A photochemical model and sensitivity study of the triple-oxygen isotopic ($\Delta^{17}O$) composition of NO$_y$, HO$_x$, and H$_2$O$_2$ in a polluted boundary layer

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Abstract

We present a photochemical model developed for the *explicit* calculation of triple oxygen isotopic compositions ($\Delta^{17}\text{O}$) of major atmospheric species. While we focus on the $\Delta^{17}\text{O}$ of HNO$_3$ and aerosol nitrate (NO$_3^-$) and its precursors such as NO, NO$_2$ and N$_2$O$_5$, the general implementation given here also provides $\Delta^{17}\text{O}$ predictions for other important atmospheric compounds such as OH, H$_2$O$_2$, and HO$_2$. Through the use of a simple aerosol surface area model, we calculate the $\Delta^{17}\text{O}$ composition of aerosol nitrate produced as a function of aerosol size and aerosol surface type. We explore the sensitivity of the $\Delta^{17}\text{O}$ of atmospheric species through a series of sensitivity studies and show that the $\Delta^{17}\text{O}$ of atmospheric compounds is affected to various degrees by environmental factors such as temperature, relative humidity, ozone concentration, NO$_x$ flux, and total ozone column density. In addition, we find that $\Delta^{17}\text{O}$ of these species is sensitive to photochemical conditions such as cloud albedo, latitude, and time of year. We compare the $\Delta^{17}\text{O}$ calculation outputs to previous methods and find significant differences in the $\Delta^{17}\text{O}$ of NO$_2$. We describe the origins of these and suggest studies that may help to resolve these differences.

1 Introduction: triple oxygen isotopic composition of atmospheric species

Oxygen has three stable isotopes ($^{16}\text{O}$, $^{17}\text{O}$, $^{18}\text{O}$) and until 1974, it was believed that all measurements of oxygen bearing species on Earth had a well defined relationship between their $\frac{[^{17}\text{O}]}{[^{16}\text{O}]}$ and $\frac{[^{18}\text{O}]}{[^{16}\text{O}]}$ ratios. Conventionally, the isotopic content of $^{17}\text{O}$ and $^{18}\text{O}$ are expressed as ratios with respect to a standard and quantified as $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ (see Appendix A) and when plotted on a so-called triple-isotope plot ($\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$), these ratios typically fall along a line with slope approximately equal to 0.52. This slope results from the fact that most physical processes that enrich or deplete the isotopic content of a system do so as a function mass and the relative depletion or enrichment
of isotopes of a given element in compounds is determined by the mass differences between the isotopes (see Thiemens, 2006). Thus, for most oxygen bearing terrestrial compounds, knowledge of $\delta^{18}\text{O}$ is sufficient for knowing $\delta^{17}\text{O}$, since these are related by $\delta^{17}\text{O} \approx 0.52 \times \delta^{18}\text{O}$ when referenced to the Standard Mean Ocean Water (SMOW) standard.

The discovery that ozone ($\text{O}_3$) produced in the lab (Thiemens and Heidenreich, 1983) and in the atmosphere (Mauersberger, 1986; Johnston and Thiemens, 1997) is anomalously enriched in $^{17}\text{O}$ has led to novel applications in the use of both $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ in measurements atmospheric compounds, where $\text{O}_3$ is a major oxidant. The anomalous enrichment in $^{17}\text{O}$, is transferred to both the direct and indirect products of ozone oxidation. For the purposes of this paper, this excess (or deficit) of $^{17}\text{O}$ is quantified as:

$$\Delta^{17}\text{O} \approx \delta^{17}\text{O} - (0.52)\delta^{18}\text{O} \quad (1)$$

Most solid and liquid oxygen bearing compounds found on Earth have $\Delta^{17}\text{O} \approx 0\%$. In recent years atmospheric compounds that have been identified as having $^{17}\text{O}$ excesses or deficits ($\Delta^{17}\text{O} \neq 0$) include CO (Huff and Thiemens, 1998; Rockmann et al., 1998), $\text{CO}_2$ (Thiemens et al., 1991), $\text{N}_2\text{O}$ (Cliff and Thiemens, 1997), $\text{H}_2\text{O}_2$ (Savarino and Thiemens, 1999a), perchlorate (Bao and Gu, 2004), molecular oxygen (Luz and Barkan, 2005), nitrate ($\text{NO}_3^-$) (Michalski et al., 2003) and sulfate ($\text{SO}_4^{2-}$) (Bao et al., 2000a,b; Lee and Thiemens, 2001; Bao et al., 2008). Most of these compounds acquire their anomalous enrichments either directly or indirectly from ozone, and measurements of the triple-oxygen isotopic composition ($\Delta^{17}\text{O}$) of these species, when combined with a detailed understanding of how the $^{17}\text{O}$ anomalies are transferred, can be used to gain direct measurements of the relative contribution of important chemical pathways. Aerosol nitrate (Morin et al., 2008; Kunasek et al., 2008; Morin et al., 2007a; Patris et al., 2007) and sulfate (Alexander et al., 2009; Bao et al., 2008; Dominguez et al., 2008), in particular, have been studied most extensively through a combination of measurements and modeling. For the purpose of illustrating some of
the novel constraints that can be provided through isotopic measurements of atmospheric compounds, in particular that of nitrate, as well as to provide additional context for understanding the motivation and significance of the work we present, we briefly previous measurements and modeling of $\Delta^{17}O$ of $\text{NO}_y (=\text{NO, NO}_2, \text{HNO}_3, \text{and NO}_3^{-})$ and $\text{HO}_x(=\text{OH, HO}_2)$ in this next section.

1.1 Recent work on $\Delta^{17}O$ of tropospheric nitrate and its precursors

The $\Delta^{17}O$ values of aerosol nitrate found in a variety of environments have been published recently. Michalski et al. (2003) first measured and modeled the $\Delta^{17}O$ bulk isotopic composition of aerosol nitrate in a polluted boundary layer using outputs of the photochemical model developed by Yvon et al. (1996). The photochemical model used by these authors included a two-stream radiative transfer model and could take inputs that included temperature, relative humidity (RH), total ozone column (TOC), NO$_x$ flux, and ozone concentrations. NO$_x$ and ozone concentrations could be held constant in the model, thus explicit treatment of ozone production was not included. By assuming a constant $\Delta^{17}O$ for ozone (=35‰) and determining the relative contribution of various oxidation pathways for NO and NO$_2$, precursors of aerosol nitrate, the authors found that the isotopic composition of aerosol nitrate has a seasonal variability attributed to shifts in temperature and actinic flux. Because the work done by Michalski et al. (2003) focused on the bulk isotopic composition of aerosol nitrate, the model predictions did not have any size dependent chemistry. Nevertheless, the authors, in general, found good agreement between their observations of the bulk isotopic composition of aerosol nitrate and their model results, although some significant differences between the model and measurements were reported. The authors attributed these differences to the possible influence of transport.

