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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The stable isotopic composition of molecular hydrogen in the tropopause region probed by the CARIBIC aircraft" *by* A. M. Batenburg et al.

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This paper by A.M. Batenburg presents a valuable examination of dD measurements performed on air samples taken in the CARIBIC project. Especially, as dD data in the upper troposphere region over Asia are presented for a first time. Several topics from Strat-Trop-Exchange to vertical transport within the troposphere during the Indian monsoon are adressed, yielding new information on the stable isotopic composition of the UT/LS region as well as demonstrating the potential and value of the CARIBIC data set.

A shortcoming of this version of the paper is, to my point of view, that the author missed

to describe a clear scientific aim of the paper in the introduction part. As mentioned above, several interesting results have been derived but the relevance and significance of these should be adressed.

Concering the english language, it could be worth to have it proofread by a native speaker. Some sections could be improved by re-formulation.

Thus, I accept this paper with minor revisions.

Specific comments

p.590 l.1-2 : "...in the upper troposphere – lower stratosphere (UTLS) region around the tropopause (TP)..." Do you want to emphasize anything special with the "around the tropopause" add-on ? If not, delete it!

p.591, l.8 "...it will lead to large-scale leakage of H2 into the atmosphere..." Do you really expect large-scale leakages? Isn't this too strong ? Certainly, considering the high volatility and an intensified use of H2, increased H2 emissions into the atmosphere are to be expected - an worth to be discussed. However, due to safety and probably fincancial reasons there will be a strong interest in minimizing leakages.

Table 1: Please explain the subscript and superscript numbers. Are these marking the errorbars ? Why are there no errors on the production terms ? All in all, the averge tropospheric mixing ratio of H2 you cite from the literature is 530 ppb - however, does this mixing ratio apply also to the upper troposphere, where the soil sink is neglectable? Your data imply much higher average H2 mixing ratios!

Section 1.2. What effects or consequences has this dD enrichment of the troposphere by STE? Just to study STE, there is a whole set of well studied more stable, long-lived trace gases which are easier to measure. Please, point out why it is worth to study the isotope effects, as well.

Though Sections 1.2 and 1.3 give a nice introduction into dD issues, the information seems to be disordered. Just a suggestion: Re-order Sections 1.2 and 1.3; one section

regarding basic dD issues and information in the tropopshere as well as in the stratopshere (e.g. p.592 l.2 - 11 + parts from 1.3) followed by an overwiew on yet performed studies and the Caribic project (e.g. p.592 l.14 -p.593, l.26). Maybe, you could even add the background values of dD (tropospheric and stratospheric) in Table 1 ?

p.595 Description of the sampling unit: Why are there two units - are parallel samples taken or are the units used on after the other ? Why does the sampling time (duration) change? Is it to adapt to the different pressures at different altitudes?

p.595,l.13-14: "Due to the regularly spaced sampling, the distribution of samples is likely representative of the different air masses encountered by the aircraft." I would say this is strongly dependent on the actual distribution (horizontal and vertical) of air masses during the flight. If there is strong filamentation or fine scale structures are observed, the sampling is not necessarily representative even though or maybe especially since you are sampling in a regular intervall. However, the number of flights and samples, regions captured by the flight tracks (...) should yield relatively robust statistics.

p.595, l. 22 averaging over 15 trajectories. Are fifteen trajectories calculated for each sampling location? Or the fifteen closest trajectories ? Please, explain.

p.597, l.20 "This estimate can be made for any sample with an m(O3) higher than at the local thermal TP". If I understand the procedure in Sprung and Zahn (2010) correctly, the O3 mixing ratio has to be higher than the average O3 mixing ratio at local thermal TP of the corresponding adjacent balloon sounding sites !? Which sounding sites have been used to derive the vertical distance to the TP, especially, for the flights over Asia? Is the procedure to derive the vertical distance above the tropopause from O3 still applicable for flights in the subtropics (lat < 35°) ? Could there be any problems with the analysis if strong horizontal gradients (streamers etc.)occur e.g. in spring to early summer !?

p.598,l.4-5 "This was repeated until the averages did not change anymore..." Just to

understand the procedure correctly: What do you exactly mean? You did not find any more data points outside the +-3s range, thus, the average was constant? Or, averages n and n+1 did not show a statistically significant difference!?

p.598, l.23: Why is it representative?

p.599,l.5ff "The difference between the m(H2) averages is less than 10 ppb, which is small compared to the 17 ppb standard deviation on the averages."

