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Isotope modeling of nitric acid formation in the atmosphere using ISO-RACM: testing the importance of NO oxidation, heterogeneous reactions, and trace gas chemistry

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Abstract

Here we present ISO-RACM, an isotope mass balance model that utilizes the Regional Atmospheric Chemistry Mechanism to predict $\Delta^{17}O$ values in atmospheric nitrate. A large number of simulations were carried out that varied atmospheric parameters that are important in altering the magnitude and range of $\Delta^{17}O$ values generated in photochemically produce nitrate. These parameters included temperature, relative humidity, actinic flux, aerosol surface area and chemical speciation, and three different N_2O_5 uptake parameterizations. Trace gas mixing ratios were also varied including CH_4, CO, NO_x, O_3, volatile organic compounds and biogenic organic compounds. The model predicts that there are seasonal, latitudinal and diurnal variations in $\Delta^{17}O$ values due to changes in actinic flux with lower values corresponding to higher actinic fluxes. There was also a minor positive correlation between higher $\Delta^{17}O$ values and increased temperature. There were distinct differences in $\Delta^{17}O$ depending on which N_2O_5 parameterization was used, mostly the result of changing relative humidity being a factor in two of the parameterization schemes. Changing CO and CH_4 mixing ratios had negligible impact on $\Delta^{17}O$ values but significant variation in magnitude and range were predicted with NO_x, O_3, and organic loading. High NO_x and O_3 generated high $\Delta^{17}O$ with a narrow (10‰) range, while high organics led to low $\Delta^{17}O$ values and a wider range of possible values. Implications for using $\Delta^{17}O$ to evaluate NO_x-NO_y chemistry and aerosol formation processes are discussed, as is needed future research.

1 Introduction

The production of atmospheric nitrate ($NO_3^-{}_{atm}$=$HNO_{3(g)}$+$NO_3^-{}_{(aq)}$+$NO_3^-{}_{(s)}$) is important in a number of atmospheric and biogeochemical systems. As a strong acid, HNO_3 is a significant and increasing component in acid rain, which has seen a resurgence in regions where emission controls remain lax (Rodhe et al., 2002; Dentener et al., 2006). Aerosol nitrate loading is expected to increase as nitrogen oxide (NO_x) emis-

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sions associated with human activities continues to grow (Galloway, 1995; Galloway et al., 2004). This increase in aerosol loading has implications for human health since nitrate aerosols are often associated with urban settings and inhalations of particulate matter has been linked to respiratory distress and increased mortality in susceptible
5   populations (Samet et al., 2000; Schwartz and Neas, 2000). Aerosols are also linked to climatic change through direct and indirect radiative forcing (Hansen et al., 2005; Myhre, 2009; Lohmann and Lesins, 2002; Haywood and Boucher, 2000) and nitrate aerosols are projected to become increasingly important in the climate system (Li et al., 2009; Bauer et al., 2007). $NO_{3\,atm}^-$ is also a nutrient, and its deposition (wet and
10 dry) can impact ecosystem function (Magill et al., 2004; Fenn et al., 2003; Paerl et al., 2001), initiating carbon uptake in some systems (Bedison and Mcneil, 2009) and retarding carbon storage in others (Scheuner and Makeschin, 2005). High nitrogen deposition can also lead to shifts in biodiversity, declines in forest health, and coastal eutrophication (Magill et al., 2004; Fenn et al., 2003; Paerl et al., 2001). Finally, $NO_{3\,atm}^-$ is
15 incorporated into snow, that in Greenland and Antarctica forms ice sheets and provides a long term (∼500 000 ybp) record of variations in $NO_{3\,atm}^-$ concentrations (Hastings et al., 2004; Gladysheva et al., 2003; Delmas, 1998). To date, however, variations in ice core nitrate concentrations (pre-anthroprocene) have yet to be linked to any specific shifts in the global nitrogen cycle over time. Such information would be vital for as-
20 sessing linkages between the global nitrogen cycle and the carbon cycle and climate system. Therefore, understanding how $NO_{3\,atm}^-$ is formed in the atmosphere and how its concentration (and formation) vary over time and space, is crucial for understanding a number of important environmental systems. In addition being able to trace the biogeochemical fate of post depositional $NO_{3\,atm}^-$ can provide insights into the linkage
25 between the atmospheric and terrestrial N cycles.

Stable isotopes can play an important role in understanding nitrogen cycling in the atmosphere including the importance of $NO_{3\,atm}^-$ formation pathways. Here we present a photochemical box model sensitivity study that examines how oxygen isotope anomalies are generated during $NO_{3\,atm}^-$ production. The model utilizes kinetic mechanisms

that trace nitric acid formation in the troposphere and an oxygen isotope transfer mechanism involving oxygen atom transfer between ozone and oxides of nitrogen. The objective is to evaluate how different combinations of atmospheric conditions, such as NO_x and organic compound concentrations, relative humidity (RH), or hours of day

5　light, might shift $NO_{3\ atm}^-$ production pathways. These shifts should then be reflected in the $\Delta^{17}O$ anomaly that is known to exist in $NO_{3\ atm}^-$ (see below). The predictions made by the model will eventually be used to select sampling sites where observations of $\Delta^{17}O$ values in $NO_{3\ atm}^-$ will be used to test the model assumptions and assess its predictive capabilities. In turn, such a model could help test hypothesis regarding

10　N_2O_5 uptake and be used to interpret $\Delta^{17}O$ anomalies in ice cores, aerosols, soils, and precipitation.

1.1　Mechanisms of $NO_{3\ atm}^-$ formation

$NO_{3\ atm}^-$ is formed by the oxidation of NO_x ($NO+NO_2$) by several different chemical mechanisms. It is initiated when nitric oxide is oxidized to NO_2 by ozone or peroxy

15　radicals (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts Jr., 2000).

$$NO + O_3 \longrightarrow NO_2 + O_2 \tag{R1}$$

$$NO + HO_2 (ROO) \longrightarrow NO_2 + OH (R) \tag{R2}$$

Here we can define an oxidation parameter α, which is the % of NO oxidized by ozone relative to peroxy radicals: α=R1/(R1+ΣR2's). The term ΣR2 arises because a number

20　of organo-peroxy radicals are capable of oxidizing NO to NO_2. NO_2 can then react with OH radicals in a 3-body reaction to generate nitric acid.

$$NO_2 + OH + M \longrightarrow HNO_3 + M = \beta \tag{R3}$$

　NO_2 can be oxidized further by ozone generating the nitrate radical. The nitrate radical can go on to extract hydrogen atoms from volatile organic compounds (VOC) such

25　as non-methane hydrocarbons (Atkinson, 2000) and biogenic VOC such as isoprene

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(Perring et al., 2009; Horowitz et al., 2007) and di-methylsulfide (DMS) (Stark et al., 2007; Yvon et al., 1996).

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \tag{R4}$$

$$NO_3 + VOC \longrightarrow HNO_3 + R = \chi \tag{R5}$$

5 Since NO_3 undergoes photolysis at wavelengths in the visible range, its daytime lifetime is short ($\sim 3\,s$) so this reaction only becomes important at night. Also at night, NO_3 can recombine with NO_2 to form N_2O_5, which is in equilibrium by thermal decomposition.

$$NO_2 + NO_3 \longleftrightarrow N_2O_5 \tag{R6}$$

N_2O_5, nitric acid anhydride, can react with gas phase water to form nitric acid. How-
10 ever, this reaction is relatively slow and is not thought to be significant under tropospheric conditions (Tuazon et al., 1983; Wahner et al., 1998). Wetted aerosol surfaces, on the other hand, have a catalytic effect and N_2O_5 can readily hydrolyze on these surfaces to form HNO_3 (Hallquist et al., 2000; Mentel et al., 1999; Mozurkewich and Calvert, 1988).

15 $$N_2O_5 \, (aerosol/H_2O) \longrightarrow 2\, HNO_3 = \varepsilon \tag{R7}$$

Recently, there has been a significant amount of controversy over what role N_2O_5 hydrolysis plays in controlling nighttime NO_x/NO_y concentrations (Brown et al., 2003, 2006). In situ data suggests that N_2O_5 uptake on aerosols seems to be a function of aerosol type (sulfate versus organic) and whether they are internally mixed (Brown et
20 al., 2006), but these results are at odds with laboratory studies that have experimentally determined N_2O_5 uptake coefficients (Mentel et al., 1999; Mozurkewich and Calvert, 1988; Wahner et al., 1998). Since this reaction is key in titrating nitrogen oxides from the atmosphere, which in turn controls daytime oxidant loads, this gap in our knowledge about NO_x/NO_y cycling is significant.

