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 your comments. Please, find below our answers. 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 (4th to 7th) revision iterations, in order to keep the track of the discussion. We believe at this stage the manuscript has reached its best shape, owing to your indefatigable industry.

With best regards,

S. Gromov and C. A. M. Brenninkmeijer

Comments:

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 [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).

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

This is illustrated in Fig. 1 (a) which presents the LMS CO-O₃ distribution of the C₂ in situ measurements overlaid with the C₁ in situ and WAS data.

Which means that we regard LMS compositions (at [O₃] 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 [O₃] below 400 nmol/mol that primarily reflect pronounced seasonal variations in the NH tropospheric CO mixing ratio.

Here “The data” implies the LMS CO-O₃ 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 [O₃], not the statistics.

Ed.-7: l. 99-100: Please change this to “The LMS data exhibit large [CO] variations for [O₃] between 300 and 400 nmol mol⁻¹, which primarily reflect ...”

Corrected.
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 [O3], 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 O3 mixing ratio. In the correction you propose, it is not clear where (at which [O3]) above 400 nmol/mol [CO] starts to level off.

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

Au.: We prefer to keep the current statement, because the symbol "\(\geq\)" 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.-7: l. 103: "from ... onwards" has no mathematical meaning. If you don't like mathematical symbols such as "\(\geq\)", please change this to "for [O3] greater than or equal to 400 nmol/mol" or "for [O3] greater than 400 nmol/mol" (depending on what you mean).

Please, explicate what is wrong with the sentence we propose. Strictly speaking, "for [O3] greater than or equal to 400 nmol/mol" implies any mixing ratio greater that 400 nmol/mol, e.g. the effect can manifest itself at 1000 nmol/mol or higher; furthermore this expression does not support continuity we imply, e.g. that the effect is continuously present starting from a certain mixing ratio towards higher ones. Interpreted this way, the expression "from ... onwards" actually has mathematical meaning. We therefore insist on keeping the current formulation.

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 [O3]), 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 O3 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 [O3] 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.

Au.: O.K.

Ed.-7: l. 105: This correction has still not been fully implemented. Please change to "In the 570−590 nmol/mol [O3] bin ..."

This correction has been implemented in the latest version (cf. acp-2014-598-manuscript-version7.pdf). Perhaps, you are referring to an earlier version?
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 δ13C(CO2) value without tracing the concomitant changes in [CO2], 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]c (derived through [CO]t and [CO]a). We further look at the changes at δ16O(CO) with respect to greater or smaller artefact input, i.e. at the constant [CO]a, whilst [CO]t varies. In a conventional application of the Keeling plot [CO]t is an equivalent of the “background” reservoir, whilst [CO]a 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 δ13C(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.


Au.: 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.-7: This sentence is still wrong. Please change this to "We use a differential mixing model (MM, originally known as the “Keeling-plot”) in combination with the parameterisation of the artefact CO component (Eq. 1) to derive the isotopic composition of artefact CO component. This approach makes no assumptions on the isotopic signatures of CO in the air portions mixed in a given WAS tank.

O.K., we will replace it according to you kind suggestion.

Ed.-4: 253: The symbol δ13C_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 δc for 13C and 18O, which the Editor requested to remove (see the comment on l. 227 of the previous version). Since distinguishing different δc, δa and δt variables is obviously necessary we return to the previous notation, e.g. 13δc, 18δc and 18δt.

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 δ13C, not 13δ. There does not appear to be any reason to adopt different notations in the same manuscript, so I suggest to use δ13C_c(CO).

Au.: We would like to specifically distinguish measured isotope compositions (e.g. δ16O(CO)) from the variables used in calculations with the MM, e.g. 18δt, 13δt, 13δc. 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 Cc, Ca, Ot, Oc, 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. δ13C(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. δ13C(CO, m). However, I don’t think this is necessary because you actually use the measured concentrations in the mixing calculations.

Au.: O.K.

