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Atmospheric
Chemistry
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Discussions

Interactive comment on "Simulation of the diurnal variations of the oxygen isotope anomaly (Δ^{17}O) of reactive atmospheric species" *by* S. Morin et al.

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We thank Becky Alexander for her detailed reading and review of our ms. In particular we appreciate that she implemented our recommendations into GEOS-Chem and was thus able to provide feedback from the global modeling community during the discussion phase of our ms. Further discussions during the discussion phase were very fruitful and are gratefully acknowledged. We hope that the revised ms contains information which can be implemented more easily in such large scale models.

1 General comments

My main issue with the paper has to do with your recommendation for global modelers. Your recommendation to global modelers could be more broadly applicable and therefore useful. For example, you suggest assigning a value of $\Delta^{17}O$ for the N_2O_5 and NO_3+H pathway of 33 and 40 ‰ respectively, but this value is dependent upon the choice of $\Delta^{17}O(O_3^*)$ and α ($\Delta^{17}O(NO_2)$). $\Delta^{17}O(NO_2)$ varies strongly with latitude, so assuming a constant value for $\Delta^{17}O$(nitrate) produced by a particular pathway would not work well in a global model. I know from Alexander et al (2009) that $\Delta^{17}O(NO_2)$ (or α) varies strongly with latitude using the PSS assumption. Does $\Delta^{17}O(NO_2)$ (or α) also vary strongly with time and space at dusk? You could probably test this in your model to see how broadly applicable your recommendations (40 ‰ and 33 ‰) are. If possible, it would be much better give your recommendation as a formula with $\Delta^{17}O(O_3^*)$ and α as variables.

The "recommendations" are now given in the form of an equation taking as arguments $\Delta^{17}O(O_3^*)$ and α.

Also, can you provide some error bars associated with the statement that Alexander et al, 2009 is biased low by 1 ‰ for the NO_2+OH pathway. I would think this could vary over space and time.

The comparison with the Alexander et al., 2009, approach, was reported in the ms on the basis of the baserun under springtime conditions. Extending the comparison to other seasons and other latitudes reveals that the error lies between 0.5 and 1.5 ‰. This has been added to the revised ms.

Your other recommendation for using a larger integration period (6:00 - 18:00) is not quite as straightforward as you make it sound. When dusk and dawn occur varies a lot in space and time, so choosing one time period would incorporate darkness into some locations (leading to an overestimate of $\Delta^{17}O(NO_2)$), while in other locations it *would not be significantly difference from what Alexander et al. (2009) did (leading to an underestimate). I haven't yet figured out a way to get around this easily in GEOS-Chem, but your suggestion is not particularly helpful in this regard.*

We have reformulated the section dealing with larger-scale model implementations. In particular, we now emphasize more strongly that a rather simple way around this issue is simply to scale the PSS α values with the the strength of the OH+NO_2 reaction rate, when computing the daily integrated isotopic signature (DIIS) of this source.

That said, I tried out your recommendation as follows. I changed my assumed $\Delta^{17}O(O_3^\star)$ from 48 ‰ to 42 ‰, so that direct comparison with your recommendation would be meaningful. I then separately assumed that nitrate produced via the N_2O_5 pathway is always equal to 33 ‰, NO_3+H is always equal to 40 ‰, and I added 1 ‰ to my calculations of the $\Delta^{17}O$(nitrate) value for the NO_2+OH pathway. I then compared the Alexander et al (2009) calculations (assuming $\Delta^{17}O(O_3^\star)$ = 42 ‰) with your recommendations. The difference between $\Delta^{17}O$(nitrate) from the NO_2+OH pathway is - 1 ‰ everywhere (expressed as Alexander et al, 2009 method - Morin et al., 2011 recommendations). The same comparison for the N_2O_5 hydrolysis and NO_3+H pathways is shown in Figure 1 (only one plot is shown because the results are identical for both pathways). Figure 1 shows the mean summer (JJA) and winter (DJF) difference between calculated $\Delta^{17}O$(nitrate) (for nitrate formed only via the N_2O_5 hydrolysis or NO_3+H pathways) at the surface from Alexander et al (2009) compared to your suggestion (expressed as Alexander - Morin). The difference ranges from 2 ‰ to -12‰ for both locations (leading to an overestimate of Δ^{17} reactions. The Alexander et al method is lower (by up to 12 ‰) in low latitude forested regions because of the nighttime source of RO2 (from reactions of O_3 with alkenes) leading to low Anight values. Differences elsewhere are small. The maximum overestimate (<2 ‰) is consistent with your results (Table 5). Figure 2 shows the same difference taking all 3 of your recommendations together for total nitrate (range of -3.6 to 0.5 ‰ difference). The largest discrepancy between the two approaches again occurs in forested regions. Elsewhere the difference is generally $<$ 1‰, in part due to the compensating effects of your recommendations. I'm not sure that your box model simulations take this additional source of RO_2 (O_3 + alkenes) into account. You could probably do a sensitivity study to examine this specific case. Although nighttime production rates of RO_2 are uncertain, this does illustrate that you cannot assume that one value (+1 ‰, 33 ‰, or 40 ‰) is appropriate everywhere. I think your sensitivity studies are useful for exploring the bias of the Alexander et al, 2009 paper for any given scenario, but may not be broadly applicable across the globe. Unless you can express your recommendations in the form of an equation with α and $\Delta^{17}O(O_3^\star)$ as variables, perhaps you should leave out your general recommendation.

