

Dominguez et al. manuscript “A Photochemical Model and Sensitivity Study of the Triple-Oxygen Isotopic ($\Delta^{17}\text{O}$) Composition of NO_y , HO_x , and H_2O_2 in a Polluted Boundary Layer” is an attempt to use an isotope mass balance and a chemical model to predict the transfer of $\Delta^{17}\text{O}$ anomalies from ozone to other compounds in the atmosphere. Understanding isotope transfer reactions involving ozone is important because the several of the end products, NO_3^- and SO_4^{2-} are deposited to the Earth's surface as snow, precipitation and dust. The $\Delta^{17}\text{O}$ anomaly can be used to trace the accumulation of nitrate and sulfate in soils, ice, and water bodies and potentially be used as an oxidation and biogeochemical tracer. However, to effectively use $\Delta^{17}\text{O}$ variations as tracers we must first understand the mechanisms in the atmosphere that generate such anomalies. This paper is an attempt to assess which atmospheric parameters are important for propagating the ^{17}O excess through trace species in the atmosphere. Our group is currently working on a similar sensitivity analysis using a different model, so I will try and limit my comments to the authors' paper and I will try not to bias them with unpublished results from ongoing work.

Overall I felt that some of the simulations were not useful, in particular the NO_y and HO_x . I say this because in the end there needs to be some validation of the model via observations. There are no observations of $\Delta^{17}\text{O}$ anomalies in OH_x and NO_y 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 NO_3^- (size, gas), SO_4^{2-} , H_2O_2 , and O_3 . In all cases the NO_3^- has the same pattern as NO_y and the NO_y are nearly the same values, so in the end I don't find the simulated NO_y enlightening, but they make the graphs more difficult to read. The same with HO_2 (see discussion below). It is not clear what the bars in the graphs mean, is daylight top or bottom? More thought should be given to graph titles. For example “Sensitivity of D^{17}O to Relative Humidity” That has no meaning unless it refers to a specific compound, which must be inferred by reading the in-graph legends. Also, all the results are MODELED.

Additional comments are in italics below

5.3.1 Size-Dependent $\Delta^{17}\text{O}$ (NO_3^-): The role of aerosol surface area types

“Types” 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 size (i.e. radius) times aerosol number density...I see no number density distribution.

For all of the data presented here, we assumed that the fine and coarse size bins had $t(F) = 6$ hours and $t(C) = 10$ days to roughly correspond to the deposition timescales expected for fine sulfate dominated particles and coarse-sized sea-salt spray.

I do not understand why the fine lifetime is shorter than the course lifetime. If the authors assuming settling velocity, the large particles would have a much shorter lifetime. If it is a wet deposition, then they would be the ~ same. Or are they assuming small particles are coagulating to course over short timescale 6 hours?

we assumed that $\alpha = 0.1$ for HNO_3 for both coarse and fine aerosol surfaces. Aqueous sea-salt particles were set to dominate the coarse aerosol surface area and the uptake of N_2O_5 ($\alpha(\text{N}_2\text{O}_5) = 0.05$) and HNO_3 produced aerosol nitrate in the coarse size-bin while only N_2O_5 was assumed to be taken up in the coarse (aqueous) aerosol size bin

This is difficult to understand, please rewrite. The authors need to provide appropriate references for these uptake coefficients.

This size-dependent aqueous surface

Is not surface and size proportionally the same thing?

residence timeprovides 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.

Is this a result of this work or a something already known? It sounds like a possible result...

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?

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.

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 $\text{O}_3 \Delta^{17}\text{O}$ values not important? Since RH is a function of T wouldn't there be an inherent T effect similar to RH (below), especially at night when RH is changing primarily as T decreases.

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)

These results suggest that actinic flux variability during sampling with high time resolutions (1-6 hours), could be sensitive to this effect, especially near strong NO_x sources. Finally, we note that the differences in ¹⁷O of 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 field...Should be discussed in terms of RH..

Fig. 2. Sensitivity of ¹⁷O to Relative Humidity

...of modeled D¹⁷O values in NO_y to relative humidity (same for "Fig. 4. Sensitivity of ¹⁷O to O₃".)

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 in turn 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 Δ¹⁷O changes with aerosol size variations mean much in this figure.

The origin of the significant ¹⁷O values of HO₂ seen here will...

Nothing has been "seen" only simulated

to be representative of those found in a polluted urban area (CITE HERE).

I agree a citation would be appropriate...

6.2 Sensitivity to [O₃]

I have concerns about what this means...is it realistic?. Holding NO_x 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 NO_x 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 "fixing" certain values for secondary pollutants that naturally vary (O₃, NO_x) 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.

7.1 $\Delta^{17}\text{O}$ of HO_2

The authors discussion of HO_2 in the transfer scheme should be rethought. It is easy to envision isotopic exchange between HO_2 and O_2 via the transition state $\text{O}_2\text{--H---O}_2$. H atom transfer reactions are common. The authors should walk next door and discuss with Sinha, who measure HO_2 isotopic exchange with ozone and O_2 . He estimated a rate constant of $<3 \times 10^{-17}$ 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 H_2O_2 for NO oxidation the exchange/reaction ratio is

$$\frac{k_2[\text{O}_2][\text{HO}_2]/k_1[\text{NO}][\text{HO}_2]}{k_2[\text{O}_2][\text{HO}_2]/k_1[\text{NO}][\text{HO}_2]} = .21 \frac{k_2/k_1[\text{NO}]}{k_2/k_1[\text{NO}]} \sim \frac{k_2/k_1[\text{NO}]}{k_2/k_1[\text{NO}]}$$

@ $[\text{NO}] 50\text{ppt} = [3 \times 10^{-17}] / [50 \times 10^{-12}] [8 \times 10^{-12}] \sim 1 \times 10^5$

even if the exchange rate constant is over estimated by a three orders magnitude, exchange is still 100 times faster. As the authors point out, H_2O_2 is mainly produced by HO_2 recombination so HO_2 can't have the high values predicted in the model, so the exchange with O_2 is probably washing out the $\Delta^{17}\text{O}$ anomaly.

Sensitivity to CH_4

For a polluted region, non methane hydrocarbon and VOC would have been an interesting simulation. Why were these not considered?