Interactive comment on "Global modelling of H_2 mixing ratio and isotopic composition with the TM5 model" by G. Pieterse et al.

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General Comments

In their manuscript, Pieterse et al. present the global modelling study on tropospheric hydrogen and its deuterium composition with the use of TM5 atmospheric chemistry-transport model. The objective of the study is the reproduction of the global H_2 mixing and D/H isotope ratios and the comparison with the newly available observational data. The sensitivity study probes different D kinetic isotope effect parameterisations and adjustment of the D/H ratios of the sources on top of unaltered H_2 budget.

Mainly due to somewhat superficial analysis of the modelling results it is difficult to reckon whether presented study gains a substantial insight into the tropospheric H_2, complementing previous findings. Regretfully, little is given on the performance of the explicit isotope chemistry reaction scheme as such; notwithstanding, the latter is the novelty in the current model application compared to the previous attempts. I believe there is room in the paper for a brief analysis similar to that of Pieterse et al. (2009), fairly abridged to principal factors, *viz.* the predicted D enrichments in CH_4 and NMHC oxidation chains and average δD of formaldehyde for the tropospheric conditions. This could benefit to the current inquiry, yielding at least preliminary conclusions on the potential of a new approach in further constraining the tropospheric budget of H_2. Alternatively, authors may omit the proposed analysis, but then the simulated isotope budget merely echoes that of Price et al. (2007).

Whereas the importance of the stratospheric input to the tropospheric isotope composition of H_2 is confirmed anew, given quantification of the exchange term is incomplete. I am perplexed by the simplism in treating the model stratospheric H_2 composition: Please justify why resorting to the arbitrarily chosen stratosphere-troposphere boundary adequately substitutes those proxies for the stratospheric domain derivable from the model available at hand, *e.g.* meteorological data and/or chemical tracers. Furthermore, performed budgeting appears to be inaccurate, thus raises questions (see specific comments).

Overall, I find the manuscript well-outlined and sized (disregarding the missing chemistry part), although leaving the reader under an obscure impression due to much general deductions, noticeable lack of terseness and some sloppy use of terminology with respect to either modelling or isotopes matters. I suggest raising the presentation quality of this work by improving the terminology, giving more detail to the results in more concise manner. This will be appreciated by the readers of the revised version, whereas I am pleased to recommend the amended manuscript for publishing in ACP.

Specific comments

1. It is unclear whether your terms in Tables 1 and 2 are comparable to those adopted from Ehhalt and Rohrer (2009). Latter table the tropospheric estimates specifically, whereas you mention the region of the atmosphere up to 100 hPa, *i.e.* you integrate over the whole modelling domain. In this case you include the stratospheric portion of the air. Whilst the surface terms remain unaltered, the photochemical terms, hence overall $\delta D(H_2)$, must be influenced. From the manuscript I get no notion whether the stratospheric mass was masked out, as you are referring to the 'tropospheric budget', 'overall budget' and 'global budget' throughout. There may be a point supporting my suspicion that the budget is incomparable as being not the tropospheric one: The OH sink term is ~20% larger than that from the previous estimates, despite that the tropospheric H_2 burden and rate of H_2+OH reaction are comparable. From this I infer that your average tropospheric [OH] is 20% higher, which is serious and does not correspond the CH_4 lifetime of 8.7 reported (apparently for tropospheric methane) in Appendix A. Thus what could add to the OH sink term?

The cardinal question is whether we are further talking about the tropospheric H_2 and the influence of the stratosphere-troposphere exchange (STE) on it, or comparing apples and oranges?

2. I do not understand why the fractionation factors in the loss processes are derived with respect to the initial state of the model instead of the equilibrium state established after a 'spin-up' (p. 5826, l. 21). This must be a misunderstanding, because then the derived α_j depend on the initial mixing ratios in the model. The initial state is usually perturbed, *i.e.* you may start too far from the composition that is to be in equilibrium with the implemented value to diagnose the effective α_j properly. From Eq. (7), I derive that the initial $[H_2]_i/[HD]_i$ ratio higher by merely 22‰ (in terms of δD) than the surface equilibrium composition at which H_2 gets deposited, is enough to skew thus calculated soil sink α_{soil} from implemented 0.943 to 0.925. Generally, I do not see why the effective fractionation factor should be different from the implemented one, as the fractionation process is independent from the isotope ratio of the tracer being removed, or any other parameter. Eq. (7) is essentially the Rayleigh process equation integrated assuming the constant fractionation factor; it relates the isotope ratios of the atmospheric and deposited reservoirs via α. Thus for the budget evaluation the implemented value (0.943) for the soil sink fractionation should be used in conjunction with the overall tropospheric $[H_2]/[HD]$ ratio. That pertains to the photochemical sink as well.