Ed.-7: Your "ok" in the Author Response is not reflected by corresponding changes in the manuscript. Please delete the indices "i" from the delta symbols where they occur in this part of the manuscript [as you had already done in version 4 of the manuscript]. Please change delta_a to delta_a(CO), delta_t to delta_t(CO) and delta_c to delta_c(CO) [with _a, _t, _c standing for subscript indices], for consistency with the notation used in the remainder of the manuscript. Please also explain that delta13C(CO) and delta18O(CO) are equal to delta13C_a(CO) and delta18O_a(CO), respectively.

l. 249, 259, 264, 275, 295, 296, 306, 310, 628, 629: Please change to delta18O_c(CO), for consistency with the notation used in the remainder of the manuscript.

l. 250, 255, 261, 303, 628: Please change to delta13C_c(CO), for consistency with the notation used in the remainder of the manuscript.

Our apologies, we have interpreted this comment as your kind suggestion only. We find, however, that notations "δ18O_t(CO)" or "δ13C(CO, m)" are as much ambiguous as "18δ_t" (originally "18Oδ_t") we propose. We expect the Reader to comprehend "18" referring to the 18O isotope, but what should "18O_t" mean? The element O_t? Ultimately, we are perplexed with what does the notation issue has to do with the content communicated by the manuscript? Do the symbols we propose really impede the Reader to understand the content, or rather it goes against personal aesthetic preferences of the Editor?

To finally resolve this issue we propose another solution that we believe will satisfy both the Editor and the Authors and spare them from further revisions. Employing the delta-notation in a rather general way, we refrain from using any indices with it, in turn distinguishing with indices the various CO components δ is being applied to. That is, instead of former [CO], and 18δ, denoting the mixing and 18O/16O isotope ratio of the contamination component, we use [CO_c] and δ18O(CO_c), respectively, and so on. We agree to remove the index ‘a’ since COa in effect doubles CO indeed. The changes have been introduced throughout the manuscript and also to the Figs. 1, 5 and 6.

Ed.-7: l. 228 etc.: The indices a, c and t should be written in upright (roman) font, not italics. Italic font is reserved for physical quantity symbols.

l. 229: Please change "isotope compositions" to "isotope deltas" or "delta values" or "relative isotope ratio differences".

Corrected.

Ed.-7: l. 231 and 236: Please change "composition" to "isotope delta" or "delta value" or "relative isotope ratio difference".

We refer here to both, mixing and isotope, ratios, so we believe using “composition” is justified.
2.2 On-line instrumentation

In addition to the WAS collection systems, both C1 and C2 measurement setups include different instrumentation for on-line detection of [CO] and [O₃] (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 O₃ 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

When comparing the CO mixing ratios in relation to those of O₃ 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-O₃ distribution of the C2 in situ measurements overlaid with the C1 in situ and WAS data. The entire C1 CO/O₃ dataset is presented in Fig. 2. For the in situ CO datasets we calculated the statistics (Fig. 1 (b)) of the samples with respective O₃ mixing ratios clustered in 20 nmol/mol bins, i.e. the median and spread of [CO] as a function of [O₃] 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 LMS data exhibit large [CO] variations for [O₃] between 300 and 400 nmol/mol, which primarily reflect pronounced seasonal variations in the NH tropospheric CO mixing ratio. With increasing [O₃], [CO] decreases to typical stratospheric values, and its spread reduces to mere 3.5 nmol/mol and less, as [O₃] surpasses 500 nmol/mol. Despite the comparable spread in C1 and C2 [CO], from 400 nmol/mol of [O₃] 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 O₃ bin, C1 [CO] of 39.7±0.7 nmol/mol contains some extra 14 nmol/mol compared to 25.6±1.1 nmol/mol typical for C2 values. Overall, at [O₃] 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 > 3·10⁶). The conventions here follow Natrelle (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 O₃ bin, respectively. The statistics include
ments in a regression analysis (detailed in Appendix A), we quantify the artefact component $\text{CO}_c$ being chiefly a function of $\text{O}_3$ mixing ratio as

$$[\text{CO}_c] = b \cdot [\text{O}_3]^2, \quad b = (5.19 \pm 0.12) \cdot 10^{-5} \ [\text{mol/nmol}], \quad (1)$$

which is equivalent to 8–18 nmol/mol throughout the respective $[\text{O}_3]$ range of 400–620 nmol/mol (see Fig. 1 (d)). Subtracting this artefact signal yields the corrected in situ $\text{C}_1 \text{CO}--\text{O}_3$ distribution conforming to that of $\text{C}_2$ (cf. red symbols in Fig. 1 (a)).

