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Letter to the Editor of the ACP Manuscript "An estimation of the $^{18}O/^{16}O$ ratio of UT/LMS ozone based on artefact CO in air sampled during CARIBIC flights" *by* S. Gromov and C. A. M. Brenninkmeijer

S. Gromov and C.A.M. Brenninkmeijer

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Dear Dr. Kaiser,

Thank you very much for the prompt answer. Please, find below our answers to your comments. We have prepared the revised version (the pages with mark-up are found at the end of this letter) and included the comments and answers from the last three (4th to 6th) revision iterations, in order to keep the track of the discussion.

With best regards,

S. Gromov and C. A. M. Brenninkmeijer

Comments:

Ed.-6: ***unambiguous:*** *As noted before the term "unambiguous(ly)" implies it is not open to other interpretations, which goes against the grain of scientific principles. If you wanted to make the statement stronger, you could say it's "very likely", maybe even "virtually certain". As you acknowledge yourself in l. 142 "Such sampling-induced mixing renders an unambiguous determination of the artifact source isotope signature rather difficult because neither mixing nor isotope ratios of the admixed air portions are known sufficiently well". And on line 354, you strive "more unambiguous verification". Unambiguous implies 100 % certainty, so it can't be more unambiguous. Would you please revise your manuscript to reflect the actual level of (un)certainty, along the lines suggested above?*

O.K., we will use "very likely" here. However, despite the absolute nature of "unambiguous", common usage doesn't strictly follow that definition. If an inference is stated to be 'less ambiguous' (which is a more commonly used expression), then it should follow that it is equivalently 'more unambiguous'. Although not often, the latter expression is also being commonly used (*cf.* the statistics on using these expressions under http://bit.ly/1AyqStq and http://bit.ly/1AyqXgW, respectively).

Ed.-4: 99: "in NH tropospheric emissions" (otherwise this would be a tautology)

Au.: We see no tautology here. The CO variations result from mixing of the little varying stratospheric [CO] and largely varying tropospheric [CO]. It is the result of mixing we discuss here. Besides, variations in tropospheric [CO] are by far more strongly determined by the presence of hydroxyl radical that by the variations in emissions.

Ed.-5: Would you please clarify how far below 400 nmol/mol this observation holds.

Au.: As stated, this observation holds below 400 nmol/mol, i.e. including tropospheric compositions.

Ed.-6: ***tautology:*** *If, as you say the observations hold for all observations below 400 nmol/mol, i.e. including tropospheric conditions, than this implies the tautological statement "tropospheric CO mixing ratios are largely affected by varying tropospheric [CO]". I agree that OH concentrations in addition to CO emissions affect to emissions affect [CO], so you might want to include both in your revised manuscript. In line with your comment on bins, this should probably be 390 nmol/mol as you don't resolve individual values between 390 and 410 nmol/mol (in Figure 1b, which is the one being discussed in this paragraph).*

In the manuscript we state (ll. 93–95 of the current version):

> This is illustrated in Fig. 1 (a) which presents the LMS CO-O_3 distribution of the C2 *in situ* measurements overlaid with the C1 *in situ* and WAS data.

Which means that we regard LMS compositions (at [O_3] greater than 300 nmol/mol in Fig.1 (a)), not tropospheric ones. We further state (ll. 99−101 of the current version):

> The data exhibit large [CO] variations at [O_3] below 400 nmol/mol that primarily reflect pronounced seasonal variations in the NH tropospheric CO mixing ratio.

Here "The data" implies the LMS CO-O_3 distribution referred to above. Thus, again, we are discussing the LMS CO that is partly influenced by tropospheric compositions, and therefore conclude no tautology to be here. Furthermore, deepening our discussion on what factors cause the variations in tropospheric [CO] (*i.e.* availability of hydroxyl radical, changes in emissions or trop. transport) is beyond the scope of this paper, which is dedicated to the UT/LMS CO. Regarding your last comment, the discussion here has nothing to do with bin alignment – we discuss observed [CO] and [O_3], not the statistics.

Ed.-4: 102: "in C1 and C2 [CO], for [O3] > 400 nmol/mol the C1 CO mixing ratios [...]"

Au.: This comment is unclear to us. We describe continuous changes in [CO] with increasing [O_3], this will change the meaning of the sentence to something we do not intend to state.

Ed.-5: Your response is also unclear to me. If you don't refer to [O3] mole fractions > 400 nmol/mol, perhaps you could clarify what you mean.

