Reply to the comments of S. Gromov

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).

[The reason why the individual reactions are not explored explicitly is that the subsequent enrichments in D proved not to be significantly different than found in our previous single box model study and experimental atmospheric data for a thorough comparison was not available at the time of the study. The pressure dependency of formaldehyde photolysis and a stratospheric parameterisation were not implemented in the previous study and were therefore considered the two most important processes to investigate in more detail. We believe that as a whole, the full reaction scheme in this study provides much more insight into the global isotope budget than provided in the study of Price et al. (2007), because in the present study the photochemical source signature was determined from a bottom up approach (using a chemistry model based on dedicated measurements) whereas in Price et al. (2007) this parameter was used to close the isotope budget.]

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).

[The reason why a stratospheric boundary condition is used is that TM5 is a tropospheric model without tracers like CFCs, Cl, and O^1D. Hence, it is not possible to implement a stratospheric reaction scheme for H_2 - like presented by Rahn et al. (2003) and Röckmann et al. (2003). Also, the coarse vertical resolution models are known to have a too fast Brewer-Dobson stratospheric circulation. For these reasons an empirical parameterisation was used as alternative.
Indeed, there are different ways to define/calculate the tropopause boundary height. The reference tropopause height was in fact chosen to be close to the pressure heights that are frequently associated with the approximate tropopause boundary. At this point and at the present level of knowledge on the STE of H_2 and HD, we prefer to use the model pressure boundaries to enable a more numerically accurate sensitivity budget study. Of course, we are aware of the limitations of the stratospheric parameterization, and therefore we investigate the impact of the "tropopause" height (2b, 2c) and the stratospheric composition (2a) above the tropopause on the composition in the modelled region up to 100 mbar in the sensitivity study. Case 2b and 2c do not lead to very different results (2‰), whereas the actual composition in the stratosphere and at the tropopause region appears a much stronger driver via the STE. The fact that the STE is overestimated by ECMWF (page 5831, line 5-10), and herewith also the quantitative impact on the isotopic composition, is clearly acknowledged, but we cannot change this in our study that uses ECMWF meteorology. Knowing these limitations, one of the

main recommendations of our study is therefore to further investigate the role of the STE in the hydrogen isotope budget using an integral global CTM for the troposphere and stratosphere.]

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.

[We will carefully revise the manuscript with special attention to the issues raised here, and in the specific comments below.]

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 dD(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 years 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?

[For the mixing ratios we can correct the budget for the known amount of mass that belongs to the stratospheric part in the atmosphere up to 100 mbar. It was not possible to do this for δD because the distribution of H_2 and HD is not equal in height within the accumulated region up to 100 mbar and therefore we chose to report the δD budget up to 100 mbar. Lifetimes for H_2 are therefore calculated using the approach mentioned in the footnotes of Table 1. The referee is correct that it should be pointed out clearly, which we will do more carefully in the revised version. The CH_4 lifetime of 8.7 years was mentioned for the entire atmosphere to show that OH is modelled adequately.]

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 $[H2]_i/[HD]_i$ ratio higher by merely 22‰ (in terms of δD) than the surface equilibrium composition at which H2 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.

[Regarding the spin-up, the initial state of the model is in fact the composition at the start of the year after a complete spin-up. We will more clearly state this in the revised version. Regarding the removal at the surface, we were also puzzled by this at first, but the issue appears to be the following: As removal occurs at the surface, the loss fluxes depend on the *surface* mixing ratios of H_2 and HD. Especially in the strong deposition regions over the continents, the surface mixing ratios are significantly different from the average value in the

budget box up to 100 mbar. This results in an apparent difference between the fractionation factor that was implemented in the sink, and the one we calculate from the modelled integrated fields and surface fluxes. We will change 'effective fractionation' to 'apparent fractionation']

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 H2 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 H2 turnover with δD = +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)?

