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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Isotope modeling of nitric acid formation in the atmosphere using ISO-RACM: testing the importance of NO oxidation, heterogeneous reactions, and trace gas chemistry" *by* G. Michalski and F. Xu

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1 General comments

Michalski and Xu have performed a large number of simulations after having implemented Δ^{17}O into the RACM atmospheric chemistry model. These simulations are aimed at identifying the main drivers for Δ^{17}O changes in atmospheric nitrate; in this regard, special attention was paid to evaluate the impact of various N_2O_5 hydrolysis

schemes. Overall, it is a little disappointing that not much progress regarding Δ^{17}O calculations has been done since the first modeling study by Michalski et al. in 2003. Given the number of new measurements and several significant experiments carried out since this pioneering study, one could have expected that the authors reevaluate their Δ^{17}O module in light of recent results. Nevertheless, I think the paper deserves publication in ACP, provided that the authors make a significant effort to improve the readability of the manuscript and the figures.

2 Specific comments

1. Title : I think "nitric acid" should be replaced by "atmospheric nitrate". "Atmospheric nitrate" is referred to on line 2 of the abstract, and it include nitric acid but not only. Also, I think "atmosphere" should be replaced by "troposphere" since this is the focus of the paper.

2. I have a major problem with the way the authors introduce the isotopic mass balance equation. Equation (1) has several problems. I don't understand what the authors mean by "$\Delta^{17}O(NO_{3\,atm}^-)$/dt". Mathematically speaking, I understand what dx/dt is, but not x/dt. In addition, the correct mass balance equation, which governs the time evolution of the isotopic composition of a species of interest (say, nitrate, here), is expressed as a function of the time derivative of $\Delta^{17}O(NO_{3\,atm}^-)\times[NO_3^-]$, not the time derivative of $\Delta^{17}O(NO_{3\,atm}^-)$ only. The correct form for the left-hand side of equation (1) is thus : "d ($\Delta^{17}O(NO_{3\,atm}^-)\times[NO_3^-]$) /dt ".

3. My second problem with equation (1) deals with the treatment of sink reactions. For a given air parcel, while it is well mentioned that source reactions "create" nitrate with a specific Δ^{17}O value (noted "$\Delta^{17}O_i$"), it should be stated clearly that sink reactions

eliminate nitrate that is already in the parcel. Ignoring possible fractionation associated with these processes does not entitle the authors to simply remove the sink term. Instead, it should be replaced with (ΣL$_j$)$\times\Delta^{17}$O($NO_{3\,atm}^-$), where Δ^{17}O($NO_{3\,atm}^-$) represents the Δ^{17}O of nitrate present in the box at a given time. The sentences "In tis sense, based on our current understanding, tropospheric production pathways control the Δ^{17}O of compounds such as nitrate" is thus wrong : the Δ^{17}O of nitrate depends also on its sink reactions, which may be summed up as its lifetime. A mathematically and isotopically correct description of the equation governing Δ^{17}O is given below:

$$\frac{d}{dt}\left([NO_3^-]\times\Delta^{17}O(NO_3^-)\right)=\Sigma_i\left(P_i\times\Delta^{17}O(NO_3^-)_i\right)-\frac{[NO_3^-]}{\tau}\times\Delta^{17}O(NO_3^-)$$

where τ is the lifetime of atmospheric nitrate. Nitrate does not accumulate for ever in the atmosphere, so that nitrate bearing a given Δ^{17}O disappears one day from a given atmospheric parcel. This is reflected in the equation above. It is unclear to me whether the authors implemented correctly the above equation but failed to reproduce it in the paper, or if they implemented in the model a description of Δ^{17}O which misses the fact that nitrate once formed in the atmosphere does not remain in a given air parcel for ever. This must absolutely be clarified before several aspects of the paper can be discussed. From line 15 to 22, the authors refer to different types of model to justify their elimination of sink terms. First of all, I think it's better if models do not interfere with the physical description of atmospheric mechanisms, and second there is no reason why dry deposition, wet deposition and so on is negligible in a 0D model and not in more complex approaches. Advection is only one term describing the elimination of nitrate from a given air parcel, among others.