Au.: No, we do describe what happens to [CO] *from* 400 nmol/mol onwards, namely that [CO] in C1 *starts* to level off at this O_3 mixing ratio. In the correction you propose, it is not clear *where* (at which [O_3]) above 400 nmol/mol [CO] starts to level off.

*Ed.-6: **O3 mole fractions:** Please change ">" to "≥" in the suggested correction. In line with your comment on bins, this should probably be 390 or 410 nmol/mol, though.*

We prefer to keep the current statement, because the symbol "≥" means "greater or equal", but not "from ... onwards". The statement we use is therefore more precise. Concerning you second comment, the subject has nothing to do with bin alignment here, please note "samples" (l. 104) used.

Ed.-4: 104: "In the 580-600 nmol/mol [O3] bin"

Au.: This comment is unclear to us. We describe to what [CO] in C1 one observes in particular bin (around 580 nmol/mol of [O_3]), this will change the meaning of the sentence to something we do not intend to state.

Ed.-5: Your response is also unclear to me. If you don't refer to the 580-600 nmol/mol bin, perhaps you could clarify what you mean because the data in Fig. 1b (the one you are referring to) are presented in binned format.

Au.: Please look more carefully at Fig. 1 – you may discover that the O_3 bins are defined around multipliers of 20. The bin we are talking about is around 580 nmol/mol, *i.e.* covering 570−590 nmol/mol of [O_3] range. What you suggest spans from the middle of one bin to the middle of the other.

*Ed.-6: **580-600 nmol/mol bin:** Please amend to 570-590 nmol/mol bin, or whichever bin you refer to.*

O.K.

Ed.-4: 160-162: This sentence duplicates the message of the previous one and can be deleted.

Au.: Please explain. The statements “[CO] from WAS and *in situ* measurements correlate well” and “anomalies in both [CO] and $\delta^{18}O(CO)$ manifest functions of $[O_3]$” do not appear duplicate to us.

Ed.-5: I referred to the sentences "However, both anomalies in [CO] and δ18O(CO) manifest clear but complex functions of the concomitant [O3]." and "That is, the C1 in situ and WAS data very likely evidence artefacts pertaining to the O3-driven effect of the same nature."

Au.: We would like (at least here) to keep our own style of communication to the Reader. We believe that the combination of these two sentences emphasises our statement better.

*Ed.-6: **l. 160-162:** I accept that you would like to adopt a level of redundancy, but it is important that the statements are clear and the second sentence is not. If you would like to retain this sentence, please clarify which C1 and WAS data (presumably [CO] and $\delta^{18}O(CO)$?) you refer to and what "of the same nature" refers to.*

“Of the same nature” means “the same” here, we believe there is no other interpretation. We reformulate this sentence as follows:

> That is, the C1 *in situ* and WAS [CO] and $\delta^{18}O(CO)$ data very likely evidence artefacts pertaining to the same O_3-driven effect.

Ed.-4: 223: Please delete "Practically" and change "resort" to "use". The Keeling plot itself does _not_ require an estimate of [CO]_c; however, your data selection criterion (for delta_true) does. Please change this sentence accordingly.

Auth.: Perhaps, the Editor has misunderstood the message of the sentence. Here we emphasise that we can employ the MM using solely the estimate of the contamination strength (*i.e.*, the amount of molecules admixed to the reservoir with some initial composition). Furthermore, do you imply that using the Keeling plot one does not require to know the amount of molecules admixed into a reservoir with known starting composition? (It obviously would be nonsense, of course, perhaps we did not understand your comment?)

Ed.-5: Indeed, the Keeling plot does not require an estimate of $[CO]_c$.

Auth.: This is strange to hear from an isotope scientist. $[CO]_c$ here is essentially the amount of molecules by which the reservoir changes, and knowing which one is able to explain (differentially) concomitant changes in isotope ratios. Imagine you observe changes in $\delta^{13}C(CO_2)$ value without tracing the concomitant changes in $[CO_2]$, then what information you get and how can you use the Keeling plot at all?

We do select samples with (nearly) identical initial composition (at least, mixing ratio) – this is one of the requirements of the Keeling plot approach. To select these we use (nearly) identical $[CO]_t$ (derived through $[CO]_a$ and $[CO]_c$). We further look at the changes to $\delta^{18}O(CO)$ with respect to greater or smaller artefact input, *i.e.* at the constant $[CO]_t$, whilst $[CO]_c$ varies. In a conventional application of the Keeling plot $[CO]_t$ is an equivalent of the “background” reservoir, whilst $[CO]_c$ is the admixed portion (“emission”) of the molecules. These are basics of applying isotope mass-balancing calculations which, we believe, do not have to be specifically emphasised – in contrast to what the Editor proposes for l. 223.

