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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 3 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.

General Comments This manuscript assesses the ethane measurement obtained using the Picarro G2201- i and tests its ability to provide meaningful data for determining

C2H6:CH4 in methane plumes, with the goal of source attribution. The instrument is tested and calibrated in the laboratory, subjected to controlled release experiments, and taken to measure real sources in the field. The authors find that, due mostly to the low precision of the ethane measurement ($\sim$ 50 ppb), the G2201-i can only realistically be used for ethane-to-methane ratios in methane peaks that are at least 1 ppm above the background. Furthermore, the measurement as presented must be taken under stationary conditions (i.e., with the mobile platform parked within a plume for $\sim$30 min) or the noise of the ethane measurement becomes unacceptably high. The use of the G2201-i for the described applications seems extremely limited, especially in light of the other available instruments that can do this type of measurement much better (LGR, Aerodyne, and other Picarro models). However, the authors do recognize that in order to use the Picarro G2201-i for ethane field measurements (which in turn are to be used only in the calculation of ethane-to-methane ratios rather than absolute ethane mixing ratios), the instrument response must be extensively characterized. This work is done, and the limitations of the G2201-i for the purposes described are appropriately determined and discussed.

1. There is a lot of information presented on the experimental details of previous work, which, in my opinion, obscures the experimental design and the main conclusions of the current manuscript somewhat. It makes it difficult for the reader to focus on the important points of the manuscript (one of which is the many conditions that need to be satisfied to obtain useful ethane information from the G2201-i). I recommend the authors try to streamline the manuscript as much as possible so that the important points are evident. Additionally, I recommend careful proofreading of the manuscript, which contains many small grammar errors, some of which are highlighted below under "Technical Comments".

A:The manuscript will be "streamlined" as suggested to present the study more clearly in order to be useful for other scientific teams which already have CRDS G2201-i and would like to use it in field conditions for measuring both δ13CH4 and ethane

to methane ratio. Thus, we will modify our manuscript for that. It can be treated as a protocol where all necessary steps are described and verified before field work. To do it, in the revised manuscript the introduction and conclusion parts will be improved to highlight the importance of the work done. Also, the method section will be rewritten to make it more straightforward and some additional explanation will be added to make it more "stand-alone" work (e.g adding scheme or conducted test before using instrument on field or adding table to equation 1, with factors A, B, C for different humidity levels).

Specific Comments 2. Lines 53-58: How does this study differ from Assan et al? Is the system just characterized better? Is the only difference, as mentioned later in lines 361+, that the instrument was put in a car (which must remain stationary within a plume for $\sim$30 mins to take a useful measurement)? If so, that should be made clear early on.

A:In our study, additional tests were made, the previously calculated correction and calibration factors were evaluated and long term drift was verified. Notably, we did not observe the time drift, contrary to Assan et al. Also, compared to Assan et al., a controlled release experiment was made. Ultimately, we wanted to check in which conditions we can measure ethane to methane ratio in short time, near-source conditions. Overall, we showed it is possible to received reliable values during short time (i.g. 30 minutes) and the instrument can be installed inside the car. Having the instrument set-up inside the car facilitates the measurement set-up as an additional place to install the stationary instrument is not required anymore. However yes the measurements are field-tested with the car idling. This explanation will be added in the method section.

3. Lines 62+: Did you use the monitoring mode in addition to the replay mode for the Aircore in the current study? I think some more information on how the Aircore was used specifically for this study should be included, although I would add this information later in the methods section.

A:Indeed, all measurements which were made during standing inside the plume were made in the monitoring mode. Also, we drived through CH4 plumes (in monitoring mode) and remeasured air accumulated in the AirCore sampler (replay mode). However, during car motion, the instrument noise increased and also crossing road bumps can cause additional fluctuation of measured C2H6. Thus, comparison of data collected in monitoring mode and replay mode, where the same plume is remeasured, can by biased due to influence of car motion for C2H6 readout in monitoring mode. This information will be added in the method section.

4. Lines 82 – 85: This background information on how ethane is measured and reported for an isotopic methane/carbon dioxide instrument should be moved to the abstract and introduction.

A:This information will be moved to the introduction section.

5. Lines 81+ (Materials and Methods section): To make each factor investigated clear, consider re-formatting with subheadings, such as, 1.1 Laboratory 1.1.1 Interference Correction on Ethane and Water Sensitivity 1.1.2 Ethane Calibration Factors 1.1.3 Precision and Allan Variance 1.1.4 Time drift Because the water vapor sensitivity tests are tests on the validity of the interference corrections, I think this should be discussed at the same time as the interference correction in general.

A:Material and Method section will be rewritten according to this comment. These changes will be followed by changed order in the results paragraph.

