Response to RC2:

Commane et al present a study comparing three commercially available analyzers for atmospheric CH4 and C2H6. Results from typical laboratory performance tests and calibrations are discussed. The authors also present results from a very short period of real-world data collected in an urban area.

The paper is well-written and clearly structured. Core results are highlighted and the logic is easy to follow. The description of the experiments is good, but could be improved slightly with some additional details. Overall, this a very good example of a study that other experimental scientists in this field can use to choose suitable equipment for future work. Testing analyzers with the combination of gases CH4 and C2H6 is very timely as there is an increasing amount of research on local atmospheric methane signals in recent years and many these studies could be improved if reliable source apportionment (thermogenic vs microbial) was done. Thus, this paper is highly suitable for AMT after minor comments are addressed.

We thank the reviewer for their helpful comments and suggestions that have improved the manuscript.

General comments:

Please consider using consistent unit for the mole fractions reported here. Sometimes it is reported as ppbv, then as ppb in the figures and nmol mol-1 in some tables. Also please add an explanation that nmol mol-1 is only equivalent to ppbv assuming ideal gases (which C2H6 and CH4 are not) or consistently report in nmol mol-1.

Sorry about this confusion. We have made the reported units consistent across the manuscript. As the reviewer mentions, the instruments measure dry mole fractions (nmol mol^{-1}) but as the analyzers report mixing ratios and these units are most commonly used in the field, we have chosen to report all units as ppbv. We have added a sentence to clarify in Section 2.1

"Each of the analyzer described below reports the dry mole fraction of methane and ethane in air using units of ppbv, parts-per-billion by volume, which is the equivalent of nmol mol^{-1} for an ideal gas."

Please specify the composition of the zero air at least once to ensure that it is not just a synthetic N2/O2 mixture but has the correct (ambient air) amount of all three matrix gases.

Thanks for catching this. The Zero tests were done with nitrogen and not zero air. To avoid confusion we have renamed Section 2.2.4 Zero-air tests to

2.2.4 Nitrogen tests

Line 245 was changed to:

"We evaluated the stability of frequent additions of nitrogen (liquid nitrogen boil-off free of methane, ethane, CO_2, etc.) for all three analyzers."

Please add to the discussion about the Picarro performance that the tests using N2 should be disregarded as their CRDS systems have been shown to be susceptible to changes in matrix gas, see Nara et al. 2012 https://doi.org/10.5194/amt-5-2689-2012 We should not expect for the CRDS system to work properly for any mixture with missing O2 or Ar.

We thank the reviewer for highlighting this point. Nara et al., 2012 calculate a +/-2 ppbv decrease in reported CH_4 due to pressure broadening effects when changing O2 and Ar from the sampled gas of a G1301 analyzer. We're not sure the same correction is observed for the wavelengths used for the detection of methane here. If it did, we should see more bias for the reported methane in Fig 3. But the Picarro does particularly well in the humidified nitrogen. We clarified in Section 2.2.4 that there may be trace levels of O2 and Ar in the LN2 (see the helpful reviewer comment below). We also edited the text at the end of the second (Picarro) paragraph in Section 3.4.

"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."

Specific comments:

Line 134: How pure is the N2 boil off? could there be other contaminant gases than CO?

It is possible that there are species other than CO (boiling point (b. p.) is -191.5°C) in the LN2 boil off (b. p. N_2 -196°C) such as argon (-186°C) or oxygen (b. p. -183°C) but we have

not measured any other species with the instruments we have used at the site. We have clarified Section 2.2.4 with the following text:

We use the boil off from a large liquid nitrogen dewar, which can be refilled on site, and which contains a variable mole fraction of carbon monoxide (~250 ppbv), and may contain trace levels of oxygen and argon.

Line 135: The units for carbon monoxide should be nmol mol-1 or ppb

Agreed. We have used ppbv throughout the manuscript for the reasons explained above.

Line 173: See general comments on use of different units throughout the manuscript

Agreed. We have cleaned up the use of units throughout the manuscript.

Line 176f: different units in table, figure and caption seems unnecessary

Agreed. We have cleaned up the use of units throughout the manuscript.

Line 213: Consider adding information about the actual measurement cycle of the Picarro. The data rates does not automatically match the measurement frequency here.

We have added the following text to Section 2.1.3

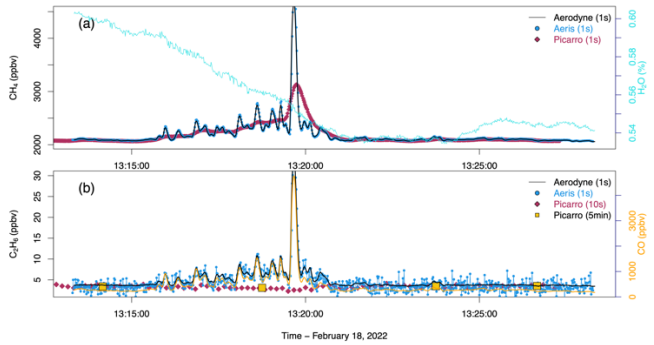
"The measurement and reporting cycle of the Picarro G2210-i are 1Hz. But the low flow rate reduces the instrument response time considerably. We have corrected for the delay and report methane at 1Hz and we have averaged the ethane to 10s and 5 minutes."