*Ed.-6: **Keeling plot (l. 223 and 348):** As you can see in Keeling (1958), he only measured the CO2 mole fraction and $\delta^{13}C(CO2)$, not the mole fraction of added CO2. Could you please change the sentence to reflect the use of the added selection criterion for the range of samples you apply the Keeling plot to? I also noted an additional error that appeared between versions 4 and 5 of the manuscript: [CO]c in the numerator of Eq. (4) should instead be [CO]t.*

Keeling (1958) The concentration and isotopic abundances of atmospheric carbon dioxide in rural areas. Geochim. Cosmochim. Acta 13, 322-334

We believe the Editor and the Authors face rather a perceptual difference of how one applies the Keeling approach than a conceptual one. The description of the Keeling plot (on ll. 228–237) is conventional now, as was requested by one Reviewer and the Editor in previous reviewing iterations. We detail the selection criteria subsequently on ll. 237–239, and do not find any reason why it should be introduced earlier once more. The typo in Eq. (4) has occurred during multiple edits and is now corrected.

Ed.-4: 253: The symbol 13delta_c has not been defined. For consistency, this should be delta13C_c(CO), or, following conventional symbol and index notation, delta_c(13C, CO).

Au.: The Editor contradicts himself here. In the previous version of the manuscript we used a consistent notation using indices to distinguish δ_c for ^{13}C and ^{18}O, which the Editor requested to remove (see the comment on l. 227 of the previous version). Since distinguishing different δ_c, δ_a and δ_t variables is obviously necessary we return to the previous notation, *e.g.* $^{13}\delta_c$ and $^{18}\delta_c$.

Ed.-5: There is no contradiction. The distinguishing indices are not necessary for the equations. However, your adopted delta notation for specific isotope deltas is $\delta^{13}C$, not $^{13}\delta$. There does not appear to be any reason to adopt different notations in the same manuscript, so I suggest to use $\delta^{13}C_c(CO)$.

Au.: We would like to specifically distinguish *measured isotope compositions* (*e.g.* $\delta^{18}O(CO)$) from the *variables used in calculations* with the MM, *e.g.* $^{18}\delta_t$, $^{13}\delta_a$ $^{13}\delta_c$. Applying the notation you propose makes them less distinguishable, furthermore the indices appear to pertain to element symbols, *i.e.* the Reader may stumble on what all C_c, C_a, O_t, O_c, *etc.* imply. Finally, the formulae (and manuscript itself) become more cumbersome, hence less easy to follow. We thus prefer to keep current notation.

*Ed.-6: **Notation (l. 253, Fig. 6 and elsewhere):** I suggested a notation that avoids the appearance of Cc, Ca, Ot, Oc, e.g. $\delta^{13}C(CO, c)$. The notation should be consistent, not distinguishable because it is confusing to use different samples for the same quantity. If you need to distinguish further between measure and modeled isotope deltas, you could use additional labels, e.g. $\delta^{13}C(CO, m)$. However, I don't think this is necessary because you actually use the measured concentrations in the mixing calculations.*

O.K.

An estimation of the $^{18}O/^{16}O$ ratio of UT/LMS ozone based on artefact CO in air sampled during CARIBIC flights

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Abstract

An issue of O_3-driven artefact production of CO in the upper troposphere/lowermost stratosphere (UT/LMS) air analysed in the CARIBIC−1 project is being discussed. By confronting the CO mixing and isotope ratios obtained from different analytical instrumentation, we (i) reject natural/artificial sampling and mixing effects as possible culprits of the problem, (ii) ascertain the chemical nature and quantify the strength of the contamination, and (iii) demonstrate successful application of the isotope mass-balance calculations for inferring the isotope composition of the contamination source. The $\delta^{18}O$ values of the latter indicate the oxygen very likely being inherited from O_3. The $\delta^{13}C$ values hint at reactions of trace amounts of organics with stratospheric O_3 that could have yielded the artificial CO. While the exact contamination mechanism is not known, it is clear that the issue pertains only to the earlier (first) phase of the CARIBIC project. Finally, estimated UT/LMS ozone $\delta^{18}O$ values are lower than those observed in the stratosphere within the same temperature range, suggesting that higher pressures (240−270 hPa) imply lower isotope fractionation controlling the local $\delta^{18}O(O_3)$ value.

