AMT-Discussions: Response to interactive review 2

Manuscript title: "In situ observations of greenhouse gases over Europe during the CoMet 1.0 campaign aboard the HALO aircraft", Gałkowski et al.
From: Anonymous Referee #2,
Review received and published: September 22nd, 2020

Note: Original reviewer's remarks are given as ***bold and italicized text***. We've assigned each comment with a code for easier reference. Responses from authors are given below the comments.

General Comments

RC 2.1. ***The manuscript presents a broad overview and analysis of results of aircraft in situ measurements (continuous greenhouse and trace gases) and atmospheric trace gas and isotopic composition measurements in onboard flask samples conducted during the CoMet 1.0 campaign. It details these two measurement systems and inter-comparisons in the context of WMO compatibility goals and presents model-data comparisons to two commonly used global modelling systems with different resolutions and meteorological drivers. The article is well written, concise, and scientifically sound, but I feel that the focus of this manuscript stretches the limits of the scope of the AMT journal. As such, and since the article is part of a special issue collection, the majority of my specific comments aim to provide more detail for important measurement techniques below.***

We thank the reviewer for that comment. As explained in our reply to reviewer #1, we are aware that some sections of our manuscript might be on the edge of the scope for AMT. We believe, however, that including some analysis of the measurements is beneficial for our manuscript and improves the overall value of the paper for the general scientific community.

We kindly refer the referees to our previous discussion of above (see RC 1.1. and RC 1.14.).

Specific Comments

RC 2.2. Section 2.2.1 describes the CRDS measurements, but there is some key information and clarification lacking from the description of this system and its operation that should be included here. For example, air sample drying and/or water vapour corrections to these greenhouse gas measurements should be discussed as these measurements are compared to dried flask sample measurements.

We kindly refer to section RC 1.8. in this document.

RC 2.3. Furthermore, 'mixing ratios' measured should be reported as dry air mole fractions: please replace 'mixing ratio' with 'mole fraction' throughout the text.

Agreed, units have been replaced as requested. See also our discussion in RC 1.9.

RC 2.4. It would also be useful to also specify how many in-flight offset-corrections occurred on average per flight as these were performed manually, and specify whether this is a single-point correction or if two calibration tanks were used.

We thank the reviewer for these remarks. We have taken them into the account when addressing point RC 1.7. See discussion there.

RC 2.5. For flask samples, please clarify the level to which air samples are dried with the magnesium perchlorate and the pressure and volume of air that is sampled in each glass flask (is this 1 L at ambient pressures?).

The air is dried to dew points below -70 °C. With regard to the pressure inside flask, the following text was modified in section 2.2.2. at approx. L159:

"(…) that provides the over-pressure necessary to flush and pressurise the flasks, up to approximately 1500 hPa."

RC 2.6. On which type of analyser were the flasks measured?

The description of the measurement instruments was expanded in section 2.2.2.:

"Gas chromatographic analysis of air in glass flasks is made with a gas chromatographic system based on two GCs (6890A, Agilent Technologies) equipped with a flame ionisation detector and a Nickel CO_2 converter (FID) for CH_4 and CO_2, an electron capture detector (ECD) for N_2O and SF_6, a helium ionisation pulsed discharge detector (D-3-I-HP, Valco Instruments Co. Inc.) for H_2, and a HgO Reduction Gas Analyser (RGA3, Trace Analytical) for H_2 and CO. Additional analyses of O_2/N_2, Ar/N_2 and isotopic composition of methane $\delta^{13}C$ -CH_4 and $\delta^{2}H$ -CH_4 were carried out in the IsoLab of MPI-BGC (Sperlich et al., 2016). The typical measurement precision of the laboratory analyses is given in Table 1."

RC 2.7. L169 states that there was a drift in the CO flask measurements between collection and measurement; for clarity, please elaborate on how you have determined this using the in situ data.

Description has been expanded following the discussion of RC 1.11 here – we kindly refer to the discussion above.

RC 2.8. L194: Please also clarify how flasks were sampled during vertical profiles; if the aircraft was only either ascending/descending over the flask fill time, the reader can infer that the air samples collected during these profiles represents an integrative mole fraction between potentially several layers of the atmosphere. It might therefore also be useful to state, on average, how long it takes to fill a flask.

Indeed, the filling time was variable with height. The altitude to which the flask was assigned to was assigned based on the box model that took into the account flow, pressure and tubing volumes, as described in L159-L163, following the work of Chen et al. 2012. We've added the following additional information into the text after 170:

"Each flask was flushed with 10 times its volume prior to closing the upstream and downstream valves. Typically, flasks were filled during descending profiles, but on some occasions also during ascents. The variable ambient pressure caused the flask fill time to vary between 100 seconds at high altitudes to 25 seconds close to the surface."