1.2 Oxygen isotope transfer model description

Direct modeling of isotope partitioning into atmospheric reactive species such as NO_x and $NO_{3\ atm}^-$ is difficult. To do so would require knowing the kinetic and equilibrium fractionation factors (isotopologue rate constants), either by experimental or theoretical determination. While equilibrium fractionation factors have been calculated for small stable molecules (Urey, 1947), they have not been evaluated for larger molecules (i.e. N_2O_5) and radicals. For kinetic isotope effects (KIE) the situation is even less favorable. Relatively few atmospherically relevant KIE's have been experimentally determined and comparisons between experimental and theoretical results often lead to different values, sometimes with opposite signs. In addition, the influence of isotopic variation in different sources that lead to $NO_{3\ atm}^-$, such as different $\delta^{15}N$ values in NO_x sources or $\delta^{18}O$ shifts in tropospheric water vapor, adds to the complexity. These difficulties have resulted in only qualitative, generalized evaluations of the mechanisms that control isotope variations ($\delta^{15}N$, $\delta^{18}O$) in NO_y (Freyer, 1991).

Modeling ^{17}O anomalies, often referred to mass independent effects, has distinct advantages over traditional isotopes fractionations (Lyons, 2001; Michalski et al., 2003). Primarily, only a handful of reactions are known to generate $\delta^{17}O$ values that do not obey the $\delta^{17}O = .52\delta^{18}O$ mass dependence rule of isotope effects (Thiemens, 2005). Deviations from this rule, the ^{17}O excess, are quantified by $\Delta^{17}O = \delta^{17}O - .52\delta^{18}O$ (Miller, 2002). The most well known system where $\Delta^{17}O$ values are generated using reactants that are mass dependent (e.g. the mass independent fractionation – MIF) is during the formation of ozone (Thiemens and Heidenreich III, 1983; Thiemens and Jackson, 1987). While MIF's have been observed in CO (Rockmann et al., 1998; Bhattacharya and Thiemens, 1989), CO_2 (Bhattacharya et al., 2000), and HO_x (Savarino and Thiemens, 1999), the effect is typically much smaller than that observed in ozone and they are often generated via UV dissociation reactions which are trivial in the lower troposphere. Therefore from a tropospheric chemistry perspective, MIF is believed to occur during the production of tropospheric ozone.

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Once $\Delta^{17}O$ values are generated in ozone (by MIF) they are propagated through to other reactive species by mass balance (Lyons, 2001; Michalski et al., 2003; Alexander et al., 2005). This is the current hypothesis for the origin of $\Delta^{17}O$ values that have been observed in nitrate (Michalski et al., 2003) and sulfate (Alexander et al., 2005) aerosols, and in tropospheric H_2O_2 (Savarino and Thiemens, 1999). This mass balance mechanism can be formulated by

$$\Delta^{17}O(NO_{3_{atm}}^-)/dt = \Sigma P_{(NO3)i} \cdot \Delta^{17}O_{(NO_3)i} - \Sigma L_{(NO_3)j} \cdot \Delta^{17}O_{(NO_3)j} \tag{1}$$

where $\Delta^{17}O(NO_3^-)$ is the ^{17}O excess observed in compound NO_3^-; $P_{(NO3)i}$ is the production of nitrate through reaction pathway i and $\Delta^{17}O_{(NO3)i}$ is the $\Delta^{17}O$ value associated with that pathway. $L_{(NO3)j}$ is the analogous terms for the loss process (j) of nitrate. For $NO_{3\ atm}^-$ the main loss processes in the lower troposphere are removal by dry and wet deposition, processes that should have minor mass dependent isotopic effects (i.e. $\Delta^{17}O=0$) so that the $\Delta^{17}O_{xj}$ terms become zero and $\Delta^{17}O_x = \Sigma P_{xi} \cdot \Delta^{17}O_{xi}$. In this sense, based on our current understanding, tropospheric production pathways control the $\Delta^{17}O$ of compounds such as nitrate. This assumption is not true for multidimensional modeling where the loss terms play an important role. For example, if an urban region, with high nitrate production, advects this nitrate to an adjacent, pristine site (cell/box) where production is trivial, the urban signal would mask pristine production from Eq. (1). If removal terms in the urban box were high, say by rainout via an intense storm, then the urban nitrate $\Delta^{17}O$ signal would not manifest itself in the pristine cell. The present model is zero dimensional (no fluxes) so only the production terms need to be considered.

2   Methods: $\Delta^{17}O$ mass balance model

The $\Delta^{17}O$ mass balance approach follows previous work that suggests ozone oxidation of NO_x to higher oxidation states (NO_y) is the main transfer mechanism for generating

positive $\Delta^{17}O$ values in $NO_{3\ atm}^-$ (Savarino et al., 2008; Michalski et al., 2003; Lyons, 2001). The transfer of one oxygen atom from ozone to NO by Reaction (R1) is followed by an assumed mass dependent photolysis of NO_2, then re-oxidation of NO by ozone, ultimately leads to NO_2 coming into near isotopic equilibrium with ozone as NO_x
5 reached photochemical steady state. This equilibrium is upset by oxidation of NO by Reaction (R2). The $\Delta^{17}O$ transfer mechanism from ozone to NO_x-NO_y can then be formulated as (using shorthand $^{\Delta}X = \Delta^{17}O$ value of compound X)

$$^{\Delta}NO_2 = \alpha\, ^{\Delta}O_3$$

$$^{\Delta}HNO_3(\beta) = {}^{\Delta}O_3(2\,\alpha/3) \tag{2}$$

10 $$^{\Delta}HNO_3(\chi) = {}^{\Delta}O_3(2\,\alpha + 1)/3 \tag{3}$$

$$^{\Delta}HNO_3(\varepsilon) = {}^{\Delta}O_3(4\,\alpha + 1)/6 \tag{4}$$

(Michalski et al., 2003) where α is the mole fraction of NO oxidized by O_3, and β, χ and ε are the mole fractions of HNO_3 produced by the Reaction pathways (Reaction R3), (Reaction R5), and (Reaction R7) respectively. Predicting $\Delta^{17}O$ values in $NO_{3\ atm}^-$ is
15 then a matter of knowing the $\Delta^{17}O$ value of O_3 and calculating the branching ratios (α, β, χ, ε) using a photochemical kinetics model such as RACM (see below). It should be noted that α is not fixed in time but will evolve based on the production time steps and the final α used is summed over all time steps (as in integrating Eq. 1).

2.1 Uncertainties in the $\Delta^{17}O$ mass balance model

20 There are still a number of uncertainties concerning the specifics of the $NO_{3\ atm}^-$ mass balance approach that need to be acknowledged. The three main uncertainties include possible $\Delta^{17}O$ transfer from HO_2, the $\Delta^{17}O$ value of tropospheric ozone, and the dynamics of NO_x oxidation.

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Since some peroxy radicals originate from oxidation reactions with ozone, one must consider whether these compounds would also have $\Delta^{17}O$ signatures due to oxygen atom transfer. Our assumption is that they are negligible, which is based on the following considerations. Organoperoxy radicals are mainly formed by H abstraction (via OH or NO_3) from organics to form R followed by recombination with O_2 to yield ROO (Finlayson-Pitts and Pitts Jr., 2000). Since the oxygen leading to the peroxide ligand is atmospheric $O_2(\Delta^{17}O\sim-0.3‰)$ (Luz et al., 1999) the radical's $\Delta^{17}O$ value should be ~0‰. The majority of HO_2 is produced by the $H+O_2$ reaction ($k_{H+O2(298)}=1\times10^{-12}\,cm^3\,molecules^{-1}\,s^{-1}$), where H is mainly generated by OH oxidation of CO. The contribution $O_3+OH\longrightarrow HO_2+O_2$ ($k_{O3+OH(298)}=6\times10^{-14}\,cm^3\,molecules^{-1}\,s^{-1}$) would be considerably smaller since CO concentrations are typically higher than O_3 and given the larger rate constant for the CO reaction (JPL, 2006). In addition, the possibility of isotopic exchange between O_2 and HO_2 (Sinha et al., 1987) would likely erase any $\Delta^{17}O$ transfer from O_3. This is analogous to OH which losses any $\Delta^{17}O$ signal by exchange with water (Dubey et al., 1997; Lyons, 2001; Michalski et al., 2003) at relative humidity typical of the troposphere. Measurements of $\Delta^{17}O$ values in H_2O_2 (~2‰) (Savarino and Thiemens, 1999), which is primarily formed by the HO_2+HO_2 recombination reaction, supports the notion that $\Delta^{17}O$ signals in HO_2 are small. Therefore in the present model, for simplicity, we assume that HO_x and ROO· do not transfer any $\Delta^{17}O$ signature to NO_x-NO_y.

Temperature and pressure experiments (Thiemens and Jackson, 1990; Morton et al., 1990) suggest that tropospheric O_3 should possess $\Delta^{17}O$ values ~35‰, tropospheric measurements, however, show a range of $O_3\Delta^{17}O$ values that span 6–54‰ (Morin et al., 2007; Krankowsky et al., 1995; Johnston and Thiemens, 1997) and do not correlate with expected temperature and pressure variations. It is not clear whether this is an artifact in the tropospheric O_3 data (sampling apparatus) or some unknown isotope effect in the recombination processes or secondary reactions in the troposphere. We believe it is due to the tropospheric sampling approach and this is currently being in-

vestigated. Acknowledging these considerations, in the present work we will choose a $\Delta^{17}O$ value of ozone based on the experimental pressure and temperature dependent studies. Ozone $\Delta^{17}O$ values in the model were derived by considering temperature and pressure experimental values. Over deviations of ±10 kPa, typical of normal surface pressure variations, the dependence of $O_3\Delta^{17}O$ variations on pressure is weak so we have ignored the pressure effect and all simulations were run at 101.5 kPa. The $O_3\Delta^{17}O$ value's dependence on temperature was parameterized using

$$\Delta^{17}O(‰) = 10*[(0.0243 \cdot T(K) + 3.7667) - 0.52 \cdot (0.035 \cdot T(K) + 4)] \tag{5}$$

(Michalski et al., 2004) based on data from Morton et al. (1990).

