**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

Interactive comment on "A photochemical model and sensitivity study of the triple-oxygen isotopic ($\triangle^{17}$O) composition of NO$_y$, HO$_x$, and H$_2$O$_2$ in a polluted boundary layer" *by* G. Dominguez et al.

G. Dominguez et al.

gdominguez@ucsd.edu

Received and published: 15 October 2009

We thank Dr.Michalski (G.M.) for his careful and thoughtful comments on our manuscript.

0.1 General Comments

G.M. wrote:

> Overall I felt that some of the simulations were not useful, in particular the

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NOy and HOx. I say this because in the end there needs to be some validation of the model via observations. There are no observations of ?17O anomalies in OHx and NOy and it is doubtful there will be any in the near future. This is primarily because these compounds have extremely low concentrations, are highly reactive, react with each other, exchange with each other, etc. I think the model should focus on what is or could possibly be observed namely NO3- (size, gas), SO42-, H2O2, and O3.

While we agree with the assessment regarding the difficulty of measuring $\Delta^{17}O$ of OH_x, we feel that it is important to at the very least attempt to rigorously trace what isotopic anomalies these species may acquire as a function of atmospheric conditions in light of their importance as precursors for the more "measurable" atmospheric components that G.M. has listed above. For example, our photochemical modeling suggests that the ^{17}O anomaly of HO_2 may be significantly greater than 0 per mil under certain photochemical conditions (See Specific Comments) and as a significant precursor to the more easily measurable H_2O_2, which is currently assumed to have a constant $\Delta^{17}O$ in modeling efforts, the modeling predictions given here for H_2O_2 indicate that there should be some variability. Thus, we argue that the simulation of $\Delta^{17}O$ of HO_2 is a necessary step for understanding the variation that has been previously observed in the $\Delta^{17}O$ of hydrogen peroxide in the atmosphere (Savarino and Thiemens, 1999).

G.M. wrote: In all cases the NO3- has the same pattern as NOy and the NOy are nearly the same values, so in the end I donÕt find the simulated NOy enlightening, but they make the graphs more difficult to read.

While it is true that both the patterns in nitrate found in fine and coarse particles are well correlated, we feel it is important to show these given the converged conditions modeled here. We note, although we do not show this here, that the coupling between NO and NO_2 may not be achieved in all conditions. This result is not obvious, but

can be shown or demonstrated if it would help convince the editor and reviewer of the importance of displaying NO_y in this paper.

> G.M. wrote: It is not clear what the bars in the graphs mean, is daylight top or bottom? More thought should be given to graph titles.

The bars in the graphs were intended to illustrate the diurnal variability of the $\Delta^{17}O$ of these species, an issue that has not been previously discussed in modeling and observations. With the exception of HO_2, atmospheric species acquired their maximum isotopic anomalies during daytime hours. Clarification of this issue will be made in the final paper through the use of more descriptive captions. We thank the reviewer for this important observation.

0.2 Specific Comments

> 5.3.1 Size-Dependent $\Delta^{17}O$(NO 3): The role of aerosol surfaces area types
>
> ÒTypesÓ implies something other than surface (singular) area, such as chemical composition. This does not seem to be what the authors are discussing however, I only see surface area and lifetime. This section also is vague on how surface area is being derived. Aerosol surface area will be a function of bin sinumber densityÉI see no number density distribution.

The sub-title was intended to be: "The role of aerosol surface area type". The main goal of this section was to discuss the role that the chemical composition of aerosol surfaces may have on the measured isotopic composition of as a function of aerosol size. Previous observations by Patris et al. (2007) in a remote boundary layer had observed modest differences between the isotopic composition of aerosol nitrate in super- and sub-micron aerosol particles. To attempt to better understand these observations, we

chose to, quite generically, model the isotopic composition of aerosol nitrate expected to be produced and recorded in aqueous aerosol particles (sea-salt spray) compared to an urban aerosol population devoid of any heterogeneous uptake of . To do this, we chose two distinct surface types with distinct uptake coefficients for nitric acid and as well as lifetimes. By specifying two surface area concentrations, we avoid having to model the time evolution of these aerosols, including growth. Our main goal was to assess how sensitive the isotopic composition of aerosol nitrate is to differences in aerosol surface types such as aqueous and non-aqueous aerosol surfaces for a variety of atmospheric conditions.

> G.M. wrote: The deposition timescales for nitrate that we labeled as coarse and fine were mistakenly reversed. These have been corrected, with coarse particles having 6 hour deposition timescales while fine particles having 10 day timescales.

