Response to CC1: Manuele Polli

I enjoyed reading this work that address the need for accurate methane and ethane analyzers to monitor natural and anthropogenic green house gas emissions. Commane R. et al. assess this need by comparing three different commercial analyzers – Aerodyne SuperDUAL, Aeris Mira Ultra LDS, Picarro G2210-i. The authors tested the water sensitivity, instrument calibration, long-term instrument stability and accuracy in ambient sampling for each instrument. The results are convincing and the methodology adopted were well described. The clear language as well as the use of appropriate figures are strengths of this paper. I suggest the authors to put more effort into the description of the need of this study as well as the conclusion following the achieved results. Based on those suggestions and the following comments I recommend that this paper by Commane R. et al. to be accepted after minor revision.

Major comments

1. Good informative title!

It may be a bit boring but it seems to work!

2. Very good, short and precise Abstract containing all the necessary information!
3. Introduction: Easy to follow even if one is not from the field, great wording! Main concern of the introduction is the necessity of this study. What research for instruments have been done before i.e. back the necessity of this study with other sources like doing in the beginning of the methods section (e.g. line 69-71 & for Picarro – line 102). Or also adding why these new commercial analyzers are better then the previous ones and the need of a intercomparison compared to previous studies.

We thank the reviewer for this suggestion. We have added some text to the introduction to highlight the relevance of this study:

As far as we can tell, there has not yet been a systematic assessment and characterization of these newly available laser-based ethane spectrometers. There is also little guidance available to those now charged with instrumenting networks and mobile platforms for methane source apportionment.

4. Good methodology, following a good structure by firstly giving technical information, then the ideal use, possible complications followed by a detailed approach to your analysis.

Thanks

5. The structure and visualization (especially Figure 4) of your results are great. The section “3.4 Long-term instrument stability” misses a discussion and is only describing the results present. Otherwise your descriptions and discussions were short & precise, well done!

Based on some of the other review comments we have added a short discussion to Section 3.4 for the Picarro performance in particular. We have also added a short discussion about the overall instrument performance.

"Using a Picarro G1301, (Nara et al., 2012) observed a pressure broadening effect when sampling gas with a range of oxygen and argon that resulted in a ~2 ppb bias in methane. We would expect to see a larger pressure broadening effect when sampling dry nitrogen free of oxygen and argon, which may explain some of the variability in Fig 3a. Indeed, there is no increased variability in methane observed by the Picarro G2210-i when sampling from a compressed air cylinder at low humidity (Fig 1(a)). For the Aeris MIRA we see different behavior for the methane and ethane. The ethane results are consistent for both compressed air and nitrogen with more ethane variability at low humidity. The methane variability is much larger when sampling humidified nitrogen and dry compressed air than seen when sampling dry nitrogen and humidified compressed air (see Fig 1 and S1). In our tests here, the G2210-i stability for methane is the best of the three analyzers when sampling humidified nitrogen boil off, which indicates that the addition of nitrogen from a dewar is possible as a long-term zero only if the flow is humidified. However, for the Aeris MIRA, we observe much more methane variability in humidified nitrogen and lots of ethane variability in dry nitrogen so we do not recommend using nitrogen as a long-term zero."

6. Conclusions and Recommendations: Brief and containing all the major findings, very good!

Thanks!

Main concern – You do not recommend the usage of Picarro compared to both other instruments but only based on the 2 unrealistic ethane measurements during the plumes. If I understand correctly all the other tests and calibrations were qualitatively indifferent or not significantly worse when using Picarro. Following those findings, I would conclude that future research on the Picarro instrument measuring ethane plumes is needed (as you "only" measured twice) rather than only recommending the other two instruments. One idea could also be to leave the ambient sampling experiment out of the paper until more samples and a concluding review can be reached.

We thank the reviewer for highlighting this point. We had struggled with how to best describe the behavior of the G2210-i fairly and now realize that we didn't include enough information. We had 4 weeks of ambient sampling in February 2022 but for the first two weeks, the G2210-i instrument either reported negative ethane concentrations or showed anticorrelation of ethane with methane (when the Aeris and Aerodyne showed positive correlations). The two examples shown in Figures 4 are just short examples of the longer-term ambient sampling, zoomed in for ease of viewing. We saw many of these type of events in Feb 2022. We have now added Fig S8 that shows 5 days of all three instruments sampling ambient air in NYC. The same G2210-i was also operated at an air quality site for over a year and showed similar behavior (negative ethane during plumes).