Finally, the simple mass balance accounting of $\Delta^{17}O$ transfer from O_3 to NO_x-NO_y also becomes more complex if ozone's internal isotope distribution, and various NO_x-NO_y-O_3 transition states, are also considered. For example, theoretical and experimental evidence suggests the ^{17}O anomaly is found in the terminal oxygen atom (Bhattacharya et al., 2008; Michalski and Bhattacharya, 2009). If the $NO+O_3$ reaction proceeds though a terminal O_3 atom transition state (Peiro-Garcia and Nebot-Gil, 2002), the $\Delta^{17}O$ transfer (Savarino et al., 2008) would be ~3/2 the bulk ozone $\Delta^{17}O$ anomaly (terminal mechanism). However, molecular beam studies have suggested that the central oxygen atom in O_3 may also be extracted with ~equal probability (Viswanathan and Raff, 1983; Redpath et al., 1978), so the transfer to NO_2 would reflect the bulk $O_3\Delta^{17}O$ value (bulk mechanism). Likewise, ab initio calculations for the NO_2+O_3 reaction (Peiro-Garcia and Nebot-Gil, 2003) suggest a terminal atom extraction but there is no experimental evidence to confirm these calculations. We conclude that there are a number of uncertainties in the mass balance model and that there are no "correct" assumptions, only assumptions. Hopefully, the number of assumptions will be reduced as laboratory, theoretical and field, studies continue and expand. In the present work we will use both the bulk ozone and terminal atom mechanisms when estimating $NO_{3\,atm}^-\Delta^{17}O$ values and evaluating the results relative to known observations. The correct transfer mechanism will not influence the trends in $NO_{3\,atm}^-\Delta^{17}O$ values, which

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depend on the branching ratios (i.e. the chemistry), only their magnitude. We discuss the impacts of these assumptions based on our simulation results in the discussion section of this paper.

2.2 ISO-RACM: linking Δ^{17}O mass balance to RACM

The Regional Atmospheric Chemistry Mechanism (RACM) model (Stockwell et al., 1997) was utilized for tracing $NO_{3\ atm}^-$ photochemical production pathways because it has a number of advantages over the Yvon et al. (1996) model used previously (Michalski et al., 2003). Its chemical scheme is more sophisticated (238 reactions versus 122), including detailed accounting of anthropogenic hydrocarbon (alkane, alkene, aromatics) and biogenic organic (isoprene, α-pinene, d-limonene) chemistry that is important in ozone chemistry in urban and forested environments respectively. It has also been extensively validated in chamber and environmental studies by comparing observed and predicted secondary pollutants (Stockwell et al., 1997; Kirchner and Stockwell, 1997), and has been evaluated relative to other chemical mechanisms (Kuhn et al., 1998; Gross and Stockwell, 2003). Also the chemical scheme (and code) is portable into widely used 1-D, 2-D, and 3-D chemical transport models (Gross et al., 2005), which will ease the transition of this Δ^{17}O mass balance model into more sophisticated integrated land-surface-chemical transport models in future investigations. The advantage of using the RACM box model in this study, instead of using a more sophisticated 3-D model (Alexander et al., 2009), is that we can explore which reactions, conditions, and parameterizations have the most pronounced impact on controlling $NO_{3\ atm}^-\Delta^{17}$O values by altering an array of chemical boundary conditions and primary pollutant mixing ratios without requiring enormous amounts of computational resources. Incorporating the isotope mass balance mixing model into RACM, in addition to ongoing work adopting other isotope mechanisms (δ^{15}N) gives an isotope photochemical model: ISO-RACM.

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2.3 Heterogeneous N_2O_5 hydrolysis parameterization in ISO-RACM

A number of small modifications to ISO-RACM were made to account for additional $NO_{3\,atm}^-$ production pathways. The main addition is a scheme to account for heterogeneous N_2O_5 uptake by aerosols. RACM is a gas phase chemical model and lacks an explicit aerosol chemistry scheme. This limitation is typically handled by parameterizing a first order heterogeneous rate constant and treating the N_2O_5+ aerosol $\longrightarrow 2\,HNO_3$ reaction as a first order gas phase reaction: $k[N_2O_5]\longrightarrow 2\,HNO_3$ (Riemer et al., 2003). We employed three schemes to parameterize the first order rate constant: one where the uptake coefficient varies with sulfate and nitrate composition, another based of aerosol surface area that varies as a function of relative humidity, and a third that uses multiple experimental data sets to derive fitting parameters for ammoniated sulfate/nitrate aerosols.

The first N_2O_5 heterogeneous reaction scheme (scheme M) depends on surface area and chemical composition (Riemer et al., 2003; Mentel et al., 1999). The first order rate constant is derived as

$$k = 1/4 c_{N_2O_5} S \gamma_{N_2O_5}$$

where c is the mean molecular velocity, S is the aerosol surface area, and γ is the aerosol uptake coefficient for N_2O_5. The uptake coefficient (γ_{N2O5}) is varied as a function of the aerosol mass ratio (f) assuming only sulfate and nitrate are present, and using the individual N_2O_5 uptake coefficients for sulfate ($\gamma_1 = .02$) and nitrate ($\gamma_2 = .002$) (Mentel et al., 1999).

$$\gamma_{N2O5} = f \cdot \gamma_1 + (1 - f) \cdot \gamma_2 \quad f = \frac{m_{SO_4^{2-}}}{m_{SO_4^{2-}} + m_{NO_3^-}}$$

The second parameterization (scheme C) was suggested by Chang et al. (1987), which uses relative humidity (RH) as a dependent variable based on the observed

lifetime of NO_3 over a range of RH's (Platt et al., 1984). The rate constant is given by

$$k_{N2O5} = \frac{1}{600 \exp\left(-\left(\frac{RH}{28}\right)^{2.8}\right) + a}$$

where RH is in units of % and the fitting variable $a=5$, which leads to a maximum k_{N2O5} of $0.003\,s^{-1}$ at RH>60%.

The third N_2O_5 uptake coefficient model (scheme D) is taken from Davis et al. (2008). In this approach, uptake coefficient for ammonium aerosols is modeled as a function of temperature, RH, particle composition, and phase state. Briefly, this model uses regression fits of experimental uptake coefficients plotted as a function of RH and T. Coefficients (see β values in Davis et al., Table 3.) are used to fit the experimental data for $(NH_4)_2SO_4(\gamma_1)$, $NH_4HSO_4(\gamma_2)$, and $NH_4NO_3(\gamma_3)$ (see Davis Eq. 1–3) that is transformed as the logit function $\ln(\gamma/1-\gamma)$. These fits are then re transformed to derive the parameterized uptake coefficient using

$$y_i = \frac{1}{1 + e^{-\lambda_i}}$$

Similar empirical equations were derived for uptake coefficients on dry particles, mixed phase particles, and ice. For complete details the reader is referred to Davis et al. (2008).

In addition to the heterogeneous chemistry we added several modifications to the gas phase chemistry. We added two reactions that initiate DMS chemistry, one of which is a loss channel for nitrate radicals and generates HNO_3, while the other is a sink for OH radicals.
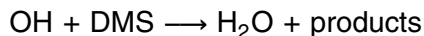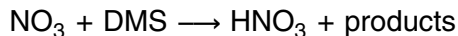
$NO_3 + DMS \longrightarrow HNO_3 + products$

$OH + DMS \longrightarrow H_2O + products$

These were added so that the importance of oceanic emissions in NO_3 radical chemistry and $\Delta^{17}O$ values might be investigated. Rate constants for all tropospheric reactions given by Stockwell et al. were checked and updated using the latest JPL guidelines for atmospheric chemistry (JPL, 2006). Changes in the latest rate constants for HONO production were the only modifications.

After tracer, N_2O_5, and rate constant updates were coded into the model a series of calibration runs were carried out to evaluate its performance relative to previous studies. The evaluation consisted of using 18 test cases that are discussed by Stockwell et al. which vary a number of trace gas concentrations and use ozone production as a validation metric. Our runs using the identical 18 test case scenarios produced the same O_3 concentrations as given by Stockwell et al. (1997) within 2% indicating that no divergences arose from the additional coding.

3 Model simulations

3.1 Sensitivity analysis

A large combinatorial simulation was carried out by changing what we perceived are likely the most important variables for impacting $\Delta^{17}O$ values. These are the starting pollutant concentrations, CO, CH_4, O_3, NO_x, non methane hydrocarbon (NMHC), and biogenic volatile organic carbon (BVOC), water vapor mixing ratio, temperature, aerosol composition, aerosol loading (surface area), and season. For each variable we selected low, medium and high values that represent the pristine, mean and extreme for various atmospheric environments, respectively. For example NO_x flux high = urban/plume, medium = rural, low = oceanic. Two seasons (winter = 1 January, summer = 15 June) were selected then the model was run for each combinatorial of the other 9 variables and their min, mean, and max values giving $\sim 3^9$ ($\sim 20\,000$) simulations.