[As stated in the reply to the general remark above, TM5 is limited in that we cannot realistically investigate STE, and therefore we cannot go further than identifying STE as an important potential candidate to close the tropospheric HD budget in TM5. Because we know the disadvantages of our approach (i.e. stratospheric parameterisation and poor ECMWF data on the STE, as stated by the referee) we think that it is not adequate to use the present study for a quantitative analysis, but we can give some more explanation here.
The stratospheric contribution presented consists of two parts: Vertical exchange with air above 100 mbar and the correction provided by McCarthy's parameterisation for the fields that are calculated by TM5 within the box up to 100mbar, but above the boundary described by Equation A4. As a consequence of the empirical parameterization, part of the stratosphere lies within the box for which the budget is calculated and therefore only part of the increase for case 2a is in fact related to the STE from the atmosphere above 100 mbar. The other part is due changing the parameterisation of the part of stratospheric HD that is inside the 100 mbar box that we are investigating.
Regarding the isotope budget, the issues in representing the stratospheric contribution (as well as horizontal transport) stimulated us to look for an alternative approach to investigate the variability in isotopic composition. Whereas the stratospheric contribution can be a sink for H_2 in one month it can become a source for H_2 in another month. The same is happening for HD. This behaviour does not enable a budget analysis in the traditional way, i.e. describing sources with signatures in ‰ and describing sinks by fractionation constants.
We can to some extent analyse the impact of the vertical exchange separately from the impact of McCarthy's parameterisation. The overall downward flux for the high-latitude boxes (HLBs) is 5.8 and 7.2 Tg/yr, respectively for the Northern and Southern Hemisphere (with an average burden of 41 and 42 Tg in the HLBs). Exchanging air in the 100 mbar NH and SH HLBs with an average composition of 117‰ and 135‰ (Fig 7) with stratospheric air with an estimated composition of 180‰ (Fig 5), coming from heights above 100 mbar, leads to an enrichment of 9‰ and 7‰, respectively. These numbers are relatively close to the numbers presented by Rhee et al., 2006, although the overall downward fluxes from heights above 100 mbar are probably smaller than at the tropopause. Thus, the actual values for the STE are expected to be at least equal or larger than these values.]

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?

[As explained in detail in the response to the last point, it includes the budget changes made by the parameterisation compared to the default output of the model and the vertical flux. Because the outward stratospheric flux is inherently entwined with the stratospheric

contribution we chose to add these two terms. We will make this very clear in the revised version.]

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 H2 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?

[We are sorry that in order to keep the manuscript concise, some of the explanation was moved to Appendix C. As written there (line 15-20 on page 5840), for the term "horizontal flux" we add the overall mass change per box (due to the seasonal changes in the surface pressure) to the horizontal flux. This is for similar reasons as for joining the vertical flux with the stratospheric contribution. We can give an example for January to show that the calculations are correct. The NH burden is 40.46 Tg and the initial concentration is 517 ppb. The vertical flux in that month is equal to +1.08 Tg/mth and the stratospheric contribution is +0.03 Tg/mth. Hence so the change will be (1.08+0.03)/40.46*517 = +14.2 ppb. For the same month, the horizontal flux is -0.65 Tg/mth. On its own this will lead to a decrease of (-0.65)/40.46*517 = -8.3 ppb. But the air mass also changes and one needs to use Equation C.1 to correct for this change. The mass in the NH box changes from $1.123 \cdot 10^9$ Tg to $1.127 \cdot 10^9$, resulting in an additional decrease of 1.9 ppb. At the same time the SH is losing 0.26 Tg to the LLB, corresponding to a decrease of 4.7 ppb when including change in air mass. We checked the incoming flux for the LLB and it is indeed the sum of both. The LLB contains 86.49 Tg at an initial concentration of 534 ppb. This leads to an increase of (0.65+0.26)/86.45=5.7 ppb. The change off mass is approximately zero (the same mass that arrives from the NH is leaving to the SH.]

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?

[The key advantage of this approach is that it is exact for sources and sinks in an open or closed system. The disadvantage is that you can only investigate variability in the budget, and not the absolute values of the different sources and sinks in the budget.]

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 H2 composition".

[This will be clarified in the revised version.]