Since then, several studies of $\Delta^{17}O$ in aerosol nitrate from a variety of environments have been published. Patris et al. (2007) measured the size-dependent values of $\Delta^{17}O$ in nitrate (and sulfate) in a remote boundary layer (Trinidad Head, CA, USA) and found modest, but statistically significant differences in the $\Delta^{17}O$ values of aerosol nitrate as
a function of aerosol size, with the coarse size fraction displaying systematically higher values (0.5–1.5‰). This systematic difference was attributed to the preferential uptake of N$_2$O$_5$ on coarse aerosol particles, although this process was not modeled by the authors. Morin et al. (2007a) studied the shift in $\Delta^{17}$O of aerosol nitrate at a coastal Arctic site and found direct evidence supporting the expectation that the concentration of ozone directly affects the $\Delta^{17}$O found in aerosol nitrate. In addition, the authors argued for the importance of BrO as an oxidant of NO$_2$ to explain their comparatively high $\Delta^{17}$O(NO$_5$) ($\approx$35‰) in the Arctic environment. Morin et al. (2007a) did not model their observations, and instead relied upon the use of analytical approximations to illustrate the need for the BrO oxidation channel to explain their isotopic data.

In an effort to better understand the variability of $\Delta^{17}$O of ice-core nitrate from Alexander et al. (2004) and its relationship to paleoclimate concentrations of O$_3$ and OH, Kunasek et al. (2008) measured $\Delta^{17}$O of snowpit nitrate and compared these measurements to the outputs of a box-model of atmospheric nitrate for over three seasons. The authors found values of a seasonal variations in $\Delta^{17}$O that ranged from $\sim$22‰ (summer) to 33.7‰ (winter). The authors modeled their data using the combination of a chemical box model (which did not include Br chemistry) supplemented with boundary conditions set by the output of the GEOS-Chem transport model (Park et al., 2004). In a manner similar to the treatment of Michalski et al. (2003), the authors calculated the $\Delta^{17}$O values of NO$_2$ and nitrate using the computed chemical production rates output from their box model. Interestingly, the authors found very good agreement between the results of their model and isotopic observations during the winter, but their model appears to underpredict the $\Delta^{17}$O of snowpit nitrate by 2–7‰ during the summer, potentially caused by the combination of assuming that $\Delta^{17}$O(OH)=0‰, the subduction of stratospheric ozone (which has a higher $^{17}$O anomaly), or the role of BrO in producing nitrate. Morin et al. (2008) measured and modeled the $\Delta^{17}$O of aerosol nitrate over an annual cycle in the Arctic. For this work, the authors employed a 0D Lagrangian box model to track the chemistry along the trajectory followed by air transiting to the sampling site. Reasonable agreement between their model and measurements are
found, although there is significant scatter in the data beyond the analytical uncertainties. Similar to previous work, the $\Delta^{17}O$ of nitrate was estimated using the outputs of a chemistry model and several simplifying assumptions to estimate the $\Delta^{17}O$ of aerosol nitrate. The authors invoked BrO oxidation of NO to explain their isotopic measurements. Most recently, Alexander et al. (2009) have presented a global-transport model of $\Delta^{17}O$ of nitrate which uses a similar methods to calculate $\Delta^{17}O$ of nitrate.

To date, there appears to be some controversy regarding the precise value of $\Delta^{17}O(O_3)$ in the atmosphere and recent laboratory experiments on the distribution of oxygen isotopes within molecules of ozone (Bhattacharya et al., 2008) has called into question some of the model assumptions made by Michalski et al. (2003). Morin et al. (2007a), for example, argue that the bulk $\Delta^{17}O$ found in tropospheric O$_3$ is closer to the 25‰ found by Johnston and Thiemens (1997) and not the 35‰ assumed by Michalski et al. (2003) and Lyons (2001). However, the enrichment of $^{17}O$ in the terminal atom position of O$_3$ (Savarino et al., 2008) may explain the good agreement between the observations and modeling of Michalski et al. (2003).

2 Motivation for present work

Given the recent increases and applications of triple-oxygen isotopic measurements in the environment, from tropical rain forests (Brothers et al., 2008) to polluted marine boundary layers (Dominguez et al., 2008), it has become clear that a systematic study of the sensitivity of $\Delta^{17}O$ of atmospheric species is needed in order to maximize the potential of $\Delta^{17}O$ measurements to provide unique and novel insights into atmospheric chemistry that are not possible using traditional concentration measurements. In this paper, we present a photochemical box model that explicitly calculates the $\Delta^{17}O$ composition of major oxygen bearing species as a function of various oxidative and photochemical conditions. While the primary driver of the present work is to better understand observations of aerosol nitrate in the environment, we also calculate the $\Delta^{17}O$ of important precursor molecules of aerosol nitrate such as NO$_2$, HO$_2$, NO$_3$,
and N₂O₅. As a consequence, we provide the first direct calculations of the Δ¹⁷O of HOₓ and H₂O₂ in the atmosphere as a function of various environmental variables.

There are several benefits and drawbacks that accompany the explicit approach taken here. First, by not resorting to approximations that simplify the analytical calculation of Δ¹⁷O of species, we avoid overlooking small contributions by precursors that may have an overall cumulative effect on Δ¹⁷O. In addition, this approach allows us to examine the effect of shorttime scale perturbations on the photochemical and oxidative conditions at a sampling site or in studies of plume photochemistry that are not possible with previous modeling approaches. The lack of transport, on the other hand, is also a drawback of the box-model approach. Finally, we should mention that the explicit tracking of Δ¹⁷O in atmospheric species, as will be described in Sect. 5.2, is computationally expensive, in essence adding an additional chemical species for each one whose Δ¹⁷O is tracked in the photochemical model. The benefits of our explicit Δ¹⁷O approach, in the end, have allowed us to identify a potentially significant oversimplification of previous work regarding the Δ¹⁷O of HO₂, a significant oxidant and precursor to nitrate in the atmosphere.

3 Overview of present work

This paper is organized as follows. First, we review the mechanisms of ¹⁷O anomaly transfer in the atmosphere using the NOₓ-O₃ system as an example. We then provide a brief overview of the isotopic photochemical box model developed and include a description of key modifications made to the precursor code such as the inclusion of aerosol and isotopic sub-models that directly tracks the propagation of Δ¹⁷O from O₃ to other other major oxygen bearing species in the atmosphere as a function of time. Using this model, we calculate the instantaneous and time-averaged values of Δ¹⁷O for a variety key oxygen bearing species in the troposphere. We should emphasize that this work, while similar in some aspects to previous modeling work reviewed in the previous section, is novel and significant. As we will show, our approach has allowed us
to identify an important consideration in the calculation of $\Delta^{17}O$ of tropospheric species that has been overlooked by previous work. The significance of this finding along with others is discussed in Sect. 8.

Before describing the photochemical model, we briefly review the mechanisms of anomalous $^{17}O$ transfer to atmospheric species, with particular emphasis on oxidized species of nitrogen, although the physical and photochemical processes described may apply to other species as well.

4 The origin of excess $^{17}O$ in atmospheric nitrate

Natural (e.g. lightning and biomass burning) and anthropogenic emissions (automobiles, powerplants, and biomass burning) of oxidized nitrogen (NO$_x$) eventually become fully oxidized in the atmosphere leading to the production of nitric acid (HNO$_3$), nitrous acid (HONO), the nitrate radical (NO$_3$), dinitrogen pentoxide (N$_2$O$_5$), peroxyacetyl nitrate (PAN,CH$_3$C(O)OONO$_2$), alkyl nitrates (RONO$_2$), and peroxyalkyl nitrates (ROONO$_2$). Nitric acid is the major product of the atmospheric oxidation of NO$_x$ (Seinfeld and Pandis, 2006).