What are the actual average tropospheric and stratospheric mixing ratios of H2 on this route ? Elevated H2 mixing ratios in tropospheric samples - many in the southern part of the flight - could those be influenced by southern hemisphere or tropical air masses (Fig.2) ? Did you calculate the tropospheric average using the complete latitude range ? Some of the stratospheric samples (at $\sim$40°N) seem to exhibit elevated H2 mixing ratios, though (Fig.2) - possible reasons!?

Section 3.1. Nice discussion of possible pollution effects! However, you write that a possible contamination by water vapour during the take off and landing phase is unlikely - why ? The fact, that intermediate canisters do also show pollution signatures could be due to other effects. As you very nicely point out, there are several possible causes. It is not necessarily only one single cause that is responsible for every contaminated flask. Fig. 3: What if one ore more of the data points with dD < 0 and 1/H2 < 1 are ommited ? What source signature do you yield in that case?

Will there be a further examination of dD signatures from aircraft exhaust?

Section 3.2

p.601 l.25 "The O3-derived altitude can be considered as a measure of the degree of mixing between low-O3 air from the troposphere and high-O3 air from the stratosphere. When it is used to plot m(H2) and dD against mean trajectory latitude and height (Fig. 4a,b)..." Sounds like you actually plot O3 vs the mean trajectory height. Maybe reformulate. Further, are you referring to the average of 15 trajectories as mentioned

in Section 2.1 or as described in Fig 4 a 5-day trajectory? Do you average the complete trajectory - sorry, guess, I did not understand your procedure! (See also under Technical Corrections referring to Fig. 4)

p.602, l.5 - 19 The correlations are compact, since - as you mention - lifetimes of the considered species are long compared to the tranport times, but what does this hace to do with the age of air ? Especially, since you link non-conserved trace gases N2O and CH4 (neithr in the troposphere nor in the stratosphere) as an "indicator of the average age of air". What do you want to tell ?

What would be an advantage using dD instead of other long-lived tracers?

p.602, l.14-15: lower stratosphere or lowermost stratosphere ?

p.603, l. 6 $\sim$25ppb is still significantly larger than the troposheric increase of $\sim$15 ppb observed by Duglogencky et al.(2009). Tropospheric CH4 has a latitudinal gradient. How do the CH4 mixing ratios compare when you look at a similar latitude range (like $\sim$43°N, where the balloon samples from Röckmann et al. (2003) were taken)?

p.605, l. 10 560ppb; is this the average mixing ratio of the non-monsoon data ?

Technical Corrections:

p 590, l. 7 and p 590, l.4 and p.596,l.10 and l.13: either use analysed or analyzed ; please check the document

p 590, l. 21: unusual to use lowering, maybe better "decrease"

p. 592 l.3: ...to constrain the H2 budget...

Please check the citition rules; parentheses or not: e.g. p.594,l. 11 - 12 , here, I would expect only the year in parentheses. p.596, l. 11 -12 ...

p.595, l.10 please use "Sampling" instead of "Collection"; re-formulate the sentence.

p.595, l.25 Please, write out the parentheses

p.596, l.16 ff use "$\sim$"

p.596 Headline of 2.3 Re-formulate to "Analysis of m(H2) and dD"

p.598, l.8 I think, at the beginning of a sentence you have to write out the numbers or re-order the sentence to omit this problem.

p.598, l.12 whether - missing h

p.598, l.17 maybe better "regions" instead of "parts"

p.602, l.28 "$\sim$" ... please check the document!

p.603, l.4-5 "The agreement between the (Röckmann et al., 2003) data and the CARIBIC data is better." i) Röckmann et al. (2003) data ii) is better. Re-formulate.

p.603 l.20 "...parameterizing dD from H2...

p.604, l. Especially,...

p.607, l. 14 Acknowledgments: "...support from the Dutch...

p.613,Table 1, Caption: ...isotope budget as estimated...

p.614, Table2: Caption: ...data sets... (m(CH4))from Rahn et al. (2003) and Röckmann et al. (2003)...

p.618 Fig 4, Caption: delete several ":" The unit of "height above TP" is missing. How is the colour of squares derived - by averaging the samples within each square? Please, describe!

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 589, 2012.