

***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.***

**Anonymous Referee #2**

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I don't think the authors have done a good job of interpreting results from the CARIBIC project with this paper. I found the paper difficult to follow from the outset starting with the title. I don't think the focus of the paper is, or should be, on analysis of “accurate  $^{13}\text{C}$  and  $^{18}\text{O}$  isotope measurements”. The paper is really about the analysis of the air samples with regard to troposphere/stratosphere mixing. I agree with the previous reviewer that the paper is too long and that the carbon cycle does not appear to be the main focus, even though the title suggests it is.

In the introduction the authors describe the main aims of the paper to be 1. Present

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CARIBIC information and measurements 2. Show how detrending of time series was performed and which air masses were sampled 3. Apply tracer-tracer correlations to demonstrate UT/LMS mixing 4. Discuss FT and UT data then compare CARIBIC data with NOAA-ESRL data 5. Discuss the future data use in models and discuss the quality of the data I don't think the structure of the paper or its contents achieve these aims as clearly as they are set out in the Introduction. I recommend the authors 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.

I made many comments on my printed copy of the manuscript, and I include these below, but I mention three specific points.

First, I don't think the detrending procedure is appropriate as implemented. In principle it is desirable to detrend but I suggest the CARIBIC-1 and CARIBIC-2 data should be detrended separately over their much shorter time periods, still using the NOAA-ESRL data, but then simply shifted to a common level using the mean offset of the two detrended sets. This would avoid using the NOAA-ESRL data for the 5 year period (2002-2007) for which there is no CARIBIC data. It may be a simple exercise for the authors to do this and compare the results from the two different detrending procedures. (See comment below RE P6009).

Second, the authors emphasize the measurements are accurate, even going so far as to state (P6000, L5) that they are “highly accurate” and (P6000, L7) “the highest precision and accuracy  $d^{13}\text{C}$  and  $d^{18}\text{O}$  data”. While the measurements may be both accurate and precise, I suspect the authors have overestimated the precision of their measurements given the emphasis in Section 2.2 on two sources of differences in  $d^{13}\text{C}$  measurements, one from different algorithms [Assonov – Allison] of -0.03 per mil, and one of -0.04 per mil based on an intercomparison between IRMM and MPI-BGC. I assume these could be significant for the precision considerations as well as the accuracy, given that Table 1 suggests a total uncertainty of 0.022 per mil for each

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datum. 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. (See also comment RE P6006 below).

Third, I would prefer to see the paper end on a section titled "Conclusion", with some conclusions drawn from the presented analyses, rather than a "Summary and Outlook" dot point list.

According to the ACP guidelines I rate the paper as: 1. Scientific Significance: Fair (3)  
2. Scientific Quality: Good (2) 3. Presentation Quality: Fair (3)

Specific Comments (P for page, L for line):

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.

P6002 L11. The comments about d18o data should contain reference to the 2 Cuntz et al papers in JGR 2003 (see below). L27. Should this be "primarily" rather than "basically" and is CARIBIC a "reactive chemistry" project?

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. L17. "fore" should be "for"

P6004 L25. Which airline operated the Boeing 767?

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.

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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. 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 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.

P6007 L8. Why were the two samples "suspect"? L17. Expand GHG to be (I assume) GreenHouse Gases. (Should this be GG rather than GHG?)

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. L19. "aver" becomes "over"

P6009 L6. The sentence starting "Later" could be changed to "Later in the manuscript we describe our selection of N2O concentration for this purpose". 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.

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

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

P6014 L1. The plots don’t show an “L” shape and the plots referred to in Figure 5 are not “vs. N<sub>2</sub>O reversed scale” they are “N<sub>2</sub>O vs.” plots. This is also an error in the caption of Figure 5 (P 6048). L24. d<sup>13</sup>C(CO<sub>2</sub>) and 1/CO<sub>2</sub> are numerical expressions relating to CO<sub>2</sub>, they don’t share source and sink properties. Also, why mention 1/CO<sub>2</sub> here?

P6015 L8. Add “(blue symbols)” after “UT/LMS mixing” and “(red symbols)” after “affected directly” to help readers. 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?

P6016 L4. The apparent SF<sub>6</sub> age should be referenced if it is not plotted. L11. Delete “also” and add a comma after “masses”. L13. Delete the “(“ before Zahn. L17. Replace “not. CO<sub>2</sub> does exchange oxygen” with “not as CO<sub>2</sub> exchanges oxygen” 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)?

P6017 L1. Which “surface” is meant? Continental surface? Oceans’ surface? L5-7. I don’t understand this sentence. Should “traces” be tracers”? L10. Change “which bears” to “more”. L13-18. This needs to be clarified. Figure 7 does not show me that positive values of CARIBIC-1 d<sup>18</sup>O(CO<sub>2</sub>) are reliable.