Importantly, since we can quantify the contamination strength using only the $\text{O}_3$ mixing ratio, the continuous in situ $\text{C}_1 [\text{O}_3]$ data allow estimating the integral artefact $\text{CO}$ component in each WAS sample and, if the isotope ratio of contaminating $\text{O}_3$ is known, to derive the initial $\delta^{18}\text{O}(\text{CO})$. The latter, as it was mentioned above, is subject to strong sample-mixing effects, which is witnessed by $\delta^{18}\text{O}(\text{CO})$ outliers even at relatively high $[\text{CO}]$ 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., $\text{O}_3$) isotope signature as well.

### 3.1 Contamination isotope signatures

We use the differential mixing model (MM, originally known as the “Keeling-plot”) in combination with the parameterisation of the artefact $\text{CO}$ component (Eq. (1)) to derive the isotope composition of the latter. This approach makes no assumptions on the isotope signatures of $\text{CO}$ in the air portions mixed in a given WAS tank. The MM parameterises the admixing of the portion of artefact $\text{CO}$ to the WAS sample with the "true" initial composition, as formulated below:

$$[\text{CO}] = [\text{CO}_t] + [\text{CO}_c], \quad (2)$$

$$\delta(\text{CO}) / [\text{CO}] = \delta(\text{CO}_t) / [\text{CO}_t] + \delta(\text{CO}_c) / [\text{CO}_c], \quad (3)$$

where indices $c$ and $t$ distinguish the components pertaining to the estimated contamination and "true" composition sought (i.e., $[\text{CO}_c]$ and $\delta(\text{CO}_c)$), respectively. Here the contamination strength $[\text{CO}_c]$ is derived by integrating Eq. (1) using the in situ $\text{C}_1 [\text{O}_3]$ data for each WAS sample. By rewriting the above equation with respect to the isotope signature of the analysed $\text{CO}$, one obtains:

$$\delta(\text{CO}) = \delta(\text{CO}_t) + (\delta(\text{CO}_c) - \delta(\text{CO}_t)) [\text{CO}_c] / [\text{CO}_t], \quad (4)$$
which signifies that linear regression of $\delta$(CO) as a function of the reciprocal of [CO] yields the estimated contamination signature $\delta$(CO) at ([CO]$^{-1}$ $\rightarrow$ 0 when invariable "true" compositions ([CO], $\delta$(CO)) are taken (the Keeling plot detailing these calculations is shown in Fig. 5). We therefore apply the MM described by Eq. (4) to the subsets of samples picked according to the same reckoned [CO] (within a ±2 nmol/mol window, n > 7). Such selection, however, may be insufficient: Due to the strong sampling effects in the WAS samples (see previous Section), it is possible to encounter samples that integrate different air masses to the same [CO] but rather different average $\delta$(CO). The solution in this case is to refer to the goodness of the MM regression fit, because the $R^2$ intrinsically measures the linearity of the regressed data, i.e. closeness of the “true” values in a regarded subset of samples, irrespective of underlying reasons for that.

[17] Higher $R^2$ values thus imply higher consistency of the estimate, as demonstrated in Fig. 6 showing the calculated $\delta$(CO) for [CO] below 80 nmol/mol as a function of the regression $R^2$. The latter decreases with greater [CO] (i.e., larger sample subset size, since tropospheric air is more often encountered) and, correspondingly, larger variations in $\delta$(CO). Ultimately, at lower $R^2$ the inferred $\delta^{18}$(CO) converge to values slightly above zero expected for uncorrelated data, i.e. C1 $\delta^{18}$(CO) tropospheric average. A similar relationship is seen for the $\delta^{13}$(CO) values (they converge around −28‰), however, there are no consistent estimates found ($R^2$ is generally below 0.4). Since such is not the case for $\delta^{18}$O, the MM is not sufficiently sensitive to the changes caused by the contamination, which implies that the artefact CO $\delta^{13}$C should be within the range of the “true” $\delta^{13}$C(CO) values. Interestingly, the MM is rather responsive to the growing fraction of the CH$_4$-derived component in CO with increasing [O$_3$], as the $\delta^{13}$C(CO) value of −(47.2±5.8)%o inferred at $R^2$ above 0.4 is characteristic for the $\delta^{13}$C of methane in the UT/LMS. It is important to note that we have accounted for the biases in the analysed C1 WAS $\delta^{18}$O(CO) expected from the mass-independent isotope composition of O$_3$ (see details in Appendix B).

