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***Interactive comment on “Analysis of accurate  $^{13}\text{C}$  and  $^{18}\text{O}$  isotope measurements of  $\text{CO}_2$  in CARIBIC aircraft air samples from the tropical troposphere, and the upper troposphere/lowermost stratosphere” by S. S. Assonov et al.***

**S. S. Assonov et al.**

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We thank reviewer-2 for his careful detailed review. We have used most of the recommendation. Below is our reply and a contribution to the discussion.

We note here that this is the first publication focused on analyses of  $\text{CO}_2$  isotope data of CARIBIC-1 and CARIBIC-2; the global coverage is comparable with largest observational programs run by NOAA and CSIRO. Both NOAA and CSIRO have published numerous papers presenting different aspects such as sampling, preconditioning of

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sampling flasks, use of driers and storage effects (CO<sub>2</sub>-exchange with water), performance of the instruments, calibration and data quality control; these complex programs were gradually optimized. All that complexity might even have necessitated backwards corrections of large data sets (e.g. Allison and Francey 2007). Though CARIBIC provides unique additional data, only a few publications cover the above mentioned aspects for greenhouse gases. Thus far there have been no CARIBIC publications for CO<sub>2</sub> isotope results (we note in response to the remark about the title, that it states the analysis of the measurement results; the analyses of the samples has been done in the lab. . .we do not see what we can improve in the title, which was considered to be hard to follow).

The content and different aspects of this manuscript are optimized to address the most important issues. It also bridges from the more traditional datasets at stations, to the UTLS region. Therefore the paper may seem a bit longish, but it is the first, as we state above, but also likely the last one. Basically, the situation is that IF these systematic data are useful to those working on the CO<sub>2</sub> cycle, and exchange with the biosphere and hydrosphere, we will consider to resume the isotope work at this amazing level of accuracy and precision (we do not think less quality data would help in any way). It may well be that this type of information is not sufficiently useful considering the effort required. The future will tell us. We do not see it as our role to “advertize” this work. We do, in the title, not claim something extreme. We are experimentalists and present and analyse the highest possible quality aircraft CO<sub>2</sub> isotope data. If colleagues elsewhere are interested in CARIBIC air samples for <sup>13</sup>C and <sup>18</sup>O analyses, we gladly supply these. The paper analyses this well defined set of measurements without using a 3D model. This may be a future application.

Replies on the general comments:

The comment suggesting “restructure the paper and trim it to a more manageable size, placing more emphasis on getting the language and grammar correct in order to convey their arguments and findings more clearly.”

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Reply: The paper is somewhat restructured, to have better connections between sections and shortened by removing repeated text. A few busy figures have been simplified and a few panels were cut. However, we stress this is a complex paper and we need all the sessions (on technical aspects, data uncertainty, inter-comparison etc) in order to provide a comprehensive introduction to the new data set and basically to the new approach (regular CO<sub>2</sub> isotope measurements by aircraft). As we note in the reply to the reviewer-1, NOAA and CSIRO have published numerous and rather long papers on similar aspects. Allison and Francey (2007) is an example discussing many technical and analytical aspects as well as introducing the data.

Comment on the de-trending procedure.

Reply: The reviewer-2 recommends on the de-trending procedure to be implemented separately for CARIBIC-1 and CARIBIC-2 and then applying certain shift. We have several notes here:

1. De-trending separately for CARIBIC-1 and CARIBIC-2 has now been implemented for N<sub>2</sub>O concentrations, avoiding to use data for 2002-2006 where there is no CARIBIC data. (Detailed description is given in the revised version). This has the only effect - masking the aspect of (calibration) consistency between CARIBIC-1 and CARIBIC-2, otherwise changes are small and do not affect the data distribution.

2. The situation is less simple for d<sup>13</sup>C and CO<sub>2</sub>. The analytical uncertainty in d<sup>13</sup>C is close to its inter-annual change, therefore constricting the trend for shorter time periods will bring a much larger uncertainty. Besides, determining the shift between median of the two distributions is not possible – in contrast to N<sub>2</sub>O, CO<sub>2</sub> has no clear peak of the distribution, its seasonality is large. Besides, the NOAA data for d<sup>13</sup>(CO<sub>2</sub>), for 2008-2009 are still not available.

3. In particular we note that common or separate de-trending for CO<sub>2</sub>, if applied to CARIBIC-1 and CARIBIC-2, cannot affect the distribution of CARIBIC data on the UT/LMS mixing plot, it cannot change the latitudinal distribution either. Other plots

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where we use de-trended data are the comparison between CARIBIC-1 and CARIBIC-2 (Keeling plot on Fig. 12) and the seasonality plot (Fig. 14); these are mostly qualitative comparisons. All other comparisons in the paper are based on non-detrended data.