4 Results and discussion

A typical simulation of $NO_{3\ atm}^- \Delta^{17}O$ values over the course of a week is shown in Fig. 1. The model suggests that that there are (instantaneous) diurnal variations in the $NO_{3\ atm}^- \Delta^{17}O$ values. These are primarily produced by an increase in the α factor, the proportion of NO oxidized by O_3 during the night when peroxy radical production has been shut down, but also by a shift away from $NO_{3\ atm}^-$ produced via the β (OH oxidation) pathway during the day towards the ε (N_2O_5) and χ (NO_3) pathways at night (Fig. 2). The shift between β, χ, and ε pathways is highly influenced by trace gas concentrations as discussed below. The predicted diurnal variation, however, becomes washed out as the $NO_{3\ atm}^-$ builds up over several days and the bulk $NO_{3\ atm}^- \Delta^{17}O$ values (cumulative) converge on a value that reflects the mass weighted mean of the day and night $NO_{3\ atm}^-$ production. Since the atmospheric lifetime of $NO_{3\ atm}^-$ is on the order of a week, diurnal $\Delta^{17}O$ variations in $NO_{3\ atm}^-$ are not likely to be observed. An exception to this may occur if $NO_{3\ atm}^-$ from urban areas is sampled diurnally directly after intense precipitation events, when $NO_{3\ atm}^-$ has been rapidly removed by rain/wash out. In this case, since the $NO_{3\ atm}^-$ reservoir is nearly completely depleted, as NO_x emissions begin to rebuild $NO_{3\ atm}^-$ over the subsequent couple of days, the diurnal variation (2–5‰) could be detected using current analytical techniques.

ISO-RACM's prediction of $NO_{3\ atm}^- \Delta^{17}O$ values across all of the meteorology and trace gas scenarios and evaluated using June photolysis parameters (20 000 simulations) is shown in Fig. 3 along with the range of observed $NO_{3\ atm}^- \Delta^{17}O$ values (excluding polar region data). The model can not reproduce the observed data in ~50% of the simulations when either the bulk $O_3 \Delta^{17}O$ transfer mechanism or the terminal atom transfer mechanism is utilized. When the model is run using December photolysis parameters (see below), however, only about 1/3 of the simulations predict $\Delta^{17}O$ values that are below the observed maximum of 32‰ when the terminal atom transfer mechanism is assumed while roughly 85% fall in the observational range using the bulk O_3 mechanism. Given the limited number of $NO_{3\ atm}^- \Delta^{17}O$ observations (primarily

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from coastal/oceanic regions) that are available for evaluating the model, it remains unclear whether the terminal atom or bulk O_3 is the valid mechanism. In either case, the ISO-RACM $\Delta^{17}O$ simulations across these diverse set of conditions predict $\Delta^{17}O$ values significantly below and above those currently observed in tropospheric mid lat-
5 itude aerosols. This highlights the need for additional isotopic analysis of precipitation and aerosol nitrate across a variety of environments that have diverse pollutant and meteorological conditions.

The importance of photolysis conditions for influencing $NO_{3\ atm}^-\Delta^{17}O$ values is shown in Fig. 4 ($\sim$20 000 runs). In this comparison of ISO-RACM runs all trace gas and me-
10 teorological conditions were identically varied, including temperature, but two different photolysis parameterizations were used (June and December). The data show that photolysis lifetime is clearly playing a role in $NO_{3\ atm}^-\Delta^{17}O$ variability. The June pho-tolysis simulations produces $\Delta^{17}O$ values that are consistently a factor .83 lower than the December values ($r^2=.85$). This effect is driven by two factors: first, the decrease
15 in daylight during the winter months leads to an increase in the α parameter meaning proportionately more NO is being oxidized by ozone (night chemistry). Second, the longer nights allow more conversion of NO_x to NO_3 and N_2O_5 which increases the probability of the χ an ε $NO_{3\ atm}^-$ production channels become active. This photolysis effect in $NO_{3\ atm}^-\Delta^{17}O$ values has been observed over seasonal cycles at mid-latitude
20 sites (Michalski et al., 2003) but should also be observable, and amplified, along latitu-dinal transects (Morin et al., 2009) as a function of season. Cloud cover and aerosol scattering may also be a factor when attempting detailed modeling of $NO_{3\ atm}^-\Delta^{17}O$ variations. The effect of photolysis on $NO_{3\ atm}^-\Delta^{17}O$ values over the course of a year is to generate a sine wave, peaking in the winter and reaching a minimum in the summer,
25 similar to the observed annual variation (Michalski et al., 2003) and predictions by a recent global model (Alexander et al., 2009).

Figure 5 shows the differences between modeled $\Delta^{17}O$ values when using N_2O_5 up-take schemes C or D relative to scheme M (using June photolysis). All three schemes predict approximately the same range of $NO_{3\ atm}^-\Delta^{17}O$ values (12–29‰) under condi-

tions detailed in Table 1. Most of the predicted $NO_{3\,atm}^-\Delta^{17}O$ values using either N_2O_5 schemes D or C are within ±0.3‰ of the values predicted using scheme M. There are, however, a considerable number of cases when the three schemes predict significantly different $NO_{3\,atm}^-\Delta^{17}O$ values. Scheme C's had a significant fraction of $\Delta^{17}O$

5 predictions that are below (22%), and a smaller fraction (16%) above, the scheme M predicted values. The under/over prediction of $\Delta^{17}O$ values by Scheme D relative to scheme M are evenly split at 13%. The magnitude of the over/under is typically on the order of 0.8% but can be as high as ±2.4‰. This under/over prediction by C and D is due to the fact that these two schemes have a relative humidity (temperature) param-

10 eter, so that as relative humidity become high, the uptake coefficient becomes large leading to more N_2O_5 hydrolysis and higher $\Delta^{17}O$ values. At low RH, the opposite is true; N_2O_5 uptake coefficients are suppressed relative to the M, which is independent of RH, and $\Delta^{17}O$ are depressed.

This is an important result because it suggests that under certain meteorological con-

15 ditions or emission scenarios the different N_2O_5 hydrolysis parameterization schemes will predict different $NO_{3\,atm}^-\Delta^{17}O$ values. This means that $\Delta^{17}O$ analysis of in situ $NO_{3\,atm}^-$ under a range of conditions may be a way of validating which N_2O_5 parameter-izations are most effective in capturing the actual atmospheric chemistry. In particular conducting $\Delta^{17}O$ analysis of nitrate collected in atmospheres with unique aerosol com-

20 positions (i.e. sulfate dominant, sulfate-nitrate, or organic-sulfate) and that have vari-able seasonal relative humidity's would be a way of validating uptake parameterization schemes. This highlights the fact that stable oxygen isotope analysis in nitrate (and sulfate) is a new way of validating chemical transport models and yields information (e.g. chemical pathway) not possible when using only concentration measurements as

25 way of validating an atmospheric chemical model's predictive capability.

There is clearly a significant temperature dependence influencing $NO_{3\,atm}^-\Delta^{17}O$ vari-ations under different trace gas concentration scenarios (Fig. 6). The trend is towards higher $\Delta^{17}O$ values, increasing by 1.5‰ to 7‰, over the temperature rise from 275 to 305 K. This temperature direction, increasing $\Delta^{17}O$ with increasing T, is opposite of that

one would expect based on the hypothesis (Michalski et al., 2003) that N_2O_5 stability in cold atmospheres is responsible for higher $NO_{3\ atm}^-\Delta^{17}O$ values in winter (i.e. low T = high $\Delta^{17}O$). Part of the temperature effect is due to the increase in $O_3\Delta^{17}O$ values via the temperature dependence of the $\Delta^{17}O$ isotope effect in ozone, but this increase is only 1.5‰(bulk) or 2.3‰ (terminal) in the terminal) over this temperature range, which can only explain the lower bound in the $NO_{3\ atm}^-\Delta^{17}O$ increase. The additional increase in $NO_{3\ atm}^-\Delta^{17}O$ values is coming from the temperature dependence in rate constants that is shifting the relative importance of the α, β, χ, and ε oxidation pathways. These oxidation parameters all exhibited some temperature induced variation, but the clearest and most consistent trend with temperature was found in β; the fraction of HNO_3 produced by OH oxidation of NO_2. High temperatures are suppressing the OH pathway so proportionately more $NO_{3\ atm}^-$ is produced by the χ and ε pathways, which increases the $\Delta^{17}O$ value. This temperature dependence may not be very important when comparing $NO_{3\ atm}^-\Delta^{17}O$ values in samples collected day to day at the same location because such a large temperature swings are not likely to occur. The temperature effect on $NO_{3\ atm}^-\Delta^{17}O$ values would be more pronounced when comparing seasonal trends, but solar flux, as noted above, has a larger influence on the $\Delta^{17}O$ value and may mask the temperature dependence. However, the effect is significant and should be considered when trying to model observed $NO_{3\ atm}^-\Delta^{17}O$ trends.