Perhaps, it is sensible to reference the comprehensive study on isotope effects in H2 production from CH4 by Mar et al. (2007) amongst other studies acknowledged in the introduction.

[That particular study is about the modelling the isotopic composition of hydrogen produced in the stratosphere. We will add a reference to the list on p. 5830, l. 12.]

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.

[We will replace default by reference throughout the manuscript.]

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

[OK.]

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.

[OK.]

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.

[The reaction flux is the product of the rate coefficient and the concentration for a certain volume in the model domain, resulting in a quantity that has units of kg/s when translated to mass units. This quantity has the same units as i.e. the fluxes of the surface sources integrated over the surface area of an element in the model domain. We will change the term to ‘reaction mass flux’.]

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.

[Both equations refer to the results presented in McCarthy et al. (2004). Indeed, some of the data shown in this study was shown in another resolution by Rahn et al. (2003). We will add a reference to the data by the latter study for Eq. (3).]

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.

[We will add the uncertainty in the isotope signatures in Table 2. The uncertainties in the emission strengths are shown in Table 1.]

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

[OK]

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?

[OK]

p. 5821, ll. 13-16: The model averages do not include emissions, they rather include those H2 depleted in D coming from the depleted sources. The term ‘isotopically depleted source regions’ is obscure.

[This will be changed to: ... whereas the model averages over a latitude band and therefore includes in the average also H_2 emitted from the isotopically depleted sources over land.]

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 δ D(H2) 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.

[We refer to the average difference and not individual differences for two reasons. The main purpose of the figure is to show the latitudinal gradient. As the data originate from different types of measurements, i.e. long-term measurements at stationary locations on land, and

single measurement on the moving ship platforms, sampling at the respective positions would result in a very incoherent picture containing a point cloud for the measurements as well as the modelled results.

The second purpose of the figure is to show the impact of the different scenario calculations on the latitudinal gradient. We therefore chose to show the modelled global latitudinal gradient. We will extend the bias range to 10‰–20‰ to represent the average difference between the model at the NH and SH, respectively.]

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.

[The comparison between isotope and mixing ratios on the global scale was done in a companion paper by Batenburg et al., (2011). In this work we aim at comparing the global signals to verify overall model performance and sensitivity in process not investigated in our previous study. However, we are working on a more site specific study at higher model resolutions where we also compare measured and modelled mixing ratios at high temporal resolution.]

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

[We meant a seasonal cycle that is disturbed by local influences. We will reformulate this sentence.]

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

[OK.]

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

[We will add the approximate numbers.]

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

[It should be clear that in this entire paper we are dealing with deuterium, so we think that it is not ambiguous here. However, we will correct this to "δD values", "depleted in D".]

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 H2 in the troposphere. I recommend removing the last part the sentence.

[Indeed the overall term and its corresponding impact on the isotopic composition is large but the isotope effect in the deposition removal process itself is relatively small compared to the isotope effect in photochemical removal. We will replace "rather weak" by "comparatively weak" to make this clear.]

p. 5824, ll. 14-15: Misuse of isotope terminology.
[This will be changed to: ... deposition indeed leads to higher δD values in the NH.]

p. 5825, l. 4: Better use 'fossil fuel usage'. Also see p. 5829, l. 2.
[OK]

p. 5825, l. 16: Remove 'again'. I presume you point to similarities with the surface [H2] dynamics?
[OK]

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 H2.

[We meant to say that it is not possible to assess the stratospheric contribution in terms of isotope signatures or fractionation constants because H_2 and HD are in some cases added or removed independently. We will reformulate this sentence.]

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?

[Sorry for the unclear statement, it will be revised to: This results in an apparent deuterium enrichment of the tropospheric reservoir.]

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.

[In principle burdens and mixing ratios are equivalent, and we prefer presenting the mixing ratios, because this can be related to measurable changes in the atmosphere.]

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.’

[OK]

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

[OK]

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.

[We meant that deposition is a stronger sink than the photochemical sink, but still the effect on the isotopic composition is stronger for photochemical removal, since the isotope fractionation is much stronger.]

