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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Analysis of accurate ^{13}C and ^{18}O isotope measurements of CO_2 in CARIBIC aircraft air samples from the tropical troposphere, and the upper troposphere/lowermost stratosphere" *by* S. S. Assonov et al.

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We thank reviewer-1 for the careful and constructive review.

We agree with most of the comments and have made corrections accordingly. The paper may appear somewhat long, though there are some other papers at ACP of similar length or longer [1-3]. However we note that systematic observation of the isotopic composition of CO2 using commercial aircraft is in development and this is the first publication we are aware of. Therefore we briefly describe some technical and logisti-

cal aspects, aspects of uncertainty and comparison with other labs, focus on the effects which can be observed (LMS/UT mixing, plumes, global CO2 trend in the remote troposphere etc) and then consider how well the first systematic observations by CARIBIC agree with these expectations. This explains the amount of material given in the paper. Although the de-trending is a more common issue in time series analyses, the filtering out of stratospheric contributions to sample air is not that a common procedure. The ER2, or balloon samples usually dealt with clear stratospheric air. Intercontinental jets cruise at in the UTLS at mid to higher latitudes. Therefore we treat this aspect in more detail and discuss which tracer is more robust.

In the revision we have focused on making better connections between different parts, in particular between the title, abstract and introduction and, and we have deleted the text that was repeated. Indeed, making a coherent story or "take-home" message running through the whole manuscript appears to be difficult, in particular connecting the UT/LS mixing analysis and the part on tropospheric data and carbon cycle analysis that follows. This manuscript as the whole might have been splitted in two or three manuscripts (data overview, UT/LS mixing and observations in the troposphere) but we have decided making one manuscript. Although a modeling study may follow, the data defensively need an introducing paper as we present now. The manuscript has two centers: (i) the point of uncertainly and data reliability, verifying whether our approach (sampling, analytics etc) is precise and accurate to catch trends and air transport at flight altitudes; (ii) brief overview of mixing structures and air transport phenomena at flight altitudes (both UT/LMS and upper tropospheric transport) as well as observed isotope trends. Our message is that CARIBIC has proven to be capable to and has recorded global CO2 isotope distribution at flight altitudes in the Northern Hemisphere. For comparison we name the complex and even longer paper by Allison and Francey [4] - they needed to give lots of technical and analytical details in order to verify stable isotope trends in atmospheric carbon dioxide for the Southern Hemisphere and data consistency with other labs, in particular with NOAA. The matter of reliable observations is really complex.

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In the revision we better explain where we see the significance of the new data. Obviously the advantage of observations by regular aircraft is that new data substantially extend the global data set accumulated by (mostly) surface observations of NOAA and CSIRO. Years ago NOAA has initiated observations by using research aircraft, or hiring small aircraft, with emphasis on vertical profiles. Though the use of commercial aircraft is advantageous, the approach has also some limits and it needs to be optimized. A particular question to be addressed is the difference between low and high resolution sampling (comparison between CARIBIC-1 and CARIBIC-2 helps here). Another program, CONTRAIL has made CO2 observations for years. The researchers in CONTRAIL consider CO2 isotope analyses as a next step. Thus, aircraft CO2 isotope data are assumed to be a valuable complimentary information to CO2 concentration measurements. We stress that significance of our new data can only be demonstrated by implementing data in models (new generation 3-d models coupling processes in the atmosphere, ocean and biosphere). This is beyond the scopes of this manuscript. The time when significant findings were based on a few measurements only appears to have gone.

We thank the reviewer to notice that, we cite: “one point that could be made more strongly in the paper, and to me the most interesting result, is that even at high altitudes, the relatively small amount of CO2 variability seems to be largely explained by fossil and biological uptake/release as evidenced by the Keeling plot intercepts. This is happening despite the fact that, at an annual mean level, ocean uptake is of the same order as terrestrial uptake, about 2 billion tons C per year, globally.” This is very interesting indeed and we discuss this now in more details. We note however that these plots are based on de-trended data. Therefore inter-annual effects have been removed by de-trending and ocean uptake appeared to be masked by de-trending. Thus one needs to consider conclusions based on these Keeling plots carefully, by considering the effect of de-trending itself and thus introduced errors. The difference in sampling resolution may also play a role here. The Keeling plot for trended data gives variability due to seasonal sources-sinks, Thereafter the agreement between on the Keeling

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plot indicates that overall budget of seasonal sources and sinks for CARIBIC-1 and CARIBIC-2 is practically the same. We discuss that by a few sentences in the revised version.

