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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).

Please note that we return to the original (*i.e.*, that of the first revised manuscript) formulation of the Abstract (ll. 8−9), namely we use "unambiguously indicate", which is not a claim of proof.

We appreciate very much the time you spent for editing this paper.

With kind regards,

S. Gromov and C. A. M. Brenninkmeijer

Comments:

The revised discussion of the contamination correction is basically acceptable now. However, you derive it in terms of number densities, which are pressure-dependent, but then use a parameterization in terms of mole fractions, which are not. You justify this as being "for convenience", but this appears to be a fundamental difference of physical quantities because the terms on the two sides of equation (A4) depend linearly on pressure ({CO}) and quadratically on pressure ({O3}^2). The corresponding parameterization in terms of mole fractions is not subject to these differences. Could you please address this in a further revision?

Thank you, this is a valid point. The regarded statement implies that we derive *b* at the air density corresponding to the C1 sampling conditions (which varies little, see our previous letter, answer to the comment on *1)*). We explicate this in the reformulated statement:

> "...; here the value of *b* in mole fraction units is derived using the air density at C1 sampling conditions for relating fitted $[CO]_c$ and observed $[O_3]^2$)."

99: "in NH tropospheric emissions" (otherwise this would be a tautology)

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.

Would you please clarify how far below 400 nmol/mol this observation holds.

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

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

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.

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.

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.

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

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.

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.

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.

105: "accommodates and extra 14 nmol/mol"

Here we meant that this [CO] contains extra 15 nmol/mol as compared to average C2 value. We adjust the statement accordingly.

Thank you for changing "accommodates" to "contains", but the difference between 39.7 and 25.6 is 14.1, which is not "some extra 15". I suggest you change this to "contains an extra 14 nmol/mol".

We change it to “some extra 14 nmol/mol”.

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

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

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."

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.

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.

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?)

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

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 δ^{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.

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).

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 ${}^{18}\delta_c$.

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 $\delta^{13}C_c(CO)$.

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.

348: Add "in combination with an empirical parameterisation of the [CO] artefact in terms of the O3 mixing ratio" after brackets, followed by "to single out ..."

We would like to keep the current formulation, as we already make a statement above (ll. 345−346) on the quantification of the artefact CO production.

A simple Keeling plot does not require a data selection criterion. The mixing effects are presumably the reason a Keeling plot without data selection fails, so the sentence does not some qualifying statement.

We do not understand the last statement ("..., so the sentence does not some qualifying statement."). The first statement is something we do not intend to put into conclusions – a Reader concerned with this particularity will find all necessary information in Sect. 3. Finally, none of these (pink) statements have anything with the statement the Editor proposed earlier for l. 348, and which we have declined. We thus would like to leave this sentence unchanged.

Fig. 6: The x-axis label should be "MM", not MMA. The legend labels should be delta18O_c(O3) and delta13C_c(O3); also in the caption.

We change the labels to ${}^{18}\delta_c$ and ${}^{13}\delta_c$, respectively, that are clearly associated with calculations with the MM. This also allows to avoid somewhat confusing $\delta^{13}C_c(O_3)$ (the carbon isotope ratio from O_3 makes no sense here).

Please be consistent with your notation and use $\delta^{13}C_c(CO)$ and $\delta^{18}O_c(CO)$. The suggestion to use O3 was a mistake.

See our answer to the comment concerning l. 253 above.

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 unambiguously indicate the oxygen 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

yet covered by specific measurements. The air samples we examine in this study were collected onboard a passenger aircraft carrying an airfreight container with analytical and air/aerosol sampling equipment on long distance flights from Germany to South India and the Caribbean within the framework of the CARIBIC project (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container, http://www.caribic-atmospheric.com).

2 Experimental and results

2.1 Whole air sampling

[4] CARIBIC−1 (Phase #1, abbreviated hereafter "C1") was operational from November 1998 until April 2002 using a *Boeing* 767-300 ER operated by LTU International Airlines (Brenninkmeijer *et al.*, 1999). Using a whole air sample (WAS) collection system, twelve air samples were collected per flight (of 8−10 hours duration at cruise altitudes of 10−12 km) in stainless steel tanks for subsequent laboratory analysis of the mixing ratios (*i.e.* mole fractions) of various trace gases, including ^{14}CO. Large air samples were required in view of the ultra-low number density of this mainly cosmogenic tracer (10−100 molecules cm^{-3} standard temperature and pressure (STP), about 0.4−4 amol/mol). Hereinafter STP denotes dry air at 273.15 K, 101325 Pa. Each C1 WAS sample (holding 350 litres of air STP) was collected over 15−20 min intervals representing the number density-weighted average of the compositions encountered along flight segments of about 250 km. The overall uncertainty of the measured WAS CO is less than ±1% for the mixing ratio and ±0.1‰/±0.2‰ for δ^{13}C(CO)/δ^{18}O(CO), respectively (Brenninkmeijer, 1993; Brenninkmeijer *et al.*, 2001). Isotope compositions are reported throughout this manuscript using the so-called delta value $\delta = (R/R_{\text{st}}-1)$ relating the ratio R of rare (^{13}C, ^{18}O or ^{17}O) over abundant isotopes of interest to the standard ratio R_{st}. These are Vienna Standard Mean Ocean Water (VSMOW) for ^{18}O/^{16}O (Gonfiantini, 1978; Coplen, 1994) and ^{17}O/^{16}O (Assonov and Brenninkmeijer, 2003), and Vienna Pee Dee Belemnite (VPDB) for ^{13}C/^{12}C (Craig, 1957), respectively. As we mention above, the oxygen isotope composition of the CO present in these WAS samples was corrupted, in particular when O_3 levels were as high as 100−600 nmol/mol.

