**Response to RC1**

**General comments**

The paper report on tests and comparison of three recent optical analyzers dedicated to measuring both CH4 and C2H6. These sensors are increasingly needed for partitioning CH4 emissions from the fossil fuel sector. This is a very timely study since CH4 emissions from the oil and gas sector are under increasing scrutiny with the potential to achieve rapid climate change mitigation results.

The study has selected three available optical sensors that represent practical option now for field measurements and offer the possibility to run long term observations as well. The authors have brought careful consideration to properly running the instruments in their test environment. The tests offer insight into water vapour dependencies and corrections, precision, short term precision and stability against zero gas. The paper provide thoughtful considerations on practical aspects and compliance of the analyzers for different scientific purposes and contexts.
Overall the paper is well written, well presented and clear.
We thank the reviewer for all their helpful comments and suggestions. They have helped to make this a much better paper and we appreciate the time they spent on this paper.

I suggest to compare succinctly metrology definitions with those used in a large network with systematic pre-deployment sensor verification such as ICOS (e.g. Yver et al 2015 www.atmos-meas-tech.net/8/3867/2015/)
We thank the reviewer for this suggestion. While the ICOS definitions are useful for standard CO2/CH4 networks with well characterized instruments, they are not ideal for new instrument testing for selectivity. Most of our tests do not fit nicely into the ICOS metrology definitions. But Figure 2 where we evaluate precision (Allan-Werle Variance) is similar to continuous measurement repeatability (CMR), which is a repeatability measure applied to continuous measurements. Figure 3 where we evaluate nitrogen sampling over time is similar to short-term repeatability. We do not asses long-term repeatability, which would take months. In any case, we have added phrases to these sections to show the relation to each of the ICOS tests.

I have three main remarks about this study :
- In this study the instruments are not compared against a reference measurement technique such as GC for C2H6. This is a missed opportunity of the study to highlight the added value of these optical analyzers against GC dedicated to light alkanes such as ease of operation and time resolution. On the other hand comparing the results of each sensor against GC performance would have been extremely instructive. Without this comparison it is less conclusive whether the best optical sensors are more adapted than GC for long term observations of background atmospheric composition or analysis of airmasses of regional representativity.
Unfortunately, we did not have access to a GC based instrument for ethane when conducting this intercomparison study. GCs are difficult to use on mobile platforms and are not widely used in the US so to be honest, we never even thought about trying to

procure one. The GC-FIDs measuring ambient ethane in New York are designed for hourly monitoring of ethane and do not measure methane. These instruments are located in state equivalent EPA monitoring sites with little space or restricted access, which makes it difficult to conduct testing and intercomparisons with those instruments. We will look into this comparison for future studies.

- The paper lacks discussion on linearity especially toward large concentrations that could be useful in the context of industrial applications. Do the three sensors perform equally linearly within the full concentration ranges that can be observed in near-source studies for both species?

We thank the reviewer for this suggestion. It was not possible to calibrate the methane and ethane to the high mixing ratios observed in these plumes as they are outside the range of our calibration standards. Instead, we have compared the Aeris and Aerodyne instruments for ambient plume sampling in Feb 20-21 at 1s for methane and 10s for ethane and the relationship is linear (Fig S9). This result is representative for the ambient sampling periods (including much more data caused the 1s data plots to be huge). While this does not directly test linearity, it is unlikely that the instruments would have identical non-linearities and therefore strong correlations between reported concentrations from the instruments likely indicates that they retain linear behavior well beyond the range of the span. We have added a discussion of the linearity of the Aerodyne and Aeris instruments at the end of Section 3.2 Instrument calibration.

