Atmos. Chem. Phys. Discuss., 14, C11929–C11938, 2015
www.atmos-chem-phys-discuss.net/14/C11929/2015/

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Simulation of the isotopic composition of stratospheric water vapour – Part 1: Description and evaluation of the EMAC model" *by* R. Eichinger et al.

R. Eichinger et al.

roland.eichinger@dlr.de

Received and published: 5 February 2015

*Reply to referee 2

GENERAL REMARKS

- *The paper describes the basic performance of a a water isotope module of the*

EMAC model in the stratosphere. The description is largely clear, but the analysis is not very deep and sometimes a bit superficial. The discussion around the tape recorder isotope effect is interesting, because some effects that could contribute to the discrepancy between published observations are discussed, even if the issue cannot be resolved.

There are two technical issues that could have been done better in the model setup. The first is rather simple: The entry value of dD in CH4 to the stratosphere was set to -68 per mill, which is clearly too high compared to high precision measurements (based on the presently accepted relation to the VSMOW scale). The value apparently originates from a previous model study that also incorporated this high value. In the comparison with this model, this therefore does not lead to problems, but in the com- parison to the data it introduces a significant shift. The authors decided not to correct for that, but it is very easy to rescale the values and I suggest to perform this correction. I suggest to correct the model entry value to the experimental value in order to show the values on the adequate scale.

The second issue is a bit more problematic, namely leaving out molecular hydrogen in the mass balance, in particular for Deuterium. The authors acknowledge the issue, but still do not take it into account. The argumentation why this is done is questionable, certainly not convincing (focussing on the stratospheric entry values should be done with the correct values). Whereas the individual fractionations are indeed partly not well quantified, the cor- relation between CH3D and HD (and CH4) is well established (see McCarthy et al., doi:10.1029/2003JD004003, 2004, Rahn et al, doi:10.1038/nature01917, 2003, cite these papers!) It should be easy to add a parameter for this effect in eq 12, where the CH3D change is translated to HDO. Basically it is not precisely 1 molecule of HDO that is formed from one CH3D, but a bit less, since some of the deuterium will be stored in HD. The correlations can be obtained from the data in McCarthy et al and conversions from the other stratospheric datasets (Rahn, *Rockmann, Rhee). In the present form, the deuterium mass balance is wrong. Although there is only 0.5 ppm of water in the stratosphere, the isotopic composition varies by several hundred per mill, so the effect is estimated to be several tens of per mill. The fact that it has not been taken into account is then cited later several times as possible cause of a discrepancy, so it is really a shame that it was not simply done!*

The comparison of HDO between the model and satellite instruments is not very strong, if it is presented without a similar comparison of HHO. The first order effects of HDO are related to HHO (more HHO, more HDO), so such a comparison should be done with HHO, where the uncertainties in the satellites are likely smaller. The dry bias of EMAC compared to some satellite datasets is discussed, but the effect on HDO is not always adequately discussed. For example, spatial changes in HDO in the stratosphere would in first order be due to spatial changes in HHO. Differences in fractionation constants will only lead to second order effects and are most likely not responsible for the larger changes in HDO that are discussed.

The fact that the incorporation of laboratory based KIEs into a global model with in- dependent OH, O1D and Cl fields leads to a very good agreement with the observed isotope-mole fraction relation as shown in Fig 3 could be discussed in more detail. It is not straightforward, since also mixing effects are important for the isotopic composition in the stratosphere.

Thank you very much for reading carefully and for giving advice and help. Please find our answers to your specific comments (in blue) in the next sections, assigned to the comments in your uploaded pdf.

SPECIFIC COMMENTS

- 23808-4 *separate from what? not clear*

  “separate“ from the actual hydrological cycle. Will be changed to “additional (and separate from the actual hydrological cycle)“

- 23808-7 *HHO and*

  Thanks, will be corrected

- 23808-7 *does it also include 18O?*

  No, it does not. ^{18}O is included in the ”physical“ hydrological cycle, chemistry has not been implemented for it, though.

- 23808-8 *also 18O?*

  No, see above.