[18] We derive the “best-guess” estimate of the admixed CO $^{18}$O signature at $\delta^{18}$O(CO) = +(92.0±8.3)%o, which agrees with the other MM results obtained at $R^2$ above 0.75. Taking the same subsets of samples, the concomitant $^{13}$C signature matches $\delta^{13}$C(CO) = −(23.3±6.6)%o, indeed at the upper end of the expected LMS $\delta^{13}$C(CO) variations of −(25–31)%o. Because of that, the MM is likely insensitive to the changes in $\delta^{13}$C(CO) caused by the contamination (the corresponding $R^2$ values are below 0.1). Upon the correction using the inferred $\delta^{18}$O(CO) value, the C1 WAS $\delta^{18}$O(CO) data agree with B96 (shown with red symbols in Fig. 3). That is, variations in the observed C18O are driven by (i) the seasonal/regional changes in the composi-
tion of tropospheric air and by (ii) the degree of mixing or replacement of the latter with the stratospheric component that is less variable in $^{18}$O. This is seen as stretching of the scattered tropospheric values ([CO] above 60 nmol/mol) towards $\delta^{18}$O(CO) of around $-10\%$ at [CO] of 25 nmol/mol, respectively. The corrected C1 $\delta^{13}$C(CO) data (shown in Fig. 7) are found to be in a $\pm 1\%$ agreement with the observations by B96, except for several deep stratospheric samples ([CO] below 40 nmol/mol). The latter were encountered during “ozone hole” conditions and carried extremely low $\delta^{13}$C(CO) values, which was attributed to the reaction of methane with available free Cl radicals (Breninkmeijer et al., 1996).

3.2 Estimate of $\delta^{18}$O(O$_3$)

[19] The contamination $^{18}$O signature inferred here ($\delta^{18}$O(CO$_c$) = $+(92.0\pm8.3)\%$) likely pertains to O$_3$ and is comparable to $\delta^{18}$O(O$_3$) values measured in the stratosphere at temperatures about 30 K lower than those encountered in the UT/LMS by C1 (see Table 1 for comparison). If no other factors are involved (see below), this discrepancy in $\delta^{18}$O(O$_3$) should be attributed to the local conditions, i.e. the higher pressures (typically 240–270 hPa for C1 cruising altitudes) at which O$_3$ was formed. Indeed, the molecular lifetime (the period through which the species’ isotope reservoir becomes entirely renewed, as opposed to the “bulk” lifetime) of O$_3$ encountered along the C1 flight routes is estimated on the order of minutes to hours at daylight (H. Riede, Max Planck Institute for Chemistry, 2010), thus the isotope composition of the photochemically regenerated O$_3$ resets quickly according to the local conditions. Virtual absence of sinks, in turn, leads to “freezing” of the $\delta^{18}$O(O$_3$) value during night in the UT/LMS. Verifying the current $\delta^{18}$O(O$_3$) estimate against the kinetic data, in contrast to the stratospheric cases, is problematic. The laboratory studies on O$_3$ formation to date have scrutinised the concomitant kinetic isotope effects (KIEs) as a function of temperature at only low pressures (67 mbar); the attenuation of the KIEs with increasing pressure was studied only at room temperatures (see Table 1, also Breninkmeijer et al. (2003) for references). A rather crude attempt may be undertaken by assuming that the formation KIEs become attenuated at higher pressures in a similar (proportional) fashion to that measured at 320 K, however applied to the nominal low-pressure values reckoned at (220–230) K. A decrease in $\delta^{18}$O(O$_3$) of about (6–8)$\%$ is expected from such calculation (cf. last row in Table 1), yet accounting for a mere one-half of the (13–15)$\%$ discrepancy between the stratospheric $\delta^{18}$O(O$_3$) values and $\delta^{18}$O(CO$_c$).