Below we give our replies on specific points given by the reviewer -1.

Comment: 1. p.6000 l.28: the claim that this data set is 'important' may be true, but this statement is not backed up in the text.

Reply: We consider that new and high quality data for unexplored region of well-mixed troposphere as well as for the UT-LMS mixing region are important.

Comment: 2. Introduction. As mentioned above, the focus in the introduction on the carbon cycle is a bit misleading, because the paper as a whole is only partially about the carbon cycle. At the very least, this discussion should be abbreviated (the first four paragraphs could be condensed to one or two), and it should be explicitly stated that the nature of the measurements (near the tropopause) do not lend themselves to information on surface-atmosphere fluxes.

Reply: We reformulate the abstract in order to better address the paper and in some degree re-focus the introduction. Still we need to describe in the introduction why carbon cycle observations are important and milestones of it. About 460 words of the introduction discuss the role of isotopes in carbon cycle observations whereas ca 580 words describe importance of aircraft observations, the CARIBIC program and introduce the paper. We disagree that measurements near the tropopause do not provide information on surface-atmosphere fluxes. Sampled are well mixed air masses which provide information on large areas; that is somewhat similar to tall towers having large fingerprinting area. Thus, based on CARIBIC data Schuck et al. [5] provided estimations of surface-atmosphere fluxes for CO2, CH4 and N2O in the Indian summer monsoon; understanding isotope data appears to be more complex.

Comment: 3. p6001 l. 16 Replace 'Carbon America' with 'North American Carbon'.

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Reply: Done.

Comment: 4. l. 23. Some references should be given for stable isotope measurements.
Reply: Done.

Comment: 5. p 6003 l. 25. I was not able to find the brief discussion of the future use of the data in models.

Reply: Indeed, at the moment CARIBIC does not have collaboration with modelers. Involvement of modeler(s) is under discussion.

Comment: 6. p 6006 l. 8. The equation should start with two 'deltas' upper-case, followed by lower-case, because this is a difference (thus upper case delta) of isotopic (lower case) delta values.

Reply: We agree, corrected.

Comment: 7. Observational data: For a paper like this, where one of the main goals is to present the data, a clear reference for the data location must be given. It appears that at least some of the data is housed at the World data center for climate. (why not the World data center for greenhouse gases?)

Reply: The data are on the CARIBIC data server and are available upon request to the project coordinator.

Comment: 8. p 6009 l19- 26. This entire paragraph is confusing to me and needs to be re-written. First, what is the consistency test that is applied to the CO2 and _13C trends? Second, isn't the _13C 'decrease rate' the same as the 'trend'? Why does one need to combine the trend with the CO2 increase rate? Also it is not clear what the y-intercepts here refer to. What exactly is being plotted?

Reply: The paragraph is rewritten. Plotted are d13C(CO2) annual means vs CO2 annual means and then the linear fit applied. Next, the d13C(CO2) increase rate is calculated based on this fit and the CO2 increase rate. (The latter is estimated simply

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by plotting CO2 (annual means) vs the year of observations.) For the years 1999-2008, the linear fit for CO2 annual means captures the trend really well (the fit to the data was also discussed with J.White). From our point of view this also provide additional check for consistency between the CO2 increase rate and the d13C(CO2) rate. There are several reasons to make the check in this way:

1. The ratio of the year-to-year changes in d13C(CO2) (the same is valid for the seasonal variability) to the analytical uncertainty is much smaller than the same value for CO2. Thus d13C(CO2) signals (annual means also) are prone to fluctuations.

2. Year to year changes in d13C(CO2) and CO2 are due to the same reason – disbalance of sources and sinks. However relative year-to-year changes for d13C(CO2) (relative to changes one expects from fossil fuel combustion) are smaller than the relative year-to-year changes for CO2, this is the effect of ocean buffering (CO2 exchange between the atmosphere and the ocean being faster than CO2 removal from the atmosphere buffers the atmospheric d13C(CO2)). At the same time actual values of year-to-year changes in d13C(CO2) and CO2 vary from one year to another and, also, may vary from one station to another (spatial inhomogeneity).

Comment: 9. Section 3.3. How are FT and UT distinguished. Could you generalize and just use 'troposphere'? Please explain and/or cite references.

Reply: Flights at mid latitudes are close to the tropopause and/or cross the tropopause; this is UT/LMS region. Correspondingly, the air masses distinguished from LMS air masses by using adequate stratosphere/troposphere tracers (N2O in our case) are named as upper troposphere (UT). The tropopause at tropics is much higher than the tropopause at mid latitudes, so that flights in the tropics sample the air being far below the tropical tropopause. Thereafter these air masses are named as free troposphere (to be precise – tropical free troposphere), in order to distinguish it from air masses being close to the tropical troposphere.