Recently, it was shown that the $\Delta^{17}O$ of aerosol nitrate found in the atmosphere can be quantified (Michalski et al., 2002) and that these measurements can be used to understand the relative role that homogeneous and heterogeneous chemistry played in the production of NO$_3^-$ in the atmosphere (Michalski et al., 2003). Here, the authors attributed the seasonal variation of the isotopic composition of bulk aerosol nitrate to shifts in the relative importance of homogeneous and heterogeneous chemistry in a polluted marine boundary layer. Specifically, the predominant homogeneous oxidation pathways used by the authors were:

$$\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3(g) + \text{M} \quad (R1)$$

$$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad (R2)$$

$$\text{NO}_3 + \text{HC}, \text{DMS} \rightarrow \text{HNO}_3(g) + \text{products} \quad (R3)$$
Gaseous nitric acid may then be taken up by aerosols to become atmospheric nitrate. The heterogeneous production of aerosol nitrate specified by Michalski et al. (2003) was given as:

$$\text{NO}_2 + \text{NO}_3 \leftrightarrow \text{N}_2\text{O}_5 + \text{H}_2\text{O(}\text{surf.}\text{)} \rightarrow \text{HNO}_3(\text{aq})$$  \hspace{1cm} (R4)

While only Reaction (R2) appears to result in the transfer of an excess of $^{17}\text{O}$ from O$_3$, a detailed examination of the NO$_x$ photochemical cycle reveals that the role of the shared precursor, NO$_2$, is important as well.

The oxygen isotopic composition of NO$_2$ and O$_3$ are expected to be linked via the following photochemical reactions:

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$$  \hspace{1cm} (R5)

$$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}^{(3}\text{P})$$  \hspace{1cm} (R6)

$$\text{O}^{(3}\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_3$$  \hspace{1cm} (R7)

An additional source of oxygen atoms for NO$_2$ are reactions with HO$_2$ or peroxy radicals (RO$_x$):

$$\text{NO} + \text{HO}_2(\text{RO}_x) \rightarrow \text{NO}_2 + \text{OH(RO)}$$  \hspace{1cm} (R8)

During daytime conditions, Reactions (R5) through (R8) occur rapidly and the oxygen isotopic composition of NO$_2$ is expected to converge and be set by the relative contributions from reactions R5 and R8 and their respective $\Delta^{17}\text{O}$ values. In general, it is assumed that $\Delta^{17}\text{O(HO}_2) \approx 0$ (Michalski et al., 2003), although we will examine the validity of this assumption later in this paper. While measurements of the isotopic composition of O$_3$ are not typically available, field measurements of its bulk isotopic composition have yielded values from as low as 21‰ to as high as 32‰ (Johnston and Thiemens, 1997). These values are lower than those assumed by previous modeling studies which assumed bulk ozone $\Delta^{17}\text{O}$ enrichments of about 35‰ (Lyons, 2001; Michalski et al., 2003; Zahn et al., 2006; Morin et al., 2007b).
Recently it was shown that Reaction (R5) results in the preferential transfer of a terminal atom in O$_3$ with a frequency >92±5\% (Savarino et al., 2008) and the magnitude of the enrichment found in the central and terminal atoms was determined experimentally by Bhattacharya et al. (2008). Here the authors found that the isotopic composition of O$_3$ made in the laboratory has a $\Delta^{17}$O≈25‰ and the terminal atoms relatively enriched, having a $\Delta^{17}$O≈35‰. These findigs are important since O$_3$ photolysis is a major source of OH in the atmosphere as shown by:

\begin{align*}
\text{O}_3 + h\nu &\rightarrow \text{O}_2 + \text{O}(^{1}D) \\
\text{O}(^{1}D) + \text{H}_2\text{O} &\rightarrow 2\text{OH}
\end{align*}

(R9) (R10)

O($^{1}$D) produced from this reaction is expected to have a large $\Delta^{17}$O and may also transfer its isotopic anomaly to other oxygen species in the atmosphere as shown by Lyons (2001).

Isotopic exchange reactions such as:

\begin{align*}
\text{H}_2\text{O} + \text{QH} &\rightleftharpoons \text{H}_2\text{Q} + \text{OH}
\end{align*}

(R11)

will also affect the isotopic composition of oxygen bearing compounds in the atmosphere and the exchange Reaction (R11) between H$_2$O ($\Delta^{17}$O=0‰) and OH and may completely erase the excess $^{17}$O of OH acquired from O($^{1}$D). Because of how rapidly this exchange reaction proceeds under tropospheric conditions (Greenblatt and Howard, 1989), it is generally assumed that $\Delta^{17}$O(OH)=0. The validity of this often used assumption will be directly tested in this paper.

4.1 The conservative nature of mass-independent isotopic signatures

Isotopic fractionation associated with most physical processes, such as the evaporation of water from a reservoir, may systematically favor the retention or depletion of “lighter” isotopomers (e.g. H$_2^{16}$O vs. H$_2^{18}$O) due to kinetic or equilibrium isotope effects. These processes will in general change the $^{16}$O, $^{17}$O, and $^{18}$O content of atmospheric
compounds, but in a mass-dependent manner and as a result the $\Delta^{17}$O composition of a reservoir of molecules is conserved unless there is mixing of additional molecules with a different $\Delta^{17}$O. A thorough review of the nature of mass-dependent and mass-independent fractionations for oxygen and sulfur was recently published (Thiemens, 2006).

5 Photochemical modeling the $\Delta^{17}$O of oxygen bearing species in a Polluted Urban Boundary (PUB) layer

The Polluted Urban Boundary Layer (PUB) model is a photochemical box model (written in Matlab) with three main components:

1. A chemical model for calculating the time evolution of over 41 chemical species using over 138 chemical and photochemical reactions as detailed in (Yvon et al., 1996).

2. An aerosol surface area distribution submodel for heterogeneous loss and chemistry (e.g. $\text{N}_2\text{O}_5+\text{H}_2\text{O}($surf$) \rightarrow \text{HNO}_3($aq$)$).

3. An isotope ratio ($\Delta^{17}$O) submodel for tracking the time evolution of the $^{17}$O anomaly in oxygen bearing species, not including water vapor, ozone, and molecular oxygen in the atmosphere.

Of particular importance to the results presented here is the inclusion of a sea-salt aerosol distribution to calculate the effects of heterogeneous production of $\text{HNO}_3$ on these particles given by Reaction (R4).

5.1 Chemical species and time dependent chemistry

The concentration of chemical species in PUB are tracked and integrated using 4th order Runge-Kutta integration (Press et al., 2002). Actinic fluxes, photolysis rates...
and quantum efficiencies are calculated for \( \text{NO}_2 \), \( \text{NO}_3 \), \( \text{H}_2\text{O}_2 \), \( \text{HNO}_2 \), \( \text{HNO}_3 \), \( \text{HO}_2\text{NO}_2 \), \( \text{N}_2\text{O}_5 \), \( \text{CH}_3\text{OOH} \), \( \text{HCO} \), \( \text{CH}_3\text{C} \) as described in Yvon et al. (1996) and Yvon and Saltzman (1993).

