**Atmospheric
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Comment

*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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I thank Greg Michalski for replying to some of the issues raised in the initial review. However, I am disappointed that several issues were not addressed in the reply ; in addition, most aspects of the reply are not convincing at all and likely erroneous. Below I am not reiterating the review posted already, for which many points remain unanswered, but highlighting issues that, to my view, require more care in addressing them than in the present reply from the authors.

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1. The reaction of $N_2O_5$ with particles (which is a large focus of the ms) produces not only nitric acid but more generally particulate nitrate. Nitric acid is widely used in atmospheric chemistry but it refers (and refers only to) $HNO_3$, which clearly is only part of atmospheric nitrate dealt with in the study. I strongly disagree with GM and suggest once more that 'atmospheric nitrate' replaces 'nitric acid' in the title and in the ms.

2. Even if one wants to compute the time evolution of $\Delta^{17}O$, the correct mass balance equation is the one given in the initial review, which predicts the time evolution of $\Delta^{17}O\times$'atmospheric concentration', and there is no way around it. Simplifications are of course possible in certain cases (photochemical steady state etc.) but the simplification provided in the ms is physically incorrect. The loss term plays a role, because nitrate that is removed from any air parcel disappears with its $\Delta^{17}O$. That loss reactions induce MDF does not imply that nitrate removed from a given air parcel disappears with a 0 $\Delta^{17}O$ (this would lead to an increase of the $\Delta^{17}O$ of nitrate remaining in the parcel, following mass conservation, and it would make no sense). Then of course if loss terms are ignored from the chemical point of view, then the loss term in the isotopic mass balance equation disappears, because the rate of nitrate removal is zero, not because the $\Delta^{17}O$ associated with it is zero.

*The absence of loss for compounds (such as ozone deposition) is common, indeed the standard practice, in zero dimensional box models*. This is the first time I see this. The authors here should provide scientific references as to why box models do no take into account deposition of long-lived species, such as ozone, nitrate etc, as mentioned just above.

Last, that $\Delta^{17}O$ reaches a *steady-state* (this word seems oddly chosen because nitrate undergoes all by 'steady-state' in the atmosphere, in contrast to $HO_x$ or $NO_x$ during the day ...) after a few days of simulation seems to indicate to me, if I understand

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correctly the way the simulations were carried out, that the production of nitrate drops precipitously after a few days of simulation (otherwise it $\Delta^{17}O$ would keep increasing for ever). To me this can only be due to an exhaustion of $NO_x$ and $NO_y$ in the box, which is not representative of atmospheric conditions. Performing box modeling does not mean that the box considered is hermetically closed : there are fluxes in and out the box, even for 0D box modeling (see e.g. box modeling studies by Sander et al., von Glasow et al., etc.). Fluxes out were ignored by the authors, although at the timescale of a week of simulation dry and wet deposition of nitrate constitutes a significant fraction of its budget. Fluxes in should likewise not be ignored, such as $NO_x$ fluxes into the box. Were those really taken to be 0 ? What is the scientific justification for this ?

4. It is not possible to use $\alpha$ at night, because photochemical steady state does not hold. This has to be fixed by the authors both in the code and in the ms.

5. [...] *since they have adopted tropospheric ozone of 25 permil to balance their model* [...]. I suspect here a large misunderstanding of the content of the study by Savarino et al. 2008. It is not a model study. It is an experimental study aimed at understanding the rate of transfer of $\Delta^{17}O$ from ozone to $NO_2$ during the bimolecular reaction $NO+O_3$. Ozone with variable $\Delta^{17}O$ was synthesized in the laboratory and reacted with equimolar amounts of NO. Thus the conclusion that NO mostly abstracts the terminal O atom from ozone does not imply any particular hypothesis about the $\Delta^{17}O$ of tropospheric ozone. The goal was simply to study one particular chemical reaction (like for measuring kinetic reaction rates, for which complex gas mixtures are likewise avoided ...). I thus do not understand at all the reply by GM here.

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

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