4. I have a problem with the implementation of the factor α in the model. This factor was first introduced by Michalski et al. (2003) and it was explicitly stated there that the equation relating Δ^{17}O(NO_2) to Δ^{17}O(O_3) using this factor α was only valid at photostationary steady-state. Morin et al. (2007) provided the full demonstration

behind this equation. At night, it is not possible to use the same equation to compute Δ^{17}O(NO_2), because then the photostationary steady-state does not hold. This was first alluded to in Morin et al. (2009, JGR) and also repeated in Morin (2009, review of Alexander et al., 2009). This problem cannot be masked to the reader and I hope the authors can find a way to clarify this issue and find a consistent method to represent Δ^{17}O(NO_2) at night. This is important because the value of Δ^{17}O(NO_2) at night drives the value of Δ^{17}O(NO_3), hence Δ^{17}O(N_2O_5), thus starting from a wrong hypothesis at this stage will have a major impact on the discussion of the impact of various N_2O_5 hydrolysis schemes. Work I'm currently carrying out shows that the error on Δ^{17}O(NO_2) can be as large as 3 to 4 permil during the night (see poster presentation at upcoming EGU 2010). This error is on the same order of magnitude than the effect of various N_2O_5 parametrizations discussed later, so discussing those without assessing carefully Δ^{17}O of NO_2 and NO_3 at night is problematic. The sentence on page 6836 from line 16 to 19 is particularly unclear.

5. The last big problem I have with this study is linked to the discussion on Δ^{17}O of ozone and how it is transferred to other gas-phase species. Indeed, it was first alluded to by Janssen (2006, ACPD comment linked with Savarino et al. 2007 ACP paper) that molecular beams studies are not really representative of the conditions prevailing in the atmosphere, in that they correspond to reactions operating at temperatures of several 1000s K. Inferring partitioning ratios between central and terminal ozone atoms based on such studies is thus highly questionable. A large review effort was carried out by Savarino et al. (2008, JCP), see e.g. Table IV of this study. It was shown that the branching ratio between central and terminal O atoms in ozone is largely dependent on temperature ; it was even possible to reconcile molecular beams studies with experiments carried out at temperatures closer to room temperature based on the literature survey. Thus relying on molecular beam studies to rule out the fact that experimental evidence has shown that ozone transfers O atoms preferably from its terminal position does not seem correct, and this has been noticed a long time ago in the literature. Also,

why do the author not use the experimental results of Savarino et al. (2008, JCP) for branching ration (ozone terminal vs. central atoms transfer) pertaining to the NO+O_3 reaction ? A reason should be given to explain why this experimental work was not given superior credence than molecular beams studies.

6. It is also a little surprising that the authors do not trust *ab initio* calculations that show similar results as the experiments by Savarino et al. (2008) in terms of the branching ratio between terminal and central oxygen atom transfer from ozone to NO_2 or NO_3, given that in Michalski and Bhattacharya (2009, PNAS), *ab initio* calculations were used as a confirmation of the authors's results, regarding the ozone + nitrite reaction... It is thus hard to follow that the authors "conclude that there are a number of uncertainties in the mass balance model and that there are no "correct" assumptions, only assumptions". I hope that the authors can provide a more balanced assessment of the current state of the knowledge in this area. Of course there are uncertain parameters, but claiming that almost nothing is known is probably going a little too far.

3 Technical corrections

Page 6830, line 6 : "produce" → "produced"
Page 6830, line 20 : "as is needed future research" is obscure to me.
Page 6831, line 1 : "continues" → "continue"
Page 6831, line 28 : oxygen isotope anomalies should be introduced in the introduction, as this is a central aspect of the ms.
Page 6832, reaction R3 : please remove the "= β" which has nothing to do in a chemical equation. Since the numbering if this equation is "R3", I don't see why the authors need to use an additional greek letter ("β") to refer to it.
Page 6833, reaction R5 : Same comment as above for the extraneous greek letter "χ"