Comment on data accuracy.

The comment by the reviewer concerning data accuracy, the systematic discrepancy between IRMM and MPI-BGC and correction due to different  $17\text{O}$  correction algorithms needs to be answered in detail (we give now some more explanation in the text). There are several reasons for potential misunderstanding.

1.  $\delta^{13}\text{C}(\text{CO}_2)$  quantity is obtained by applying correction for the  $17\text{O}$  contribution to the signal measured on mass 45. Historically, a simple correction algorithm has been applied (after Craig 1957, modified by Allison et al., 1995). Later it was recognized that this is not accurate as it ignored  $17\text{O}$ - $18\text{O}$  relationships in natural materials. Also new, more accurate determinations of the  $17\text{O}$  isotope abundance have become available. However this correction was officially recommended until recently. Based on their re-determination of  $17\text{O}$  abundance, Assonov and Brenninkmeijer (2003a, b) re-considered the  $17\text{O}$  correction algorithm. The 13th  $\text{CO}_2$  expert meeting (see reference in the paper) recommended using the  $17\text{O}$  correction after (Assonov& Brenninkmeijer, 2003), in 2010 this algorithm has been officially recommended by IUPAC (Brand et al., 2010; available at <http://iupac.org/publications/pac/asap/PAC-REP-09-01-05/>). Though the recommendation was first released in 2005 (13th  $\text{CO}_2$  expert meetings), NOAA has continued reporting data based on the correction after Allison et al. (1995). Accordingly the NOAA data needed to be corrected for the bias between the two  $17\text{O}$  correction algorithms; the same was applied to the CARIBIC-1 data which were also based on Allison et al. (1995). The last data release by NOAA in 2009 is already on the newly recommended  $17\text{O}$  correction, we use these data in the revision.

2. Concerning the  $\delta^{13}\text{C}$  offset of  $-0.04$  per mil between IRMM and MPI-BGC – unfor-

tunately, this offset is rather normal. Please do understand this correctly. In one sense it is not normal, because few laboratories attain the sufficient high degree of precision and accuracy to detect such an offset. On the other hand, “it is rather normal” means that it will be hard to get rid of such extremely small discrepancies. For years CSIRO, SCRIPPS and NOAA had to deal with much larger, often unexplicable discrepancies and offsets. Thus the offset between CSIRO and NOAA was observed at -0.05 per mil for d13C and about 1 per mil for d18O (Allison and Francey 2007; Vaughn et al., 2010). The d18O calibration of NOAA has been re-adjusted only recently (Vaughn et al., 2010). We wrote in the manuscript “This is much less than the variability discussed in the present paper, and less than inter-laboratory scale discrepancies recently published (e.g. Levin et al., 2007).” First, the d13C scale discrepancy between well established laboratories is known to be up to 0.08 per mil (Levin et al., 2007), solving this matter is beyond the scope of the paper; second, given that IRMM and MPI-BGC have used different approaches to evaluate instrumental corrections and the offset we found is close to the two sigma values for IRMM and MPI-BGC, the situation is still satisfactory; third, the correction for this offset was applied only to 28 samples analyzed at MPI-BGC which cannot effect the data consistency. However we should note all these aspects as these may effect future data integration in models. The d18O offset between IRMM and MPI-BGC of -0.06 per mil is much smaller than discrepancies observed between well established laboratories, these account for up to 0.4 in many cases (Levin et al., 2007). We note that we reach a level where different labs determine the 1.1% 13C in atmospheric CO2 with a uncertainty of 40 per meg (our 2- $\sigma$  value). For 18O it is even more difficult. The CO2 experts review and will continue reviewing how to get better performance and improve the criteria regularly.

3. The comment by reviewer-2, we cite: I’m also “uncertain” that it is necessary to compare accuracy with another laboratory for the interpretation of the CARIBIC results. Surely the most important criterion is the relative precision of individual measurements that will be affected by the long term (i.e. period of CARIBIC project) internal precision of the IRMM and MPI-C measurements.”

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Reply: Foremost is the internal consistency of all our data, that is true. However, we remark that another reviewer might have equally well stated exactly the opposite, if we had not done that, namely how well do these data compare to other datasets. We consider that discussing and analysing results (as the title states) of systematic measurements, signal variability and making comparison with NOAA data is not possible without overview of the data uncertainty. This is important to do now for several reasons (i) CARIBIC-1 measurements at MPI-C were terminated. (ii) CARIBIC-2 measurements at IRMM have been also stopped. Later, if our data are to be used, the present paper is important for full documentation. In particular modelers may wish to ascertain how the different data sets compare. This is one of the important aspects of this paper. For colleagues wishing to start such measurements, our paper is a useful document as well.