Input parameters include temperature \( T \), relative humidity \( \text{RH} \), \( \text{NO}_x \) flux, \( \text{O}_3 \) concentration, boundary layer height \( \text{BLH} \), total ozone column density, and cloud albedo. These factors are known to affect the oxidative conditions of the marine boundary layer and can be changed or held constant in the model. Combined with the oxygen isotopes submodel (Sect. 5.2) they can be used to probe the sensitivity of \( \Delta^{17}\text{O} \) in atmospheric species to environmental variables. The results of these sensitivity tests are presented in Sect. 6.

### 5.2 Oxygen isotopes submodel

The PUB model calculates the time dependent \( \Delta^{17}\text{O} \) values of a chemical species using a weighted average approach that provides isotopic mass-balance. This procedure calculates the \( \Delta^{17}\text{O} \) of a chemical species \( X \) as follows:

\[
\Delta^{17}\text{O}(X(i + 1))[X(i + 1)] = \Delta^{17}\text{O}(X(i))[X(i)] + \sum_{\text{sources}, j} d[X_j(i)]\Delta^{17}\text{O}(d[X_j(i)])
\]  

(2)

where \( [X(i)] \) represents the concentration of species \( X \), \( \Delta^{17}\text{O}(X) \) is the isotopic anomaly associated with species \( X \), \( d[X_j] \) is an infinitesimal change in that concentration from a chemical/photochemical reaction \( j \), and \( \Delta^{17}\text{O}(d[X_j(i)]) \) is the anomaly transferred by that source. We assume that all sink reactions do not affect the \( \Delta^{17}\text{O} \) of species, which is equivalent to saying that they are mass dependent.

The amount of \( \Delta^{17}\text{O} \) transferred by source reaction \( j \) will depend on the number of oxygen atoms in the product \( X_j \) derived from the reactants and the \( \Delta^{17}\text{O} \) associated with these. For example, the \( \Delta^{17}\text{O} \) of the homogeneous Reaction (R1) is given by:

\[
\Delta^{17}\text{O}(d[\text{HNO}_3(g)]) = \frac{2}{3}\Delta^{17}\text{O}(\text{NO}_2) + \frac{1}{3}\Delta^{17}\text{O}(\text{OH})
\]

(3)
The origin of any excess $^{17}\text{O}$ found in atmospheric species is assumed to originate from $\text{O}_3$ and is propagated to other atmospheric species and warrants further discussion.

5.2.1 $\Delta^{17}\text{O}$ of $\text{O}_3$, $\text{O}(^{1}\text{D})$, $\text{NO}_2$, and $\text{OH}$

Following the suggestion by Savarino et al. (2008) and in agreement with previous isotopic measurements of the $\Delta^{17}\text{O}$ of tropospheric $\text{O}_3$ (Krankowsky et al., 1995; Johnston and Thiemens, 1997), the $\Delta^{17}\text{O}$ of bulk ozone was assumed to be constant and fixed at 25‰. The central and terminal position anomalies were determined using a linear fit to the inferred relationship between the bulk and terminal as well as central positions of the $\Delta^{17}\text{O}$ of $\text{O}_3$ reported in (Bhattacharya et al., 2008):

$$\Delta^{17}\text{O}(\text{O}_3\text{(terminal)}) = (0.97 \pm 0.1 \, (2\sigma))\Delta^{17}\text{O}(\text{O}_3\text{(bulk)}) + 13 \, \%$$

$$\Delta^{17}\text{O}(\text{O}_3\text{(central)}) = (0.91 \pm Y \, (2\sigma))\Delta^{17}\text{O}(\text{O}_3\text{(bulk)}) - 25 \, \%$$

These details on the distribution of $^{17}\text{O}$ in $\text{O}_3$ are important since in the UV photolysis of $\text{O}_3$,

$$\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(^{1}\text{D}) \quad \text{(R12)}$$

it is expected that on average $\text{O}(^{1}\text{D})$ originates from the terminal position at least 91% of the time, resulting in an elevated heavy isotopic enrichment $\text{O}(^{1}\text{D})$. For our calculations, we assumed that:

$$\Delta^{17}\text{O} \left( \text{O}(^{1}\text{D}) \right) = 0.91 \times \Delta^{17}\text{O} \left( \text{O}_3\text{(terminal)} \right) + 13367$$
0.09 × Δ\(^{17}\)O (O\(_3\) (central))

\[ \begin{align*}
\text{(6)} \\
34.76 \%^\circ
\end{align*} \]

With the exception of water vapor (Δ\(^{17}\)O=0‰), molecular oxygen (Δ\(^{17}\)O= 0‰), and ozone (Δ\(^{17}\)O(bulk)=25‰) which we consider to be infinite reservoirs here, all other starting values of Δ\(^{17}\)O were assumed to equal zero initially, but were allowed to acquire an \(^{17}\)O excess via their precursors and isotopic exchange as described in Eq. (2) and Reaction (R11). We neglect the effect of chemical reactions such as CO+OH→CO\(_2\)+H and H+O\(_2\)+M which are known to produce CO\(_2\) and HO\(_2\) with Δ\(^{17}\)O≠0 (Huff and Thiemens, 1998; Rockmann et al., 1998; Savarino and Thiemens, 1999b). Of particular importance to species like Δ\(^{17}\)O(OH), whose precursor O(\(^{1}\)D) has a large \(^{17}\)O anomaly, the exchange Reaction (R11) is treated numerically as a chemical reaction that takes away OH with Δ\(^{17}\)O≠0 followed by a production of the same amount of OH with a Δ\(^{17}\)O=0. A list of exchange reactions considered in our numerical implementation of isotopic exchange are given below Reactions (R13–R15) and their respective rate constants are summarized in Table 1.

\[ \begin{align*}
\text{QH} + \text{H}_2\text{O} &\rightleftharpoons \text{OH} + \text{H}_2\text{Q} \\
\text{NQ} + \text{OH} &\rightleftharpoons \text{NO} + \text{QH} \\
\text{HOQ} + \text{OH} &\rightleftharpoons \text{HOO} + \text{QH}
\end{align*} \]

(R13) (R14) (R15)

5.3 Aerosol surface area submodel

To examine the role that differential uptake of precursors of nitrate may have on the Δ\(^{17}\)O of aerosol nitrate as a function of size, the PUB model aerosol submodel can be used to specify an arbitrary number of aerosol size bins, each with chemical compound specific uptake coefficients. For the purpose of examining the maximum contrast between Δ\(^{17}\)O of nitrate as a function of aerosol size, we specified two surface area size bins, a fine (F, Diameter≤1.5µm) and a coarse (C, Diameter>1.5µm). For each of
these size bins, deposition losses are calculated by specifying a deposition timescale, \( \tau_d \). For all of the data presented here, we assumed that the fine and coarse size bins had \( \tau_d(F) = 6 \text{ h} \) and \( \tau_d(C) = 10 \text{ days} \) to roughly correspond to the deposition timescales expected for fine sulfate dominated particles and coarse-sized sea-salt spray. The concentration and isotopic composition of nitrate in each of these size bins are treated exactly like the gas-phase species in the PUB model and we assume that the deposition process does not fractionate our aerosol nitrate in a mass-independent manner.