A large number of simulations were run to test which trace gas concentrations are important for controlling the chemistry that dictates $NO_{3\ atm}^-\Delta^{17}O$ values. These included another set of conditions that examined low, pre-anthropogenic type atmospheres as detailed in Table 1. In order to simplify the data interpretation we selected N_2O_5 scheme M as the test case and used June photolysis parameterization. Since water mixing ratio (scheme C) and percent bisulfate aerosol mass (scheme D) are not used in scheme M's uptake coefficient calculation, those variables were kept constant (1% and 0%, respectively) as were temperature (298 K) and % sulfate (80%).

There seems to be little impact on $NO_{3atm}^- \Delta^{17}O$ values when CO and CH_4 concentrations are varied to low, pre-anthropogenic values (Fig. 7), but changing VOC mixing ratios induces large effects (Fig. 8). When CO and CH_4 are decreased to 25 ppbv and 750 ppbv respectively, the same range and pattern in $\Delta^{17}O$ values were produced as when present day mixing ratios (200 ppbv, 1700 ppbv) were used. This is because the relative rate of NO_x-O_3 catalytic cycling in much slower for the carbon monoxide and methane cycles relative to VOC or biogenic organic reactions. Conversely, when VOC concentrations increase, $NO_{3\ atm}^- \Delta^{17}O$ values tend to decrease. In fact the extremely low $\Delta^{17}O$ values, (ones yet to be observed by in situ measurements), are under high VOC mixing ratio scenarios. This VOC effect is due to a decrease in α with increasing VOC via enhanced oxidation on NO by organic peroxy radicals. A similar effect is observed with increases in biogenic VOCs for the same reasons. Such high VOC concentrations are only going to be found in highly VOC polluted urban regions (Houston e.g.) or in plumes (air craft, ships, stacks). This ISO-RACM prediction of decreasing $NO_{3atm}^- \Delta^{17}O$ values with increasing VOC could be tested by conducting isotope analysis of $NO_{3\ atm}^-$ collected at the surface, down wind of oil refinery or by sampling plumes.

Mixing ratios of NO_x and O_3 are also predictors of the final range of $NO_{3\ atm}^- \Delta^{17}O$ values that might be generated. When NO_x mixing ratios are low (10–20 ppt) and the system is in an ozone destruction regime, simulated $NO_{3\ atm}^- \Delta^{17}O$ spans a wide range of values depending on other trace gases, primarily VOC/biogenic mixing ratios (Fig. 9). However, as NO_x mixing ratios increase to 100 pptv the $\Delta^{17}O$ values become more constrained and by 2 ppbv NO_x, only a narrow range of $\Delta^{17}O$ values are observed regardless of VOC/biogenic mixing ratios. Similarly, high O_3 mixing ratios (20, 50 ppbv) produce elevated $\Delta^{17}O$ values (Fig. 10) that span a somewhat narrow range (~5–10‰). But as O_3 mixing ratios drop to 5 ppbv or lower, the absolute values decrease and the range begins to expand (~15‰) and at uncharacteristically low O_3 mixing ratios (<1–5 ppbv) $NO_{3\ atm}^- \Delta^{17}O$ values are typically less than 10‰ but can approach zero.

In these types of simulated atmospheres, very low O_3/high VOC/biogenic would not be typical of the troposphere and such low $\Delta^{17}O$ values are not likely to be observed in $NO_{3\ atm}^-$ in the troposphere. Indeed, O_3 mixing ratios at mid-latitudes rarely drop below 10 ppbv, therefore our model suggests that it is unlikely that $NO_{3\ atm}^-\Delta^{17}O$ values below 15‰ would be observed in the troposphere.

The range of $NO_{3\ atm}^-\Delta^{17}O$ values in predicted by ISO-RACM is similar to those predicted by other models, but there are some noteworthy differences. One difference worth mentioning is Alexander et al. (2009)'s predication of nitrate $\Delta^{17}O$ values below 10 in the tropics (see Fig. 3 in Alexander et al., 2009). As discussed above, our model does not predict $\Delta^{17}O$ values below 15% under realistic conditions in the troposphere. These low estimates must be driven driven by peroxy radial oxidation, which may be higher in GEOS-Chem relative to ones predicted by ISO-RACM under high biogenic emission scenarios. Unfortunately there are no published seasonal measurements of aerosol or precipitation nitrate $\Delta^{17}O$ values from these tropical regions for evaluating the two models predictive capability. ISO-RACM estimates that $NO_{3\ atm}^-$ produced by the N_2O_5 hydrolysis span 10 to 80% and is highly dependent on NO_x mixing ratios, aerosol surface area, and relative humidity. This is similar to our previous model results (Michalski et al., 2003), but significantly higher than the range estimated by Alexander et al. (2009) (5–50%). This difference is likely due to high heterogeneous N_2O_5 oxidation under urban and plume conditions that are not well represented in the global model. The $NO_{3\ atm}^-\Delta^{17}O$ values are sensitive to temperature, NO_x, O_3, and VOC mixing ratios. These a strong function of boundary layer height, particularly in urban regions. This suggests comparing multiple year/site in situ $\Delta^{17}O$ data with $\Delta^{17}O$ predications by single year 2-D and 3-D model analysis will also likely suffer biases as a function of model grid size and annual local variations in these trace gas parameters. Point sources and chemical plumes in large scale grids will appear chemically dilute with respect to the chemistry creating $NO_{3\ atm}^-$. Small, regional models such as CMAQ (grid size as small as 1 km^2) would likely be more effective at capturing the actual chemical pathways and may be a better approach for modeling $\Delta^{17}O$ in modern

atmospheres.

5 Conclusions and future work

One of the objectives of this study is to use the model $\Delta^{17}O$ predictions as a basis for selecting field sites, archived samples (such as the National Atmospheric Deposition Program or US-EPA $PM_{2.5}$ archive), and collection techniques; $HNO_3(g)$ vs. particulates. Based on these modeling results we expect to observe seasonal oscillations in $NO_{3\ atm}^-\Delta^{17}O$ values driven by changes in actinic flux that alters, primarily the α parameter. This oscillation would likely vanish near the tropics and become step like at higher latitudes mirroring seasonal actinic flux variations. Daily oscillations could be observed with high analytical precision (±0.3‰) or when $NO_{3\ atm}^-$ is rapidly removed by rain after which NO_x emission would rebuild $NO_{3\ atm}^-$ over the subsequent days. In urban areas where NO_x and ozone are elevated the model suggests a narrow range of $\Delta^{17}O$ values in $NO_{3\ atm}^-$, with elevated absolute values. In rural-pristine areas, a slightly wider range and lower absolute value of $\Delta^{17}O$ in $NO_{3\ atm}^-$ is expected, reaching the lowest values under high organic loading and low NO_x/O_3. This might be expected in the rural sites in the southern USA where isoprene emissions are significant due to emissions by deciduous trees but NO_x can remain low. If relative humidity is important in N_2O_5 hydrolysis, then we expect more significant $\Delta^{17}O$ variations in regions with high and variable RH (Midwestern USA) relative to those with low, near constant RH such as desert regions in the southwestern USA.

Simulating the dependence of $NO_{3\ atm}^-\Delta^{17}O$ values in different aerosol sizes would require a more sophisticated aerosol model, but some information can be gleaned from the present modeling results. Since N_2O_5 hydrolysis requires an aerosol surface for the reaction to occur, and that this pathway leads to higher $\Delta^{17}O$ values in the resulting $NO_{3\ atm}^-$, at first blush one could conclude that the size fraction that dominates the aerosol surface area would have $NO_{3(s)}^-$ with the higher $\Delta^{17}O$ values. This effect,

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however, would depend on the air mass and aerosol characteristics. The equilibrium between $HNO_{3(g)} \longleftrightarrow NH_4NO_{3(s)}$ occurs on the order of minutes and is a strong function of temperature. Morino et al. (2009) showed there were strong diurnal, seasonal, and altitudinal shifts in equilibrium due to the temperature (and RH) dependency of the equilibrium. For example, during daytime in the summer nearly 90% of $NO_{3\ atm}^-$ can be gaseous HNO_3. Therefore even though $NO_{3\ atm}^-$ may be formed on aerosol surfaces at night via Reactions (R6) it would transition to the gas phase during the day. Chemical equilibrium will also be dependent on aerosol composition. The large shift in the gas-particle equilibrium usually assumes NH_4^+ is the dominant cation, which is not always the case. In coastal or open ocean air masses NaCl can be the dominant contributor to the surface area. In this case, due to chloride displacement as HCl, N_2O_5 hydrolysis would lead to $NaNO_3(s)$ formation, not $H^+ + NO_3^-$. Here the equilibrium towards the gas phase is very weak, and nitrate would remain bound on sea salt particles, therefore one might expect high $\Delta^{17}O$ values in the sea salt size fraction (>2.5 micron) (Patris et al., 2007; Morin et al., 2009) relative to smaller aerosols that might have higher surface area, but are also often acidic. By the same arguments, however, uptake of $HNO_{3(g)}$ onto sea salt particles would also be thermodynamically favorable, therefore loss of $HNO_{3(g)}$ formed by $NO_2 + OH$ (with low $\Delta^{17}O$ signatures) would readily mix with N_2O_5 reactions on the same particles. One situation where it may be possible to use $\Delta^{17}O$ measurements to see the Reactions (R3) and (R6) in different aerosol sizes is in mid latitude agricultural regions in the Midwest during winter. In these regions there is often high NH_3 emissions that would facilitate the $HNO_{3(g)} + NH_3 \longrightarrow NH_4NO_3$ and the cold temperatures would retain it in the aerosol phase. Because this is a gas to particle reaction, this would be seen in the Aiken size fraction or accumulation mode. However, aerosol surface area is still dominated by sub micron dust, sulfate, and biogenic aerosols arising from agriculture and coal combustion in the region. These particles would facilitate the N_2O_5 hydrolysis reaction and lead to high $\Delta^{17}O$ values in $NO_{3(s)}^-$. Much would depend on the chemical characteristics of the different aerosol size distributions and modeling this would require an explicit aerosol dynamics module that

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incorporates the isotope mass balance model.

