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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.

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1 General comments

We thank S. Morin for his careful and detailed review of our manuscript. The most significant comment, and change to the manuscript, is in the calculation of D17O(NOx) for the nighttime nitrate formation reactions. We have made this change in our calculations and the manuscript, which represents an important improvement. It does not change any of our conclusions. Details of this change and why it does not alter our conclusions are discussed in more detail below. All other comments were relatively minor, and are addressed explicitly and in detail below.

2 Specific comments

2.1 Structure and content

Sections 1 and 2 have been merged. We have kept the discussion of the oxygen isotopic composition of ozone in the introductory section to present this important issue upfront. Waiting to include a discussion of this material until the results section seems awkward, especially since we address this issue in the “Model description” section, where we initially mention our sensitivity studies covering a range D17O(O3) = 25 – 35‰Ålso, since we say in the beginning that D17O(nitrate) depends on D17O(O3) we think it is important to address the range of observations of both species.

We have also included the description of the NOx and nitrate chemistry (including Figure 1) in the introductory section.

We have included a supplementary table including all sample information and the total range in observed D17O(nitrate). The range in D17O(nitrate) does not always cover the full annual range since many of the observations do not cover one full year. The observations that do cover one full year are plotted in Figure 5.

We have removed the detailed description of the measurements from the COCA campaign, including the supplementary table. We agree that even more detail would be needed to show for example that oxidation of organics by H2O2 doesn’t alter the isotopic composition of nitrate (according to our testing, it does not). We have referred to this data as (Alexander et al., unpublished data) as we have not yet begun to write this up in more detail. We think it is important to include here however due to the paucity of low latitude D17O(nitrate) data, as you also noted.

2.2 Model description

The first sentence of the “Model description” section was changed to: “We utilize the GEOS-Chem global 3-D model of coupled aerosol-oxidant chemistry (Park et al., 2004) to simulate nitrate D17O and compare with observations.”

We have indicated the chemical timestep (1 hour) at the end of this first paragraph.

Equation 2a, calculating D17O(NOx) now uses instead of D17O(O3). A description, following [Morin et al., 2007] is included following the equation. We agree that this makes the calculation more clear. This was also changed in Equations 3a-d. We chose to keep Equations 3a-d to make clear the use of throughout the D17O(nitrate) calculations, and the distinction between Aday and Anight (described below), which is different from that used by (Michalski et al., 2003) and (Kunasek et al., 2008). Also, the aforementioned references do not include an equation for stratospheric nitrate, so we think it is important to explicitly show our assumptions here regarding the D17O value of stratospheric nitrate.

The calculation of D17O(nitrate) does include transport, which is explicitly stated. We changed the sentence beginning on page 11193 (line 15) to the following to try to make this more clear: "D17O(nitrate) is calculated according to the local importance of O3 in NOx cycling (A) and the relative abundance of each nitrate tracer (from transport and local production) according to the following:"

2.3 Scientific issues

2.3.1 Bias due to available data

It is true that the GEOS-Chem model has been extensively evaluated in the northern mid-latitudes and much less so in polar-regions. There is currently extensive work being done comparing the GEOS-Chem model to observations in the Arctic as part of the ARCTAS campaign, but this work is not yet published. Because the model has not been evaluated much prior to this work doesn't preclude us from comparing the polar observations with the model. In fact, such comparisons will ultimately improve the model's representation of polar chemistry. For example, the comparison suggests the need to implement BrO chemistry in relation to reactive nitrogen cycling in polar-regions, something we are working on at present. Such comparisons with the isotopes (in any location) are useful for improving and validating the model's chemistry in a way

that comparisons with concentration measurements cannot.

We specifically note the discrepancies in polar regions that maximize in springtime due to a combination of the lack of the effect of PSC sedimentation on polar nitrate and the lack of reactive BrO chemistry. We have not ignored this issue! These discrepancies are apparent in Figure 5. Showing the seasonality (where observations are available) is very useful for understanding model discrepancies, which is why we've included Figure 5.