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1 Introduction

[1] Accurate determination of the atmospheric carbon monoxide (CO) content based on the collection of air samples depends on the preservation of the mixing ratio of CO inside the receptacle, from the point of sampling to the moment of physicochemical analysis in a laboratory. A well known example in our field of research is the filling of pairs of glass flasks at South Pole

2.2 On-line instrumentation

[6] In addition to the WAS collection systems, both C1 and C2 measurement setups include different instrumentation for on-line detection of [CO] and [O_3] (hereinafter the squared brackets [] denote the mixing ratio of the respective species). *In situ* CO analysis in C1 is done using a gas chromatography (GC)-reducing gas analyser which provides measurements every 130 s with an uncertainty of ±3 nmol/mol (Zahn *et al.*, 2000). In C2, a vacuum ultraviolet fluorescence (VUV) instrument with lower measurement uncertainty and higher temporal resolution of ±2 nmol/mol in 2 s (Scharffe *et al.*, 2012) is employed. Furthermore, the detection frequency for O_3 mixing ratios has also increased, *viz.*, from 0.06 Hz in C1 to 5 Hz in C2 (Zahn *et al.*, 2002; Zahn *et al.*, 2012).

2.3 Results

[7] When comparing the CO mixing ratios in relation to those of O_3 for C1 and C2, differences are apparent in the LMS, where C2 [CO] values are systematically lower. This is illustrated in Fig. 1 (a) which presents the LMS CO-O_3 distribution of the C2 *in situ* measurements overlaid with the C1 *in situ* and WAS data. The entire C1 CO/O_3 dataset is presented in Fig. 2. For the *in situ* CO datasets we calculated the statistics (Fig. 1 (b)) of the samples with respective O_3 mixing ratios clustered in 20 nmol/mol bins, *i.e.* the median and spread of [CO] as a function of [O_3] analysed. The interquartile range, IQR, is used in the current analysis as a robust measure of the data spread instead of the standard deviation. The data exhibit large [CO] variations at [O_3] below 400 nmol/mol that primarily reflect pronounced seasonal variations in the NH tropospheric CO mixing ratio. With increasing [O_3], [CO] decreases to typical stratospheric values, and its spread reduces to mere 3.5 nmol/mol and less, as [O_3] surpasses 500 nmol/mol. Despite the comparable spread in C1 and C2 [CO], from 400 nmol/mol of [O_3] onwards the C1 CO mixing ratios start to level off, with no samples below 35 nmol/mol having been detected, whereas the C2 levels continuously decline. By the 570−590 nmol/mol O_3 bin, C1 [CO] of $39.7^{+0.7}_{-1.3}$ nmol/mol contains some extra 14 nmol/mol compared to $25.6^{+1.2}_{-1.1}$ nmol/mol typical for C2 values. Overall, at [O_3] above 400 nmol/mol the conspicuously high [CO] is marked in about 200 *in situ* C1 samples, of which 158 and 69 emerge as statistically significant mild and extreme outliers, respectively, when compared against the number of C2 samples ($n > 3 \cdot 10^5$). The conventions here follow Natrella (2003), *i.e.* ±1.5 and ±3 IQR ranges define the inner and outer statistical fences (ranges outside which the data points are considered mild and extreme outliers) of the C2 [CO] distribution in every O_3 bin, respectively. The statistics include the

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[10] Differences between the WAS and *in situ* measured [CO] – a possible indication that the $\delta^{18}O(CO)$ contamination pertains specifically to the WAS data – average at $\overline{\Delta}$(WAS−*in situ*) = (5.3±0.2) nmol/mol (±1 standard deviation of the mean, $n = 408$) and happen to be random with respect to any operational parameter or measured characteristic in C1, *i.e.* irrespective of CO or O_3 abundances. The above mentioned discrepancy remained after several calibrations between the two systems had been performed, and likely results from the differences in the detection methods, drifts of the calibration standards used (see details in Brenninkmeijer *et al.*, 2001) and a short-term production of CO in the stainless steel tanks during sampling. The large spread of Δ(WAS−*in situ*) of ±3.5 nmol/mol (±1σ of the population) ensues from the fact that the *in situ* sampled air corresponds to (2−4)% of the concomitantly sampled WAS volume, as typically 6−7 *in situ* collections of 5 s were made throughout one tank collection of 17−21 min. The integrity of the WAS CO is further affirmed by the unsystematic distribution of the artefact compositions among tanks (in contrast to that for $\delta^{18}O(CO_2)$ in C1 discussed by Assonov *et al.*, 2009). Overall, the WAS and *in situ* measured CO mixing ratios correlate extremely well (adj. $R^2 = 0.972$, slope of 0.992±0.008 (±1σ), $n = 408$). However, both anomalies in [CO] and $\delta^{18}O(CO)$ manifest clear but complex influences of the concomitant [O_3]. That is, the C1 *in situ* and WAS [CO] and $\delta^{18}O(CO)$ data very likely evidence artefacts pertaining to the same O_3-driven effect. Below we discuss and quantify these influences.