We have clarified the discussion regarding the choice and justification for uptake coefficients that the reviewer found difficult to understand. We agree that the choice of words may have obscured the points we were trying to make in this section. For example, the reviewer commented on the following phrase: " The size-dependent aqueous surface". Here, we were merely trying to say that the aqueous surface intended to model sea-salt aerosols was assumed to only be found in the coarse aerosol size bin.

> G.M. wrote "residence time É..provides inertia for rapid changes in the average isotopic composition of aerosol nitrate and this effect is also accounted for in the aerosol sub-model as a sink reaction for aerosol nitrate in the fine (F) and coarse (C) size bins."

To atmospheric chemists accustomed to thinking about reservoirs and their sensitivity to isotopic shifts, this statement is obvious. If the reviewer feels that this is not the case,

our subsequent results and comparison of the variability of HNO_3 compared to aerosol nitrate is a direct demonstration of this. We can state this as a finding if the reviewer believes that this result is not obvious and merits highlighting.

> G.M. wrote: ... most species display large diurnal variations in both their concentration and isotopic composition, which are expected to be due to the photochemical production of OH and isotope exchange with water vapor during daylight. (Fact or is this one of your conclusions?)

Fact. We are stating these as findings in our paper.

> G.M. wrote: Since this is an electronic only journal it would not hurt to give a complete list of the reactions in the model and rate constants used, some of these constants may have been updated by JPL since the Yvon et al. work and a discussion of any rate constant would be appropriate.

We would be more than happy to include a list of reactions modeled here as an appendix if the editor feels it is appropriate. Given the lengthy reactions and reference made to the source of chemical reactions, these were not included in the original.

Before submission of a final paper, we will review the updated JPL photochemical database and assess the significance of any of these changes.

> G.M. wrote: Given that rate and equilibrium constants have a temperature dependence, Im surprised no sensitivity on temperature is shown. This could be very relevant seasonally and diurnally. Does the model change the rate constant over the course of the day as T changes? Why is the T dependence of O3 D17O values not important? Since RH is a function of T wouldnÕt there be an inherent T effect similar to RH (below), especially at night when RH is changing primarily as T decreases.

This was surprising to us too, at first. However, upon further thought, it is important to note that many of these reactions have large activation energies that parameterize their reaction rates. The range of temperatures relevant for tropospheric reactions (-30-30 C) is not significant enough to change the reaction rates appreciably. We agree that this is an important observation. We note that the model does not, in its current implementation, change T as a function of time of day (or insolation). This choice was made in order to explicitly isolate the effect of temperature alone. We explicitly stated this in the paper and left open the real possibility that some variables such as T and RH may be tightly coupled. We chose to treat the effect of RH as a separate variable in this paper for simplicity.

We agree that the T dependence of O_3 may be an additional source of variability that we have not tested here. These shifts as a function of temperatures representative of tropospheric conditions are likely to introduce small shifts, but if the reviewer and editor find that an explicit treatment of this factor is justified, we can implement a temperature dependence on the $\Delta^{17}O$ of ozone for the final paper.

> G.M. wrote: Figure 1 Is there only one scale for the two parameters? If so these OH concentrations seem very high. How do these compare with OH measurements/models in similar environments from other authors ? Also the ozone is at 1 ppm? EPA O3 limits are 75 ppb, is a 200 times over EPA limits realistic? This is likely the reason for high OH?(see your figure 4)

We agree that the O3 concentration used is not the most representative of typical ambient conditions. We will replace this figure with a more realistic figure in final version of the paper.

> G.M. wrote: These results suggest that actinic flux variability during sampling with high time resolutions (t 1-6 hours), could be sensitive this effect,

especially near strong NOx sources. Finally, we note that the differences in 17O nitrate produced in fine and coarse particles did not differ by more than 0.3 ‰for all of the environmental conditions that we probed in this study. What does actinic flux have to do with relative humidity?? This paragraph seems to come out of left fieldÉShould be discussed in terms of RH..

We agree. These sentences were erroneously left in the paper from an earlier version.

G.M wrote: Fig. 2. Sensitivity of $\Delta^{17}O$ to Relative Humidity . ..of modeled D17O values in NOy to relative humidity (same for Fig. 4. Sensitivity of $\Delta^{17}O$ to O3 .)

We don't know what the reviewer means to communicate here. Does he mean that the two captions are too similar to each other and wishes for an expanded description of these?