We are not sure why you say that there are relatively few measurements in mid-latitudes. Evidence provided in Figure 2 is used to choose the appropriate value of D17O(O3) and the isotopic transfer function. The original Figure 2 included a total of 84 data points, exactly half of which are in low to mid-latitudes. Figure 5 only includes sites where year-round observations are available, and thus does not include all of the data that appears in Figure 2. We have now included a comparison of the model results with observations from (Morin et al., 2009) in Figure 2. Figure 2 now includes a total of 106 data points, well over half (64) of which are in the mid- to low-latitudes.

We believe that it is clear from Figure 2 that the same conclusions apply regarding D17O(O3) and the isotopic transfer functions even if the polar data are removed. We have attached an alternate version of Figure 2 here that includes only the non-polar observations (64 data points), to see if we reach the same conclusions. As you can see, this leads us to the same conclusion regarding D17O(O3) and the isotopic transfer mechanism. We explicitly state in the manuscript that this is no substitute for direct observations of D17O(O3) and more information on the isotopic transfer function during oxidation reactions from laboratory experiments is needed. However, given the available information, the statistics suggest that D17O(O3)=35‰ with the (Savarino et al., 2008) transfer function applied to both the NO+O3 and NO2+O3 reactions is the most appropriate choice. We then go on from here to discuss the global variability in D17O(nitrate). Note that we did not include data from (Patris et al., 2007) because they only report size-resolved (not bulk) observations. GEOS-Chem does not explicitly resolve the aerosol size distribution.

We do not place too much weight on the discrepancy with the Princeton data set, but suggest that since this data set represents event based rainwater samples, comparison with monthly mean model results may not be adequate. This is stated in the manuscript. We note that other mid-latitude data sets that better represent the monthly-mean state due to the nature of continuous aerosol collection show much better agreement with the model.

We of course do not think that our model is correct everywhere all the time; and we discuss possible model biases that could impact Figure 2. No model is perfect, but that does not mean that they are not useful (though climate skeptics like to use this argument). However, we do note that these model biases (which can apply to any model) are highly variable in space and time. For example, if the fractional contribution of N2O5 hydrolysis is biased high, then we would expect this to most impact wintertime data in the mid- to high-northern latitudes. Tropical and southern ocean data would be much less affected. We see a consistent result at all locations and time periods in Figure 2, which makes it hard to attribute one particular model bias for skewing the conclusions regarding this figure. This we think is one advantage of using a global model for this purpose.

2.3.2 D17O(O3) and transfer

We strongly disagree that the (Savarino et al., 2008) study showed that D17O(O3)=25‰. They showed that the NO is preferentially oxidized by the terminal atom of ozone, and showed the isotopic significance of this. They speculate that D17O(O3)=25‰ based on (Michalski et al., 2003); but as we now discuss in the manuscript, the (Michalski et al., 2003) paper is likely biased high regarding the importance of N2O5 hydrolysis, which strongly impacts their isotopic calculations.

Figure 2 has been changed to show the model results assuming D17O(O3)=25‰ and D17O(O3)=35‰ each with the statistical and the (Savarino et al., 2008) isotopic transfer function applied to both the NO+O3 and NO2+O3 reactions. We agree that this is the appropriate choice. The text has been modified accordingly and the conclusions regarding the choice of the D17O value of O3 clearly remain the same.

2.3.3 D17O(NO2) calculation

You are correct that we are assuming that isotopic steady-state holds when calculating D17O(NO2). We realize of course that this is not always the case at night. We assumed that since the lifetime of NOx is $\sim$1 day (longer at high latitudes), NOx will equilibrate during the day achieving isotopic equilibrium with daytime oxidant levels. We did acknowledge in the manuscript that daytime isotopic equilibrium won't always hold, and estimated the impact of this assumption on calculated D17O(nitrate) values by performing a sensitivity study using 24 hour average NO2 production rates via O3, HO2 and RO2 (compared to the 10am-2pm average in the base simulation). As stated in the manuscript, the difference is small (generally < 2‰ due to the strong diurnal variability in NO2 production rates.