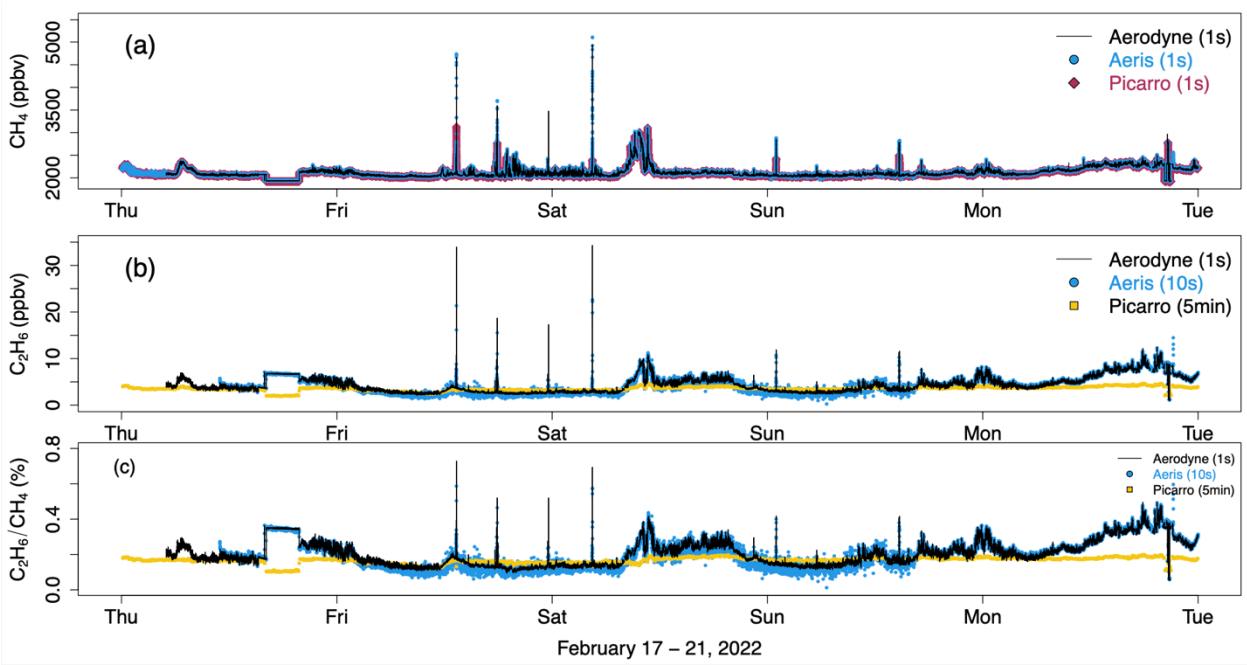

Fig S8: Time series of ambient sampling of all three instruments for Feb 17 – 21, 2022 (Time in UTC). (a) Methane (CH_4, ppbv), (b) ethane (C_2H_6, ppbv) and (c) ethane/methane ratio (C_2H_6/CH_4, %). Compressed air tanks were sampled on Thursday and Monday. The Aerodyne SuperDUAL data (black line) is shown at 1s, the Aeris MIRA (blue circle) is a 10s average and the Picarro G2210-i is 1s for (a) CH_4 and (b) 5 minute average for C_2H_6. All three analyzers observed plumes of methane on Friday night (Feb 18th) into Saturday morning (Feb 19th). While the Aerodyne SuperDUAL and Aeris MIRA also saw increases in ethane that identified these plumes as natural gas, the Picarro G2210-I did not. The Picarro G2210-i also reported a decrease in ethane when sampling a compressed air cylinder, contrary to the increase reported by the Aerodyne SuperDUAL and Aeris MIRA.

As stated in the response to Reviewer 1:

We struggled with how to represent the behavior of the Picarro fairly and may have erred on the side of not including enough information. We have no reason to believe that the behavior described here is specific to this analyzer. In the few papers that reported using the G2210-i analyzer (e.g. Lebel et al., 2022), no ethane data has ever been plotted/shown in a figure. Methane reported by the analyzer is within spec provided by Picarro and the methane isotopes (not evaluated here) also seem to be reporting accurately (based on some brief testing at the isotope lab in Rochester).