### 5.3.1 Size-dependent \( \Delta^{17}O(\text{NO}_3^-) \): the role of aerosol surfaces area types

Previous triple-oxygen isotope measurements of \( \text{NO}_3^- \) in size-segregated aerosols in a pristine MBL by Patris et al. (2007) found that nitrate found in coarse particles (\( \text{NO}_3^-(C) \)) had a consistently higher \( \Delta^{17}O \) compared to nitrate found in fine particles (\( \text{NO}_3^-(F) \)). These results were interpreted as direct evidence of \( \text{N}_2\text{O}_5 \) uptake onto sea-salt particles. In their work, Michalski et al. (2003) used a single aerosol surface area concentration (\( \mu\text{m}^2\text{ cm}^{-3} \)) to track their aerosol nitrate and thus provide no specific insight into the relative importance of this process.

For the sensitivity studies described in the next section, the available aerosol surface area was represented simply as a combination of an urban (<1.5 \( \mu\)m) and a sea-salt aerosol distribution (>1.5 \( \mu\)m) and the uptake of gas-phase species \( X \) is calculated using the first-order reaction rate for uptake:

\[
\frac{d[X]}{dt} = \frac{\gamma}{4} c[X] A \tag{R16}
\]

where the molecular speed \( c = \sqrt{\frac{8k_B T}{\pi m_X}} \), \( m_X \) is the mass of species \( X \), \( \gamma \) is the sticking probability of species \( X \) of the surface of aerosols with a surface area concentration \( A \), and \( k_B \) is Boltzmann’s constant. For the calculations we present here, we assumed that \( \gamma = 0.1 \) for \( \text{HNO}_3 \) for both coarse and fine aerosol surfaces. Aqueous sea-salt particles were set to dominate the coarse aerosol surface area and the uptake of \( \text{N}_2\text{O}_5 \)
γ(N₂O₅)=0.05) and HNO₃ produced aerosol nitrate in the coarse size-bin while only N₂O₅ was assumed to be taken up in the coarse (aqueous) aerosol size bin. This size-dependent aqueous surface may potentially produce size dependent Δ¹⁷O values in aerosol nitrate (Seinfeld and Pandis, 2006).

The residence time of aerosols, while not directly a factor in determining their isotopic composition, 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.

6 Sensitivity study of Δ¹⁷O of atmospheric species

Conventionally, sample size requirements for the triple-oxygen isotopic analysis of aerosol nitrate have demanded that aerosol sampling be done over time periods ranging from 12–36 h for typical aerosol nitrate concentrations. During this time, environmental parameters such as temperature, relative humidity, NOₓ flux, etc. may vary. Advances in analytical capabilities have reduced the sample size and the potential for high time-resolution measurements of the triple-isotopic composition of atmospheric species exists (Kaiser et al., 2007). At either range of time-scales, the oxidizing conditions and hence the Δ¹⁷O of atmospheric species may have substantially diurnal variability. Finally, regional and long-range transport of species may also influence the isotopic composition of NOₓ and HOₓ species, further motivating the study of Δ¹⁷O as a function of geographic and anthropogenic factors. To explore these issues, we specified baseline conditions and changed variables individually to probe the numerical sensitivity of Δ¹⁷O of major oxygen bearing species to these factors. The list of environmental variables and their baseline values are summarized in Table 2.

The sensitivity of the following NOₓ species: NO, NO₂, NO₃, HNO₃, N₂O₅, and fine (NO₃(F)) and coarse aerosol nitrate (NO₃(C)) are reported in the next section. The range of observed Δ¹⁷O of other oxygen bearing trace species (e.g. PAN, HNO₂,
HNO₂) calculated by the PUB model are summarized in Table 3.

The bulk of our discussion will focus on major species whose Δ¹⁷O have previously been measured or inferred and used in calculations of important precursors to measured species. These precursors include: OH, H₂O₂, HO₂, NO, NO₂, HNO₃, N₂O₅, and aerosol NO₃⁻. To control for model dependence on initial conditions, the model was first run for 150 h to ensure numerical convergence. While the daily average Δ¹⁷O are typically well converged at this timescale, 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 conditions. To illustrate this dynamic, we plot the concentration of [OH] and Δ¹⁷O of HNO₃ vs. time for a baseline run where [O₃]=1 ppmv in Fig. 1.

We provide plots of Δ¹⁷O of NOₙ as well as OH and HO₂ for a select number of the variables tested in our study. For all other variables, we summarize their influence on Δ¹⁷O of oxygen bearing species in Sect. 6.7. When reporting the results of our sensitivity study in plots, we will report both the time-average Δ¹⁷O values of species for the last 24 h of model run time (out of 150) as well as the diurnal variation (min,max) of these using diagonal or vertical bars.

6.1 Sensitivity to relative humidity

6.1.1 NOₙ

Depending on geographic location and associated meteorology, the diurnal range in relative humidity (RH) can be mild or extreme. We plot the sensitivity of Δ¹⁷O vs. RH of key NOₙ species in Fig. 2. Examination of this plot shows that Δ¹⁷O is relatively sensitive to humidity, especially at low RH values, but decreases at higher RH. The inverse correlation between Δ¹⁷O and RH is not surprising given that the abundance of water vapor in the atmosphere directly influences both the rate of isotopic exchange between H₂O vapor and OH as well as the abundance of OH. This interplay between
[OH] and oxygen bearing species was seen in all of our simulations, and contribute to the significant variability of $\Delta^{17}$O(HNO$_3$). These results suggest that actinic flux variability during sampling with high time resolutions ($\Delta t \sim 1–6$ h), could be sensitive to this effect, especially near strong NO$_x$ sources. Finally, we note that the differences in $\Delta^{17}$O 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.

6.1.2 HO$_x$ and H$_2$O$_2$

In exploring the effects of RH on $\Delta^{17}$O values of HO$_x$ and H$_2$O$_2$ shown in Fig. 3, we make note of several things:

- The time-averaged $\Delta^{17}$O(HO$_2$) is significantly greater than 0‰ and has significant diurnal variability.
- The time-averaged $\Delta^{17}$O(OH) becomes significant (25‰) as RH→0.
- The time-averaged $\Delta^{17}$O(H$_2$O$_2$) is a function of RH, converging at about 2‰ RH≥30 %.

The origin of the significant $\Delta^{17}$O values of HO$_2$ seen here will be discussed later in this paper (See Sect. 7.1).

6.2 Sensitivity to [O$_3$]

6.2.1 NO$_y$

Plots of $\Delta^{17}$O vs. [O$_3$] for NO$_y$ and aerosol NO$_3^-$ are shown in Fig. 4. The lower end of O$_3$ concentrations was chosen to reflect the oxidative conditions present in a relatively pristine environment such as a rain forest or a remote marine boundary layer, while the higher end were chosen to be representative of those fond in a polluted urban
area (CITE HERE). In examining Fig. 4, it is clear that $\Delta^{17}O$ of aerosol nitrate and its precursors are sensitive non-linear functions of $O_3$ concentrations.

6.2.2 $HO_x$ and $H_2O_2$

Interestingly, the time-averaged $\Delta^{17}O(HO_2)$ does not appear to be sensitive to $[O_3]$, while the $\Delta^{17}O(H_2O_2)$ appears to be sensitive to $[O_3]$ (see Fig. 5).