"We evaluated the linearity of the instruments outside our range of calibration standards by comparing the instrument response for the Aerodyne SuperDUAL and Aeris MIRA during the high plumes (as discussed in Section 3.5 below). Fig S3 shows the linearity of 1s methane and 10s ethane for Feb 20-21, 2022 with the Aeris MIRA and Aerodyne SuperDUAL. The methane fit (Slope 1.002) is slightly closer to 1 than the ethane fit (Slope: 1.048 +/- 0.002). The slow response of the Picarro G2210-i meant that it could not represent plumes of ethane at sufficient resolution to allow for valid comparison. While this does not directly test linearity, the strong correlations between reported concentrations from the instruments likely indicates that they retain linear behavior well beyond the range of our calibration standards. "

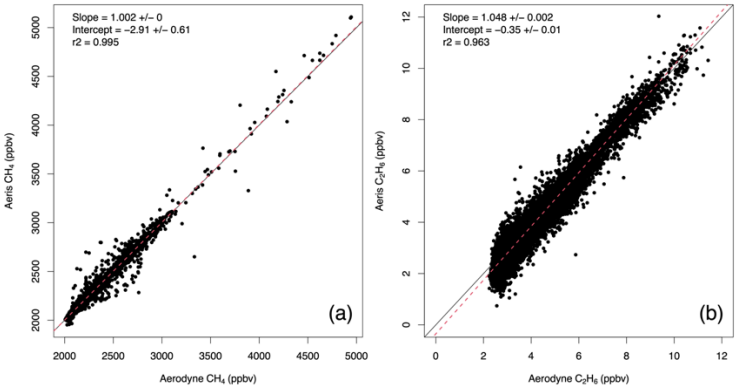



Figure S3: Linearity of (a) methane (1s data) and (b) ethane (10s aggregated data) for two days in February 20-21, 2022. The 1:1 line is shown in black. The slope and intercept calculated from an ordinary least squares with 95% confidence intervals are shown in the top left. The calculated slope and intercept are shown as a red dashed line.

- The obvious problem about the Picarro not detecting the ambient air 10ppb C2 peaks is a major concern (section 3.5). Is it representative of a shortcoming of the G2210 model, or is it just a problem with this particular unit at that particular time, mishandling

or poor quality control at the factory by the manufacturer? This is an important concern that is opened by this study but is frustratingly not really addressed. Such a poor performance is useful to publish since this particular case suggest that the instrument do not work according to expectations. However if this is behaviour is not representative of the G2210 model it cannot left as it is. Further work is needed that investigates whether this poor performance is to be attributed either to shortcomings of the G2210 model or to another reason (and if there is another reason, is there hope that it can be corrected by the manufacturer or the user). In my opinion, before this paper is published this work should really be completed to address this point. Ideally by running in parallel another G2210 unit that could maybe be borrowed from the manufacturer or elsewhere. This could be done even through a few days worth of measurements close to a known C1/C2 emitter (natural gas industrial site) with only the 2 picarros.

We thank the reviewer for this comment. 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, Defratyka et al., 2021), 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 to the PI 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."