Page 6833, reaction R6 : you can use `\leftrightarrow` to produce symbol $\leftrightarrow$
Page 6833, reaction R7 : Same comment as above for the extraneous greek letter "ε"
Page 6834, line 1 : "NO_x", "NO_y" and other shorthands should be defined at least once in the ms (preferably the first time they are used).
Page 6836, section 2 : the authors introduce the shorthand $^{\Delta}$X to refer to Δ^{17}O(X), for a given species X. This shorthand is only used in this page of the ms, so I suggest removing it as it is more confusing than helping the reader.
Page 6838, equation 5 : I suggest giving values of $\Delta^{17}O(O_3)$ corresponding to typical temperatures. Also, I strongly suggest that the authors perform their analysis at a fixed $\Delta^{17}O(O_3)$ value to disentangle the temperature effect pertaining to $\Delta^{17}O(O_3)$ variations and that due to chemical kinetics.
Page 6840, line 22 : please split the equation in two parts. I think there should be a space between γ_2 and f.
Page 6841, line 11 : I believe the authors wanted to write $\ln(\gamma/(1-\gamma))$
Page 6841, line 13 (equation) : What is is y_i ? What is λ_i ? I think more details can be given here. This section is quite confusing.
Page 6842, line 24: what is the latitude of the simulation ?
Page 6843, line 8 : the sentence starting with "The shift ..." would be easier to read if the authors substitute the greek letters referring to reaction pathways with the actual reaction number (R3, R4, R5 etc.) or write down the name of pathway in plain English.
Page 6846, line 5: "(terminal) in the terminal" should be rephrased.
Page 6849, line 8 : "This oscillation would [...] become step like at higher latitudes" : observations supportive of this speculation exist in the peer-reviewed literature, no need to speculate here (see e.g. Kunasek et al. 2008, JGR, or Morin et al., 2008, Science). Records from the tropics are not (yet) available in the peer-reviewed literature.
Page 6850, line 20 to 27 : please give some references to support the claims.

Figures

Figure 1 : in the caption please add the "$^-$" to NO_3 to make it an ion. Also, please subscript the "3". It would be nice if tick marks were spaced by 12 or 24 hours, this would correspond to the length of one day.
Figure 2 : Please subscript numbers in chemical species (e.g. N2O5 $\rightarrow$ N_2O_5). Same comment as above for tick marks on the x-axis.
Figure 3 : I'm not sure that the fact that the model predicts Δ^{17}O values that have not been observed is solely due to the "paucity of in situ data". It could also well be that certain combinations of parameters for the model runs are not representative of actual atmospheric conditions.
Figure 6 : It would be good if dashes lines link together actual model results corresponding to the same settings except for temperature. For instance I don't understand why the Δ^{17}O values on the order of 12 permil are not connected to values obtained at higher temperatures. I wonder how the dashed lines were drawn.
Figure 10 : First of all I'd recommend swapping the x- and y-axis of this figure (then it would really be Δ^{17}O vs. O_3 mixing ratio). Also, I wonder how much sense it makes to use the ozone mixing ratio at the end of the simulation. Doesn't it vary over time during a given simulation ? What if the simulation ends during the night as opposed to during the day ? The instantaneous ozone mixing ratio after one week of simulation seems to be a weird proxy to relate Δ^{17}O of nitrate to photochemical activity. Could the authors elaborate on their choice ?

References

There are a few issues with the reference list.
Missing references:
Thiemens (2005) (appearing on Page 6834, line 18) is absent from the reference list.
Morino et al. (2009) (appearing on Page 6850, line 3) is absent from the reference list.
Couples of references from the same year:
There are two references from Wahner et al. in 1998, as well as two references from Savarino and Thiemens in 1999. These are not labelled a and b as they should be, so

in the text the reader does not know to which specific reference the authors point to.
Other issues :
The text refers to JPL, 2006. It turns out that this reference appears to be referenced as Friedl et al. 2006. This must be changed to improve consistency.
I leave it to the editorial staff to check the references further. For instance, the journal title for Atkinson (2000) is missing. Additional issues involve style of chemical species (absent subscripts, e.g. Davis et al. 2008 N2O5 instead of N_2O_5) or isotopic ratios (see e.g. Freyer 1991), latitudes (e.g. Morin et al. 2009) or greek symbols (missing ν in Redpath et al. 1978, e.g.). Please consider improving the spelling of Peìro-Garcìa in the two corresponding references (2002 and 2003), as well as Röckmann instead of Rockmann.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 6829, 2010.