6.3 Sensitivity to $NO_x$ Flux

6.3.1 $NO_y$

The rates of $NO_x$ flux into the atmosphere can vary by orders of magnitude ($1-10^4 \mu$moles m$^{-2}$ dy$^{-1}$) and these are dominated by anthropogenic activities (GEIA-ACCENT Database, 2005). To explore the sensitivity of $\Delta^{17}O$ of $NO_y$ and aerosol nitrate to this variable, we varied $NO_x$ flux from 0–200 $\mu$moles m$^{-2}$ dy$^{-1}$. These results are shown in Fig. 6. It should be noted that in all of our simulations, $O_3$ concentrations were fixed to explore the role that increases in $NO_x$ flux have of $\Delta^{17}O$ for the species we studies. We acknowledge that holding the concentration of $O_3$ constant while increasing $NO_x$ fluxes may be unphysical, but this treatment avoids the complexities of generating ozone via organic precursors while still allowing us to probe the numerical consequences of increasing $NO_x$ flux. It is interesting to note that both $O_3$ and $NO_x$ flux are significant influences in the $\Delta^{17}O$ of $NO_y$ species and that this contrast appears to saturate in environments with strong $NO_x$ sources.

6.3.2 $HO_x$ and $H_2O_2$

We note that the $\Delta^{17}O$ of $H_2O_2$ in high $NO_x$ flux environments (Fig. 7) goes to zero, suggesting a source of variation for the $\Delta^{17}O$ of $H_2O_2$ measurements in the environment. The $\Delta^{17}O$ values of $HO_2$ and OH appear to increase systematically as a function
of NOx flux. This effect would explain some, but not all, of the associated increases in $\Delta^{17}O$. In any case, these results suggest that assessments of the $\Delta^{17}O$ calculations of the $\Delta^{17}O$ of atmospheric species in plumes will likely require explicit numerical isotopic determinations such as these.

6.4 Sensitivity to CH4

6.4.1 NOy, HOx and H2O2

Global methane levels, as deduced from ice core data, show that methane concentrations have ranged from about 0.350–0.700 ppmv over the last 420 000 (Petit et al., 1999). Strong regional sources of methane are known to exist (Owens, 1991). With this variability in mind, we plot the $\Delta^{17}O$ of NOy and aerosol NO3– as a function [CH4] in Fig. 8. These results indicate that local oxidizing conditions perturbed by significant amounts of methane, such as agricultural centers, may have a significant effect on $\Delta^{17}O$ of NOy. In contrast, increased methane concentrations appear to have a mild effect on $\Delta^{17}O$ of HOx(Fig. 9).

6.5 Sensitivity to latitude

6.5.1 NOy

The sensitivity of $\Delta^{17}O$ of NOy and aerosol NO3– to the latitude of their production are shown in Fig. 10. Changes in latitude are equivalent to changes in zenith angle and illustrate the potential sensitivity of NOy species to the geographic location where these species are oxidized. These results also suggest that NOy transported from sources at different latitudes may be distinguished from locally produced NOy species if isotopic exchange or mixing between these is precluded. The asymmetrical dependence seen in Figs. 10 and 11 is due to the baseline Julian Day chosen for this run (Julian Day=5), and indicates that this sensitivity is enhanced during during the winter season for both
the Northern and Southern Hemispheres. We note that if the simulations had been run at either Spring or Fall Equinox, we would expect a symmetrical dependence on latitude.

6.5.2 HO_x and H_2O_2

It is interesting to note that the $\Delta^{17}O$ of HO_2 is also strongly dependent on latitude, while H_2O_2 is relatively insensitive except at the highest latitudes, where it decreases to zero in our simulations.

6.6 Sensitivity to cloud albedo

6.6.1 NO_y

We explored the sensitivity of $\Delta^{17}O$ vs. cloud albedo of NO_y and aerosol NO_3^- by varying the cloud albedo. These results are shown in Fig. 13. Over the range of 0-1 for cloud albedo, we find that values below 0.5 have a negligible effect on the $\Delta^{17}O$ of NO_y with the sensitivity being increasingly non-linear at cloud albedo values above 0.5. These results suggest that cloud albedo is a significant variable in determining the $\Delta^{17}O$ of NO_y and aerosol nitrate.

6.6.2 HO_x and H_2O_2

It is interesting to note that while the $\Delta^{17}O$ of HO_2 increases as cloud albedo $\rightarrow$ 1, the $\Delta^{17}O$ of H_2O_2 decreases to zero.

6.7 Other sensitivities

We summarize results of other sensitivity tests in Table 4. Some variables such as Temperature and cloud base height appear to have very little effect on the $\Delta^{17}O$ of
aerosol NO$_3^-$ while ozone column density, boundary layer height, and Julian Day do have a measurable effect.

While we have not treated the formation of aerosol sulfate in our modeling study, we note that increases in the flux of atmospheric S in the forms of Dimethylsulfide (DMS) and H$_2$S both led to increases in the $\Delta^{17}$O of NO$_y$ and aerosol NO$_3^-$. An examination of model output [OH] concentrations as a function of these two variables suggest that the additional inputs of S into the atmosphere, some of which become SO$_2$, in turn lead to systematic decreases in the concentration of [OH] and a decrease in the fraction of all aerosol nitrate produced by Reaction (R1). Further studies using a coupled N and S isotopic model should be carried out to further investigate the possibility of this being a significant factor in $\Delta^{17}$O studies.

7 Comparison with analytic determinations of $\Delta^{17}$O of HO$_2$ and NO$_2$

7.1 $\Delta^{17}$O of HO$_2$

Our explicit calculations of $\Delta^{17}$O(HO$_2$) suggest that the time averaged $\Delta^{17}$O of HO$_2$ has a large diurnal variation and is significantly higher ($\Delta^{17}$O$\sim$10–30‰) than zero for a wide range of atmospheric conditions. The concentration averaged values, on the other hand, are closer to zero, though these are still significantly higher than zero. The source of this surprising result merits further discussion as the sources of HO$_2$ considered in our model are:

\[
\begin{align*}
H + O_2 + M & \rightarrow HO_2 \quad [\Delta^{17}O \approx 0\%] \quad (R17) \\
OH + O_3 & \rightarrow HO_2 + O_2 \quad [\Delta^{17}O \gg 0\%] \quad (R18) \\
OH + H_2O_2 & \rightarrow HO_2 + H_2O \quad [\Delta^{17}O \approx \frac{1}{2}\Delta^{17}O(H_2O_2)] \quad (R19) \\
HO_2NO_2 & \rightarrow HO_2 + NO_2 \quad [\Delta^{17}O = \Delta^{17}O(HO_2NO_2)] \quad (R20)
\end{align*}
\]
Estimates of the relative importance of these sources for representative atmospheric conditions experienced in the simulations run are summarized in Table 5. Based on the concentrations of ozone, H, and OH, it is clear that Reaction (R20) is a significant production pathway for HO₂ in the atmosphere, especially at night when photochemical production channels of OH and H diminish and the photolysis of HO₂ ceases. The major question regarding the production of HO₂ via Reaction (R20) is what should the Δ¹⁷O of the HO₂ produced be, given that the major source of HO₂NO₂ is:

\[ \text{HO}_2 + \text{NO}_2 \rightarrow \text{HO}_2\text{NO}_2 \] \hspace{1cm} (R21)

In our numerical scheme (Sect. 5.2), the Δ¹⁷O of newly produced HO₂NO₂ by Reaction (R21) is given by:

\[ \Delta^{17}O(\text{d}[\text{HO}_2\text{NO}_2]) = \frac{1}{2} \left[ \Delta^{17}O(\text{HO}_2) + \Delta^{17}O(\text{NO}_2) \right] \] \hspace{1cm} (R22)

This scheme is responsible for the higher than expected Δ¹⁷O values for HO₂ even in the absence of the mass-independent chemistry that has been previously reported for HOₓ formation (Savarino and Thiemens, 1999b).

