

AMT-Discussions: Response to interactive review 1

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 #1,

Review received and published: September 17th, 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.

RC 1.1. This paper presents a nice overview and synthesis of the two kinds of measurements made on the CoMet Aircraft, in-situ continuous and flask measurements, including isotopes. It also presents some analysis of the data, which in my view stretches a bit the goals for this journal, although I have definitely seen this type of thing before in AMT. The conclusion did a nice job of tying things together when really the results cover a lot of different topics, ranging from how well a global model reproduces vertical gradients to the isotopic value of the USCB. Very broad!

We thank the reviewer for this comment. Indeed, we spent quite some time thinking about the appropriate journal. We finally decided to put the measurement results at the core of our study. With this in mind, we thought that the demonstration of the usefulness of our measurements would fit our narrative, and comparison against widely-used state-of-the-art global models provided an excellent opportunity.

Other than that, it is well-written so I have very few editorial remarks below, and a few requests for more explanation of some of the measurement techniques, such as if and how water vapor was removed for the in-situ system.

Details:

RC 1.2. L69 ref to Varon is a satellite paper - this sentence reads as if it is a study using aircraft measurements.

We have moved the sentence in question to a paragraph discussing remote sensing techniques (after the text in L59).

RC 1.3. L94 should read "instruments"

Corrected.

RC 1.4. L115 tolerance

Corrected.

RC 1.5. L117 remove "so-called". I think working tanks is fine on its own.

Agreed.

RC 1.6. L121, were these two cylinders at different values?

Indeed, they were. We've added the information on the mole fractions of the calibration mixtures. Additionally, in L122, a minor correction regarding the length of calibration cycles was introduced. The respective fragment now reads:

"The instrument calibration was monitored during the mission with the use of two reference in-flight cylinders that contained dry mixtures of atmospheric air of known composition, for each tracer at a high and a low mole fraction, namely 373.4 -- 397.4 $\mu\text{mol mol}^{-1}$ for CO_2 , 1661.0 -- 1917.1 nmol mol^{-1} for CH_4 , and 77.4 -- 139.5 nmol mol^{-1} for CO . These were analysed several times during each flight. The calibration cycle consisted of two intervals, each three minutes in length. The first minute of each interval was discarded in subsequent analyses due to pressure equilibration effects within the regulators."

RC 1.7. L 128, to be clear, the data itself was not adjusted for these in-flight calibration runs? Drift was assessed, was any drift found? If so, was it corrected? Why/why not? Were these in-flight calibrations noisier than expected so they were not used (see Karion et al., Long-Term Measurements of GHSs from Aircraft, AMT, 2013, for example)?

Indeed, in-flight calibrations were used exclusively to monitor for drifts. No significant drift was found. The flight-to-flight variation of each low- and high-span measurement during the period prior to the instrument malfunction on June 7th was slightly larger than expected for CO_2 , but not for other gases.

We added the following paragraph to the result section (3.1, approx.. L266 in the revised manuscript) of the manuscript, describing this in more detail:

"Results from in-flight measurements of the two reference cylinders showed no significant drift, however the flight-to-flight variation of each low- and high-span measurement during the period prior to the instrument malfunction on June 7th was slightly larger than expected for CO_2 : low-span measurements varied by 0.10 $\mu\text{mol mol}^{-1}$, 0.4 nmol mol^{-1} , and 1.0 nmol mol^{-1} , while high span measurements varied by 0.14 $\mu\text{mol mol}^{-1}$, 0.3 nmol mol^{-1} , and 0.8 nmol mol^{-1} for CO_2 , CH_4 and CO , respectively. The likely cause for this are the silicon rubber membranes used in the pressure regulators (Filges, 2015), which are known to cause diffusion of CO_2 (Hughes, 1995). Given that species other than CO_2 did not show unexpected behaviour, we did not apply any correction of the measurements resulting from the in-flight measurements of the reference cylinders. For this reason, we also did not apply any correction of drift within each flight, in contrast to the experience of Karion et al. (2013b).

RC 1.8. Was the sample dried prior to measurement by the Picarro? If so, does the calibration gas also pass through the drying system? If not, how was the effect of water vapor removed?

