

Interactive comment on “Quantifying atmospheric nitrate formation pathways based on a global model of the oxygen isotopic composition ($\Delta^{17}\text{O}$) of atmospheric nitrate” by B. Alexander et al.

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We thank reviewer #2 for his/her helpful comments. We have added a discussion of how biases in transport (such as convection) may impact our isotopic results. Detailed comments are addressed below.

1) The relevance of the lack of a systematic global bias is related to our conclusions regarding Figure 2. Other groups have assumed $\text{D17O}(\text{O3})=25\text{‰}$ and in this paragraph we are trying to explain possible model biases that could make our results look like $\text{D17O}(\text{O3})=35\text{‰}$ when it may not be so (e.g. what could be a model bias that could contribute to this isotopic difference?). Although there are certainly regional biases in

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concentrations of any simulated species, because at each location where we compare with observations $\text{D17O}(\text{O3})=35\text{‰}$ gives the best agreement, a bias in any one species such as ozone would have to exist at each location where there are observations. This is why we are concentrating on global, and not regional biases in this section. It is beyond the scope of this paper (or almost any paper!) to compare our model results with all available ozone observations (of which there are many); however, many other papers using the same model have addressed this issue on the regional scale (e.g. Wang et al., 2009; Hudman et al., 2009; Zhang et al., 2008; Terao et al., 2008; Wu et al., 2007), so we cite these papers instead of repeating their work.

One distinct advantage of the isotopic calculations is that they are normalized to concentration data. If the model gets nitrate concentrations wrong we don't immediately know why. There could be something wrong with NO_x emissions, with deposition rates, with the thermodynamic or kinetic partitioning between gas-phase and particulate nitrate, or nitrate formation rates could be incorrect, among other things. For example, nitrate concentrations will also be influenced by emissions and concentrations of NH_3 and sulfate, as the presence of these species will impact the thermodynamic partitioning of nitrate, and can have large uncertainties in and of themselves. See (Park et al., 2004) for a detailed discussion of this in the GEOS-Chem model. $\text{D17O}(\text{nitrate})$ is advantageous because it is indicative of only the chemistry of NO_x cycling and nitrate formation from its precursor, NO_2 . It is independent of thermodynamic partitioning for example, because this will fractionate the isotopes in a mass-dependent fashion, leaving $\text{D17O}(\text{nitrate})$ intact. Observations and modeling of $\text{D17O}(\text{nitrate})$ can shed light on whether the simulation of reactive nitrogen chemistry may be contributing to model discrepancies with observations of nitrate concentrations. A detailed comparison with nitrate concentrations is beyond the scope of this paper. There are many more observations of nitrate concentrations than of $\text{D17O}(\text{nitrate})$, and other papers such as (Park et al., 2004) have addressed this issue in detail. Discrepancies at the surface are partly attributed to inaccurate emissions inventories of NH_3 , which will not impact $\text{D17O}(\text{nitrate})$ in the current parameterization.

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It would be an insurmountable task to compare our model with all observed NO_y concentrations, but other papers, such as (Park et al., 2004) have compared surface observations in different regions with simulated nitrate concentrations. We are unable to plot nitrate concentration data in Figure 5 in 3 of 6 locations. The model simulates gas-phase and particulate nitrate, whereas the observations often represent nitrate deposition, such as in rain or snow. Therefore direct atmospheric concentrations are not available. The Summit and Princeton data set are from snowpit and rainwater samples respectively, which do not contain direct atmospheric concentration information. I was only able to get the number of micromoles of nitrate per sample from the author of the La Jolla data set. This allowed me to weight the monthly mean D17O(nitrate) calculations by concentration, but does not give me direct information on atmospheric concentrations. Also, the model will likely not reproduce the seasonality of nitrate concentrations in Antarctica since it does not include snowpack photodenitrification.

2) and 3) This distinction has been made more clear in the manuscript revisions. We do not distinguish between tropospheric and stratospheric-derived D17O(O₃) within the troposphere. Since nitrate production is dominant in the boundary layer, we expect this error in general to be small at the surface at low altitudes where most of the observations of D17O(nitrate) are located, but could be of seasonal importance in the mid-to high-latitudes. Please see revised manuscript for a more detailed discussion (second to last paragraph in section 2).

4) There was an error in the DDU plot in Figure 5 that has been fixed. The symbols for the gammaN₂O₅=0 simulation and organic nitrate calculations were inadvertently switched.

5) Observations on the synoptic time scale are generally not available (with the exception of the Princeton and Bermuda rain water samples). Due to the relatively large amounts of nitrate required for D17O analysis (particularly for the silver salt pyrolysis method), the observations themselves are often representative of significant time averaging (generally > 1 day). It would be computationally expensive and not necessarily

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useful to run the model for every year of observations that are available. If one was looking at details in one particular region this may be useful, but the goal of this paper is to provide a global perspective. We now include 2 data sets (COCA and Atlantic cruises) at daily resolution for 2 different years, 2003 (at 2°x2.5° horizontal resolution) and 2007 (at 4°x5° horizontal resolution), compared to 2005 at 4°x5° horizontal resolution for the rest of the model-observation comparisons.

6) We will work with ACP to make Figure 5 larger. We have removed one symbol showing the results of the sensitivity study using gammaN₂O₅=0 (and instead discuss in the text) which makes Figure 5 less cluttered. We will work with ACP to get a more informative running title.

References:

Park, R.J., Jacob, D. J., Field, B. D., Yantosca, R. M., and Chin, M.: Natural and transboundary pollution influences on sulfate-nitrate-ammonium aerosols in the United States: implications for policy, *J. Geophys. Res.*, 109, D15204, 10.1029/2003JD004473, 2004.

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