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Atmospheric
Chemistry
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Discussions

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

**S. Morin et al.**

morin.samuel@gmail.com

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We thank Reviewer #1 for his/her positive appreciation of this work.

Replies to his/her remarks and suggestions are given below.

*First, the paper presents many of its results in table format. While this is certainly clear, it would be more useful to the reader and perhaps easier for the casual reader to understand if some of these tables were converted to graphics (e.g., bar graph format). I leave this as a suggestion for the authors.*

We have taken good note of the reviewers's suggestion, but we prefer keeping tables for displaying the results of the different simulations carried out under different isotopic or chemical assumptions. In the tables, actual numbers are given, which is what will

be needed by the colleagues who will hopefully use these results for their own models. For the more general audience, the other plots provide illustrations to the concepts introduced in the ms.

*Second, the paper has a section on open questions or unknowns. It appears to me that the recent discover y that $N_2O_5$ leads to large production of $ClNO_2$, which is photolabile and recycles $NO_x$, has changed the conventional picture of the atmospheric chemistry of nighttime formation of $NO_3$. This chemistry has not been conisered here in terms of its isotope anomaly, but perhaps should be.*

It is true that the paper focusses on "classical" atmospheric chemistry, and does not consider explicitly recent developments relevant to the heterogeneous reactions involving $NO_y$ and reactive halogens. It would of course be very interesting to test how such reactions impact the isotope anomaly of reactive species. However, the present manuscript focusses on methodological developments rather than a detailed exploration of the many new interesting aspects of reactive atmospheric chemistry (this would make the ms even lenghtier).

*Specific comments:*

*Reactions R1-R4: This set of reactions pertains to inorganic nitrate only. The authors may wish to distinguish inorganic from organic nitrate in the sentence that precedes it.*

This has been clarified in the introduction (first occurrence of "atmospheric nitrate").

*Section 3.2.1: $NO_2$ + $O_3$ is assumed to have the same mechanistic characteristics as NO + $O_3$. Is this justified? Are there any experimental data at all?*

This issue has required a significant update between the initial acpd ms and the revised ms, taking advantage of results of new laboratory experiments made available to us. It turns out that the $NO_2$+$O_3$ reaction possesses different mechanistic characteristics than NO+$O_3$. Full details on this are given in the revised ms and shall not be duplicated here.

*Also, it is not clear why photolysis of $N_2O_5$ or $HNO_4$ should differ from thermal dissociation in terms of isotopic scrambling. Either process, it seems, would simply break the weakest bond in the molecule. Why would one expect a difference?*

This issue has been tackled in the revised version of the ms. We now simply explore the impact of scrambling upon both photolysis and thermal decomposition. In the basic hypothesis, scrambling is not supposed to happen. We have then tested the case where scrambling occurs for both ways of dissociating $N_2O_5$ and $HNO_4$.

One motivation for this was that one previous study (Dominguez et al., ACPD 2009) assumed scrambling for all such processes, and we wanted to test how critical this assumption was.

*Section 4.1.1 The diurnal variation of HONO seems inconsistent with most field data that show it to be larger at night that during the day. Why the difference? Is the only source of HONO here due to OH + NO rather than heterogeneous reactions of $NO_2$?*

As explained above, in order to focus as much as possible on the methodology, only gas phase reactions were considered. This explains why HONO is indeed only forms through the OH + NO reaction, as summarized in the supplement to the paper.

*Section 4.2.3 Is the $NO_x$ mixing ratio changed by a factor of $10^5$, or by 100, as stated in the conclusion? An initial $NO_x$ of 2 ppbv (i.e., 2 nmol mol$^{-1}$) would seem more reasonable than 20 ppmv (20 $\mu$mol mol$^{-1}$) and would be consistent with the conclusion.*

Yes, the correct value is 2 nmol mol$^{-1}$. This was changed in the text and in the caption of the relevant table.

*Typographical:*

All typographical errors indicated were fixed in the revised ms.