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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Quantifying atmospheric nitrate formation pathways based on a global model of the oxygen isotopic composition (Δ^{17}O) of atmospheric nitrate" *by* B. Alexander et al.

Anonymous Referee #2

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The manuscript describes global model simulations Δ17O of nitrate and a comparison of simulated data with observations. The study is highly original and the subject of the paper is well within the scope of ACP. The results are described and discussed clearly.

Discrepancies between modelled and observed Δ17O are discussed in terms of chemical reactions that are neglected in the model (bromide) or missing sources (release of NOy from snow). However, discrepancies between modelled and observed MIF can also be attributed to potential errors in sources, transport pathways, stratosphere-troposphere interactions etc. I miss a discussion on the potential influences of the dynamics of the atmosphere on the Δ17O of nitrate. For example: NOx in the upper

troposphere has a longer life time than NOx close to the surface, and will react relatively less efficiently with OH. Therefore a different A will apply for NOx in a model with spurious convection than in a model with less efficient convective transports. Further, a bit more information on the general model performance regarding ozone and NOy distributions is required. Specific comments follow below.

1) It is mentioned (p. 1197 line 22-25) that simulated ozone has no systematig global bias. However, with NOx and nitrate lifetimes upto a few days, regional aspects are more relevant here. More information on the general model performance regarding ozone and NOy distributions would be helpful for a better appreciation of the simulated isotope signatures and discrepancies with measurements (Fig. 5). For example, what can be deduced if Δ17O for nitrate is simulated consistently with the measurements but absolute concentrations (or deposition amounts) are not? Or the other way around?

2) The MIF of ozone in the stratosphere is prescribed with 40 permille, and in the troposphere with 25 or 35 permille. It is not entirely clear from the manuscript if the tropospheric value is kept fixed in the simulations, or is it adapted by influx of and mixing with stratospheric ozone? In the latter case it would be interesting to show a figure of the zonal and/or horizontal distribution of the computed Δ17O of ozone.

3) Stratosphere-to-troposphere transport of ozone is a highly regional process. Tropopauze foldings occur in specific regions, lower stratospheric air is transported rapidly to the surface and mixes irreversibly with tropospheric air, with different effects on atmospheric chemical processes as result. See for example some of the papers produced in the STACCATO project that investigated cross-tropopauze transports of O3 (http://www.forst.tu-muenchen.de/EXT/LST/METEO/staccato/). STE thus may carry relatively high Δ17O (O3) into the lower troposphere, and is therefore a process with a potentially significant impact on Δ17O (NO3). However, relatively fine model resolutions are required for a good dynamical representation of STE otherwise the synoptic transports can not be resolved and mixing between stratospheric and troposheric air is too fast. The resolution applied in GEOS-CHEM in this study (4x5

degrees) may be too coarse for this. Can this play a role in the overestimation of Δ17O (NO3) at Princeton in winter/spring?

4) You explain why neglecting N2O5 hydrolysis leads to a larger MIF in the winter/spring NH, but why does it produce a smaller MIF in SH (DDU)?

5) If I understand correctly the model meteorology is for 2005. The model-measurement comparisons in the figures reflect annual and monthly averages. Is it possible to include one or two figures with selected time series of observed and simulated values? This would illustrate the performance of the model on synoptic scales, more consistent with the NOy life time.

6) Technical: I found Figure 5 a bit small, difficult to discern the symbols. Also choose a more informative running title.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 11185, 2009.