So why has this pathway been previously overlooked? In part, assuming that \( \Delta^{17}O(\text{HO}_2) \sim 2\% \) seems reasonable given that \( \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 \) is a major production pathway of \( \text{H}_2\text{O}_2 \) and the finding by Savarino and Thiemens (1999a) that \( \Delta^{17}O(\text{H}_2\text{O}_2) \sim 2\% \).

### 7.2 Δ¹⁷O of NO₂

Here we compare the Δ¹⁷O produced using our explicit calculations and those obtained using the approximations and chemical partitioning approach used by others (Michalski et al., 2003; Kunasek et al., 2008). To control for differences in the details of producing aerosol nitrate production, we focus on the Δ¹⁷O of NO₂. In general previous work has
approximated the $\Delta^{17}O$ of NO$_2$ by using the outputs of chemical models, calculating a partition ratio $A$. Following Kunasek et al. (2008), this partition variable is:

$$A = \frac{\left( \frac{d[NO_2]}{dt} \right)_{O_3\text{path}}}{\left( \frac{d[NO_2]}{dt} \right)_{\text{total}}}$$

$$= \frac{k_1[O_3][NO]}{k_1[O_3][NO] + k_2[HO_2][NO] + k_3[RO_2][NO]}$$

(8)

(9)

The $\Delta^{17}O$ of NO$_2$ is then calculated as:

$$\Delta^{17}O(NO_2) = A \times \Delta^{17}O(O_3 - \text{trans.})$$

(10)

Here $\Delta^{17}O(O_3\text{-trans.})$ is the average value transferred to NO$_2$ from ozone. To directly compare to the results of Kunasek et al. (2008), $\Delta^{17}O(O_3 - \text{trans.})$ will be assumed to be 35 ‰. The rate constants used are:

$$k_1 = 3 \times 10^{-12} \exp(-1500/T)$$

(11)

$$k_2 = 3.5 \times 10^{-12} \exp(250/T)$$

(12)

As prescribed in Kunasek et al. (2008), we also assume that $k_3[RO_2][NO] = \frac{1}{2}k_2[HO_2][NO]$.

So how do the analytic and explicit calculations compare? Using concentrations provided by the PUB model chemical submodel, we calculate the expected $\Delta^{17}O(NO_2\text{-anal.})$ and compared these to the results provided by PUB’s isotopic sub-model (See Sect. refsec:isotopesubmodel). The difference between our presumably more exact treatment of $\Delta^{17}O$ anomaly transfer and the analytic approximations used is defined as:

$$\epsilon(NO_2) = \Delta^{17}O(\text{numeric}) - \Delta^{17}O(\text{anal.})$$

(13)
In general, we found significant differences in the $\Delta^{17}$O calculated by our numeric approach compared to the partition ratios method used by others. Not all of these differences can be attributed solely to the effect of having a non-zero $\Delta^{17}$O for HO$_2$ since the calculated differences ($\epsilon$(NO$_2$)) ranged from about $-7\%$ to $+3\%$. The origins of these differences are subtle, likely reflecting systematic changes in the $\Delta^{17}$O values and concentrations of HO$_2$, H, and OH. To illustrate the non-linear nature of these differences, we plot $\epsilon$(NO$_2$) as a function of relative humidity and total ozone column density in Figs. 14 and 15.

8 Conclusions

We have developed and presented a simple isotopic photochemical box model for explicitly calculating the $\Delta^{17}$O of major oxygen bearing species in the atmosphere. Using this photochemical model, we have probed the sensitivity of the triple-oxygen isotopic compositions ($\Delta^{17}$O) of important oxygen bearing species to atmospheric conditions that may vary at the local, regional, and global scales.

As a result of these sensitivity tests, we have shown that the $\Delta^{17}$O of aerosol NO$_3^-$ is expected to vary as functions of environmental factors such as relative humidity, cloud albedo, anthropogenic influences and urban setting and that these shifts and their diurnal variation are significant in the precursors of aerosol nitrate. Some of these variables may or may not vary independently of each other (e.g. relative humidity and cloud cover), but by varying each of these factors individually, we have isolated their potential contributions to atmospheric sample variability.

The results presented on the relationship between NO$_x$ flux and $\Delta^{17}$O in nitrate are consistent with the observations of Alexander et al. (2004), which found a shift in the $\Delta^{17}$O of Greenland ice-core NO$_3^-$ ($\approx 2\%$) that was directly tied to an increase in pre-industrial biomass burning in North America.

The sensitivity of $\Delta^{17}$O of NO$_y$ species to ozone and total ozone column density suggest a potential source of variability in Antarctic samples. Photochemical models.
of $\Delta^{17}O$ of NO$_y$ should consider the contribution that both of these factors make. The results of $\Delta^{17}O$ of NO$_3^-$ versus total ozone column density suggests that these may be correlated, not anti-correlated as suggested by McCabe et al. (2007).

In all of our tests, we found that the $\Delta^{17}O$ of nitrate in fine and coarse aerosols rarely deviated from each other by more than 0.3‰. These results strongly suggest that size-dependent deviations exceeding this amount may indicate the mixing of distinct sources of NO$_y$ with distinct oxidative conditions.

We have found, as result of our explicit numerical calculations, that contrary to assumptions regarding the $\Delta^{17}O$ of OH, H$_2$O$_2$ and HO$_2$ made by previous authors (Michalski et al., 2003; Savarino and Thiemens, 1999a; Alexander et al., 2004; Kunasek et al., 2008; Alexander et al., 2009), our explicit tracking of $\Delta^{17}O$ for these species and their precursors shows that their $\Delta^{17}O$ is expected to vary as a function of NO$_x$-O$_3$ environment. In addition, we have shown that HO$_2$ can have $\Delta^{17}O$ values that are significantly greater than zero.

As a result of our explicit calculations of the $\Delta^{17}O$(NO$_2$), we have shown that analytical approximations used by previous models of NO$_x$ chemistry may significantly under or overestimate the $\Delta^{17}O$ of NO$_y$ species as well as HO$_2$ and our overall results suggest that other factors such as methane and S sources may need to be considered when interpreting $\Delta^{17}O$ measurements of atmospheric species.

Given our explicit calculations, we provide the first calculations of atmospheric H$_2$O$_2$. These calculations show that the $\Delta^{17}O$ of H$_2$O$_2$ obtains some if not all of its anomaly through O$_3$. In this context, it should be noted that previous modeling work by Zahn et al. (2006) predicted non-zero values for HO$_2$ in the middle atmosphere while Lyons (2001), by considering the isotopic exchange reaction between HO$_2$ and O$_2$, found that this completely erased the $^{17}O$ anomaly. More laboratory measurements of poorly constrained isotope exchange rates, as suggested by Zahn et al. (2006), are needed to provide a definitive answer to this question, but our results suggest that the entire anomaly found in atmospheric H$_2$O$_2$ does not require chemical mass-independent ori-
gins as suggested by Savarino and Thiemens (1999b).