[20] Lower $\delta^{18}$O(CO$_c$) values could result from possible isotope fractionation accompanying the production of the artefact CO. Although not quantifiable here, oxygen KIEs in the O$_3 \rightarrow$ CO...
conversion chain cannot be ruled out, recalling that the intermediate reaction steps are not iden-
tifiable and the artefact CO represents at most 4% of all O$_3$ molecules. Furthermore, the yield
$\lambda_{O_3}$ of CO from O$_3$ may be lower than unity (see details in Appendix A). On the other hand, the
inference that the contamination strength primarily depends on [O$_3$] indicates that the kinetic 
fractionation may have greater effect on the carbon isotope ratios of the artefact CO produced 
(the $\delta^{13}C(CO_c)$ values) in contrast to the oxygen ones. That is because all reactive oxygen avail-
able from O$_3$ becomes converted to CO, whilst the concomitant carbon atoms are drawn from a 
virtually unlimited pool whose apparent isotope composition is altered by the magnitude of the 
$^{13}$C KIEs.

[21] Besides KIEs, selectivity in the transfer of O atoms from O$_3$ to CO affects the resulting 
$\delta^{18}O(CO_c)$ value. The terminal O atoms in O$_3$ are enriched with respect to the molecular (bulk) 
O$_3$ composition when the latter is above $+70\%$ in $\delta^{18}$O (Janssen, 2005; Bhattachar-
nya et al., 2008), therefore an incorporation of only central O atoms into the artefact CO mole-
cules should result in a reduced apparent $\delta^{18}O(CO_c)$ value. Such exclusive selection is, howev-
er, less likely from the kinetic standpoint and was not observed in available laboratory studies 
(see Savarino et al. (2008) for a review). For instance, Röckmann et al. (1998a) established the 
evidence of direct O transfer from O$_3$ to the CO produced in alkene ozonolysis. A reanalysis of 
their results (in light of findings of Bhattacharya et al. (2008)) suggests that usually the terminal 
atoms of the O$_3$ molecule become transferred (their ratio over the central ones changes from the 
bulk 2:1 to 1:0 for various species). Considering the alternatives of the O transfer in our case 
(listed additionally in Table 1), the equiprobable incorporation of the terminal and central O$_3$ 
atoms into CO should result in the $\delta^{18}O(O_3)$ value in agreement with the “crude” estimate based 
on laboratory data given above.

[22] Furthermore, the conditions that supported the reaction of O$_3$ (or its derivatives) followed by 
the production of CO are vague. A few hypotheses ought to be scrutinised here. First, a fast 
O$_3 \rightarrow$ CO conversion must have occurred, owing to short (i.e., fraction of a second) exposure 
time of the probed air to the contamination. Accounting for the typical C1 air sampling condi-
tions (these are: sampled air pressure of 240–270 hPa and temperature of 220–235 K outboard 
to 275–300 K inboard, sampling rate of 12.85·10$^{-3}$ mol s$^{-1}$ corresponding to 350 L STP sam-
pled in 1200 s, inlet/tubing volume gauged to yield exposure times of 0.01 to 0.1 s due to vari-
able air intake rate, [O$_3$] of 600 nmol/mol), the overall reaction rate coefficient ($k_e$ in Eq. (A3) 
from Appendix A) must be on the order of (6·10$^{-15}$/t$_c$) molecules$^{-1}$ cm$^3$, where $t_c$ is the exposure 
time. Assuming the case of a gas-phase CO production from a recombining O$_3$ derivative and
an unknown carbonaceous compound X, the reaction rate coefficient for the latter ($k$ in Eq. (A2) in Appendix A) must be unrealistically high, at least $6 \cdot 10^{-10}$ molec$^{-1}$ cm$^3$ s$^{-1}$ over $\tau_c = 1/100$ s. This number decreases proportionally with growing $\tau_c$ and $[X]$, if we take less strict exposure conditions. Nonetheless, in order to provide the amounts of artefact CO we detect, a minimum mixing ratio of 20 nmol/mol (or up to 4 µg of C per flight) of X is required, which is not available in the UT/LMS from the species readily undergoing ozonolysis, e.g. alkenes.

Second, a more complex heterogeneous chemistry on the inner surface of the inlet or supplying tubing may be involved. Such can be the tracers’ surface adsorption, (catalytic) decomposition of O$_3$ and its reaction with organics or with surface carbon that also may lead to the production of CO (Oyama, 2000). Evidence exists for the dissociative adsorption of O$_3$ on the surfaces with subsequent production of the reactive atomic oxygen species (see, e.g., Li et al., 1998, also Oyama, 2000). It is probable that sufficient amounts of organics have remained on the walls of the sampling line exposed to highly polluted tropospheric air, to be later broken down by the products of the heterogeneous decomposition of the ample stratospheric O$_3$. Unfortunately, the scope for a detailed quantification of intricate surface effects in the C1 CO contamination problem is very limited.