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

[If a source has almost the same isotopic composition as the reservoir, it will not change the isotopic composition reservoir significantly.]

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?

[See comments above. It was included in the stratospheric component.]

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?

[OK]

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).

[OK]

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

[This will be rewritten as follows: The effect on the average tropospheric δD value is profound (an increase of 12‰). Evidently, H_2 produced in the stratosphere is highly enriched in D (Rahn

et al., 2003; Röckmann et al., 2003). The back-flux of stratospheric hydrogen can significantly enrich H_2 in the troposphere, as was already concluded from the results in Table 2 and Fig. 8 in Sect. 3.4.]

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

[OK]

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.

[This sentence is correct because it proves that only the STE at the mid-latitudes has an enriching effect on the tropospheric composition.]

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.

[This will be revised to: The simulated change in δD compared to the reference scenario....]

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

[This will be revised to: Hence, the model results are not very sensitive to changes in the isotopic composition of biologically produced H_2.]

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

[This will be revised to: Again, the global average change of δD due to a change in the δD source signature of H2 from biomass burning relative to the reference scenario is small.]

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.

[This will be revised to: Thus, all sub-scenarios of case 4, which explore the previously reported ranges of uncertainty in the source signatures, do not lead to a significant change in global average δD values.]

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.

[We will add an explanation. For instance, changes in deposition will have more impact on the NH concentration than on the SH. In the case that one must lower the modelled SH concentration whereas the NH concentration is well predicted, lowering deposition can solve the SH bias but will introduce a negative bias on the NH.]

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

[This will be revised to: The KIE of the molecular channel of the photolysis reaction of formaldehyde, the fractionation constant for deposition, and finally the isotopic composition around the tropopause used as an upper boundary condition for the calculations. Missing NMHC emissions of e.g. the monoterpenes and methanol could potentially also have an effect.]

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.

[McCarthy´s parameterisation leads to the measured values in the tropopause up to the stratosphere. So strictly speaking it is not a boundary condition. We will reformulate this sentence.]

p. 5834, ll. 11 and 19-20: McCarthy et al. (2004) do not provide the parameterisation for the stratospheric H2 composition, they report the relationship between the CH4 and HD and mixing ratios observed in the stratosphere. Please refer to the shortcomings in the parameterisation introduced in this study.

[This will be revised to: ....the parameterization based on McCarthy et al. (2004).]

p. 5835, l. 15: Did you mean the *tropospheric* lifetime of CH4?

[No, we meant the overall lifetime as stated in this sentence, but for better compatibility with the current study we will replace it by the chemical lifetime up to 100 mbar. We will clarify this in the revised manuscript]

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.

[The average value is highly variable in time and location (see example Figure 1). Depending on the time of the year, the overall average values up to 100 mbar are in the range $0.79\text{-}1.11\cdot10^{6}$ cm^{-3} and in the range $0.84\text{-}1.20\cdot10^{6}$ cm^{-3} up to 200 mbar. The lower values correspond to the overall average value in January whereas the upper values correspond to the overall average value for in July. This is well within the range of reported values, e.g. Lawrence et al., 2001 or Wang et al. 2008, so we have no reason to doubt the photochemical lifetimes of CH$_4$ and H$_2$.]