However, we think you have a very good point about the relevance of this assumption, since NOx cycling will continue near twilight when peroxy radical concentrations are much lower than during the day, raising the A value. We have therefore changed the calculation so that the D17O(nitrate)R5 is calculated using A values between 10am-2pm (now Aday), and D17O(nitrate)R6,R7 and D17O(nitrate)R6,R8 using Anight, which is calculated using nighttime (midnight to 2am) NO2 production rates. The global range of Anight values is 0.50 – 1.00; however, the lower values are quite rare and most are between 0.9-1.0. This may result in an overestimate in of calculated D17O(nitrate) due to a broadening of the peroxy radical diurnal cycle from photolysis of species other than ozone (e.g. HCHO, HONO, H2O2, CH3O2H) (Fleming et al., 2006;Carpenter et al., 1997), but this overestimate is likely to be small on the global scale. As you can see in Figure 2, our conclusions regarding the value of D17O(O3) and the isotopic transfer function are the same. The reason this change has a relatively small impact on our calculations can be explained by comparing two very different locations, polar and tropical regions. In polar-regions, due to the 24 hour-a-day presence of (or lack of) sunlight (e.g. it is night from 10am-2pm during polar winter), A values were already at their nighttime values. As you noted, this change will affect calculated A values most in the tropics; however, in the tropics the daytime reaction (R5) dominates nitrate production, minimizing the impact on calculations of D17O(nitrate). We have modified all figures, equations, and resulting discussion using Anight for the nighttime reactions and Aday for the daytime reactions. We greatly appreciate this suggestion.

2.3.4 D17O of OH

We are confused by this point because we explicitly discuss this issue, and cite (Morin et al., 2007) and (Kunasek et al., 2008) on page 11200, line 25.

2.3.5 Analytical techniques

Regarding the denitrifier method and organic nitrate issue, I surveyed all users of the denitrifier method that I know of on this issue. I asked whether or not it was possible that Pseudomonas aureofaciens would convert organic nitrates, in addition to inorganic nitrate, into N2O. All groups with the exception of one replied “maybe” or “it is possible” (the one other group replied “no”). One group said that they had initial evidence in their lab of the answer being “yes”, but hadn’t yet followed through on those experiments to validate their initial findings. Another group pointed me to references demonstrating biological degradation of RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) producing N2O as a by product, which suggests that biological degradation of dissolved organic nitrate producing N2O as a by-product is possible. We now include a reference (Hawari et al., 2000) of biological degradation of RDX producing N2O as scientific evidence that this is generally possible. I refer specifically to soluble organic nitrates, not PAN as you mention. Due to its insolubility, I doubt that PAN would pose a problem. If Pseudomonas aureofaciens is utilizing soluble organic nitrates, then I wouldn’t expect any differences in the O2/N2 ratio (that should depend only on the decomposition of the biologically produced N2O into O2 and N2 and not on how N2O was produced).

The organic nitrate issue should only be important in low latitude forested regions, or mid-latitude forested regions during summer. If you don’t detect an issue with organic nitrates in polar-regions or in the MBL, this is not surprising as you wouldn’t expect a significant fraction of soluble organic nitrates in these regions. As far as I know, none of the published measurements from your group would be expected to contain a significant fraction of soluble organic nitrates. You are correct that it has not been shown that organic nitrates will be utilized by Pseudomonas aureofaciens, but it has not been shown that they do not use organic nitrates. Including organic nitrates in calculations of D17O(nitrate) can make a large difference (up to 10‰. An easy test would be to compare the two analytical methods on samples collected in a low latitude forested region. This may not be an issue, but it should be proven so.

We removed the discussion of the DDU data set. We noticed an error in our calculated monthly-mean D17O(nitrate) values for the observations at this location for the month of May. The corrected observational data now show a similar seasonality and magnitude as other polar observations.

2.4 Update to Kunasek et al., 2008

We have now included a discussion of the (Michalski et al., 2003) and (Kunasek et al., 2008) papers. We discuss why their box models achieve good agreement with the D17O(nitrate) observations using D17O(O3)=35‰ using the statistical isotopic transfer function, and we do not. Please see the revised manuscript for details.

3. Technical corrections

We will work with ACP to get a more descriptive running title.