4 Conclusions

Recapitulating, the in situ measurements of CO and O$_3$ allowed us to unambiguously quantify the artefact CO production from O$_3$ likely in the sample line of the CARIBIC−1 instrumentation. Strong evidence to that is provided by the isotope CO measurements. We demonstrate the ability of the simple mixing model (“Keeling-plot” approach) to single out the contamination isotope signatures even in the case of a large sampling-induced mixing of the air with very different compositions. Obtained as a collateral result, the estimate of the $\delta^{18}$O(O$_3$) in the UT/LMS appears adequate, calling, however, for additional laboratory data (e.g., the temperature-driven variations of the O$_3$ formation KIE at pressures above 100 hPa) for a more unambiguous verification.

Appendix A. Contamination assessment

We quantify the C1 CO contamination strength (denoted [CO$_c$], obtained by discriminating the C1 outliers from respective C2 data) in a sequence of regression analyses. We foremost ascertain that no other species or operational parameter (e.g. temperature, pressure, flight dura-
tion, season, latitude, time of day, etc.) measured in C1 appear to determine (e.g., systematically correlate with) [COc], except that for [O3]. We hypothesise therefore that a production of artefact CO molecules was initiated by O3 (via either its decomposition or a reaction with an unknown educt) and proceeded with incorporation of carbon (donated by some carbonaceous species X) and oxygen (donated by O3 or its derivatives) atoms into final CO. Despite that neither the actual reaction chain nor its intermediates are known, it is possible to describe the artefact component COc produced (hereinafter brackets {} denote number densities) as

\[ \{\text{CO}_c\}_v = \lambda_{\text{O}_3} v \tau_c, \]  

(A1)

where the yield \(\lambda_{\text{O}_3}\), a diagnostic quantity, relates the amount of artefact CO molecules produced to the total number of O3 molecules consumed in the system, \(\tau_c\) denotes the reaction time (period throughout which sampled air is exposed to contamination), and \(v\) stands for the overall rate of the reaction chain. The latter, being regarded macroscopically (empirically), is parameterised to account for the order of reaction chain rate with respect to hypothesised reactants (McNaught and Wilkinson, 1997) as

\[ v = k \{X\}^\kappa \{\text{O}_3\}^\kappa, \]  

(A2)

where \(\kappa\) and \(K\) are the partial orders with respect to X and O3 number densities, respectively, and \(k\) is the rate coefficient. Here it is implied that changes to \(\{X\}\) and \(\{\text{O}_3\}\) are negligible throughout the exposure time \(\tau_c\) (typically < 0.1 s for C1 sample line). As stated above, we find that variations in \(\{\text{CO}_c\}\) correlate exclusively with variations in \(\{\text{O}_3\}\), hence Eq. (A2) can be reduced by assuming constancy of \(\{X\}\) and \(K\) to:

\[ v_c = k_c \{\text{O}_3\}^\kappa, \]  

(A3)

Here, \(k_c = k \{X\}^\kappa\) (often referred to as pseudo-first-order or “observed” rate coefficient) quantifies the rate of reaction chain exclusively propelled by O3. Finally, using Eqs. (A1) and (A3), the artefact \(\{\text{CO}_c\}\) component is expressed as

\[ \{\text{CO}_c\}_v = \lambda_{\text{O}_3} k_c \tau_c \]  

(A4)

where the constant proportionality factor \(b\) integrates the influence of the unknown (and as we explicate below, likely invariable) \(\{X\}\), \(k\), \(K\) and \(\tau_c\).