The results presented here suggests that $\Delta^{17}O$ analysis in $NO_{3\ atm}^-$ is potentially an important new tool for understanding in situ NO_x-NO_y chemistry and aerosol production mechanisms, but additional studies need to be conducted to effectively utilize this stable isotope tool. Foremost, is the need for additional measurements of $\Delta^{17}O$ in a diverse set of locations where $NO_{3\ atm}^-$ formation pathways are expected to vary and interact with different oxidation intermediates. Oceanic, tropical, desert, forested and rural areas are not well represented in the current data sets, which itself is incredibly limited. One of the key shortcomings of the model is the uncertainty in the O_3-NO transfer mechanism and how that relates to tropospheric O_3 $\Delta^{17}O$ values. An experimental determination of $\Delta^{17}O$ generated in NO_x through the Leighton reactions would be a significant advance. Experimental evidence for any isotope effect associated with the $NO+HO_2$ reaction would also limit much of the uncertainty in the current assumptions in the mass balance model. Clearly there is room for improvement in the modeling aspects. Given the short lifetime of $NO_{3\ atm}^-$ and the importance of point sources and plume chemistry, large grid scale global models may not be as effective in predicting $NO_{3\ atm}^-$ $\Delta^{17}O$ when influenced by human emissions as more detailed, regional models such a CMAQ or WRF-Chem. Finally, more effort is needed to incorporate the other isotopic tracers in $NO_{3\ atm}^-$, $\delta^{15}N$ and $\delta^{18}O$, into model simulations. This adds complexity because it requires not only understanding the kinetic and equilibrium isotope effects that occur during NO_x-NO_y cycling, but also $\delta^{15}N$ variations arising from NO_x sources and $\delta^{18}O$ variations arising from water vapor, which has distinct $\delta^{18}O$ values as a function of time and space.

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Table 1. ISO-RACM simulations initial conditions.

Flux	High	Med	Low
NO_x/CO flux ($\mu mol/m^2$/day)	6	0.6	.006
NMHC flux ($\mu molC/m^2$/day)	1000	100	1
BVOC flux ($\mu mol/m^2$/day)	2000	100	1
Initial conditions			
$[H_2O]$	3%	1%	0.5%
Temp. (K)	310	298	270
Aerosol mass ($\mu g/m^3$)	100	10	1
% aerosol SO_4^{2-}	95	60	10
% NH_4HSO_4	100	50	10
N_2O_5 scheme	1	2	3
NO_x (ppbv)	1	10	30
O_3 (ppbv)	10	50	80
CO (ppbv)	100	200	300
CH_4 (ppbv)	1600	1750	1800
VOC (ppbv as C)	10	100	1000
BVOC (ppbv as C)	1	10	200
Pre-anthroprogenic			
NO_x (pptv)	10, 20	100	2000
O_3 (ppbv)	1, 10	20	50
CO (ppbv)	25, 50	100	200
CH_4 (ppbv)	750, 900	1100	1700
VOC (ppbv as C)	1	10	100
BVOC (ppbv as C)	1	10	200
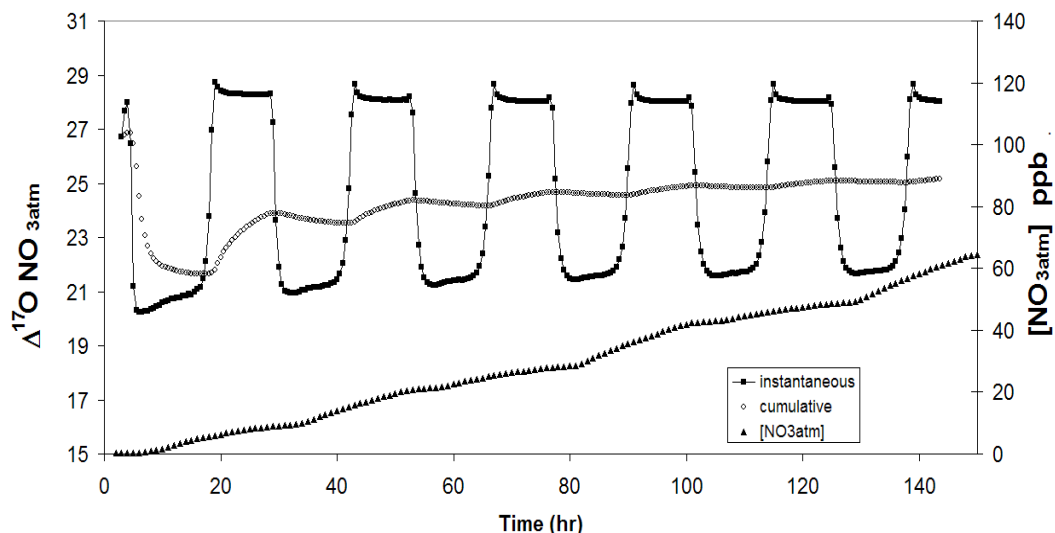
Fig. 1. Simulated instantaneous and cumulative change in $NO_{3\ atm}^-$ $\Delta^{17}O$ values (in ‰) using test case 1 (time(0)=0600). The minima in the simulated instantaneous $\Delta^{17}O$ values of ~21‰ correspond to $NO_{3\ atm}^-$ production dominated by the reaction $OH+NO_2$ during the daytime. Instantaneous maximums at night are primarily due to increases in NO oxidation by O_3 at night and by $NO_{3\ atm}^-$ production via N_2O_5 hydrolysis. Diurnal variation in the modeled cumulative $\Delta^{17}O$ signal are washed out by day 3 as $NO_{3\ atm}^-$ accumulates in the atmosphere resulting in a mean $\Delta^{17}O$ values of ~25‰ under test case 1 conditions.