Finally, our model results suggest that explicit calculations of the $\Delta^{17}O$ of atmospheric oxygen bearing species, using the general algorithm presented (Eq. 2) here should be implemented in the global chemistry models of $\Delta^{17}O$ (e.g. Alexander et al., 2005) and point to the importance of local and regional conditions in determining the isotopic composition of aerosol nitrate, NO$_y$ and HO$_x$species in the atmosphere.

Appendix A

Notation

The isotopic ratios of a sample (SA) can be quantified with respect to an isotopic standard (ST). For oxygen, the Standard Mean Ocean Water (SMOW) standard is used and the isotope ratios of samples are quantified as:

$$\delta^{\text{x}O}(\%o) = \left( \frac{x_{R_{SA}}}{x_{R_{ST}}} - 1 \right) \times 1000$$

(A1)

where $x_{R_{SA,ST}} = \frac{[\text{xO}_{SA,ST}]}{[\text{16O}_{SA,ST}]}$ and $x=17$ or 18.

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Table 1. Isotopic exchange reactions included in PUB model. References used: a=(Greenblatt and Howard, 1989), b=(Dubey et al., 1997), c=(Dransfeld and Wagner, 1987).

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<th>Reaction</th>
<th>$k$ (cm$^{-6}$ s$^{-1}$)</th>
<th>Reference</th>
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<tr>
<td>R13</td>
<td>$1.6 \times 10^{-13} \exp(-2100/T)$</td>
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</tr>
<tr>
<td>R14</td>
<td>$1 \times 10^{-11}$</td>
<td>b</td>
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<tr>
<td>R15</td>
<td>$1.7 \times 10^{-11} \exp(-400/T)$</td>
<td>c</td>
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Table 2. Baseline Environmental Variables and their Values.

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<th>Value</th>
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<td>Julian Day</td>
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</tr>
<tr>
<td>$\gamma$(N$_2$O$_5$)</td>
<td>0.05</td>
</tr>
</tbody>
</table>
**Table 3.** Oxygen bearing trace species and their $\Delta^{17}O$ values.

<table>
<thead>
<tr>
<th>Trace Species</th>
<th>$\Delta^{17}O(‰)$ range</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$O</td>
<td>[0–25]</td>
</tr>
<tr>
<td>CH$_3$O$_2$</td>
<td>[13–27]</td>
</tr>
<tr>
<td>CH$_3$O$_2$H</td>
<td>[1–22]</td>
</tr>
<tr>
<td>HCHO</td>
<td>[2–15]</td>
</tr>
<tr>
<td>CHO</td>
<td>[0–15]</td>
</tr>
<tr>
<td>PAN</td>
<td>[18–31]</td>
</tr>
<tr>
<td>HNO$_2$</td>
<td>[19–31]</td>
</tr>
<tr>
<td>CH$_3$CO$_3$</td>
<td>[19–31]</td>
</tr>
</tbody>
</table>
**Table 4.** Summary of Environmental Sensitivities of $\Delta^{17}O(NO_3^-)$. Sensitivities for precursors of aerosol nitrate also follow similar trends and offsets.

<table>
<thead>
<tr>
<th>Variable (units)</th>
<th>Range</th>
<th>$\Delta^{17}O(NO_3^-)$‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone Column (DU)</td>
<td>[200–500]</td>
<td>[20.1–26.1]</td>
</tr>
<tr>
<td>Boundary Layer Height (km)</td>
<td>[0.5–3]</td>
<td>[29.9–21.1]</td>
</tr>
<tr>
<td>Cloud Base Height (km)</td>
<td>[2–6]</td>
<td>[22.2–21.4]</td>
</tr>
<tr>
<td>DMS Flux ($\mu$moles m$^{-2}$dy$^{-1}$)</td>
<td>[0–50]</td>
<td>[19.0–24.3]</td>
</tr>
<tr>
<td>H$_2$S Flux ($\mu$moles m$^{-2}$dy$^{-1}$)</td>
<td>[0–30]</td>
<td>[21.4–23.8]</td>
</tr>
<tr>
<td>Julian Day</td>
<td>[0–185]</td>
<td>[21.5–17.1]</td>
</tr>
</tbody>
</table>
Table 5. Sources of HO$_2$ in Model and Significance. Production % estimates based on typical model outputs for [OH], [O$_3$], [H].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k(T=298\text{ K})$ cm$^{-6}$ s$^{-1}$</th>
<th>Production % Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>R17</td>
<td>$1.06 \times 10^{-11}$</td>
<td>$\sim 0.99-0%$</td>
</tr>
<tr>
<td>R18</td>
<td>$6.82 \times 10^{-14}$</td>
<td>$\ll 1%$</td>
</tr>
<tr>
<td>R19</td>
<td>$1.69 \times 10^{-12}$</td>
<td>$\ll 1%$</td>
</tr>
<tr>
<td>R20</td>
<td>0.23</td>
<td>$\sim 0-0.99%$</td>
</tr>
</tbody>
</table>
Fig. 1. Diurnal variation of [OH] and Δ^{17}O of HNO₃ typically seen in model output. Output shown for [O₃]=1 ppm and baseline values for other variables.
Fig. 2. Sensitivity of $\Delta^{17}$O to Relative Humidity.
Fig. 3. Sensitivity of $\Delta^{17}$O of HO$_x$ and H$_2$O$_2$ to Relative Humidity. We note that in the limit of 0% RH, the $\Delta^{17}$O of OH converges to 26‰.
Fig. 4. Sensitivity of $\Delta^{17}\text{O}$ to $\text{O}_3$. 

$\Delta^{17}\text{O}$ Model and Sensitivity Study

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Fig. 5. Sensitivity of $\Delta^{17}\text{O}$ of HO$_x$ and H$_2$O$_2$ to [O$_3$].
Fig. 6. Sensitivity of $\Delta^{17}O$ to NO$_x$ flux.
Fig. 7. Sensitivity of $\Delta^{17}O$ of HO$_x$ and H$_2$O$_2$ to NO$_x$ flux.
Fig. 8. Sensitivity of $\Delta^{17}\text{O}$ to $[\text{CH}_4]$. 
Fig. 9. Sensitivity of $\Delta^{17}O$ of HO$_x$ and H$_2$O$_2$ to CH$_4$ concentration.
Fig. 10. Sensitivity of $\Delta^{17}O$ to Latitude.
Fig. 11. Sensitivity of $\Delta^{17}$O of HO$_x$ and H$_2$O$_2$ to Latitude.
Fig. 12. Sensitivity of $\Delta^{17}O$ to Cloud Albedo.
Fig. 13. Sensitivity of $\Delta^{17}O$ of HO$_x$ and H$_2$O$_2$ to Cloud Albedo.
Fig. 14. Error in $\Delta^{17}$O(NO$_2$) as a function of Relative Humidity. The large differences at low relative humidity are contributed in part by the fact that the $\Delta^{17}$O (OH) becomes significantly greater than 0 at very low humidities.
Fig. 15. Error in $\Delta^{17}\text{O}(\text{NO}_2)$ as a function of total ozone column density.