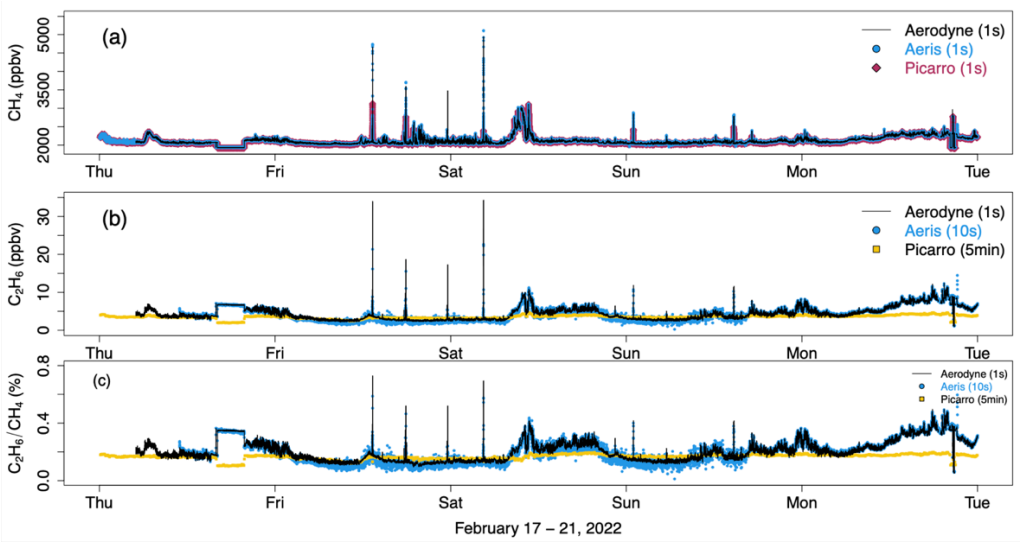



Fig S8: Time series of ambient sampling of all three instruments for Feb 17 – 21, 2022 (Time in UTC). (a) Methane ($CH_4$, ppbv), (b) ethane ($C_2H_6$, ppbv) and (c) ethane/methane ratio ($C_2H_6/CH_4$, %). Compressed air tanks were sampled on Thursday and Monday. The Aerodyne SuperDUAL data (black line)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

We have no opinion on how the G2210-i will do at natural gas industrial sites. That is not the topic of this study and we disagree with the Reviewers suggestion that two G2210-i analyzers should be tested at a natural gas source. We are specifically discussing here that these analyzers are not suitable for *urban* environments or areas with natural gas *combustion*, both of which have large possible interferents for the ethane reported by the analyzer. It is important that any analyzer for use in an urban or combustion environment would be evaluated in that specific environment. We edited a line in Section 3.4 to emphasize this point.

"Our results indicate that the Picarro G2210-i should not be used to selectively measure ethane near combustion sources such as flares, or natural gas power plants or in urban areas that combust natural gas on a large scale. Indeed, care should be taken to ensure that thermogenic sources are not erroneously attributed to biogenic sources with the Picarro G2210-i in urban areas."

## Specific comments

Abstract - I would encourage the authors to provide numeric values for precisions in the abstract

We made a conscious decision not to list precisions in the abstract. All instrument precisions are in the sub-ppb range for both methane and ethane but the Picarro isn't selectively measuring ethane in ambient air, which is the most important metric. Listing precisions could give a false sense that the Picarro actually works (which it doesn't). We can list the precisions if the editor requires it but we would prefer not to for the reasons stated above.

L44 the statement could reflect the nuance that biomass burning co emits CH4 and ethane

Good point. We have edited the text as follows:

"The incomplete combustion of liquid (e.g. natural gas) or solid (e.g. coal, wood) fuels can co-emit high concentrations of carbon monoxide (CO) and other Volatile Organic Compounds VOCs."

L81 please explain the values of 2 and 1.45

The water broadening coefficient is a correction applied to the fitting of the absorption spectra that is a function of the water vapor observed in the cell. The coefficient is experimentally determined by the manufacturer and applied to generate the dry mole fraction reported methane and ethane. A similar correction is used in all laser-based spectrometers. We have edited the text as follows:

"We use the default water broadening coefficient (WBC) for all species (WBC = 2), except CO (WBC = 1.45)."

L81 define footprint in this context

We meant the table top area needed for the instrument but we have edited the text to avoid confusion:

"The analyzer is large and heavy"

L95 typically could an external ush pump solve the problem?

Yes! And I believe a group at Scripps are currently working with Aeris to develop a "tower ready" version of the instrument with an external pump to avoid this problem in future. But it's not possible to do right now because of interactions with the internal pump.

L114 should be lowest humidity or driest air,

Good catch. Corrected to lowest humidity.

L243 it should be noted here that the G2201-i, unlike the G2210 is not intended for ethane measurements. Is the value reported for Defratyka et al. applying any specific correction? Are the two sensors similarly configured in terms of laser wavelengths?

Despite asking, we never did get the ethane wavelength for the G2210-i so we can't answer this question. After re-reading the Defratyka et al paper, we noticed that we mis-quoted the precision, which should have been 12 ppbv (1 minute). We have removed the following sentence as the comparison is not helpful and, as the reviewer states, the G2201-i was not designed to measure ethane (even if Defratyka et al do an amazing job quantifying the ethane response).