It would also be useful to state the relative importance of each nitrate formation pathway. For example, the largest discrepancy between your detailed calculations and the PSS assumption occurs for the N_2O_5 hydrolysis and NO_3+H pathways (according to Figure 5). What is the relative importance of these 2 pathways for total nitrate? According to Alexander et al (2009), globally (annual mean) the NO_2+OH pathway dominates (76%), but the N_2O_5 hydrolysis pathway can dominate (up to 74%) over high northern latitudes over continents and over the Arctic. The NO_3+H pathway is relatively minor (4% globally, annual mean).

We disagree with this argument. Indeed, our goal is to be able to simulate as precisely as possible the Δ^{17}O signature of each nitrate formation pathway, regardless its relative importance. It is only at this expense that it is the possible then to use the isotope tool to apportion the nitrate production channels, or, in forward modeling approaches such as Alexander et al., ACP 2009, to check that the output of a given atmospheric chemistry model is consistent with measured values of both concentrations and Δ^{17}O values as a method to provide a more robust evaluation of the proportions between nitrate sources.

Our work is motivated by methodological issues ; given that heterogeneous reactions were not included for the sake of simplicity, it is not possible to compare the model output to atmospheric measurements. The future implementation of heterogeneous reactions into this model will make it a tool of choice to compare its output to atmospheric measurements, for instance gathered during intensive field campaigns.

I somewhat agree with the first reviewer that there are a lot of tables that could be replaced with some figures, but the advantage of tables is that it is possible to get actual numbers.

Our reply to this point is given in our reply to Reviewer #1.

Although we don't know what the isotopic transfer function is for the NO_2*+*O_3 *reaction, in the absence of better information I think it's justified to use the same transfer function as for the NO+*O_3 *reaction as there is no reason to think that it would be any different.*

Our reply to this point is given in our reply to Reviewer #1. It is a very important point that has undergone significant modifications during the revision process.

I dislike the constant referral to 'case 1', 'case 2', etc. I am constantly flipping back and forth trying to remember what these are. If you could put some information about each 'case' within the text, e.g. replace 'case 2' with 'case 2 (explicit NOx)', that would be helpful. Also, refer to the specific reaction formula rather than giving an obscure reaction number that forces the reader to flip through numerous tables trying to figure out what reaction you are talking about.

We have tried to make more explicit linkages to the different cases and reactions dealt with.

2 Grammatical issues:

We thank Becky Alexander for her detailed inspection of the grammar of our ms. We are sorry for inappropriate use of plurality in some words of the original ms. This has been fixed and thoroughly proof-checked in the hope that the revised ms is grammatically improved. Trivial fixes were all carried out. Other suggestions are dealt with below:

Page 30415 lines 2-7: This is a confusing and awkward sentence. I'm not sure what you're trying to say here.

This sentence has been removed.

Page 30422 line 1: either describe the 'simple parameterization' or provide a reference

The sentence was changed to : “Photolysis rate coefficients are calculated by the model (Sander et al., 2005)”.

Page 30422 lines 6-9: It is not entirely clear what you are doing here. Of course 36 hours is between 24 and 60 hours, but aren't you looking at the diurnal variability? This sentence makes it sound like you are looking at one snapshot in the model (36 hours after initialization), and it is not clear to me what and why you are doing anything at 36 hours.

A 24 hours time windows does not allow to visualize a full diurnal cycle. For instance, if the 24 time windows runs from 0 to 24h local time, the nighttime variations are somewhat difficult to observe. In contrast, 36 hours allow to visualize a full day and a full night continuously (see e.g. Figure 4).

Remove the following sentence. “First of all, general equations are derived from textbook physical principles.” Of course they are, so this sentence provides no useful information. This statement sounds personal to me.

This sentence was removed.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 30405, 2010.