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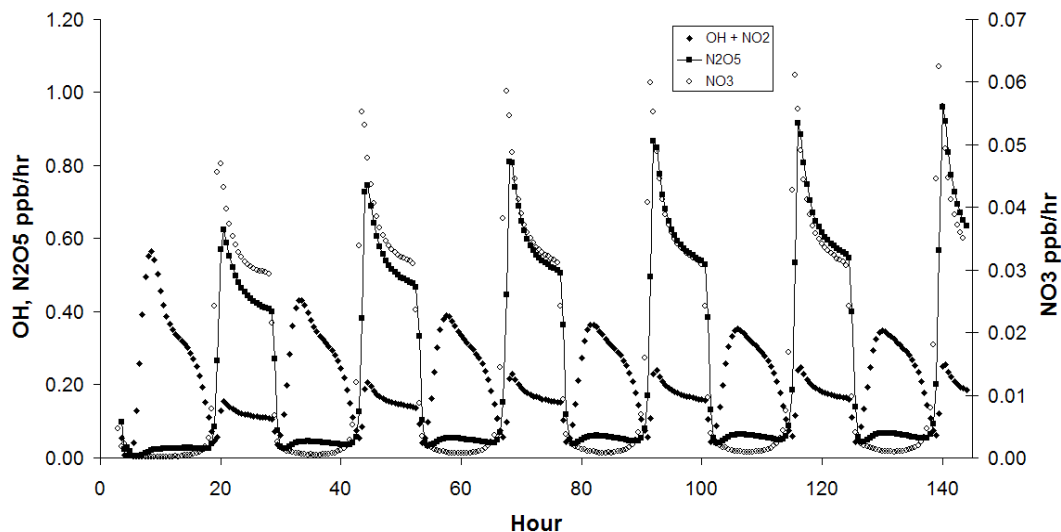
Fig. 2. $NO_{3\ atm}^-$ produced in ppb/hr (using a fixed mixing height) by the three formation pathways. The β pathway (OH) dominates during the day while ε (NO) is the main pathway at night with the χ pathway (NO$_3$) contributing only a few percent under these conditions (note the scale difference of χ on the secondary axis, which is used for clarity).
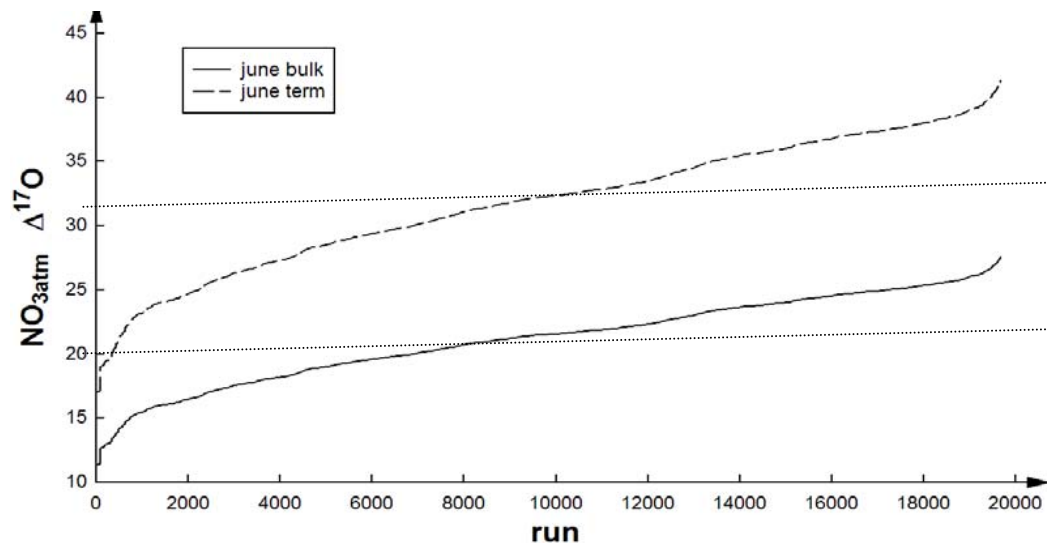
Fig. 3. Predicted $\Delta^{17}O$ values for $NO_{3\ atm}^{-}$ for June at 35° N latitude using bulk and terminal atom transfer mechanisms. Range of observed mid-latitude $NO_{3\ atm}^{-}$ $\Delta^{17}O$ values are bracketed by the dotted lines. Either transfer mechanism produces $\Delta^{17}O$ that have not been observed due to the paucity of in situ data.
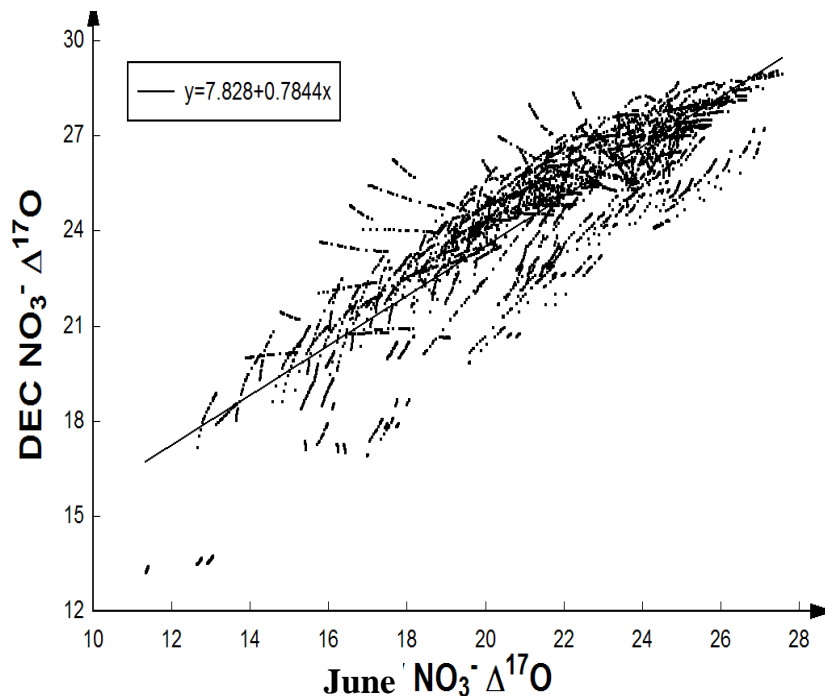
Fig. 4. The influence of photolysis on $NO_{3\ atm}^{-}$ $\Delta^{17}O$ values are only 78% (r^2=.88) as high as those in December. Since all other parameters were varied the same in each run (temperature, trace gas, RH, etc.) this difference is only due to change in HNO_3 production driven by the seasonal difference photolysis lifetimes of O_3, NO_2 and NO_3. values. Each point represents the $\Delta^{17}O$ after a one week simulation. The June $NO_{3\ atm}^{-}$ $\Delta^{17}O$ values are only 78% (r^2=.88) as high as those in December. Since all other parameters were varied the same in each run (temperature, trace gas, RH, etc.) this difference is only due to change in HNO_3 production driven by the seasonal difference photolysis lifetimes of O_3, NO_2 and NO_3.