~~"The Picarro G2210-i ethane precision is similar to that observed with a Picarro G2201-i analyzer (0.8 ppbv at 1 minute; (Defratyka et al., 2021))."~~

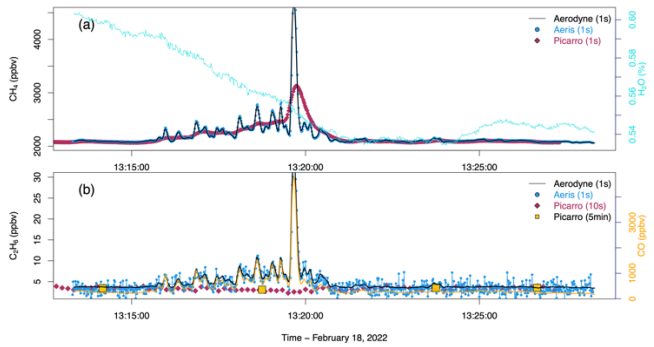
Section 3.4 Would measuring a gas cylinder with concentration typical of ambient air yield similar or different conclusion about long term stability?

We have added more discussion to Section 3.4 to include discussion of the comparison with the compressed gas cylinder experiments (Fig 1, 2, S4- S7). The Aeris results are consistent for both the air and nitrogen for ethane but not methane. The Picarro results are different for methane and at the suggestion of another reviewer, we have included a new paragraph discussing those results.

"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."

L287 : difficult to see the longer CH4 peak duration in the figure

We have added Figure S9 to the supplement with a zoomed in 20 mins around the peak of this plume. Fig S9 shows the slower reduction in methane from the Picarro vs the other instruments. At the request of another reviewer, we also included water vapor and CO to the plot.




"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."

L289 This is noticeably incompatible with the 0.8ppb precision reported in previous sections
Agreed. This result suggests that precision alone is insufficient to determine instrument viability for a given environment. It is important to also determine *selectivity* in order to understand instrument performance.

L304: For the picarro, not being applicable close to sources is a strong problem when considered the 0.8ppb C2H6 precision: such a precision orients the applicability of this analyzer to near-source measurements
As stated above, we are specifically discussing here that these analyzers are not suitable for *urban* environments or areas with natural gas *combustion*, both of which have large possible interferents for the ethane reported by the analyzer. It is important that any analyzer for use in an urban or combustion environment would be evaluated in that specific environment. As stated above we have edited this line to emphasize this point.
"Our results indicate that the Picarro G2210-i should not be used to selectively measure ethane near combustion sources such as flares, or natural gas power plants or in urban areas that combust natural gas on a large scale. Indeed, care should be taken to ensure that thermogenic sources are not erroneously attributed to biogenic sources with the Picarro G2210-i in urban areas."

L328, continuing on my general comments: is this problem specific to a deficient unit or representative of all G2210? as it is, it cannot be concluded whether the picarro technique is performing poorly or if this particular unit has a problem. Has it been check with the manufacturer? It would be useful to reproduce test with another unit.
We believe this behavior described here is not just for this analyzer. Please see the discussion above. It has been checked by the manufacturer and I disagree with suggesting someone else should buy one a G2210-i to measure ethane in an urban environment.

**Editorial**
Table 1 Aeris CH4 formula: would there be a way to better present the different formulas: linear vs quadratic Fig 2 x axis would be more useful labelled in seconds.
We have changed the x axis label.
We struggled with how best to represent the different formulas in Table 1 and this was the best we could think of due to the non-linearity of the Aeris methane. If anyone has a better suggestion, we'd be happy to change the table.

L242 please choose unit ppb or nmol mol-1
Done. Sorry about that.

Fig 4 there seems to be a technical problem with the figure: it might be not well constructed.
It was fine when we uploaded and printed it but we will work with the editors to ensure it is clear before publication.

L327 TestS plural
Done.