P6018 L1. What are the “new” data? CARIBIC-2 or data selected using a criterion of

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d<sup>13</sup>c(CO<sub>2</sub>) = -8.2? L2. I would hope that d<sup>13</sup>c(CO<sub>2</sub>) and d<sup>18</sup>o(co<sub>2</sub>) reflect air mixing in a similar way to CO<sub>2</sub>! L8. Add “but no long term trend” after “gradient” and take it out of L9. L18. Add “but contain the same features” at the end. L22. “because of” becomes “for” and delete “being” L25. I can’t see a gradient in the CO<sub>2</sub> (Figure 8) and neither can the authors (P6020 L5).

P6019 L4. Where is the data on the NOAA website? Give the URL and an access date. L6. Should the last sentence include a reference to the Schuck et al 2010 paper? L9. For surface stations a statement such as “well mixed free troposphere” could be added to highlight the difference from stratosphere. L20. Does adding the few CARIBIC-1 data add value to the figure and/or discussion?

P6021 L9. The comment in brackets should be deleted. L10. Add “in” after stations. This section is hard to read as many of the data subsets are not discernable on Figure 9. L27. “Regardless the fact that” becomes “Although”.

P6022 L3. “demonstrating a” becomes “show” L4. “and are used qualitatively only”. L6. The high d<sup>18</sup>O(CO<sub>2</sub>) values might suggest SH air; “apparently” is a loose term. 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 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. 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.

P6024 L21. Replace “large. The reasons for this” with “and”

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

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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.

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

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

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

P6028 L5. "applied" becomes "used" 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. L10. "basically in agreement" means there is some noticeable disagreement. Is that correct? L16. "Though the modelling studies of Miyazaki et al (2008, 2009) . . ." L18. Delete the parentheses. L20-25. It is not clear what these 2 studies contribute to the analysis of the CARIBIC results. L23. First use of STE, expand the abbreviation. L28. "our final figure" is not needed.

P6029 L3. "labs" becomes "laboratories". "lag" should be "difference" or "separation". L6. This is the first mention of the 2000 ppb (2 ppm) H<sub>2</sub>O and CO<sub>2</sub>>125ppb filters. (Are ppb and ppm explained?) 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"? 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

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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".

P6030 Section 4.5 "Future use of data . . ." does not mention any future use of the data.

P6031 L15. Where are the data available?

P6032 L2. Should N<sub>2</sub>O be referred to as the most suitable or appropriate tracer, rather than the most adequate? L3. Remove parentheses. L4. Add "(H<sub>2</sub>O > 2 ppm)" after "plumes". 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. L19. Point 6. I find this confusing. Do the authors mean something along 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. 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?

P6033 L6. Narciss should be capitalized to NARCIS as it is an abbreviation.

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

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(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.

P6046 The panels are too small; they're very hard to read.

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.

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

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.

P6056 The caption needs to be rewritten to make sense and to remove errors (e.g. Mauna Low). Also, the data shown are  $\delta^{18}\text{O}(\text{CO}_2)$  yet the reference is to GLOBALVIEW-CO<sub>2</sub>C13. I suspect the real reference for this data should be White & Vaughn (2009).

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 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.

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 CO<sub>2</sub> for Isotopic Study) RM (Reference

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Material)

Extra references for the authors to consider that I mention above: Cuntz, M., P. Ciais, G. Hoffmann, and W. Knorr (2003a), A comprehensive global three-dimensional model of  $\delta^{18}\text{O}$  in atmospheric CO<sub>2</sub>: 1. Validation of surface processes, *J. Geophys. Res.*, 108, 4527, doi:10.1029/2002JD003153.

Cuntz, M., P. Ciais, G. Hoffmann, C. E. Allison, R. J. Francey, W. Knorr, P. P. Tans, J. W. C. White, and I. Levin (2003b), A comprehensive global three-dimensional model of  $\delta^{18}\text{O}$  in atmospheric CO<sub>2</sub>: 2. Mapping the atmospheric signal, *J. Geophys. Res.*, 108, 4528, doi:10.1029/2002JD003154.

White, J. and B. Vaughn (2009), University of Colorado, Institute of Arctic and Alpine Research (INSTAAR), Stable Isotopic Composition of Atmospheric Carbon Dioxide (13C and 18O) from the NOAA ESRL Carbon Cycle Cooperative Global Air Sampling Network, 1990-2007, Version: 2009-06-01, Path: <ftp://ftp.cmdl.noaa.gov/ccg/co2o18/flask/event/>.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 10, 5999, 2010.

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