We prefer to keep the current title. The title you suggest will only attract the isotope community. Our title should attract a broader audience, those that are interested for example in the global importance of nitrate formed via N2O5 and its impact on NOx using more recent parameterizations for DN2O5 than (Dentener and Crutzen, 1993).

Thank you for noticing the error on the longitude of Alert. This has been fixed.

“Bromine” on page 11200, line 6 has been changed to “BrO”.

The definition of NOX used on page 11201, line 16 is consistent with the (Dentener and Crutzen, 1993) paper. This paper is widely cited for the impact of N2O5 hydrolysis on the tropospheric NOX burden (though often it is confused with NOx). It is important to be consistent in the definitions in order to allow for direct comparison.

The range of D17O(O3) we report is the range of the mean of all measurements at any given location. We have added the absolute range. The sentence now reads: “Observations of the mean D17O value of tropospheric ozone (D17O(O3)) at different locations range from 25 – 35‰ (Johnston and Thiemens, 1997;Krankowsky et al., 1995); the absolute variability is much larger (6 – 54‰ (Morin et al., 2007).”

We didn’t think it was appropriate to discuss the Zahn et al. [2006] study, which discusses calculations of D17O(O3)stratosphere, in a paragraph which is discussing D17O(O3)troposphere. We instead removed the reference to the Lyons [2001] calculation of the value of D17O(O3) at the tropopause.

We don’t say that BrONO2 results in a higher D17O value than nitrate formed via the other pathways, we say it has a higher D17O value than O3, and this is due to preferential oxidation by the terminal atom of ozone.

We have changed “simulate observations” to “compare with observations”.

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. The model will likely not reproduce the seasonality of nitrate concentrations in Antarctica since it does not include snowpack photodenitrification.

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 NOx 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 NH3 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. D17O(nitrate) is advantageous because it is indicative of only the chemistry of NOx cycling and nitrate formation from its precursor, NO2. It is independent of thermodynamic partitioning for example, because this will fractionate the isotopes in a mass-dependent fashion, leaving D17O(nitrate) intact. So if a model does not get nitrate concentrations right, this does not make D17O(nitrate) calculations useless as you suggest. Indeed it 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 D17O(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 NH3, which will not impact D17O(nitrate) in the current parameterization.

References:

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Alternate version of Figure 2. Scatter plot of monthly-mean model calculations at the surface versus observations. Observations include: Bermuda (black circles), La Jolla (red triangles), Chile (purple diamond), Princeton (purple open circles), Ecuador (purple square), COCA (blue open triangles), and an Atlantic cruise (black open squares). Each panel uses different assumptions regarding the bulk isotopic composition of ozone and the isotopic transfer mechanism during ozone oxidation: a) D17O(O3)=35‰ and statistical D17O transfer, b) D17O(O3)=25‰ and statistical D17O transfer c) D17O(O3)=35‰ and (Savarino et al., 2008) transfer applied to NO+O3 and NO2+O3, d) D17O(O3)=25‰ and (Savarino et al., 2008) transfer applied to NO+O3 and NO2+O3. The linear least-squares regression (thick), y = x (solid), y = 2x and y = 0.5x (dashed) lines are shown. Inset is the regression equation and R2 values.

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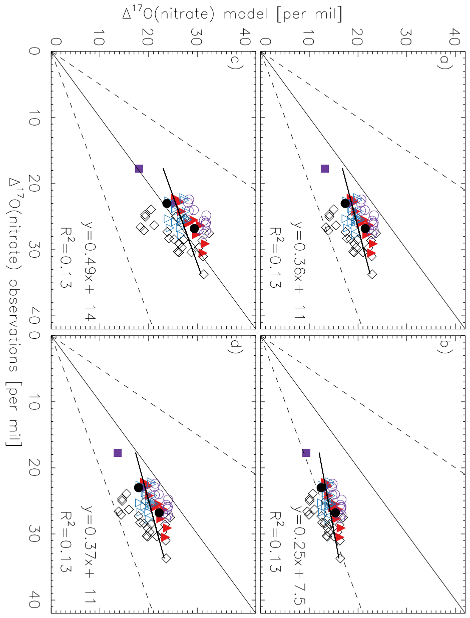

Fig. 1. Alternate version of Figure 2, without polar data.