3. There is no estimate of the STE given by the authors. In my opinion, it is adamant to quantify this term and list it in the isotope budget, along with the average δD of the exchanged stratospheric H_2 portion. That is a deficit of the previous studies too, with the exception of Rhee et al. (2006) who duly report their estimate. I will, however, attempt to comprehend the results of the sensitivity study case 2a and derive the STE term here. From a +20‰ perturbation of the stratospheric $\delta D(H_2)$, the resulting overall +12‰ implies that in effect the amount of ~60% of the tropospheric H_2 turnover with $\delta D = +147\%$ must be exchanged. This result is constrained well by the cross isotope mass-balance of the reference and case-2a simulation results. Putting that in the budget, it is ~47 Tg/yr, a fairly large amount. Rhee et al. (2006) give an estimate of 25 Tg/yr (+168‰). From Price et al. (2007), by closing their budget, I calculate ~31 Tg/yr (+180‰) STE that only fits their simulated +37‰ effect from the stratosphere. This does not agree with their reported 0.15 Gg/yr flux of [HD], despite that the stratospheric signature is high. Similarly, to close the isotope budget of Ehhalt and Rohrer (2009), one needs ~38 Tg/yr (+200‰) to be exchanged, a factor of 3 greater than their given 11 Tg/yr. Could you excurse more into this in the revised version of the manuscript and compare your STE estimate with those from the alternative studies, *e.g.* Seo and Bowman (2002)?

4. Although I like very much the concept of the analysis presented in Fig. 8, I am afraid I do not completely understand the consistency of result and its potential application. In particular, what is attributed to the 'stratospheric contribution' term? Does it reflect exclusively the changes to the H_2 mixing ratios parameterised in the stratospheric domain? It is interesting to see Fig. 8 conferring the estimates for the surface model layer. In that case, I fear, it is not feasible to obtain the 'stratospheric contribution' and transport terms without considering the vertical transport?

Furthermore, the calculations for mixing ratios look somewhat suspicious. For example, grey bars in lowermost left panel of Fig. 8 are surprisingly large, reckoning the fraction of the stratospheric mass of ~9% of the total mass enclosed in the model. Given an overwhelming variability of ±50 ppb per month for the stratospheric H_2 mixing ratio, one should yield the mass-weighted term for the entire SH box less than ±5 ppb, whereas I note +12 ppb in some months. The 'horizontal flux' terms, which I interpret as the latitudinal advection of H_2 from one box to another, are negative in January for the high-latitude boxes (HLBs), implying that H_2 is transported into the low-latitude box (LLB). The aggregate ~15 ppb lost from the HLBs are expected to arrive as ~30 ppb into the LLB. Here I take into account that the masses of HLBs and LLB relate as 2:1, assuming equal air density distribution with height in the boxes. Nonetheless, the depicted respective positive 'horizontal flux' term for LLB is of 5-6 ppb. Could you reconcile these estimates? Does the computation conserve the global mass of the advected tracer?

At last, the derived *dR/dt* in your method (Eq. (C5)) appears to account for the fractionations in the closed system, but you are dealing with the open system (Rayleigh process) when looking at the sinks, for example. Hence, can you quantify the inaccuracies introduced by this approximation?

5. Other comments:

I suggest clarifying the headings of Sections 2.3, 3.3, 3.4, 3.5. Thus, for example, Sect. 2.3 could be entitled “Parameterisation of the stratospheric H_2 composition”.

Perhaps, it is sensible to reference the comprehensive study on isotope effects in H_2 production from CH_4 by Mar et al. (2007) amongst other studies acknowledged in the introduction.