6. Lines 147+: I have some confusion about what Protocol 1, 2, and 3 are. Are these described clearly somewhere? I would add relevant details here in the methods section.

A:Protocols 1,2,3 are arbitrary made protocols to describe which correction factors were used. Thus Protocol 1 is when no interference correction was used, Protocol 2 when interference correction was used for high humidity case and Protocol 3 for low

humidity case. However, as Protocol X is always followed by a short description of cases, in the revised manuscript we will remove “Protocol X” and will mention for which case results are presented (i.g. “no correction”, “high humidity” or “low humidity”).

7. Lines 151-152: Delete “The measurement setup used here is the same as in the field” and only mention in section 2.3.

A:This correction will be applied.

8. Lines 154-159: The point that true “mobile” measurements are not conducted (i.e., while the vehicle is moving) should be highlighted earlier in the manuscript. It is an important point that is somewhat hidden here. Also- please add information here about the specifics of the Aircore setup as used in this study (e.g., flow rates, different modes, car stopped or moving).

A:This information will be added in the method section (question 3). Also the details about how to use AirCores will be added.

9. Line 174- 178: I question whether any of the information about the failed bag measurements should be included in the main manuscript, especially given the issues with sampling and bag preparation mentioned later (in lines 284+). Maybe make a very abbreviated reference to them, and then move all other bag information to the supporting information.

A:During preparing the manuscript, we considered the same question. In the revised manuscript, we will move this bag samples part to Appendix and leave only a short explanation in the main text.

10. Lines 195+, Section 3.1: Suggest headings that are the same as those suggested above for section 2.1 to help organize the information.

A:The heading will be changed and text will be rewritten according to suggestion in question 5.

11. Line 201: Can you specify what a “low amount of C2H6” means?

A:This working gas was fulfilled with dried ambient air, thus C2H6 concentration was similar to concentration of 2.2 ppb in working gas used to measurements of CMR and Allan Deviation. In the revised manuscript, used working gases will be better numbered and better described.

12. Line 356: Please clarify what “10 mins of ambient air collection was measured during 20 minutes” means.

A:Sentences in lines 356-358 will be rewritten to make it clean and consistent. The sentence in line 356 will be rewritten: “For GC-FID, ambient air was collected 10 minutes and during following 20 minutes the instrument analysed the input air.”

13. Lines 384-390: Please revise this section on Aircore and CRDS flow rates for clarity. How are the Aircore and CRDS flows related? Were there reasons for the chosen flows?

A:In the set-up used in this study, the CRDS had flow 160 mL/min and this flow rate was used in the monitoring mode. Then in the replay mode, using the needle valves, the flow rate decreased to about 50 mL/min. It caused the three times increase of the number of measurement points. In our set-up, the instrument flow rate in monitoring mode was increased (by default, in CRDS G2201-i the flow rate is equal to 25 mL/min) to achieve faster instrument response during mobile measurements. Then, the flow rate in the reply mode was chosen as optimal solution between increasing the number of measurement points and having enough air for each zone sampled. With 50 mL/min flow rate, one AirCore analysis lasts about ten minutes. Smaller flow rate would allow to increase the number of measurement points and thus instrument precision, but also requires longer time to use replay mode and measure air stored in AirCore. The AirCore tool was also used inside Paris city and we decided to keep 10 minutes sampling time of replay mode. As Paris is a crowded city with numerous traffics, it would not be possible to stop the car for longer analysing time to measure CH4 plume in the replay

mode. The additional explanation of AirCore and CRDS flow rates will be added.

14. Line 398: Do you mean the “first comparisons” of ethane mixing ratios with GC-FID match up in a relative sense? The word “indicative” is confusing here.

A:In this line we mean first comparison between CRDS sampling according to the protocol presented in the manuscript with GC-FID. The sentence will be rewritten for clarity.

15. Line 431: Please clarify what the “flushing issue” to be solved is.

A:Here, by flushing issue we mean a too small decrease of the flow rate. A stronger decrease of the flow rate will result in an increase of measurements points and an improvement of instrument accuracy. Further decreasing flow rate could solve the problem of observed differences between AirCore and actual ethane to methane ratio (discussion in lines 382- 390). In line 431 it will be rephrased for clarity.

16. Technical Comments Line 43: “source” should be “sources” Line 54: “measure of” should be “measurement of” Line 60: Change “allows to improve time resolution” to “allows improvement of time resolution” Line 77: Change “instrument to ethane” to “instrument for ethane” Line 165: Change “find” to “found” Line 167: Change “emission flux” to “gas flow rate” Line 168: Change “could vary” to “were varied”

A:All suggested grammar corrections 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.

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