Comment on recommendation to make concussions instead of summary and outlook.

Reply: We can draw several conclusions from the presented data analyses, namely that N<sub>2</sub>O can be used as adequate tracer to separate data, new isotope data reflect UT-LMS mixing and atmospheric circulation in the troposphere and also some based on comparison with the NOAA data. However much more work is needed for complete data interpretation, also with models; this paper is only an introduction. We consider giving a summary of the present status and outlook a logical conclusion of the paper.

- Replies on the specific comments are listed along with the original comments:

Comment: P6001 L15. “The need for large numbers of measurements” is not really exemplified by another project that generates large numbers of measurements; the need is from other parameters, e.g. density of model points.

Reply: We partly agree. In this statement we note that more and more measurements are carried out. This obviously is necessary to get a better grip on the complex system. See also the paper by Corinne Le Quere and about 30 co-authors in Nature Geosciences (Le Quere, 2009). Surely how best to measure, where and when, and

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even the usefulness of isotope measurements as such is a matter that is hard to judge. Existing large programs have been tailored together with data users/modelers. Besides, on P 6002 L 16-18 we refer to modelers, namely “Patra and co-authors (Patra and Maksyutov, 2002; Patra et al., 2003) concluded on the need to extend the network by optimally located stations in continental South America, Africa and Asia”.

Comment: P6002 L11. The comments about d18O data should contain reference to the 2 Cuntz et al papers in JGR 2003 (see below).

Reply: We thank the reviewer for the reference. However our statement that (P 6002, L11) “However, 18O data have not been generated and used to the same degree by far. . .” appears to be valid – in contrast to d13C, 18O of CO2 data have not been used widely; the generation of reliable 18O data started in 2000s only. Perhaps the 18O signal is too complex to ever be decisive. More papers like those by Cuntz surely are a guidance as what and where to measure, and what we can learn from the data. We think that aircraft measurements at 10 km altitude are useful, not for instance for inverse modeling, but because there represent larger air masses. This also makes it necessary to have the best possible quality data.

Comment: L27. Should this be “primarily” rather than “basically” and is CARIBIC a “reactive chemistry” project? (Our sentence was “Although CARIBIC basically is an atmospheric chemistry project, CO2 measurements are part of its large measurement package.”)

Reply: No, the word “basically” is the right word, CARIBIC deals with many aspects. But in the first instance it is an atmospheric chemistry project. We do not know what the referee would mean with a reactive chemistry project, because to opposite would be a non-reactive chemistry project, a contradiction in terminus.

Comment: P6003 Paragraph starting line 2. How did the in situ CO2 analyser compare with the flask measurements? The justification for the stable isotope work does not mention a scientific benefit.

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Reply: The in situ analyzer is in test phase, comparison with the flask data is beyond the scope of the paper. A comparison is shown however in the paper by Schuck et al. (2009) on the GHG analyses.

Comment: L17. “fore” should be “for”

Reply: Corrected.

Comment: P6004 L25. Which airline operated the Boeing 767?

Reply: This is LTU, now specified.

Comment: P6005 Section 2.2. There are a number of measurement differences in this section, e.g. the difference from NOAA-ESRL (equation on P6006 L8) and the -0.04 per mil difference from MPI-BGC, that cast a shadow over the repeated assertion that the CARIBIC stable isotope measurements are accurate.

Reply: See the answer to the general comment-2 above. Accurate is a relative concept. The CARIBIC measurements belong to the most accurate measurements ever made.

Comment: P6006 L12. Expand MPI-C. L14. NARCIS is an abbreviation and should be capitalized and expanded (Mukai, 11th WMO Experts Meeting, GAW-148). Expand MPI-BGC, it isn't explained anywhere else.

Reply: MPI-C is given in the abbreviation list. However we cannot give all details in the paper; interested reader can find some more details on the method and calibration tests (also the comparison with NARCIS-CO<sub>2</sub>) in other publications we refer to (Assonov et al., 2009 a,b).

Comment: L23. The description of uncertainty raises two issues for me. First, the data presented in Table 1 could easily be incorporated into the text. Second, and more importantly, I don't believe the uncertainty estimate to be correct. The reference for the uncertainty is Assonov 2009b and after reading that paper I think some reassessment of the uncertainty treatment is required. A number of factors in the uncertainty analysis

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need consideration; the CARIBIC mass spectrometer analysis used 5 measurement cycles giving a sigma-5 value not a sigma-10 as given, for instance, for the NIST RMs used for the calibration; no analytical uncertainty appears to be used in the total uncertainty budget (p 827 of Assonov 2009b: the description of the uncertainty budget in that reference is not clear to me). I do, however, note that an estimate of uncertainty is not critical to this paper as the data do not appear to be used quantitatively.