This particular G2210i analyzer was operating for over a year at a background site where it was reporting somewhat unexpected behavior (negative ethane concentrations, anticorrelations of ethane with methane, etc). The instrument was returned to Picarro for service, where it was kept for a few months before it was returned and we conducted this study soon after. When we received the analyzer, we were assured by Picarro engineers that it was functioning as expected and completely within specifications. What we don't show here is all the negative ethane concentrations and the anticorrelation with methane (obviously a malfunction) that we observed in the first two weeks of our study. We contacted Picarro after the two weeks and spent over ten hours on various meetings with engineers and scientists at Picarro trying to understand the behavior described here, specifically showing them the negative response for ethane vs the other analyzers. We informed them that we were working on this manuscript and gave them opportunity to

deal with the problem before we submitted. However, they failed to identify a problem, other than it *might* be a CO or VOC interference from the combustion, and no solution was presented. They never offered to send a second analyzer for additional comparison and we would not suggest that anyone should spend money buying one. The analyzer was returned to the background site (with little CO) after this study and seems to be operating within specifications since then.

We have added the following (blue) text to Section 3.5:

"In order to test the suitability of each analyzer to report accurate methane and ethane mole fractions in ambient air, we ran all instruments sampling ambient air from the CUNY Observatory in Harlem, NY, for 3-4 weeks in February 2022. In general, air is cold and very dry in New York City in winter and it took some time to learn that we had to humidify the Aeris MIRA and Picarro G2210-i sample flows in order to record valid data (see instrument characterization experiments described above). The Picarro G2210-i was oftenreporting negative ethane and negative correlations of ethane with methane for the first two weeks of observations. We then requested that Picarro engineers check the instrument and they assured us it was performing as expected. So we have focused on Feb 17-22, 2022 (see Fig S8), when the G2210-i was confirmed to be performing to specification. Figure 4 shows typical zoomed in examples of the ambient methane and ethane mole fractions observed by all the analyzers when sampling ambient air in February 2022."

{minor comments}

General comment: You're talking about concentrations of methane and ethane, so I suggest to add that in the text e.g. Line 57: "Here, we evaluated three laser- based spectrometers that are marketed to measure ambient ethane and methane "concentration".

Technically the instruments report dry mole fractions of those gases (ppbv) and not concentration (molecule cm^{-3}) so we have added the text:

"Here, we evaluated three laser-based spectrometers that are marketed to measure ambient dry mole fractions of ethane and methane.

General comment: Be consistent using either ppbv or ppb (e.g. Table 1 & Figure 1 contain ppb but description and text contains ppbv)

Done. Sorry about that confusion.

General comment: Keep the capitalization within your titles consistent (e.g. Line 163 "Characterization of water sensitivity" or Line 126 "Instrument stability")

Corrected.

Abstract: Good and compact but some sentences (e.g. starting Line: 13, 16, 21) are very lengthy which could be rephrased into two sentences.

We shortened a number of sentences in the abstract.

"The Aerodyne SuperDUAL instrument performed best of the three instruments but it is large and requires expertise to operate… The more compact Aeris MIRA can, with careful use, quantify thermogenic methane sources to sufficient precision for mobile or short term deployments in urban or oil and gas areas. We weighed the advantages of each instrument, including size, power requirement, ease of use on mobile platforms, and expertise needed to operate the instrument. We recommend the Aerodyne SuperDUAL or the Aeris MIRA Ultra LDS depending on the situation."

Line 9 – No point after the title Abstract

Done.

Line 12 – different sources not difference

Done.

Introduction: Explain the term nocturnal boundary layer as it gets mentioned a few times in the result & discussion section.

We reworded those sentences in the Discussion to make it less jargony. Instead we used terms like "build up in the urban atmosphere overnight".

Line 46 – add sources "to many studies"

Done.

Line 50 – no "e.g." needed

Done.

Line 52 – source?

Added a list of sources for Boston, DC, LA, and Indianapolis.

Methods: Line 71 – sentence is very lengthy.

We have split the sentence in two:

These spectrometers use a continuous wave interband cascade laser (ICL) based spectrometer to measure methane, ethane and water vapor. They are often used in a two laser system alongside a continuous wave quantum cascade laser (QCL) to measure dry mole fractions of carbon dioxide (CO_2), carbon monoxide (CO), and nitrous oxide (N_2O).

Line 90 – "There are..." what should this sentence contribute to the understanding of Aeris technology?

