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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.

Anonymous Referee #2

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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 comparison 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 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 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 independent 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.

Further detailed comments are included in the annotated manuscript

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/14/C10314/2014/acpd-14-C10314-2014-supplement.zip

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