[5] CARIBIC−2 (Phase #2, referred to as "C2") started operation in December 2004 with a Lufthansa *Airbus* A340-600 fitted with a new inlet system and air sampling lines, including perfluoroalkoxy alkane (PFA) lined tubing for trace gas intake (Brenninkmeijer *et al.*, 2007). No flask CO mixing/isotope ratio measurements are performed in C2.

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 580 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 samples in bins with average

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adj. $R^2 = 0.83$, red. $\chi^2 = 4.0$; here the value of b in mole fraction units is derived using the air density at C1 sampling conditions for relating fitted $[\mathrm{CO}]_c$ and observed $[\mathrm{O_3}]^2$). At last, we ascertain that the best regression results are obtained particularly at $\kappa = 2$, as indicated by the regression statistic (R^2 and χ^2) that asymptotically improves when a set of regressions with neighbouring (*i.e.* below and above 2) integer values of κ is compared. The low uncertainty (within ±3%) associated with the estimate of b confirms an exclusive dependence of the contamination source on the O_3 mixing ratio, as well as much similar reaction times τ_c. The regressed value of $[\mathrm{CO}]_c$ as a function of $[\mathrm{O_3}]$ is presented in Fig. 1 (d) (solid line). It is possible to constrain the overall yield $\lambda_{\mathrm{O_3}}$ of CO molecules in the artefact source chain to be between 0.5 and 1, comparing the magnitude of $[\mathrm{CO}]_c$ to the discrepancy between the $[\mathrm{O_3}]$ measured in C1 and C2 (±20 nmol/mol, taken equal to the $[\mathrm{O_3}]$ bin size owing to the N_2O–O_3 and H_2O–O_3 distributions matching well between the datasets). Lower $\lambda_{\mathrm{O_3}}$ values, otherwise, should have resulted in a noticeable (*i.e.*, greater than 20 nmol/mol) decrease in the C1 O_3 mixing ratios with respect to the C2 levels.

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Appendix B. Corrections to measured δ^{13}C(CO) values due to the oxygen MIF

[27] Atmospheric O_3 carries an anomalous isotope composition (or mass-independent fractionation, MIF) with a substantially higher relative enrichment in ^{17}O over that in ^{18}O (above +25‰ in $\Delta^{17}\mathrm{O} = (\delta^{17}\mathrm{O}+1)/(\delta^{18}\mathrm{O}+1)^{\beta}-1$, $\beta = 0.528$) when compared to the majority of terrestrial oxygen reservoirs that are mass-dependently fractionated (*i.e.*, with Δ^{17}O of 0‰) (see Brenninkmeijer *et al.* (2003) and refs. therein). CO itself also has an unusual oxygen isotopic composition, possessing a moderate tropospheric MIF of around +5‰ in Δ^{17}O(CO) induced by the sink KIEs in reaction of CO with OH (Röckmann *et al.*, 1998b; Röckmann *et al.*, 2002) and a minor source effect from the ozonolysis of alkenes (Röckmann *et al.*, 1998a; Gromov *et al.*, 2010). A substantial contamination of CO by O_3 oxygen induces proportional changes to Δ^{17}O(CO) that largely exceed its natural atmospheric variation. On the other hand, the MIF has implications in the analytical determination of δ^{13}C(CO), because the presence of C^{17}O species interferes with the mass-spectrometric measurement of the abundances of ^{13}CO possessing the same basic molecular mass (m/z is 45). When inferring the exact C^{17}O/C^{18}O ratio in the analysed sample is not possible, analytical techniques usually involve assumptions (*e.g.*, mass-dependently fractionated compositions or a certain non-zero Δ^{17}O value) with respect to the C^{17}O abundances (Assonov and Brenninkmeijer, 2001). In effect for the C1 CO data, the artefact CO produced