The technical specification of the Pico is very similar to the Ultra. So we have added the phrase:

There are few descriptions of the Aeris MIRA but Travis et al., 2020 described a similar, portable version of the instrument with an onboard battery (MIRA Pico, not evaluated here).

Line 111 – sentence is very lengthy.

We have split the sentence:

A counter flow of air was drawn through the Nafion at ~2000 sccm using a vacuum pump. The inlet to the counter flow was alternatively sampling the top of a container of water that was at a temperature slightly warmer than the observatory or dry air-conditioned air in the observatory.

Line 120 – Reword "calibrated" as it appears 2 times in the same sentence.

Agreed. We have reworded the sentence:

"Each of the instruments sampled two ambient range cylinders calibrated by…"

Line 129 – why was the regular zero not performed? – give reasoning

We stopped the zeros to allow or a direct comparison of all analyzers. If the laboratory temperature is stable (as on this day), a 4 hour time period without zeros is not detrimental to the performance of the SuperDUAL as seen in Fig 2. We have edited the text to:

"During this time the regular zero for the Aerodyne SuperDUAL was not performed to allow for direct comparison of all instruments."

Line 136 – Rewrite that sentence for clarity, i.e. I don't understand the meaning behind it.

We have rephrased the sentence:

"Regular nitrogen sampling is not required for the long-term operation of either the Picarro G2210-i or the Aeris MIRA. We evaluated the performance of the Aeris MIRA and Picarro G2210-i when sampling dry and humidified nitrogen."

Results and Discussion: Well written first paragraph (Line 160)!

Thank you!

Line 178 – Figure caption misses a point in the end.

Done.

Line 182 – Missing indent

Done.

Line 186 – Do you have a source to the possibility of laser wavelength drift?

We have seen similar behavior with the SuperDUAL when the reference lock is disabled. So it's a possibility but without a laser wavelength monitor (which we do not have), I don't know how we would confirm that theory. We discussed the problem in depth with engineers at Aeris Technologies and they have developed a fix for this problem by changing the lock to either the stronger water line (often saturated in normal operation) or locking to the methane. We have updated the text as follows:

"After discussion with engineers at Aeris Technologies, we learned that there are two water vapor peaks in the spectral window. So this problem could be mitigated when sampling dry cylinders by locking to the stronger water vapor absorption peak, which is often saturated during normal operation, or to the methane line directly. Note that locking to the methane line would prevent running zero methane or nitrogen samples as discussed in Section 3.4 below. Either change can be implemented upon request when ordering new analyzers."

Line 195 – Source to the Aeris engineers is missing

The document provided by Aeris Technologies was emailed to the authors. We have added personal communication as the citation.

The findings from (i)&(ii) (Line 183-196) are not very well visible in the graphs, maybe a zoom in to the respective "noise sections" would help.

The data for the other two instruments is so linear that we just increased the y axis to include the full scale of Aeris data.

Line 208 – remove "of"

Done.

Line 215 – Description of Table 2: describe the meaning of "Slope +/-, Intercept +/- and r2".

We have clarified the caption and added 95% CI to the headers in the Table

Table 2. Calibration span (slope) and zero (intercept) calculated for each instrument reporting at 1 Hz when sampling the NOAA calibration standards. The 95% confidence intervals (CI) for the slope and intercept of an Ordinary Least Squares (OLS) fit are also shown. **The ethane Picarro G2210-i calibration was calculated from the mean of each cylinder measurement (two-point calibration).

Figure 2 – y-axis label is not centered.

Centered.

Table 3 – Add sources of quoted CH4 & C2H6 precision

We clarified the wording:

Table 3: Summary of various instrument performance metrics. The quoted precisions are from the Product Datasheet for each analyzer except *Aerodyne Superdual Quoted Precision from Kostinek et al., 2019

Line 232-243: very good description and discussion

Thanks

Figure 3 – increase the spacing between the upper and lower graph (axis overlap)

We have added more space between the figures

Line 283 – remove “during”

Done.

Line 297-304 – very good discussion

Thanks!

Conclusion and Recommendations: Line 309 – replace “or” with “of”

Done.

Conclusion: This paper is very well written and offers a clear structure to follow. The two main drawbacks lie in the description of the need of this study based on previous research and the conclusion being based on the results of only one experiment.

We thank the reviewer for their helpful comments. We have added more motivation for the study. We believe we have clarified the extent of the ambient sampling that extends the comparison beyond a single experiment.