RC 2.9. Throughout the manuscript, the Jena CarboScope model is referred to as TM3, but in L235, it is mentioned that it will be referred to as "CarboScope" – please choose one or the other for consistency.

The plots and captions have been updated and now use CSc in place of TM3.

RC 2.10. It is mentioned in Section 4 that the flask measurements are compatible, by WMO standards, with the G2401 measurements but this does not seem to be the case. The in situ-flask differences, given uncertainties, fall outside of WMO surface compatibility goals for CO2 (0.1 ppm) and CH4 (2 ppb). As compatibility between measurement systems is mentioned as one of the scientific goals of the CoMet 1.0 mission, it seems necessary to state these compatibility goals for CO2 and CH4 as defined by WMO.

Thank you for this remark. In line 257 we have stated that the results are the difference is "still close to the WMO compatibility goal". However, the later statement in the "Conclusions" section was incorrect. This has been changed into (L508):

"Comparison with flask samples analysed in the laboratory confirm that the measurement data are close to compliance with the WMO compatibility goals (average bias smaller than 0.15 μmol mol^{-1} and 3 nmol mol^{-1} for CO_2 and CH_4, respectively)"

We have added the requested information on WMO compatibility goals in L285:

"The comparison between flask and in situ measurements is available for all except one flight (no. 5). From the 96 samples collected and analysed, 84 had simultaneous in situ measurements available from JIG that could be used for a bias assessment. Here, we compare bias between both our datasets to the 'network compatibility goal', defined by World Meteorological Organization as "the scientifically-determined maximum bias among monitoring programmes that can be included without significantly influencing fluxes inferred from observations with models" (WMO, 2019). WMO specifies this compatibility goal as equal to 0.1 μmol mol^{-1} for CO_2 (in the northern hemisphere) and 2 nmol mol^{-1} for both CH_4 and CO."

RC 2.11. Figure 3 does not define the differences shown (i.e. are flask – in situ values shown)? I also wonder why these results are shown by flight number rather than something more informative for understanding differences between the two systems (e.g. difference vs. altitude or difference vs. mole fraction), separating flights 1-7 and 8-9. I would suggest a figure showing these differences as a function of either of these parameters (perhaps in SI) to shed light on why differences are seen between in situ and flask greenhouse gases.

In the course of data analysis, we have investigated the mismatch between JIG and JAS in detail and found no clear relationship of in situ vs. flask mole fractions with either altitude or mole fraction (see figures below).

For both CO_2 and CH_4, the distribution of difference seems to be largely independent of altitude (Fig. A). Three outliers with very negative bias for methane (below 10 nmol mol^{-1}) are observed around 10 km, however even for high altitudes most of the differences are in the typical reported range (approximately -5 to 0 nmol mol^{-1}, with the mean of -2.93, nmol mol^{-1}).

As shown in Fig. B., the variability of JIG-JAS difference seems to be slightly higher closer to the higher end of the observed mole fraction range, however no clear trend can be observed. For methane, small biases are observed in the lower mole fraction ranges (below 1850 nmol mol^{-1}) with outliers for very low values of methane seemingly less biased than the ones observed in the typical tropospheric range (1900-1950 nmol mol^{-1}).