Please refer to your reference simulation/setup as the ‘reference simulation/setup’; this should replace different terms used throughout the manuscript alike ‘default scenario’, etc.

p. 5815, l. 7: “Experimental evaluation” sounds equivocal; also ‘spatial’ may be omitted.

p. 5816, l. 7: I believe it is better to use ‘D/H isotope ratio’ instead of ‘isotope composition’ talking about potentially larger depletion in D of this source.

p. 5816, l. 12-15: The term ‘reaction flux’ does not pertain to atmospheric chemistry, I do not understand what is meant to be said in this sentence, please reformulate.

p. 5817, ll. 10-12: Eq. (3) refers to Rahn et al. (2003), whereas Eq. (2) relates to the results of McCarthy et al. (2004), please correct the referencing.

p. 5818, ll. 7-11: Is it possible to conclude the uncertainty of the overall emission strength and respective isotope composition signature? That could also indicate the overall model uncertainty, omitting the photochemical terms that are difficult to estimate.

p. 5819, l. 14: This sentence is redundant, please remove it.

p. 5819, ll. 18-20: The deposition scheme appears to be more sophisticated than usually employed constant deposition velocity. Can you place the typical span of the velocities calculated in the model and compare those used in other studies? Does the deposition velocity vary with the soil moisture content in the model?

p. 5821, ll. 13-16: The model averages do not include emissions, they rather include those H_2 depleted in D coming from the depleted sources. The term ‘isotopically depleted source regions’ is obscure.

p. 5821, ll. 16-20: It is indisputable that the observations from the individual stations do not represent the latitudinal average. I wonder why you compare the latter from the model with the point station data. Perhaps due to averaging, I do not notice biases of 10‰–15‰, but 15‰–30‰ in $\delta D(H_2)$ reproduced by the model in the SH. I suggest adding to Fig. 3 the modelled values sampled in the respective station location grid cells to be able to compare the results to the observations properly. It is necessary to complement Fig. 3 with the panel depicting the respective mixing ratios. Otherwise, isotope ratios cannot be compared on top of unknown mixing ratios. This also concerns the comparison given in Fig. 4.

p. 5822, l. 11: What is meant by ‘disturbed seasonal cycle’?

p. 5822, l. 26: Perhaps, use ‘period’ instead of ‘number of months’.

p. 5823, l. 6: Either reformulate or quantify the limit for the difference between the model results and measurements.

p. 5823, l. 23-27: Misuse of terminology: ‘isotope values’, ‘isotopically depleted’, etc. without specifying the respective isotope is useless.

p. 5824, ll. 6-7: In my opinion, the KIE in soil sink is not weak, providing that this is the dominant removal term for H_2 in the troposphere. I recommend removing the last part the sentence.

p. 5824, ll. 14-15: Misuse of isotope terminology.

p. 5825, l. 4: Better use ‘fossil fuel usage’. Also see p. 5829, l. 2.

p. 5825, l. 16: Remove ‘again’. I presume you point to similarities with the surface $[H_2]$ dynamics?

p. 5826, ll. 3-5: Note: I do not see the problem in masking the stratospheric composition in the model, at least resorting to the concept of the 'stratospheric parameterisation' you use for H_2.

p. 5827, ll. 7-9: I do not understand what is meant by "significant positive bias towards the actual tropospheric value". A bias of what, and why it should be biased towards the *tropospheric* value, if the "large high latitude fraction of the *stratospheric* mass" is included?

p. 5827, ll. 20-21: I believe presenting the burdens for these large model domains instead of the average mixing ratios in Fig. 7 will be more consistent.

p. 5827, ll. 27-: Malformed sentence. I suggest replacing it with 'We can analyse the H_2 isotope budget in the model in more detail by calculating the individual contribution of each source and sink process to the change of the H_2 mixing ratio and isotopic composition on the monthly basis.'

p. 5828, l. 16: I suggest changing to '… negative contribution to the monthly mixing ratio change'.

p. 5828, l. 19-22: Did you mean that the deposition is the stronger *sink* rather than the *source*? From the figure I do not notice the effect of the dry deposition being smaller than that of the chemical loss. I recommend omitting the last part of the sentence.

p. 5828, l. 27: The first part of the sentence is unclear. What do you mean by "isotope leverage"?

p. 5829, l. 9-11: I do not notice any estimates of the vertical flux presented in Fig. 8, as well as in the following sensitivity study. Was it actually evaluated, except of looking at Fig. 5?