Reply: Concerning the Table, we think it makes the paper easier to read, when this is not embedded in text. Concerning the uncertainty, here we sense there is some misunderstanding. First, the data of CARIBIC-1, though each measurement was characterized by the sigma on  $n=5$ , have been obtained by independent measurements (on different days) vs two working reference CO<sub>2</sub> gases having different isotope compositions. Second, the total uncertainty given for CARIBIC-1 has been based on the statistical treatment of the two data sets (distribution of the difference between the two data sets) and also included the calibration uncertainty. Third, all calibrations (both on NBS-19-CO<sub>2</sub> and NIST RMs) were obtained by numerous measurement runs with ( $N=10$  and  $20$ ) and than grand averages were taken. Finally, d<sub>18</sub>O calibration uncertainty was adjusted based on measurements of NIST RMs; these demonstrated better reproducibility than runs on NBS-19-CO<sub>2</sub> extractions.

Comment: P6007 L8. Why were the two samples “suspect”?

Reply: Several samples were analyzed repeatedly. These two samples were suspect due to their d<sub>18</sub>O behavior in repeated analyses (problems with the CO<sub>2</sub> extraction at the very beginning of measurements at IRMM). In that sense they are exceptions, the only 2.

Comment: L17. Expand GHG to be (I assume) GreenHouse Gases. (Should this be GG rather than GHG?)

Reply: The abbreviation GHG stands for green house gases which is in use in numerous publications. The abbreviation is listed in the Appendix, the section Abbreviations.

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Comment: P6008 Paragraph starting L3: I find the description of the flights to be clumsy. For example, “We note that the return flights start initially at lower altitudes and reach over Europe deeper into the LMS”. What does this mean? Don’t all flights start at lower altitudes.

Reply: This place is re-formulated, means that return flights reach over Europe deeper into the LMS.

Comment: L19. “aver” becomes “over”

Corrected.

Comment: P6009 L6. The sentence starting “Later” could be changed to “Later in the manuscript we describe our selection of N<sub>2</sub>O concentration for this purpose”.

Corrected.

Comment: Section 3.2. The detrending would be better done on the 2 stages, CARIBIC-1 and -2, separately and then shifted. By detrending over time when there are no data available there is an implicit assumption that the trend over the period NOT sampled is the same as that over the periods for which there are data. This may be very wrong and could lead to erroneous conclusions.

Reply: See the answer to the general comment-2 above. It is applied to N<sub>2</sub>O but cannot be applied to CO<sub>2</sub>. In fact the use of de-trended data is qualitative only so that we cannot expect wrong conclusions.

Comment: P6012 L16. The reasons given are not compelling; they are simply reasons.

Reply: Here we ask for some freedom to write the way we want. There are strong reasons, convincing reasons, actually compelling reasons, and we give these. This quantifier we use to indicate that in our opinion these reasons are important.

Comment: P6013 L6. CARIBIC-1 data show the same features “but the peak is below 320 ppb”.

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Corrected.

Comment: L11. The CARIBIC-1 N<sub>2</sub>O increase rate was adjusted up by 20%. This is hardly a slight increase. Why not drop the CARIBIC-2? What would have been the impact of using different rates?

Reply: True, it is a substantial increase in a very barely resolved signal. Now the de-trending for N<sub>2</sub>O is applied as recommended by the reviewer-2; see also the answer to the general comment-2 above. In fact we use de-trended data only qualitatively.

Comment: L16. I don't think a "small N<sub>2</sub>O scale inconsistency" should be raised and then simply put outside the scope of this paper. This paper is all about using N<sub>2</sub>O and the authors should address the issue once they raise it, even if only briefly.

Reply: The paper argues that using distribution of N<sub>2</sub>O signals can help to separate UT and LMS samples and gives reasons for this. Namely we stress that N<sub>2</sub>O is rather homogeneously distributed in the troposphere, has very limited seasonality and has main sink in the stratosphere. That is in contrast to for instance ozone, which has large seasonality in LMS. Our idea is to use N<sub>2</sub>O is based on its compact distribution peak and tailing towards LMS. The added value is that previously nobody has used N<sub>2</sub>O to separate air masses aimed analyses of CO<sub>2</sub> isotope data, the N<sub>2</sub>O filter can easily be implemented in models. However note that one will not use de-trended data in models!, this de-trending was introduced simply because we do not use a model.

Resolving all aspects of long-term N<sub>2</sub>O calibration, stability of calibration mixtures etc is definitely beyond the scope of this paper. Besides, CARIBIC-1 and CARIBIC-2 has use different sampling systems, different sampling containers and have had different sampling resolution. Besides, even different routes may have slightly different mean value for tropospheric N<sub>2</sub>O, as N<sub>2</sub>O sources are not equally distributed, and for instance at high latitudes the influx from the stratosphere takes place. We do not rise the discrepancy issue in the revision.