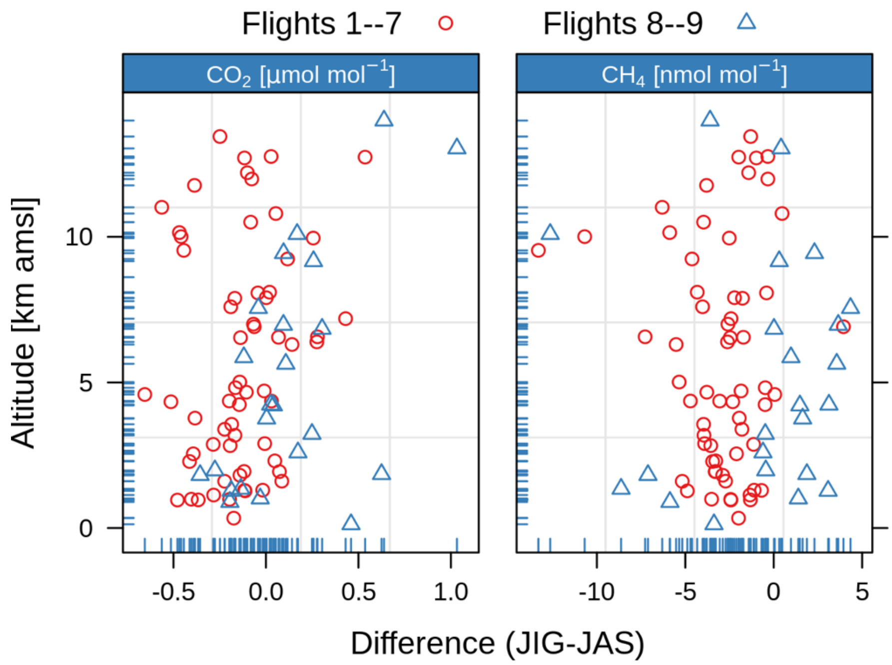

Figure A. Difference between JIG in situ and flask values, and their dependence on altitude, presented separately for flights 1—7 (red) and 8—9 (blue). Notches added to X and Y axes to display distribution of values (these are not colour-labeled).

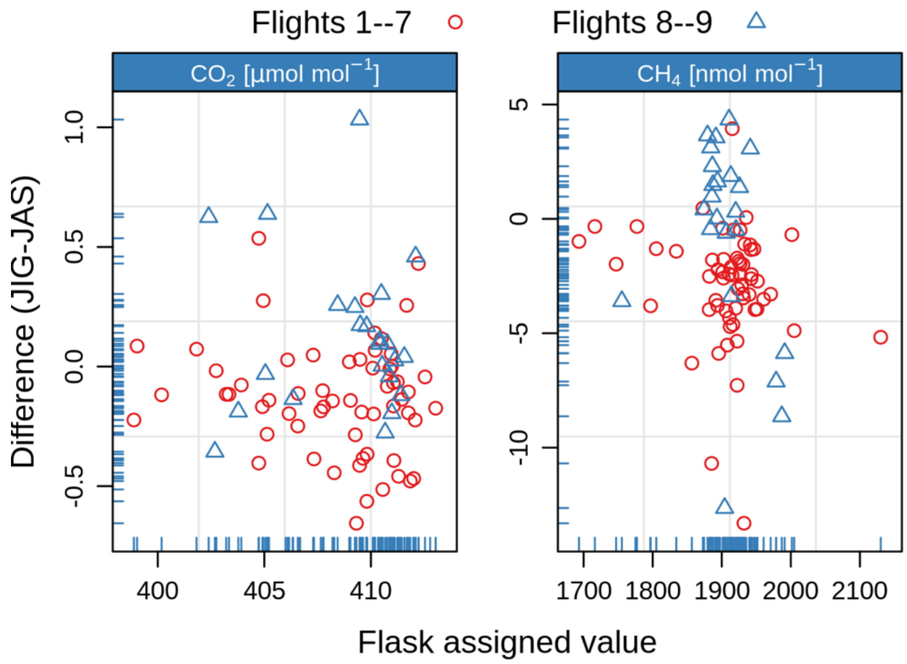

Figure B. Difference between JIG in situ and flask values plotted as a function of mole fractions. Notches were added to X and Y axes to display the distribution of values (notches are not colour-labeled).

We've therefore decided that we want to emphasize first and foremost the change in the mean offset in flights 8—9, and to present the day-to-day variability, which is done in Figure 3 of the manuscript.

The plot has been updated in the following manner: i) difference is now clearly defined with the Y label axis; ii) units changed to µmol mol^{-1} and nmol mol^{-1} for CO_2 and CH_4, respectively, for consistency with the rest of the text (c.f. RC 2.3).

RC 2.12. L290: Please describe how it was evidenced that a stratospheric intrusion was crossed.

'Stratospheric intrusion' in this sentence is meant to describe stratospheric air being pulled below typically observed altitude ranges. This is supported by comparison of CAMS model predictions and our in situ observations for all greenhouse gases (Fig. 4), where we see a clear segment of airmass with significantly reduced mole fractions, which is probably a potential vorticity (PV) filament that has been brought down by the outflow of the convective system. While we did not measure the ozone concentrations that are typically associated with stratospheric intrusions, and the observed air mass clearly doesn't reach deep into the troposphere, we believe that the very high correlation between observations and the model allows us to identify the phenomenon by stratospheric air presence at the flight level.

The text at L290 has been expanded, with stratospheric intrusion changed to 'stratospheric filament' in order to prevent confusion with the dry intrusions associated with large-scale tropopause folds:

"Immediately before the descent to Monte Cimone it crossed a stratospheric air filament, possibly brought down to the flight level by the outflow of a deep convective system active in the area in the afternoon on that day. This is corroborated by CAMS model results, which show a clearly defined air-mass structure, depleted in mole fractions for all the observed compounds, stretching from the stratosphere at 200 hPa down to approximately 400 hPa (corresponding to roughly 13 km and 8 km a.m.s.l., respectively)."