The sample was not dried externally. The water correction was performed based on online measurements of H_2O and followed the procedure described by Filges et al. (2015), which is

consistent with a more recent study from Reum et al. (2019). We have added this information in section 2.2.1. (after L118 in the revised manuscript). It reads:

“The instrument reports dry mole fractions, defined as number of molecules of each species in moles per one mole of dry air, with typical observed ranges expressed in $\mu\text{mol mol}^{-1}$ for CO_2 (equal to one part per million, ppm) and in nmol mol^{-1} for CO and CH_4 (equal to 1 part per billion, ppb). As the collected air was not dried in the sampling line, a water correction was applied based on the online measurements of H_2O mole fraction, following the approach described in previous studies of Filges et al. (2015) and Reum et al. (2019).

RC 1.9. Somewhere in Sec 2 should be mentioned the quantity being measured, i.e. the dry air mole fraction of the species, with the definition that it is the moles of the species per mole of dry air, and define ppm as parts per million, or micromoles of CO_2 per mole of dry air... etc. These are formalities but they are useful so we keep the work accessible and clear.

We have added the short definition in subsection 2.2.1. together with the information on water correction (c.f. RC 1.8. above).

RC 1.10. L145-155, and throughout. Units should all be in metric, I see a lot of inches (") here. Inches I believe should be abbreviated as in. Perhaps give in cm with inches in parentheses?

Agreed, now OD given in mm with inches in parentheses.

RC 1.11. L169- how was this drift discovered, was it by comparing the flask analysed value from the lab with the in-situ system during flight? How big is "significant" (curious)?

The first occurrence of the issue was observed when comparing the flask values against corresponding in situ observations done with JIG. Mean bias between these two was equal to $-9.4 \pm 1.2 \text{ nmol mol}^{-1}$ for flights 1—7 and $-11.0 \pm 2.6 \text{ nmol mol}^{-1}$ for flights 8—9, much larger than expected. For several flask samples analysis repetitions were made after a few days that yielded systematically higher CO results ($1.5 - 3 \text{ nmol mol}^{-1}$ within 2 – 20 days indicating drift rates of up to $1 \text{ nmol mol}^{-1} \text{ d}^{-1}$).

To find the reason for that discrepancy, we have analysed flasks that were not filled during the campaign, which still contained the conditioned air samples from Jena. As the GasLab at MPI-BGC carefully maintains the mole fractions of these conditioning mixtures, we were able to diagnose that indeed the CO values of these flasks were drifting.

Following on these initial results, a lab experiment was performed in early 2019, where 10 flasks were equipped with different configurations of the sealing caps. One of the flasks tested was equipped with the same type of sealing caps as the flask set used during CoMet (namely 7 PCTFE type). It was found that for this type of cap the drift in CO was significantly larger than for those of the regular flask pool used in other field measurements supported by GasLab in Jena (about $2.9 \text{ nmol mol}^{-1} \text{ month}^{-1}$ per cap). No extra effect was observed for other gases.

As the exact reason behind this extra drift couldn't be established, and a precise correction function could not be calculated, we have decided to discard the CO measurements.

We have added some of the extra information to the manuscript in section 2.2.2:

"A significant (approximately 10 nmol mol⁻¹) bias in CO mole fractions was observed when comparing in situ measurements from JIG against gas flasks collected using JAS. Control laboratory experiments run after the campaign have shown that this bias was a result of a growth in CO mole fractions in the period between sample collection and subsequent laboratory analysis. This enhancement of the mole fraction could be attributed to new valve sealing polymer but could not be accurately corrected, therefore we have decided to discard these results. Careful quality control and additional tests did not show any sign of other gases being affected."

RC 1.12. L258: first time a broken mounting is mentioned, earlier it is referred to a roll-out malfunction. Perhaps either give a little detail or keep referring to it as a malfunction? I think a sentence would be nice as to what happened exactly?