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3 Discussion

[11] Three factors may lead to the (artefact) distributions seen for C1 *in situ* [CO] at LMS O_3 mixing ratios, namely:

[12] (i) Strong (linear) natural mixing, such as enhanced stratosphere-troposphere exchange (STE), when a [CO] outside the statistically expected range results from the integration of air having dissimilar ratios of the tracers' mixing ratios, *viz.* [O_3]:[CO]. For example, mixing of two air parcels in a 16%:84% proportion (by moles of air) with typical [O_3]:[CO] of 700:24 (stratospheric) and 60:125 (tropospheric), respectively, yields an integrated composition with [O_3]:[CO] of 598:40 which indeed corresponds to C1 data (this case is exemplified by the mixing curve in Fig. 1). Nonetheless, occurrences of rather high stratospheric CO mixing ratios (in our case, 40 nmol/mol at the concomitant [O_3] of 500−600 nmol/mol compared to the typical 24−26 nmol/mol) are rare. For instance, a deep STE similar to that described by Pan *et al.* (2004) was observed by C2 only once (*cf.* the outliers at [O_3] of 500 nmol/mol in Fig. 1), whereas the C1 outliers were exclusively registered in some 12 flights during

ments in a regression analysis (detailed in Appendix A), we quantify the artefact component $[CO]_c$ being chiefly a function of O_3 mixing ratio as

$$[CO]_c = b\cdot[O_3]^2,\ b = (5.19\pm0.12)\cdot10^{-5}\ [\mathrm{mol/nmol}], \qquad (1)$$

which is equivalent to 8−18 nmol/mol throughout the respective $[O_3]$ range of 400−620 nmol/mol (see Fig. 1 (d)). Subtracting this artefact signal yields the corrected *in situ* C1 CO−O_3 distribution conforming to that of C2 (*cf.* red symbols in Fig. 1 (a)).

[15] Importantly, since we can quantify the contamination strength using only the O_3 mixing ratio, the continuous *in situ* C1 $[O_3]$ data allow estimating the integral artefact CO component in each WAS sample and, if the isotope ratio of contaminating O_3 is known, to derive the initial $\delta^{18}O(CO)$. The latter, as it was mentioned above, is subject to strong sample-mixing effects, which is witnessed by $\delta^{18}O(CO)$ outliers even at relatively high [CO] up to 100 nmol/mol. Accounting for such cases is, however, problematic since it is necessary to distinguish the proportions of the least modified (tropospheric) and significantly affected (stratospheric) components in the resultant WAS sample mix. Since this information is not available, we applied an *ad hoc* correction approach, as described in the following. This approach is capable of determining the contamination source (*i.e.*, O_3) isotope signature as well.

3.1 Contamination isotope signatures

[16] We use the differential mixing model (MM, originally known as the “Keeling-plot”), because it requires only the estimate of the artefact component mixing ratio, but no assumptions on the (unknown) shares and isotope signatures of the air portions mixed in a given WAS tank. The MM parameterises the admixing of the portion of artefact CO to the WAS sample with the "true" initial composition, as formulated below:

$$[CO]_a = [CO]_t + [CO]_c\ , \qquad (2)$$

$$ {}^i\delta_a\,[CO]_a = {}^i\delta_t\,[CO]_t + {}^i\delta_c\,[CO]_c\ , \qquad (3)$$

where indices a, c and t distinguish the mixing ratios and isotope compositions ${}^i\delta$ (${}^{18}\delta$ and ${}^{13}\delta$ for ^{13}C and ^{18}O, respectively) pertaining to the analysed sample, estimated contamination and “true” composition sought (*i.e.*, $[CO]_t$ and ${}^i\delta_t$), respectively. Here the contamination strength $[CO]_c$ is derived by integrating Eq. (1) using the *in situ* C1 $[O_3]$ data for each WAS sample. By rewriting the above equation with respect to the isotope signature of the analysed CO, one obtains:

$$ {}^i\delta_a = {}^i\delta_c + ({}^i\delta_t - {}^i\delta_c)\,[CO]_t/[CO]_a\ , \qquad (4)$$

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