p. 5830, l. 1: Can you include the estimates of the resulting photochemical production signature in the model from the cases 1a and 1b? Is it also possible to mention the resulting average D content of HCHO here?

p. 5830, ll. 2-7: Please refer reader to Appendix A4 for the pressure-dependent KIE approximation (*i.e.* equation given in Tables 3, A1).

p. 5830, ll. 11-14: Malformed terminology, please rewrite the sentence.

p. 5830, ll. 17: Please put '(2b)' in front of 'the STE at higher latitudes' for clarity.

p. 5830, ll. 20-26: If the changes near the TTL were not expected to affect the tropospheric composition, why the results of both cases show similar effect? The next two sentences do not follow from the first one.

p. 5832, ll. 6-7: Unclear. What means 'observed change'? I assume, 'the change to the simulated composition'? There are no changes listed in Table 3.

p. 5832, ll. 7-8: This sentence is indeed senseless.

p. 5832, l. 15-16: It is obscure what 'global signals of the isotopic composition' means.

p. 5832, ll. 17-19: Imprecise conclusion of the result. You indeed test for the different estimates, but not the uncertainties reported for them. Please clarify.

p. 5834, ll. 2-4: Please detail the specific role of the latitudinal gradient in constraining the H_2 budget on the global scale, if this is stated.

p. 5834, l. 6: Missing methanol and monoterpenes emissions were not probed in this study, thus you cannot conclude that.

p. 5834, ll. 8-9: The isotopic composition around the tropopause apparently was not used as the upper boundary condition, you contradict yourself in Sect. 2.3. However, it is vitally important to quantify the STE, δD of the respective exchanged term and the isotope composition around the tropopause for the reference and case 2a-2c simulations. Please tabulate these values either here, or Sect. 3.6 and in Table 2.

p. 5834, ll. 11 and 19-20: McCarthy et al. (2004) do not provide the parameterisation for the stratospheric H_2 composition, they report the relationship between the CH_4 and HD and mixing ratios observed in the stratosphere. Please refer to the shortcomings in the parameterisation introduced in this study.

p. 5835, l. 15: Did you mean the *tropospheric* lifetime of CH_4?

p. 5835, l. 17: In view of the specific comment #1, please present the average tropospheric and overall modelled OH, better in number density units.

p. 5836, ll. 9-11: Can you lay out the branching ratio values for the typical atmospheric temperatures?

p. 5840-5841: I propose to clarify the derivation of the method significantly; I hardly comprehend what is given. Should not you account for the overall mass change on the monthly basis, not seasonally, if you analyse the monthly terms (*e.g.*, Fig. 8)? Using 'budged fluxes', 'production fluxes' is senseless, please use 'terms'. What is meant by 'bi-directional processes'? Do the individual mixing ratio change terms depend on dm_{air}?

Finally, please provide separate examples of the calculation of the individual contributions of the mass-exchanging and mass-conserving processes escorted with KIEs and not. These are, *viz.*, inward-outward advection, emission and chemical loss. The examples should be for both, mixing and isotope ratio terms.

Please note that the definition of the D/H isotope ratio in Eq. (C3) is incorrect for the diatomic H_2. One should read $R \equiv [HD] / (2[H_2]+[HD])$, from this, Eqs. (C4) and (C5) are to change accordingly. Alternatively, R can be introduced as the ratio of the isotopologues' mixing ratios, but then Eq. (C6) should be adjusted appropriately.

Technical corrections

Is it possible to reduce the colour scale in Figs. 5, 6, 9, 10 to a number of 12-16 discrete levels, so that it would be much easier to analyse the plots?

p. 5813, l. 16: Apparently, you refer to Table 1?
p. 5815, l. 5-6: Remove the article before 'from'.
p. 5817, ll. 17-18: Reference standard is already introduced at p. 5814, thus may be omitted.
p. 5824, ll. 7-9: Double use of 'again'.
p. 5837, l. 5: Doubled 'directly'.
p. 5838, l. 23: Misprinted 'where there'.
p. 5859, Fig. 4: Provide the coordinates of the respective observation location, either in the panels or figure caption. Please thicken the line pertaining to the reference simulation result or use another colour, as the black lines are barely distinguishable.
p. 5842-5849 References: please check for the outdated entries, *e.g.* Nilsson et al. (2009).

References

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