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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 1 for his comments that helped us to improve our manuscript. We provide below a detailed reply to the Reviewer's comment on the utility of our work. Manuscript will be clarified accordingly.

The stated main objective of this paper: is to evaluate the performance of the CRDS2201-i and the applicability of making short-term, direct, continuous, mobile measurements of ethane in methane-enriched air, with sufficient precision during near

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source (“pollution plume conditions”) surveys. The authors did a commendable amount of work characterizing their instrument and in presenting all the limitations of this instrument. This is to their credit, and to this end the work described herein achieves its objectives. However, with that being said, this reviewer finds very limited applications where the G2201-i analyzer can be employed in measuring ethane/methane slopes in real world situations. As stated, peak ethane enhanced values of at least 100 ppb and peak methane values of at least 1 ppm are needed on stationary platforms for meaningful slopes. Unless one is directly at a well head or at a compressor source, this type of performance is not very useful. Also, more discussions of the 30 ppb bias in their ethane measurements, its sources, and its variability are needed. Despite the body of work here, this reviewer does not find any utility in publishing this paper with very limited real world applications for the G2201-i analyzer in terms of ethane/methane slopes. This reviewer recommends that the authors instead focus on a similar concerted effort to characterize their CRDS 2210-i analyzer, which they briefly mention, and shows superior performance for ethane.

A:We think that the full characterization of CRDS 2201-i analyzer to measure ethane to methane ratios proposed in our paper is useful and worth publishing for the following reasons: 1. Valuable opportunities exist for using this instrument beyond its intended application (i.e. measuring ethane together with isotopic composition on a single analyzer), but this requires a prior specific characterization. In our study we focused on the characterization of CRDS G2201-i for ethane measurements, as some previous studies already used this instrument during field campaigns to measure ethane to methane ratio in fixed settings such as a shelter (described in paragraph 4 discussion). Thus our purpose was to evaluate limitations and possibilities to use this instrument to measure ethane to methane ratio in a car setting (one conclusion was that, indeed, it needs to be stationary during measurements but is mobile over a site). This study is useful for other scientific teams, which do not have an instrument dedicated for ethane measurements, but already have the CRDS G2201-i and would like to use it in field conditions for measuring both δ13CH4 and ethane to methane ratio. According to our

knowledge, outside our team, two other research teams in Europe use CRDS G2201-i during mobile measurements (Heidelberg University and AGH University of Science and Technology). Possibly, more institutions use it as well. Thus, our manuscript can be viewed as a protocol where all necessary steps are described and verified before field work. On a side note, the CRDS 2210-i briefly discussed was only tested in our colleagues' laboratory but was on loan from another institute. It was not available for us to test in field conditions.

2. Large enhancements necessary to use CRDS G2201-i can be found for many sources. As you note, using CRDS G2201-i to calculate ethane to methane ratio requires relatively large CH4 and C2H6 enhancement. Indeed, these conditions do not happen often during long-term stationary measurements on a fixed station located remotely from sources. However, high enhancements are observed near-source surveys for most types of methane point or site-scale sources like coal mines, natural gas or oil, waste water treatment plants, landfills, geological sources (e.g. Zazzeri et al. 2015; Lopez et al. 2017; Hoheisel et al. 2019; Lowry et al. 2020). Moreover, recent studies (Lan et al. 2019; Turner, Frankenberg, and Kort 2019; Yacovitch, Daube, and Herndon 2020) showed varying ethane to methane ratios for different facilities, even at a local scale, which shows the important role of near-source measurements of ethane to methane ratio. Having an additional model of analyzer to measure this ratio increase the possibilities to perform systematic repetitions of these measurements that can be used to observe possible changes of ratios over time

3. Ethane to methane ratios are important to better estimate methane sources from different emitting processes and every instrument counts in this matter. Mobile near-source measurements of C2H6:CH4 ratio also allows for partitioning sources between biogenic (e.g., landfill, farms) and thermogenic (e.g., oil and natural gas facilities) on a small scale, as biogenic sources do not co-emit ethane (Yacovitch et al. 2014; Assan et al. 2017). So far, to achieve it, δ13CH4 is commonly used, as typically, biogenic sources are more depleted than thermogenic sources (Nisbet et al. 2019; Turner,

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Frankenberg, and Kort 2019; Saunois et al. 2020). However, recent studies showed that some fossil fuel sources can also emit more depleted CH4 (Schwietzke et al. 2016; Sherwood et al. 2017; Yacovitch, Daube, and Herndon 2020). These more depleted 13C values are caused by the biogenic origin of the extracted gas. Based on the current database, 14% of conventional natural gas samples have a biogenic origin (δ13CH4 < -55‰ (Sherwood et al. 2017). In this case, it is crucial to use an additional tracer to portion CH4 sources during mobile near-source measurements. For this purpose, C2H6:CH4 measurements can be performed during mobile near-source surveys and using existing instruments in the different networks provides a bonus instead of waiting for their replacement with more recent and accurate instruments (e.g. 2210-i). Considering the crucial role of near-source measurements of ethane to methane ratio, our method, even with some limitations, can give rapid and qualitative results to determine the origin of methane emission.

In the revised version of the manuscript we will discuss in details the observed 30 ppb bias, which comes from the instrument various terms of uncertainty. We will also improve the introduction and discussion part to highlight the opportunities arising from our research for the scientific community and we will make more clear the motivation of our study.

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