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Comment: P6014 L1. The plots don't show an "L" shape and the plots referred to in Figure 5 are not "vs. N2O reversed scale" they are "N2O vs." plots. This is also an error in the caption of Figure 5 (P 6048).

Reply: As L shape we consider folded line connecting stratospheric and tropospheric end-members. Even on the CO-N2O plot (Fig 5, right upper panel, here N2O is used instead of O3) the mixing line does not show the ideal L shape, it is simply folded. CO2 isotope plots vs N2O (Fig 5) look very similar, they also have a fold at the same value of stratospheric tracer N2O as on the CO-N2O plot.

Comment: L24.  $d^{13}C(CO_2)$  and  $1/CO_2$  are numerical expressions relating to  $CO_2$ , they don't share source and sink properties. Also, why mention  $1/CO_2$  here?

Reply: Here there made a miss print, it should have been  $CO_2$  instead of  $1/CO_2$ . However  $d^{13}C(CO_2)$  and  $CO_2$  share source and sink properties.

Comment: P6015 L8. Add "(blue symbols)" after "UT/LMS mixing" and "(red symbols)" after "affected directly" to help readers.

Reply: We think that we should not put part of the figure captions in the text.

Comment: L13-15. Aren't "seasonal variations" and "different degrees of mixing of air masses affected by source and sinks and background air masses" the same?

Reply: No, these are not the same. Here we mean seasonal variations in the UT; and "mixing of air masses affected by source and sinks and background air masses" means air masses being recently in contact with surface/fresh uplifted plumes.

Comment: P6016 L4. The apparent SF6 age should be referenced if it is not plotted.

Reply: Corrected; the reference to unpublished data is given.

Comment: L11. Delete "also" and add a comma after "masses". Corrected.

Comment: L13. Delete the "(" before Zahn. Corrected.

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Comment: L17. Replace “not. CO<sub>2</sub> does exchange oxygen” with “not as CO<sub>2</sub> exchanges oxygen”

Reply: No, we prefer shorter sentences.

Comment: L28. Was the starting point +0.5 per mil or about +0.5 per mil? Explain why this value was selected here. Is it the annual mean NH tropics value (P6017 L4)?

Reply: The construction of this plot is better explained in the revised version.

Comment:P6017 L1. Which “surface” is meant? Continental surface? Oceans’ surface?

Reply: This is explained in revised version.

Comment: L5-7. I don’t understand this sentence. Should “traces” be tracers”?

Reply: Some misprinting, corrected.

Comment: L10. Change “which bears” to “more”.

Reply: This place is re-worded.

Comment: L13-18. This needs to be clarified. Figure 7 does not show me that positive values of CARIBIC-1 d<sub>18</sub>O(CO<sub>2</sub>) are reliable.

Reply: Is now re-worded. Based on expertise of our and many other labs, positive d<sub>18</sub>O(CO<sub>2</sub>) values cannot be artifact due to CO<sub>2</sub>-water exchange, storage and/or any analytical problem.

Comment: P6018 L1. What are the “new” data? CARIBIC-2 or data selected using a criterion of d<sub>13</sub>C(CO<sub>2</sub>) = -8.2?

Reply: Yes, CARIBIC-2 data.

Comment: L2. I would hope that d<sub>13</sub>C(CO<sub>2</sub>) and d<sub>18</sub>O(CO<sub>2</sub>) reflect air mixing in a similar way to CO<sub>2</sub>!

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Reply: Indeed. However variations are sometimes so small that only high quality measurements can demonstrate it. This statement is a general one, an introductory statement, that's why we state "clearly" one could have written obviously, but this would be to obvious.

Comment: L8. Add "but no long term trend" after "gradient" and take it out of L9.

Is corrected.

Comment: L18. Add "but contain the same features" at the end.

Is corrected.

Comment: L22. "because of" becomes "for" and delete "being"

No.

Comment: L25. I can't see a gradient in the CO<sub>2</sub> (Figure 8) and neither can the authors (P6020 L5).

Is corrected.

Comment: P6019 L4. Where is the data on the NOAA website? Give the URL and an access date.

Reference is now given.

Comment: L6. Should the last sentence include a reference to the Schuck et al 2010 paper?

Reply: When our manuscript was submitted, the Schuck et al 2010 paper was not online. Now we refer to it.

Comment: L9. For surface stations a statement such as "well mixed free troposphere" could be added to highlight the difference from stratosphere.

Reply: Perhaps we did not clearly formulate this, our apologies. The word "contrast"

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may be misleading. Meant is that when there is no CO<sub>2</sub> gradient, no <sup>13</sup>C gradient is expected. At the surface, both have gradients. We have changed this formulation.