[26] Eq. (A4) defines the regression expression using which we attempt to fit the values of \(\{\text{CO}_c\}\) as a function of \(\kappa\), \(\{\text{O}_3\}\) and \(b\). In the first regression iteration we keep both \(\kappa\) and \(b\) as free parameters, which provides best approximation at \(\kappa = 2.06 \pm 0.38\), suggesting reactions of two O3 molecules in case elementary reactions constitute the reaction mechanism, or two elementary steps involving O3 or its derivatives in case a stepwise reaction is involved.
In a subsequent regression iteration we set $\kappa = 2$, which yields better (as opposed to the first iteration) estimate of $b$ of $(5.19 \pm 0.12) \times 10^{-5}$ mol/nmol ($\pm 1\sigma$, 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 [CO] and observed [O$_3$]). At last, we ascertain that the best regression results are obtained particularly at $\kappa = 2$, as indicated by the regression statistic ($R^2$ and $\chi^2$) that asymptotically improves when a set of regressions with neighbouring (i.e. below and above 2) integer values of $\kappa$ is compared. The low uncertainty (within $\pm 3\%$) 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 $\tau_c$. The regressed value of [CO] as a function of [O$_3$] is presented in Fig. 1 (d) (solid line). It is possible to constrain the overall yield $\lambda_{O_3}$ of CO molecules in the artefact source chain to be between 0.5 and 1, comparing the magnitude of [CO]$_c$ to the discrepancy between the [O$_3$] measured in C1 and C2 ($\pm 20$ nmol/mol, taken equal to the [O$_3$] bin size owing to the N$_2$O−O$_3$ and H$_2$O−O$_3$ distributions matching well between the datasets). Lower $\lambda_{O_3}$ 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.

Appendix B. Corrections to measured $\delta^{13}$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 $+25\%_\circ$ in $\Delta^{17}$O = $(\delta^{17}$O+1)/$(\delta^{18}$O+1)$^{\beta}$−1, $\beta = 0.528$) when compared to the majority of terrestrial oxygen reservoirs that are mass-dependently fractionated (i.e., with $\Delta^{17}$O of 0$\%_\circ$) (see Brenninkmeijer et al. (2003) and refs. therein). CO itself also has an unusual oxygen isotopic composition, possessing a moderate tropospheric MIF of around $+5\%_\circ$ in $\Delta^{17}$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 $\Delta^{17}$O(CO) that largely exceed its natural atmospheric variation. On the other hand, the MIF has implications in the analytical determination of $\delta^{13}$C(CO), because the presence of C$^{17}$O species interferes with the mass-spectrometric measurement of the abundances of C$^{13}$O 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 $\Delta^{17}O$ value) with respect to the C$^{17}O$ abundances (Assonov and Brenninkmeijer, 2001). In effect for the C1 CO data, the artefact CO produced from O$_3$ had contributed with unexpectedly high C$^{17}O$ abundances that led to the overestimated $\delta^{13}C(CO)$ analysed. The respective bias $\delta_b$ is quantified using

$$13\delta_b = 7.26 \cdot 10^{-2} \Delta^{17}O(CO), \quad (B1)$$

where the actual $\Delta^{17}O(CO)$ value is approximated from the natural CO MIF signal $^{17}\Delta_n$ and the typical O$_3$ MIF composition $^{17}\Delta_c$ as

$$\Delta^{17}O(CO) = \left( ^{17}\Delta_n \left( [CO] - [CO_c] \right) + ^{17}\Delta_c [CO_c] \right) / [CO]^{-1}. \quad (B2)$$

Here $[CO]$ and $[CO_c]$ denote the analysed CO mixing ratio and contamination magnitude, respectively, used in the contamination assessment (see Appendix A, Eq. (A4)) and in calculations with the MM (see Sect. 3.1). For the purpose of the current estimate it is sufficient to take $^{17}\Delta_n$ of $+5\%$ representing equilibrium enrichments expected in the remote free troposphere and UT/LMS. For the O$_3$ MIF signature $^{17}\Delta_c$, the value of $+30\%$ (the average $\Delta^{17}O(O_3)$ expected from the kinetic laboratory data at conditions met along the C1 flight routes, see Sect. 3.2 and Table 1) is adopted. The coefficient that proportionates $^{13}\delta_b$ and $\Delta^{17}O$ in Eq. (B1) is derived by linearly regressing the $\delta^{13}C(CO)$ biases (simulated using the calculation apparatus detailed by Assonov and Brenninkmeijer, 2001) as a function of $\Delta^{17}O(CO)$ varying within a (0–30)$\%$ range for the CO with initially unaccounted MIF (e.g., the sample is assumed to be mass-dependently fractionated). It therefore quantifies some extra $+(0.726 \pm 0.003)\%$ in the analysed $\delta^{13}C(CO)$ per every $+10\%$ of $\Delta^{17}O(CO)$ excess. The most contaminated C1 WAS CO samples at [O$_3$] above 300 nmol/mol are estimated to bear $\Delta^{17}O(CO)$ of (6–12)$\%$ corresponding to fractions of (0.10–0.27) of the artefact CO in the sample. Accordingly, the reckoned $\delta^{13}C(CO)$ biases span (0.5–0.9)$\%$. Although not large, these well exceed the $\delta^{13}C(CO)$ measurement precision of $\pm 0.1\%$ and were corrected for, and therefore are taken into account in the calculations with the MM presented in Sect. 3.1.