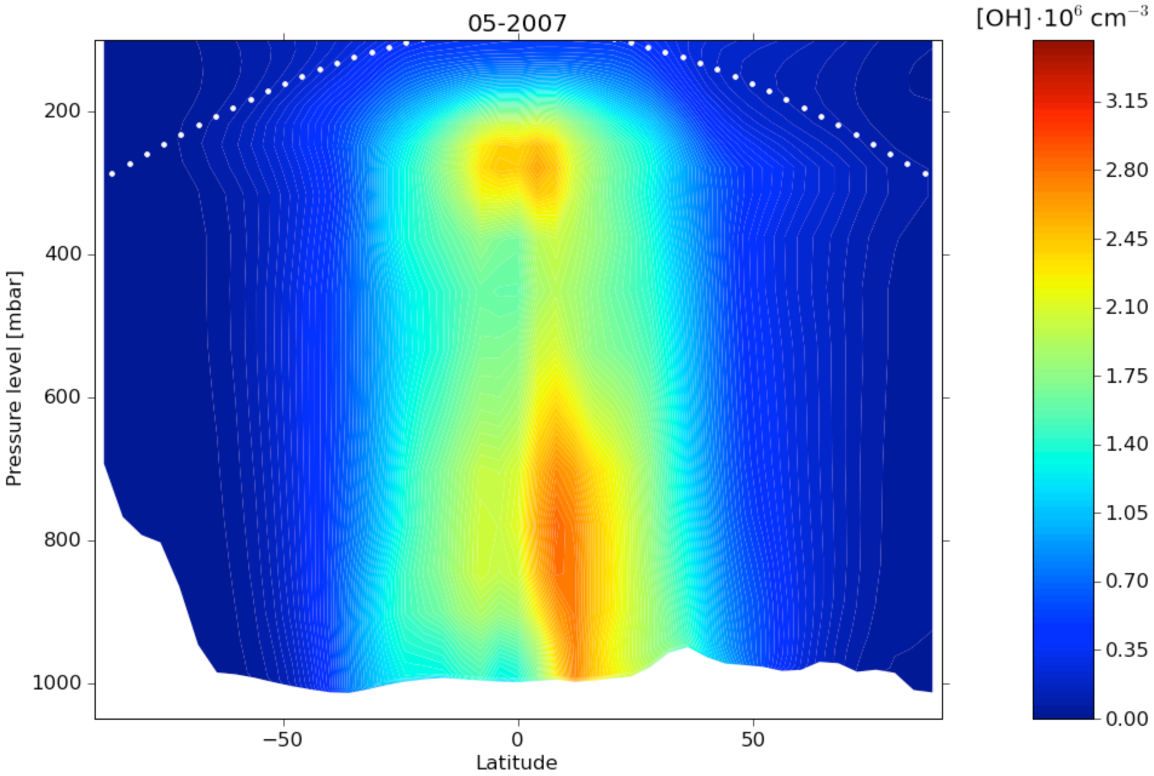

Figure 1 Zonal mean concentration of OH in May 2007. The dotted line denotes the tropospause.

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

[The typical branching ratios can be found in Pieterse et al. (2009).]

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 ‘bidirectional processes’? Do the individual mixing ratio change terms depend on *dmair*? 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.

[line 14: “seasonal” will be replaced by “monthly”.]

[line 19/20: “change in the budget mass” will be replaced by “change in H_2 (by mass)”.]

[line 20: “budget fluxes” will be revised to “flux terms in the budget”.]

[p3841: “fluxes” will be replaced by “flux terms”.]

[Since the abundance of H in HD is orders of magnitude smaller than in H_2, we approximate $R \equiv [HD] / (2[H_2]+[HD]) \sim [HD] / 2[H_2]$. Indeed, we forgot to include the factor 2 in the equation. It is a habit to correct HD automatically and therefore it is easy to forget to mention it in an equation. We did however use it for all calculations shown in the paper.]

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?

[We prefer to use continuous scales in this work because it facilitates qualitative analysis of subtle features in the calculated fields.]

p. 5813, l. 16: Apparently, you refer to Table 1?

[Yes, it will be corrected.]

p. 5815, l. 5-6: Remove the article before ‘from’.

[OK]

p. 5817, ll. 17-18: Reference standard is already introduced at p. 5814, thus may be omitted.

[OK]

p. 5824, ll. 7-9: Double use of ‘again’.

[OK, it will be corrected.]

p. 5837, l. 5: Doubled ‘directly’.

[OK, it will be corrected.]
p. 5838, l. 23: Misprinted ‘where there’.

[OK, it will be corrected.]

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.

[OK]

p. 5842-5849 References: please check for the outdated entries, *e.g.* Nilsson et al. (2009).

[We will check our references in the final version. This reference was deliberately mentioned because the pressure sensitivity of the KIE in the molecular channel is mention in this work.]