Comment: 10. p6012 l12. Should the first instance of 'N2O' be 'CO'?

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Reply: No, here we refer to the plot of N2O.

Comment: 11. p6016 l26. Is the line fit in Fig. 7 forced through a point where N2O = 150 ppb? If so, the corresponding d18O value can not be 0.5 per mil as the text seems to imply. Please explain. Also, what were the bases for choosing 150 ppb and +0.5 per mil as stratospheric 'starting points'? Reply: Explanations on constraining N2O vs d18O(CO2) plot is now given explicitly.

Comment: 12. p6021 l17. The reference CONTRAIL is impossible for a reader to follow and find the source.

Reply: Actually, CONTRAIL data are removed from the plot.

Comment: 13. p6022 l5. Should be 'qualitatively'

Reply: Corrected.

Comment: 14. p6023 l25. The last sentence is unnecessarily vague and is in conflict with p6024 l 12-13. As mentioned in the general comments, more can be said of the rather remarkable similarity of the Keeling plots, between Caribic 1 and 2 and even to a lesser degree between seasons.

Reply: The sentence is removed. More explanations on Keeling plots are given.

Comment: 15. p6024 l 11-13. The 0.1 per mil range can be interpreted (more accurately, perhaps) as an indicator of rather strong atmospheric mixing of different source and sink processes since time of 'emission', as opposed to simply the 'large scale similarities' of the source and sink processes. E.g., we know that ocean uptake results in a much different isotopic signature than terrestrial uptake.

Reply: Here we want to stress that observed correlated variability of signals is demonstrated within the very limited range (0.1 per mil) only, which indirectly confirms quality of sampling, storage, CO2 concentration measurements and CO2 isotope measurements; otherwise observing such correlations would have been impossible.

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Comment: 16. l 27. As mentioned above the value of -14 per mil is not explained clearly.

Reply: It is now explained in more details. The value of -14 per mil is the effect of ocean buffering (CO2 exchange between the atmosphere and the ocean being faster than CO2 removal from the atmosphere); this buffers the atmospheric d13C(CO2)) compared to the CO2 increase caused by fossil fuel combustion.

Comment: 17. p6025 l7-8. This similarity is very qualitative. What are the actual values?

Reply: This is really qualitative. At any station in NH the annual seasonal cycle has a variable slope on the Keeling plot; we plot MHD as example. Actual values of slopes depend on a local (seasonal) balance of CO2 sources and sinks.

Comment: 18. p6027 l 10. Change to 'help in understanding'

Reply: Corrected.

Comment: 19. l 21. How was it known that the flights 'crossed large plumes'. Please explain or give a reference.

Reply: It is based on other tracers such as total water, CO, HNMC; is explained in more details in the revised manuscript.

Comment: 20. p6030 l 8. The expert group recommendations citation is very awkward.

Reply: Corrected.

Comment: 21. Figure 9 is quite cluttered. Perhaps remove the symbols from the NOAA stations.

Reply: Corrected

Comment: 22. Figure 10 upper panel. Plot the regression line and print the slope, intercept and r2.

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Reply: Corrected.

Comment: 23. Figure 14. Remove the box-whisker legend from the plot and explain in the caption, instead.

Reply: Corrected.

Technical comments:

Comment: 1. Throughout the paper, the formatting of citations is often incorrect. E.g. '. . . paper by Callendar (Calendar, 1938). . .' should be '. . .Calendar (1938). . .'

Reply: Citations have been corrected throughout the paper.

REFERENCES:

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2. Langford B. et al.: Fluxes and concentrations of volatile organic compounds above central London, UK. Atmos. Chem. Phys., 10, 627–645, 2010.

3. Croft, B. et al. Influences of in-cloud aerosol scavenging parameterizations on aerosol concentrations and wet deposition in ECHAM5-HAM. Atmos. Chem. Phys., 10, 1511-1543, 2010.

4. Allison, C. E. and R. J. Francey: Verifying Southern Hemisphere trends in atmospheric carbon dioxide stable isotopes. J. Geophys. Res. 112: D21304,doi:21310.21029/22006JD007345, 2007.

5. Schuck, T. J. et al.: Greenhouse Gas Relationships in the Indian Summer Monsoon Plume Measured by the CARIBIC 2 Passenger Aircraft, Atmos. Chem. Phys., 10, 3965-3984, 2010.

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