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Fig. 1. (a) Distribution of CO mixing ratios as a function of concomitant O₃ mixing ratios measured by CARIBIC in the LMS ([O₃]>300 nmol/mol). The shaded area is the two-dimensional histogram of the C2 measurements (all C2 data obtained until June 2013) counted in 5×1 nmol/mol size [O₃]×[CO] bins, thus darker areas emphasise greater numbers of particular CO–O₃ pairs observed. Small symbols denote the original C1 in situ measurements (black) and corrected for the artefacts (red); the C1 WAS analyses (11 of total 408) are shown with large symbols. Thin and thick step-lines demark the inner and outer statistical fences (ranges outside which the data points are considered mild or extreme outliers, see text) of the C2 data, respectively. The dashed curve exemplifies compositions expected from the linear mixing of very different (e.g., tropospheric and stratospheric) end-members. (b) Statistics on CO mixing ratios from C1 and C2 data shown in box-and-whisker diagrams for samples clustered in 20 nmol/mol O₃ bins (whiskers represent 9th/91st percentiles). (c) Sample statistic for each CARIBIC dataset (note the C2 figures scaled down by a factor of 1000). (d) Estimates of the C1 in situ CO contamination strength [COc] as a function of [O₃] (solid line) obtained by fitting the difference Δ[CO] between the C2 and C1 in situ [CO] (small symbols) as detailed in Appendix A (Eq. (A2)). Step line shows the Δ[CO] for the statistical averages (the shaded area equals the height of the inner statistical fences of the C2 data). Large symbols denote the estimates of [COc] in the C1 WAS data (slight variations vs. the in situ data are due to the sample mixing effects, see Sect. 3). Colour denotes the respective C1 WAS δ¹⁸O(CO) (note that typically 6–7 in situ measurements correspond to one WAS sample).
Fig. 4. Measured C1 WAS δ¹⁸O(CO) (not corrected for artefacts) as a function of concomitant O₃ mixing ratio. Symbol colour denotes the artefact CO component (integral [CO₃] per each WAS); symbol size scales proportionally to the WAS CO mixing ratio corrected for artefacts (see Sect. 3 for details).
Fig. 5. Keeling plot of the data used in the calculations with the mixing model (MM). The C1 WAS isotope CO measurements are shown with symbols, solid lines denote the linear regressions through the various sets of samples selected by the MM ($n = 80$ sets are plotted). Colours refer to the δ$^{13}$C (red) and δ$^{18}$O (green) data, colour intensity indicates the coefficient of determination ($R^2$) of each regression, respectively. Darker colours denote higher $R^2$ values, with maxima of 0.92 for δ$^{18}$O and 0.54 for δ$^{13}$C data, respectively. The inferred contamination signatures $\rho$ (CO) are found at $([\text{CO}])^{-1} \rightarrow 0$. Regression uncertainties are shown in Fig. 6. Note that because different subsets of samples contain same data points, some of the symbols are plotted over (i.e., not all symbols contributing to a particular regression case may be seen).
Fig. 6. Results of the regression calculation with the MM. Shown with symbols are the contamination source isotope signatures $\Delta^{18}O(\text{CO}_2)$ as a function of the respective coefficient of determination ($R^2$). Colour denotes the number of samples in each subset selected. Solid and dashed lines present the best guess $\pm 1$ standard deviation of the mean for the $\Delta^{18}O(\text{CO}_2)$ and $\Delta^{13}C(\text{CO}_2)$ estimates. Dashed circles mark the estimates obtained at highest $R^2$ for $\Delta^{18}O(\text{CO}_2)$ regression (above 0.9). See text for details.