

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

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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

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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 discovery 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 considered 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 lengthier).

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.

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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 than 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 formed 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 ppbv ($20 \mu\text{mol mol}^{-1}$) 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.

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