Comment: L20. Does adding the few CARIBIC-1 data add value to the figure and/or discussion?

Reply: Yes, because not much data are available for SH, in particular at flight altitudes.

Comment: P6021 L9. The comment in brackets should be deleted.

Done.

Comment: L10. Add “in” after stations. This section is hard to read as many of the data subsets are not discernable on Figure 9.

Reply: Is corrected. Some data subsets from Fig. 9 are removed.

Comment: L27. “Regardless the fact that” becomes “Although”.

Reply: No, we write our paper in the style we want to write our paper

Comment: P6022 L3. “demonstrating a” becomes “show”

OK.

Comment: L4. “and are used qualitatively only”.

Is now corrected.

Comment: L6. The high d<sup>18</sup>O(CO<sub>2</sub>) values might suggest SH air; “apparently” is a loose term.

Reply: No, “apparently” is a strong statement of logical consequence. Non native speakers can learn to remember this by linking it to “it appears that” It is not like “seemingly”, which means it seems to be. A very bad word, used unfortunately is “suggest”

Comment: L8. Paragraph starting here. Is only one year of station data shown in Figure 9? According to the caption, data are extrapolated from 01/01/2008 to 04/01/2009

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based on 2008 and annual increase rates. Does this mean over 1 year's data are synthetic? If so, it is misleading to base arguments on this as the real data may be very different.

Reply: Stations data are from 1999 to 2007 inclusive. What is plotted for from 01/01/2008 to 04/01/2009 is based on extrapolated data for the year 2007. We have removed these extrapolations from this busy plot.

Comment: L24. Delete "in". I find Section 4.2.2 confusing. This needs to be rewritten. For instance a Keeling plot will not trace important sources and sinks; it can be used to identify the isotopic composition of a single source, or the apparent isotopic composition of a complex mixture of sources.

Reply: The whole section is re-written.

Comment: P6024 L21. Replace "large. The reasons for this" with "and"

Reply: No, we prefer short sentences.

Comment: P6025 L17. "flights 186 to 189". How many flights were made? This could be added to the initial description of the CARIBIC project. Paragraph starting L22 needs rewriting to correct the grammar and to make the intent clearer. Figure 12 gives the "all seasons detrended data" intercepts for CARIBIC-1 and CARIBIC-2 as -26.4 and -25.6 respectively. These could (i.e. should) be mentioned in the text to compare with the season and location specific range of -29 to -24 given in Figure 10.

Reply: The number of flights is given, the section is re-written as suggested.

Comment: P6026 L10. The use of isotopes directly reveals the causes for CO<sub>2</sub> variability to be what?

Reply: It was meant that use of isotopes reveals variability due to sources and sinks. Now we have deleted this sentence.

Comment: L25-27. Global scale measurements of d<sup>18</sup>O(CO<sub>2</sub>) have been made for



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decades by Scripps, NOAA and CSIRO and some modelling has already been done, see Cuntz et al, 2003a and Cuntz et al, 2003b. Does using "accurate" here imply that these older measurements are not accurate? I don't think so.

Reply: The story is not so simple. For many years NOAA' and CSIRO' samples were taken without drying, flasks were not specifically preconditioned/preheated, thereafter many d18O data have suffered from CO<sub>2</sub>-water exchange in flasks, even extracting procedures were not optimized to get highest quality of d18O data. Two keystone paper focused on this are Gemery et al. (1996) and Masari et al. (2001); then several papers by W.Brand and colleagues in 2002-2005 . Thus, though CO<sub>2</sub> stable isotope measurements have accumulated large data sets over years, the quality of many d18O is not as good as obtained during the last years. Also d18O calibration of NOAA was biased for 0.8 per mil and only recently the data were corrected backwards (Vaughn et al., 2010).

Comment: P6027 L4. "implies" becomes "suggests" and "to be" becomes "is to be"

No.

Comment: L5. Comparison with the station data needs to be tempered with the statement that these are monthly "baseline" values and the station may have considerable variability in higher frequency data that is removed in producing the monthly value, or not measured.

Reply: The description has been corrected.

Comment: P6028 L5. "applied" becomes "used"

Reply: Why can we not use "apply", because the reviewer wants us to apply "use"? Would we ask him or her to use apply when he or she applied use? There are cases in the English language, in which we cannot use apply, namely when we have to apply use. Thus it is for instance wrong to say "we applied to use apply" one should in this case indeed apply use, and write "we used to use apply" or also possible is "we used

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to apply use”

Comment: L6. Sentence could be changed to “Miyazaki et al (2009) concluded that “. . .”. It is not necessary to say “we cite”, that’s what quotation marks are used for.