G.M. wrote: Figure 2. This result is opening up a can of worms because aerosol surface area will change dramatically with RH, particularly above 70% when salt deliquescence takes off. This inturn depends of chemical composition, which is often a function of aerosol size (ie, small = NH4HSO4, Large = NaCl). Because of this I would not be confident in the ?17O changes with aerosol size variations mean much in this figure.

We agree with G.M. that the issue of deliquescence is an important factor which could in turn have a large effect on the uptake of N_2O_5 on sea-salt particles. This was not modeled in the present paper. We propose placing a statement in the figure caption pointing to this factor and appropriate citations.

G.M. wrote: 6.2 Sensitivity to [O3] I have concerns about what this means‐Éis it realistic?. Holding NOx constant and widely varying O3 concentrations does not seem intuitively sound because they are intimately linked. The baseline NO concentration is 50 ppt and I am gathering this is a fixed value since there is no NOx flux in the baseline. Can you produce 15 ppb of O3 with a NO of 50 ppt? This would require some large amount of VOC to produce this amount of O3, which in turn would change the organic radical oxidation of NO. I think there is danger of getting some false results by Òfix‐ingÓ certain values for secondary pollutants that naturally vary (O3, NOx) This type of model should largely be driven by initial conditions and fluxes of primary pollutants that generate secondary pollutants and realistic concentrations of these pollutants is a check on the validity of the simulation.

As G.M. points out, VOCs could also produce the amount of O3 simulated here. By fixing the NO concentration, we can directly see the influence of O3 as one of a few key photochemical reactions that influences the $\Delta^{17}O$ of NO$_y$ species. This simplified treatment avoids the complexities that would be introduced by simulating VOC chemistry. Since the purpose of this paper was to explore sensitivities such as these in general, we feel that this level of treatment is appropriate and the importance of various environmental factors that we have identified will be valuable for future studies. We propose to add in a discussion to the final paper to explicitly make clear that VOC chemistry may be an important consideration for future work.

G.M. wrote: 7.1 ?17O of HO2 The authors discussion of HO2 in the transfer scheme should be rethought. It is easy to envision isotopic exchange between HO2 and O2 via the transition state O2 –H—O2 H atom transfer reactions are common. The authors should walk next door and discuss with Sinha, who measure HO2 isotopic exchange with ozone and O2. He estimated a rate constant of <3x10-17 which is relatively slow, but must be

considered in the context of competing reactions. The two of interest in the current work are oxidation of NO and recombination to form H2O2 for NO oxidation the exchange/reaction ratio is k2[O2][HO2]/k1[NO][HO2]/ =.21k2 /k1[NO]   k2/k1[NO] @ [NO] 50ppt = [3?10?17] /[50 x 10-12][8x10-12]   1 x105 even if the exchange rate constant is over estimated by a three or-ders magnitude, exchange is still 100 times faster. As the authors point out, H2O2 is mainly produced by HO2 recombination so HO2 canÕt have the high values predicted in the model, so the exchange with O2 is probably washing out the anomaly.

We respectfully disagree with G.M. on this point. While it is true that $\Delta^{17}O$ of HO$_2$ is high in our models, we also note that the $\Delta^{17}O$ produced in atmospheric H_2O_2 remains consistent with the work of Savarino et al. that measured $\Delta^{17}O$ in H_2O_2. What may be unclear to the reviewer, based on the discussion given in the paper, is that the *concentration averaged* $\Delta^{17}O$ of HO$_2$ is actually smaller than the time-averaged values.

If we accept that HO$_2$ is a/the major precursor to H_2O_2, then we have to accept that HO_2 has a non-zero $\Delta^{17}O$ and that this anomaly is not completely washed out by exchange with O$_2$.

We agree that the isotopic exchange reaction between HO2 and O2 should be ex-plored, but inserting poorly known exchange rates into the photochemical modelcan also lead to the prediction that NO$_3$ should have no isotopic anomaly, which is clearly not true.

G.M. wrote: Sensitivity to CH4 For a polluted region, non methane hydro-carbon and VOC would have been an interesting simulation. Why were these not considered?

We agree that these could have been addressed in a simulation. VOCs were not considered for the reasons given previously in relation to ozone concentration. Non

methane hydrocarbons were not simulated due to space considerations, but we would consider implementing if desired by reviewer and editor.

References

Patris, N., Cliff, S. S., Quinn, P. K., Kasem, M., and Thiemens, M. H.: Isotopic analysis of aerosol sulfate and nitrate during ITCT-2k2: Determination of different formation pathways as a function of particle size, Journal of Geophysical Research (Atmospheres), 112, 23 301–+, 10.1029/2005JD006214, 2007.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 13355, 2009.