Thank you for pointing this out. Detailed description of the malfunctions is given in L134-141. The text (L288 in the revised manuscript) has been clarified and now reads:

"After the malfunction (see section 2.2.1.), i.e. for flights no. 8 and 9, these mean offsets were equal to 0.127 (68) μmol mol⁻¹ and -0.64 (91) nmol mol⁻¹ for the respective gases. While the difference of values as compared to flights 1--7 is statistically significant, it is still close to the WMO compatibility goal.

RC 1.13. L289 and elsewhere, I would think approximately should be spelled out.

Agreed.

RC 1.14. L300 and Section 3.4: I am starting to wonder if AMT is the appropriate forum for his extensive model-data comparison, as we are moving well beyond measurement techniques here.

We thank the reviewer for this remark. Partial answer to that question has been given already in our comment to the initial statement (RC 1.1.).

We would like to further underline that our intention in sections 3.2 – 3.4 was primarily to use the models to assist in interpreting the collected measurements. Thanks to that, we believe we can simultaneously:

- a) Further increase the confidence in our measurement results (e.g. when observing positive or negative peaks in both the model and observations we can with more certainty assume that this is due to large- or regional-scale physical processes rather than equipment issues or local effects)
- b) Better understand the causes behind the observed signals which would then allow us and scientific community in general to improve the measurement strategies for the future campaigns.

These goals can only be achieved if we can trust in the model results, hence a more detailed discussion was necessary. Perhaps the model comparisons included in sections 3.3 and 3.4 might not directly be related to measurement techniques, but we have decided to use this opportunity and expand the discussion, as we believe a mutual benefit for both modelling and observational communities could be thus achieved.

RC 1.15. *Fig 8 These are impressive 3D renderings - this kind of data is difficult to visualize. But I am a little lost - if the plots on the right correspond with the flights on the left, then why are there more points in the Miller-Tans plots than on the left (i.e. the lower should only have 4 points then correct?). Something I am missing here?*

Thank you for that comment. Miller-Tans plot on the right is done using a combined sample set from both flights shown on the left. We have excluded samples collected in higher layers of the atmosphere (above 3 km altitude), as we assumed that they represent an air mass of different origin due to large-scale transport phenomena. Based on the wind analyses and supporting modelling results we assume that we can aggregate both sample sets and treat them as representative of a mean source from the USCB. This is stated in L424-427. Two panels on the Miller-Tans plot are not plotted separately for two measurement days, but present $\delta^2\text{H}$ and $\delta^{13}\text{C}$ values measured in the combined dataset, i.e. each panel contains eight observations.

We have modified the caption of Fig. 8 for further clarification, and also added “data combined” in the panel label. We have also corrected a minor mistake in the data subset description: the altitude threshold for flasks used in Miller-Tans plots was previously given as 4 km; the correct value is 3 km.

The new caption now reads:

“Left: Visualisation of CH_4 measurements over USCB during flights no. 6 (a) and no. 7 (b). For flight no. 7, only data from below 4 km altitude is plotted for clarity. Coloured lines represent mole fractions along the flight path, with the first plotted measurement marked with 'x', triangles show the flask sampling locations. Both in situ and flask mole fractions are coloured using the same scale. c) Miller-Tans model of isotopic source signatures for $\delta^2\text{H}$ and $\delta^{13}\text{C}$, based on eight flask samples collected below 3 km over the USCB during flights no. 6 and 7 together. See text description for details. The dashed line is the linear fit calculated using the Williamson-York formula (Cantrell, 2008). Values of fit parameters are given with 1- σ uncertainty in the parentheses”.

References added to the revised manuscript:

Karion, A., Sweeney, C., Wolter, S., Newberger, T., Chen, H., Andrews, A., Kofler, J., Neff, D., and Tans, P.: Long-term greenhouse gas measurements from aircraft, *Atmospheric Measurement Techniques*, 6, 511–526, <https://doi.org/10.5194/amt-6-511-2013>,

Reum, F., Gerbig, C., Lavrič, J.V., Rella, C.W., Göckede, M., 2019. Correcting atmospheric CO_2 and CH_4 mole fractions obtained with Picarro analyzers for sensitivity of cavity pressure to water vapor. *Atmos. Meas. Tech.* 12, 1013–1027. doi:10.5194/amt-12-1013-2019