Reply: Is now changed, yet it was not wrong, we cite Webster.

Comment: L10. “basically in agreement” means there is some noticeable disagreement. Is that correct?

Reply: Yes, it can be stated as there is some noticeable disagreement. Is reformulated.

Comment: L16. “Though the modelling studies of Miyazaki et al (2008, 2009) . . .” L18. Delete the parentheses.

Done.

Comment: L20-25. It is not clear what these 2 studies contribute to the analysis of the CARIBIC results.

Reply: We could mention these papers in the introduction, but we think that it is better to mention them here.

Comment: L23. First use of STE, expand the abbreviation.

Reply: The abbreviation has been expanded now.

Comment: L28. “our final figure” is not needed.

Reply: We think that authors have some freedom.

Comment: P6029 L3. “labs” becomes “laboratories”. “lag” should be “difference” or “separation”.

Reply: Lag usually refers to time, so it is the correct word. Often “time lag” is used.

Comment: L6. This is the first mention of the 2000 ppb (2 ppm) H<sub>2</sub>O and CO<sub>2</sub>>125ppb

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filters. (Are ppb and ppm explained?)

Reply: This is (semi-)arbitrary level we selected to make separation of air masses as based on H<sub>2</sub>O and CO distribution plots; has now been explained in more details. Ppb and ppm is in all trace gas papers.

Comment: Was this done for any other data or just the data used to generate the box plot in Figure 14? How many data points is “just a few”?

Reply: It is stated in the text that only data for UT and FT air are used for this plot. No additional treatment, only filtering out the data of obvious plumes by using CO and H<sub>2</sub>O.

Comment: L25. I don't think the 0.02 per mil is an accurate estimate of the total uncertainty. I have read the Assonov et source paper and think that the uncertainty should be closer to the 2 sigma value, 0.044 per mil, presented in that paper. This carries through to the discussion on.

Reply: Here we give the 1-sigma values as clearly stated (P6029, L25, also Table 1) and as in practice by other monitoring laboratories (e.g. Vaughn et al., 2010); However, Assonov et al. (2009a,b) have given 2-sigma.

Comment: P6030 where the d<sup>13</sup>C(CO<sub>2</sub>) offset of 0.04 per mil from MPI-BGC is discussed. The description of the offset between MPI-BGC vs. NOAA is slightly confusing: if the offset is limited, it is not established to be stable. Also, an offset between the NOAA “scale” and that of CARIBIC is meaningless, there is no CARIBIC “scale”; the CARIBIC-1 ‘scale’ is an MPI-C “scale” and the CARIBIC-2 scale is an IRMM “scale”.

Reply: Indeed, we need to specify that CARIBIC-1 ‘scale’ is an “MPI-C scale” and the CARIBIC-2 scale is an “IRMM scale”. We stress that we have not made direct inter-comparisons with NOAA, only with MPI-BGC. Namely, the MPI-C scale was compared with MPI-BGC for d<sup>13</sup>C and the IRMM scale was compared for d<sup>13</sup>C and d<sup>18</sup>O. However in the paper we qualitatively compare our data with NOAA. We want to say that

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tracing back (the stability of) the offset between MPI-BGC and NOAA is beyond the scope of this paper, but it can be done and by this way the offset between IRMM and NOAA can be traced back.

Comment: P6030 Section 4.5 “Future use of data . . .” does not mention any future use of the data. P6031 L15. Where are the data available?

Reply: We have deleted the section 4.5, placing some text in another section. The data are stored on CARIBIC data server and can be available upon request to the project coordinator.

Comment: P6032 L2. Should N<sub>2</sub>O be referred to as the most suitable or appropriate tracer, rather than the most adequate?

Reply: Indeed, we have corrected this..

Comment: L3. Remove parentheses.

OK

Comment: L4. Add “(H<sub>2</sub>O > 2 ppm)” after “plumes”.

Reply: Could be corrected, in fact combination of H<sub>2</sub>O, CO and sometimes NMCH is used to recognize fresh plumes. There no single tracer for this.

Comment: L14. When will climate change “show up” in d<sup>18</sup>O(CO<sub>2</sub>)? How will it show up? Is this a summary of what was covered earlier or a new statement? This is the second mention of “climate” and the first mention of “climate change” in the paper.

Reply: Perhaps climate change has “showed up” but we had no data for the past, also even recent years. The best data by NOAA demonstrate some d<sup>18</sup>O variations in the last years (e.g. Vaughn et al., 2010) which still need to be understood. In the future, climate change, and biosphere changes will affect d<sup>18</sup>O.