RC 2.13. Figure 4, at times (L292, and elsewhere) is described in kilometers, but the figure itself is denoted in pressure altitude. The text would be more consistent with this figure if it were describing events in pressure levels as well.

Agreed. The text has been updated to use pressure levels together with altitudes.

RC 2.14. Figure 5 shows modeled vertical profiles, which seems redundant with Figure 6. In addition, these model vertical profiles are not ever discussed. I would suggest removing these panels.

We respectfully disagree. We believe that showing modelled profiles also in Fig. 5. gives a one-look visual comparison as to the nature of model vs. observation difference that would require careful, simultaneous analysis of both figures by the reader. Additionally, it also allows one to identify the distinct differences between CarboScope and CAMS products at the profile locations.

Technical Corrections:

RC 2.15. L14: Uncertainties are given in parentheses and not quotes, please rephrase.

Corrected.

RC 2.16. L83: Please define 'HALO' if this is an acronym

Agreed. Also defined in the abstract.

RC 2.17. L101: G4201-m should be G2401-m, I believe.

2.17. Indeed. We thank the reviewer for pointing this out.

RC 2.18. L101: 'fulfil' is missing ans 'l'

'Fulfil' is an acceptable form, used primarily in British English. (Oxford Advanced Learner's Dictionary, 7th Edition). We have left it as is.

RC 2.19. ***L115: Please change 'tollerance' to '*****tolerance*****'***

Corrected.

RC 2.20. ***L200: Please change to 'boundary'***

Corrected.

RC 2.21. L222: Please eliminate "when possible" and "when not"

Sentence now reads:

“In order to estimate the background signature, we have used measurements from air samples collected in the immediate vicinity of the target plume, either from the upwind air masses or from outside of the main plume.”

RC 2.22. L244: Change ‘these’ to ‘and’

Modified sentence now reads:

“Data from 51 vertical profiles are available, out of which 21 have simultaneous flask measurements. They are listed in the supplement (Table S1).”

RC 2.23. L253: Change ‘brackets’ to ‘parentheses’

Corrected.

RC 2.24. Figure 2 caption: please define what red/blue shading means. Black crosses are hard to see – perhaps a thicker line would suffice. Altitude should be specified as km ASL.

The caption was updated according to reviewer’s suggestions. The plot was also updated, with the crosses now 20% thicker and 20% larger; a small black dot was added in the centre on the top of the observations (blue line) to exactly define the value for 12.06.2018, where some of the crosses are largely covered by the data series. The width of the blue line was reduced by 30% to further make the crosses more visible. Similar changes were applied to Figure S2.

RC 2.25. L273-275 might be more easily understood if (a)-(d) were noted on Figure 4.

Agreed.

The plot has been updated in the following manner: i) markings for periods a—d were added to the bottom three panels of the plot; ii) units have been changed to mole fractions, consistent with the rest of the manuscript; iii) vertical coordinate label switched to hPa. Caption and manuscript have been adjusted accordingly.

RC 2.26. Figure 5 denotes CH4/CO/CO2 mole fractions as ‘X[ ]’, which is somewhat mis-leading as XCH4/XCO/XCO2 typically denote total-column mole fractions.

We have used a Greek letter χ, which has been used before (instead of c) to denote mole fractions. See e.g. Röckmann et al., 2016. Similar notation was also used in Karion et al., 2013. This has been left as is.

RC 2.27. L369-370: The offsets in the 3-10 km range are actually responsible for the tail.

We have clarified the description:

“Interestingly, the distribution of the mismatch in this altitude range is a positively skewed Gaussian curve (Fig. 6, bottom-right panel), with the values in the main peak almost symmetric around 0 µmol mol^{-1}, and the mean offset in the 3 – 10km range driven by the values in the tail of the distribution.”

RC 2.28. ***Figure 8 caption “For flight no. 7 on the four flasks…” (plural)***

No longer relevant, as this caption has been modified following to RC 1.15.

RC 2.29. Figure S2: Please increase line width for purple crosses, as these are difficult to see.

Figure S2 was updated similar to figure 2 (see RC 2.24 above). The label “TM3” was also replaced with Carboscope / CSc for consistency. The caption was updated accordingly.

References added to the revised manuscript:

Sperlich, P., Uitslag, N. A. M., Richter, J. M., Rothe, M., Geilmann, H., van der Veen, C., Röckmann, T., Blunier, T., and Brand, W. A.: Development and evaluation of a suite of isotope reference gasesfor methane in air, Atmospheric Measurement Techniques, 9, 3717–3737, https://doi.org/10.5194/amt-9-3717-2016, https://www.atmos-meas-tech.net/9/3717/2016/, 2016