- 23809-11 *to*

  Thanks, will be corrected

- 23810-27 *stratospheric balloon*

  Thanks, will be corrected

- 23812-19 *this should be delta values (so isotope ratio differences) not mixing ratios*

  Indeed, thanks.

- 23814-11/13 *CH4*

  Not sure what you are referring to here. Here we denote the CH4 submodel, hence the 4 is not a subscript. We will add submodel behind it to make it more clear.

- 23814-21 *pseudeo first order rate coefficiets*

  Thanks, will be corrected

- 23817-7 *Effect of HD*
  23817-15 *This is an important constraint. Whereas the individual fractionations are indeed not well quantified, the correlation between CH3D and HD (and CH4) is well established (see McCarthy et al., doi:10.1029/2003JD004003, 2004, Rahn et al, doi:10.1038/nature01917, 2003, cite these papers! It is relatively easy to add a parameter for this effect in eq 12, where the CH3D change is translated to HDO. In the present form, the deuterium mass balance is wrong. Although there is only 0.5 ppm of water in the stratosphere, the isotopic composition varies by several hundred per mill, so the effect is estimated to be several ten per mill.*

  Thank you very much for your help. We will approximate this parameter for our calculation, with:

  $$\partial[HD]\partial t = -6.32\cdot 10^{-5}\cdot\partial[CH_4]\partial t$$

  derived from McCarthy et al. (2004). With

  $$\partial[HDO]\partial t = -\partial[CH_3D]\partial t - \partial[HD]\partial t,$$

  this yields for our equation 12:

  $$\partial[HDO]\partial t = -\frac{\partial[CH_3D]}{\partial t}y + 6.32\cdot 10^{-5}\cdot\frac{\partial[CH_4]}{\partial t}y$$

  with $y = \frac{M_{air}}{M_{HDO}}\left(\frac{1}{1-HDO}\right)^2$ only dependent on HDO.
  We will perform this correction, carry out another simulation, replot everything present it and change the concerned paragraphs accordingly.

- 23818-1 *I cannot find quickly where this value originates from, but it is wrong. I fear that in one of the earlier publications the digits were transposed from -86. This is what many high precision measurements show, -68 is far too high (see Umezawa, www.atmos-chem-phys.net/12/8095/2012/ , Rice et al., doi:10.1029/2002JD003042, 2003 , Rockmann et al., 2011). You have cited the last one, should also cite the others. The Irion paper does not really provide information of acceptable quality and is not valid as validation.*

  Thank you. We will perform another simulation and use the value -86‰, as indicated in Rhee et al. (2006). We will replot all the figures and change the text accordingly.

- 23819-16 *???*

  Reformulated to: allows to evaluate various isotope fractionation effects

- 23821-4 *Too high, see above, but for model comparison not a problem*

  For this figure we will still use the -68‰, in order to have the direct comparison.

- 23821-15 *what does at first mean here*

  Thanks, not sensible, we delete ”at first”.

- 23821-23 *there are many more, in the cited paper, and in Rice et al., JGR 2003. I see, below you say flights, not samples.*

  Change “samples” to “altitude profiles”.

- 23822-3 *showing*

  Thanks, will be corrected.

- 23822-3 *as function of*

  Thanks, will be corrected.

- 23822-11 *??? This would be a decrease, when you start at -68 you probably mean 100 and 200 and 0 and 100. BUt at least the simulaiton at GAP also shows values up to 150*

  Indeed, we confused the signs, thank you.

- 23822-20 *What does it mean? You focus on the strat entry values? You seem to compare the entire stratosphere. And if you focussed on the entry values, you should take a lower value.*

  Sentence will be deleted.

- 23823-5 *This may also be related to omitting H2 and HD, since it could be that in the upper stratosphere a large fraction of the originally very heavy H2 was converted to CH4 in these samples.*

  Thank you, we will add this possible explanation in the text.