Comment: L19. Point 6. I find this confusing. Do the authors mean something along

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the lines of “When considering future observations by aircraft, optimising sampling resolution and analytical uncertainty will be critical to achieving the planned goals .High-resolution sampling may be required to study UT/LMS mixing and inter-hemispheric transport in detail, but it may be less applicable for studying the remote FT and UT on the global scale when used in combination with transport models. Mathematical treatment of high resolution data to provide data for a more coarse scale (lower resolution) could be used.”? I think so.

Reply: That is correct. When one can take a number of x samples over y kilometer distance, would one take x samples over y/x kilometer, or take x samples over a lesser distance?

Comment: L24. Point 7. I’m confused. Do I understand correctly that IRMM cannot continue their involvement but a new sampling system is about to be deployed anyway? Is CARIBIC continuing without the stable isotope analyses?

Reply: The word “should” is our opinion, but it is not so realistic. We doubt that this high quality word can and will be repeated.

Comment: P6033 L6. Narciss should be capitalized to NARCIS as it is an abbreviation. OK, done.

Comment: P6044 The two upper panels are almost unreadable. I suggest the authors use color to identify the flights rather than symbols, as done in the lower panel. Also, change the x-axis scale and labels of these 2 figures to be more legible and more logical. For example, the top panel could have 1999, 2000, 2001, 2002 and 2003 as the major (horizontal labels). The next panel could be 2007, 2008, 2009 and 2010, and could be slightly shorter to indicate the shorter time for the CARIBIC-2 data and offset.

Reply: Figures are corrected to improve readability. I

Comment: P6046 The panels are too small; they’re very hard to read.

Reply: Figures are corrected to improve readability. However the figure size has been

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determined by the size of ACPD pages.

Comment: P6048. The caption states “CO<sub>2</sub> isotope data vs. N<sub>2</sub>O”. There is no plot of this. There is a plot of “N<sub>2</sub>O vs. CO<sub>2</sub> isotope data”. Only the O<sub>3</sub> vs. CO<sub>2</sub> plot has an “L” shape.

Reply: Corrected to “N<sub>2</sub>O vs. CO<sub>2</sub> isotope data”. The d<sup>13</sup>C(CO<sub>2</sub>) plot has visible L shape (from right to left), the L-shape for d<sup>18</sup>O is indeed less visible. Here we give typical flight, sometimes L-shape is more visible for d<sup>13</sup>C, sometimes for d<sup>18</sup>O. Shall we give more plots?

Comment: P6052 This is a really busy figure. Too busy. I cannot identify the series. The x-axis needs to be relabelled.

Reply: This busy figure is now optimized for better readability, some data removed, the axis will be relabeled.

Comment: P6053 Change x-axis of top left figure to be the same as the 2 lower panels, i.e. 1000/CO<sub>2</sub>. Increase the font size.

Reply: The figure is optimized as suggested.

Comment: P6056 The caption needs to be rewritten to make sense and to remove errors (e.g. Mauna Low). Also, the data shown are d<sup>18</sup>O(CO<sub>2</sub>) yet the reference is to GLOBALVIEW-CO<sub>2</sub>C13. I suspect the real reference for this data should be White & Vaughn (2009).

Reply: The caption is re-written as suggested; the reference is corrected, also in accordance with the latest recommendations given on the NOAA ftp server.

General comment about the Figures I printed a copy for reading “offline” as I suspect many readers shall. Basically, I found the figures unreadable. The axis labelling needs to be larger and more logical. (See comment RE P6044) Dates should be in an acceptable format and a larger font size should be used for clarity. Also, many of the figures

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contain far too much data for comfortable viewing and understanding (e.g. P6052). This may be addressed in the next stage of publication but it should have been done as a matter of course by the authors before submitting the manuscript.

Reply: The figures are optimized as suggested.

Comments about citations: The previous reviewer has already identified that the use of citations needs to be corrected to Author (year) in many places. Comments about abbreviations: There is extensive use of abbreviations in the text. Some of them are presently not explained and should be. The ones I have noticed (and not mentioned above) are: NIST (National Institute of Standards and Technology) NARCIS (NIES Atmospheric Reference CO2 for Isotopic Study) RM (Reference Material)

Reply: Citations have been checked and systematically corrected, in accordance with the ACP style. All abbreviations as suggested by the reviewer-1 and reviewer-2 are clarified. However we believe that nowadays some abbreviations are of common use and should not be clarified, such as ppm, ppb (see comment to P6029 L6 above), NIST and RM or NIST-RM. In many publications it is given without explaining these abbreviations (examples are Ghosh et al., 2005 and numerous papers by W.Brand and co-authors see [http://www.bgc-jena.mpg.de/service/iso\\_gas\\_lab/publications/](http://www.bgc-jena.mpg.de/service/iso_gas_lab/publications/)) but with proper references as we did also.

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