Line 249 - Figure3: See comments on using CRDS analyzers for a non-natural air matrix

Agreed. Edited text is mentioned above.

Line 273 - Figure4: As water vapour has been shown to be a critical component please add the H2O levels to the plot. Are there any changes in H2O reported by the Picarro during the expected C2H6 peaks. Previous studies have shown strong dependencies. https://doi.org/10.5194/amt-14-5049-2021

We have corrected each instrument for water vapor dependence (as per Section 3.1). But, unlike Fig 3 in Defratyka et al., 2021, the water vapor dependence of the ethane reported by the G2210-i was negligible (See Figure 1) so we do not expect a water vapor response in the ethane signal. Adding water to Fig 4 was a bit messy so we have shown the reported water in the zoomed in version (Fig S9). We also added CO to highlight the combustion character of the plume.



"Figure S9: Time series of ambient sampling of all three instruments for 13:10 – 13: 30 UTC Feb 18, 2022. (a) Methane (CH_4, ppbv) and water vapor (cyan, % measured on SuperDUAL, 1Hz), (b) ethane (C_2H_6, ppbv) and carbon monoxide (CO, ppbv; measured on SuperDUAL, 1Hz). The Aerodyne SuperDUAL data (black line) is shown at 1s, the Aeris MIRA (blue circle) is 1s average and the Picarro G2210-i is (a) 1s, (b) 10s and 5 minute average. This is a zoomed in version of Figure 4 (a) and (b). The Picarro G2210-i CH_4 is slow to return to background concentrations due to the low flow rate. The C_2H_6 reported by the Picarro G2210-i is reduced during the increase observed by the Aeris MIRA and Aerodyne SuperDUAL instruments plume."

Line 303: Generally restricting the use of G2201-i Picarros in certain regions seems an extreme suggestion given that the real-world test period was extremely short and only performed in one region.

We do not comment on the G2201-i as it was not evaluated here. We are asserting that the G2210-i evaluated here is not appropriate for use in some conditions such as the specific urban polluted air as sampled here. We have added a new Figure S8 to show some of the longer time series of observations when all three instruments were sampling ambient air and 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."

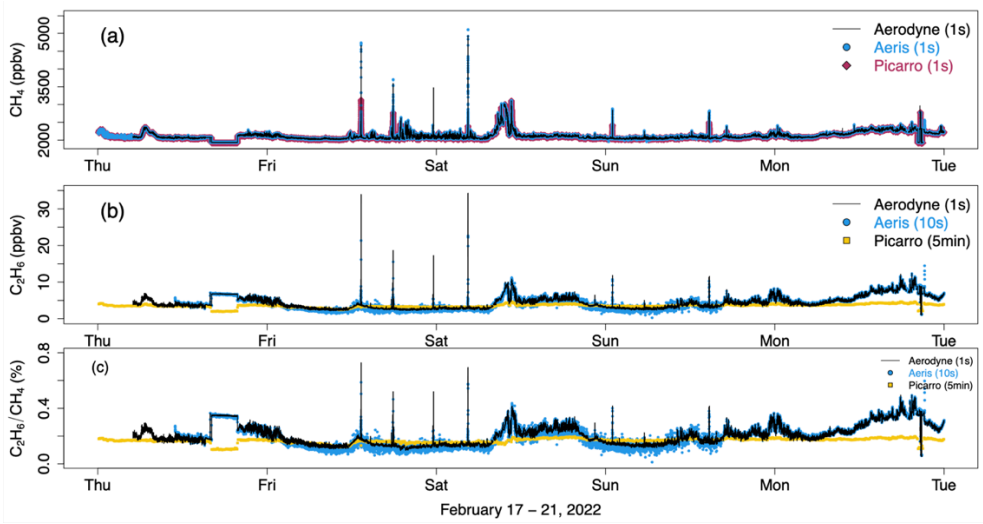


Fig S8: Time series of ambient sampling of all three instruments for Feb 17 – 21, 2022 (Time in UTC). (a) Methane (CH_4, ppbv), (b) ethane (C_2H_6, ppbv) and (c) ethane/methane ratio (C_2H_6/CH_4, %). Compressed air tanks were sampled on Thursday and Monday. The Aerodyne SuperDUAL data (black line) is 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 for 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 every 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.

Line 313: Please provide the citation for the study that established the performance equivalency of the Aerodyne and Aerodyne 'mini' system.

We have added a link to the Aerodyne spec sheet for the mini that shows the precision and edited the text as follows:

There is a smaller size instrument from Aerodyne – the Aerodyne "mini" – which has a methane/ethane precision between that of the SuperDUAL and the Aeris MIRA but this also requires an external chiller and large pump (see https://www.aerodyne.com/wp-content/uploads/2021/11/Ethane.pdf; 60s precision of 0.05 ppbv CH_4 and 0.015 ppbv C_2H_6).