- 23824-26 *HDO is so much influenced by HHO, that an "evaluation" of the HDO mole fractions without HHO is not a very strong evaluation, and maybe it is better done with HHO than with HDO. It makes more sense in the Lossow study because of the spectroscopic challenges, but the model has no measurement artifacts...*

  23825-11 *I assume that EMAC is then also simply dryer in HHO. If not, it would reflect a different isotope RATIO, which would be more worthwhile to study.*

  23826-4 *See comments above, so there is a dry bias in HHO in EMAC compared to MIPAS, so it is not a surprise that there is also a dry bias in HDO*

  Thank you, this is indeed a very important point, which we did not consider enough. We will add a comparison of satellite and model data of HHO in the same

  manner as presented here for HDO and, depending on the outcome, change the results, discussion and conclusion sections accordingly.
  In fact, the H_2O profiles and their deviations from the satellite measurements are very similar to the HDO profiles and deviations. First order differences will certainly have to be due to this, fractionation effects and also the lack of the incorporation of HD seem to play a minor role.

- 23827-13 *If the delta value is -500 per mill and matches the observations, then the dry bias must be the same for HHO and HDO, not be higher in HDO.*

  Will be corrected to: in H_2O and HDO.

- 23829-1 *applied here*

  Thanks, will be corrected.

- 23829-3 *Bot you showed that H2O is also dry biased*

  Yes, but this effect could especially change HDO and thus increase $\delta D(H_2O)$ in the lower stratosphere during boreal summer, when the differences in $\delta D(H_2O)$ between model and satellite observations are largest. We will add a sentence, in order to clarify this.

- 23829-6 *Also here, the comparison has to be made relative to the HHO change. If this also increases stronger as in the satellite observations, than this has nothing to do with fractionation, but total chemical conversion.*

  Thank you very much, we will add this, see above.

- 23829-16 *cite Rahn et al 2003*

  Thanks, will be included.

- 23829-24 *As mentioned above, it could be taken into account as a relatively simple modification to the conversion equation from CH3D to HDO, no need for explicit fractionations in all steps*

Thanks, see above

- 23830-13 *could that not also be due to seasonality of convection?*

  We do not expect a general phase shift of convection in EMAC compared to reality. Simulated patterns of moisture on the 390 K isentrope compare well with the observations of Randel et al. (2013, Nature Geosci.) in the time evolution of minimum and maximum values due to the seasonal shift of convection. Yet, the seasonal cycle of convection can only be evaluated indirectly by an analysis of the distribution of precipitation or by the redistribution of heat, momentum and moisture in the atmosphere. This kind of analyses have already been performed for the EMAC and ECHAM models and published in (see Tost et al., 2006, ACP; Hagemann et al, 2006, J. Climate). They found that the seasonal cycle of zonal mean precipitation (convective and large-scale clouds) and integrated water vapour, which were evaluated from different EMAC and ECHAM model simulations are in accordance with observations.
  Though, we found that due to the coarse vertical resolution of the MIPAS retrieval, there might be a possible delay in the retrieved tape recorder of up to 1 month at maximum possible in the MIPAS data.

- 23831-3 *allow*

  Thanks, will be corrected.

- 23831-9 *in which study? DO you mean the present study? Or a future study?*

  Will be changed to: In the present and in the companion study...

- 23831-19 *This could be discussed more thoroughly in the paper*

  Thank you for the hint, we will add more information about this.

- 23831-26 *As mentioned above, it can be more than just fractionations*

  Yes, will be taken care of, see above.

SUPPLEMENT

- Page 3 *reformulate*

  Will be reformulated to: to evaluate various isotope fractionation effects

- Page 4 *why do you show the only the absolute differences, This suppresses potentially interesting information.*

  The display would become confusing and thus hard to interpret. Anyway, the regions which show large discrepancies are evaluated in detail in Fig. 3.

- Page 7 *???*

  Sentence reformulated to: The simulated averages of δD(H_2O) in precipitation in Antarctica (in T42L90MA resolution) in Fig. 5 are compared with the results from the ECHAM5-wiso model (in T159L31 resolution) in Werner et al. (2011).

- Page 8 *Why don't you show the Werner et al data for comparison?*

  We will use the data from Werner et al. (2011) and replot the figure for the manuscript. Showing the figure directly would have caused license issues with JGR.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 23807, 2014.