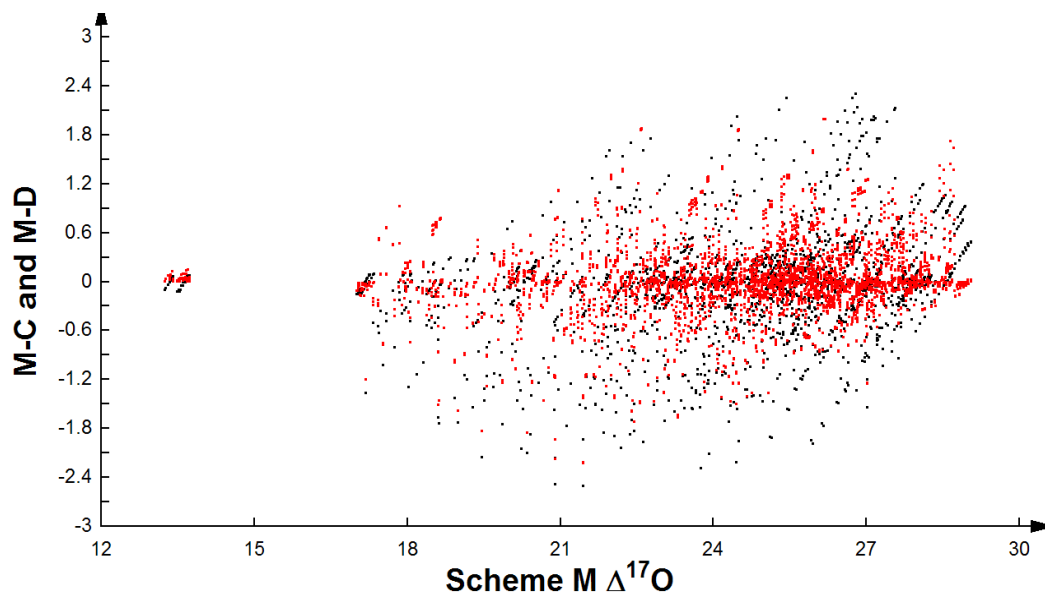
Fig. 5. Y-axis is the difference in $\Delta^{17}O$ values of $NO_{3\ atm}^-$ produced (1 week simulation) using Scheme C relative to Scheme M (M–C, red) and Scheme D relative to Scheme M (M–D, black) all normalized to the $\Delta^{17}O$ value produced using Scheme M (x-axis).
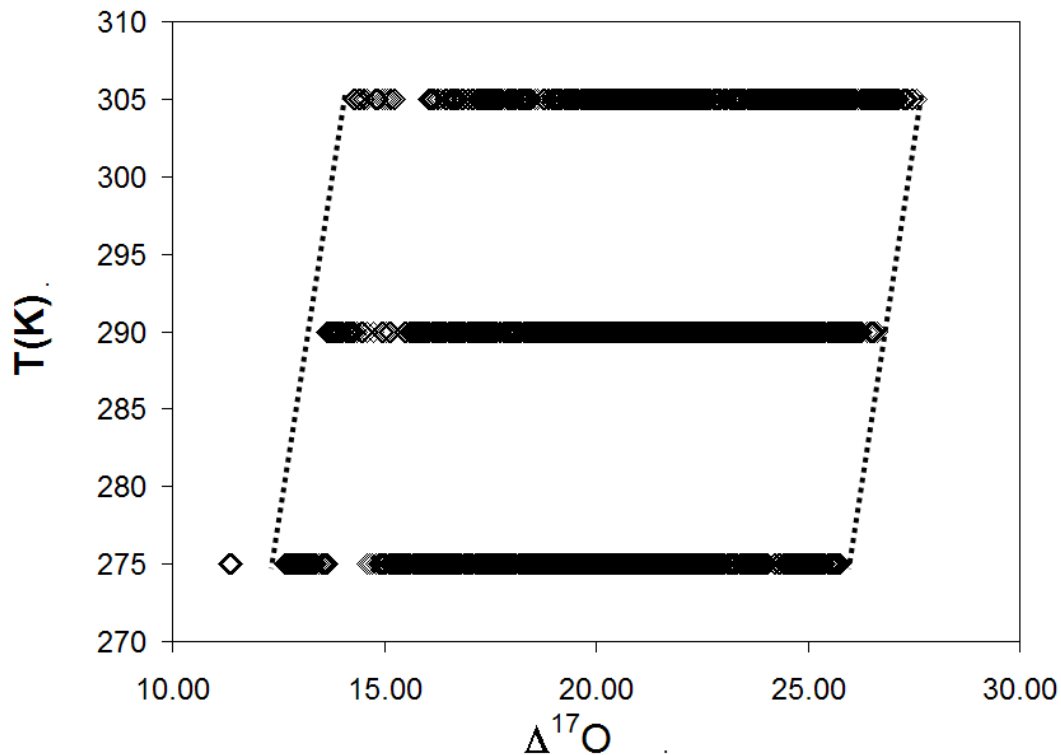
Fig. 6. Temperature dependant increases in $NO_{3\ atm}^-$ $\Delta^{17}O$ values. Starting concentrations of NO_x, O_3, VOC, aerosol mass, and sulfate % are all varied between high, medium, and low values (Table 1) while all other parameters are held constant. Dashed lines connect $NO_{3\ atm}^-$ $\Delta^{17}O$ values with the same initial concentrations but different simulation temperatures. Slope of the dashed line is a measure of the strength of the temperature effect.
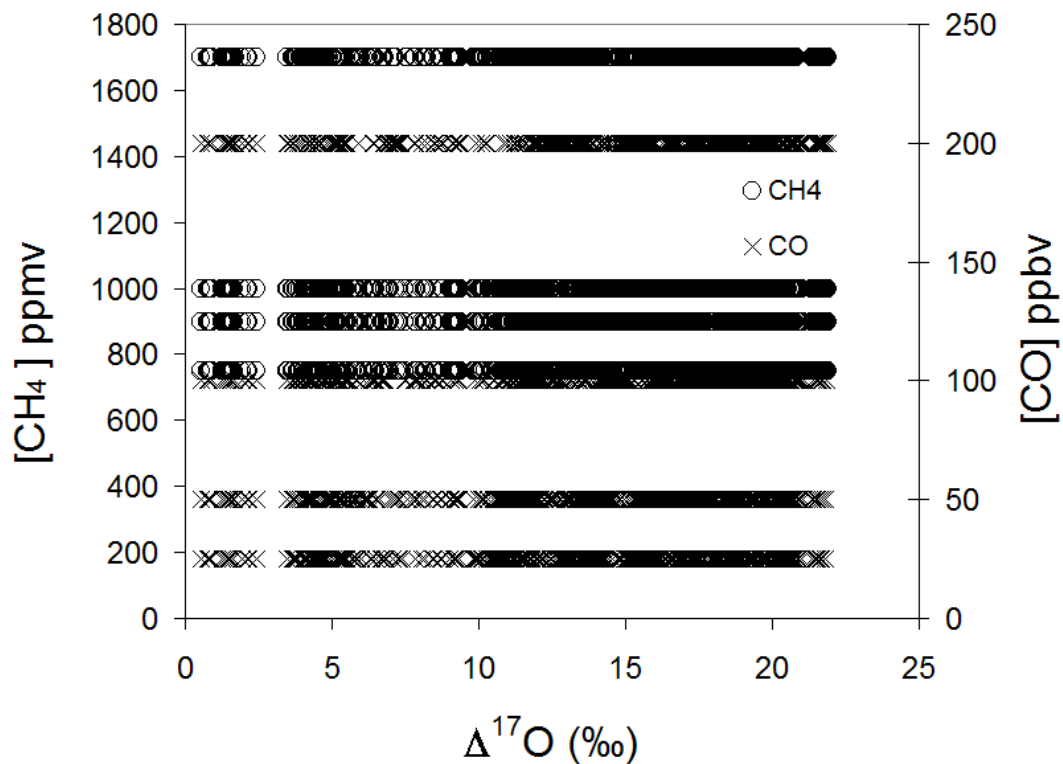
Fig. 7. Patterns and ranges of $NO_{3 \ atm}^{-}$ $\Delta^{17}O$ under radically different methane and carbon monoxide mixing ratios appears to be negligible.
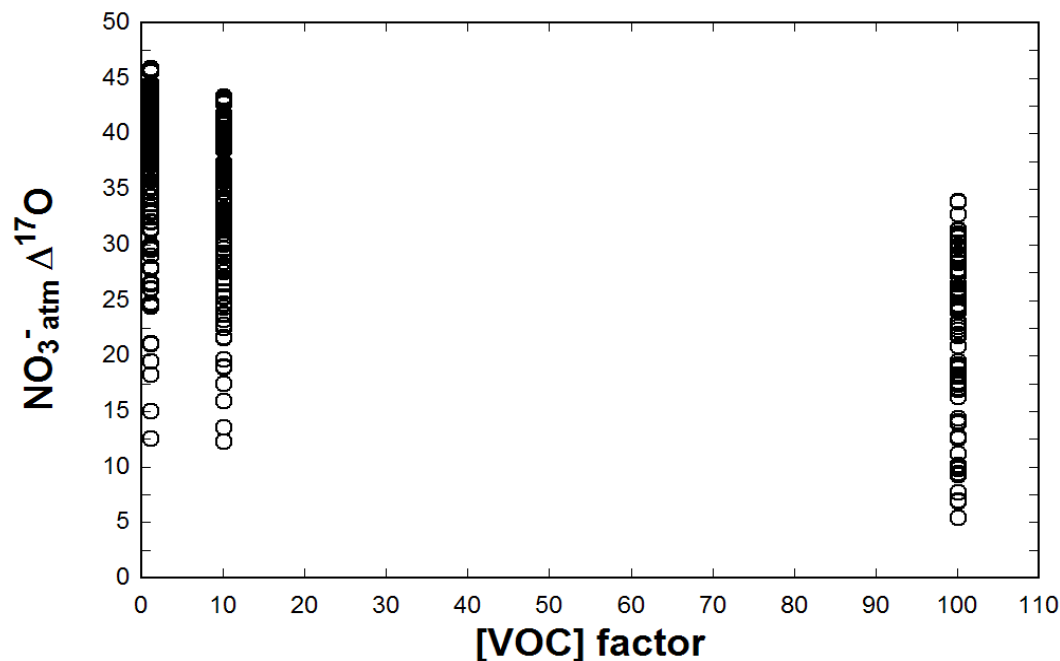
Fig. 8. $NO_3^-{}_{atm}$ $\Delta^{17}O$ values using December photolysis parameters and varying VOC mixing ratios. The VOC mixing ratio for any given simulation is determined by scaling the low VOC mixing ratio (Table 1) by the VOC factor (1, 10, and 100). December photolysis generates and the terminal O_3 mechanism generates high $\Delta^{17}O$ values, relative to observations. High VOC mixing ratios combined with low O_3 and NO_x can suppress the $\Delta^{17}O$ values to less than 10‰, but such conditions may not be atmospherically "realistic".
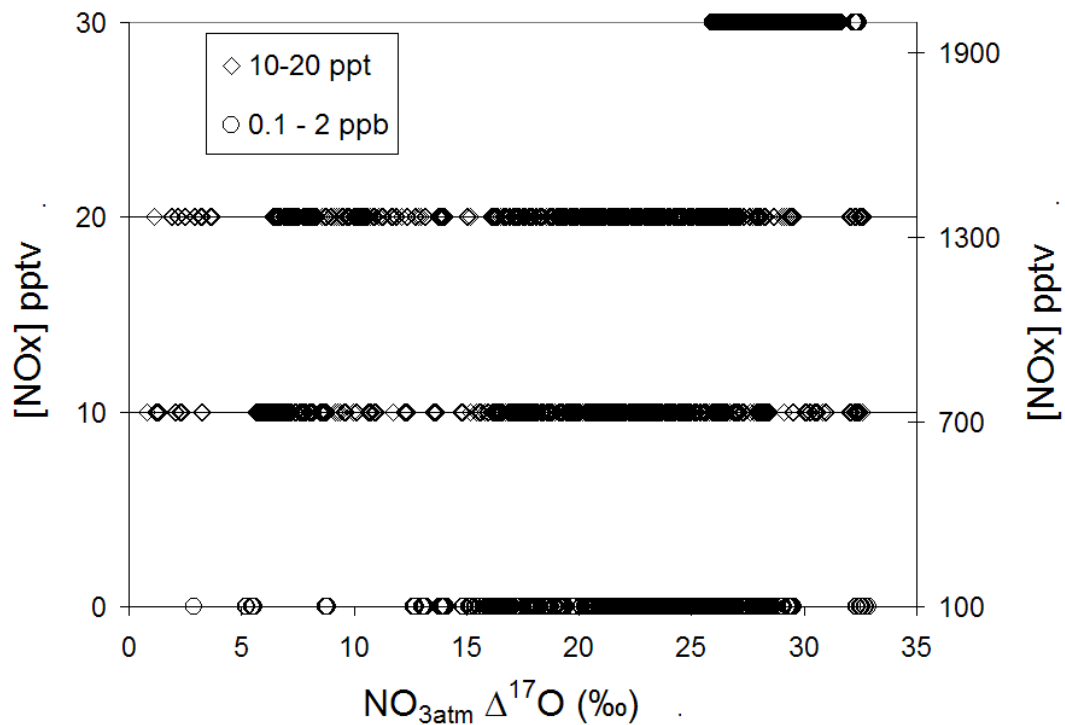
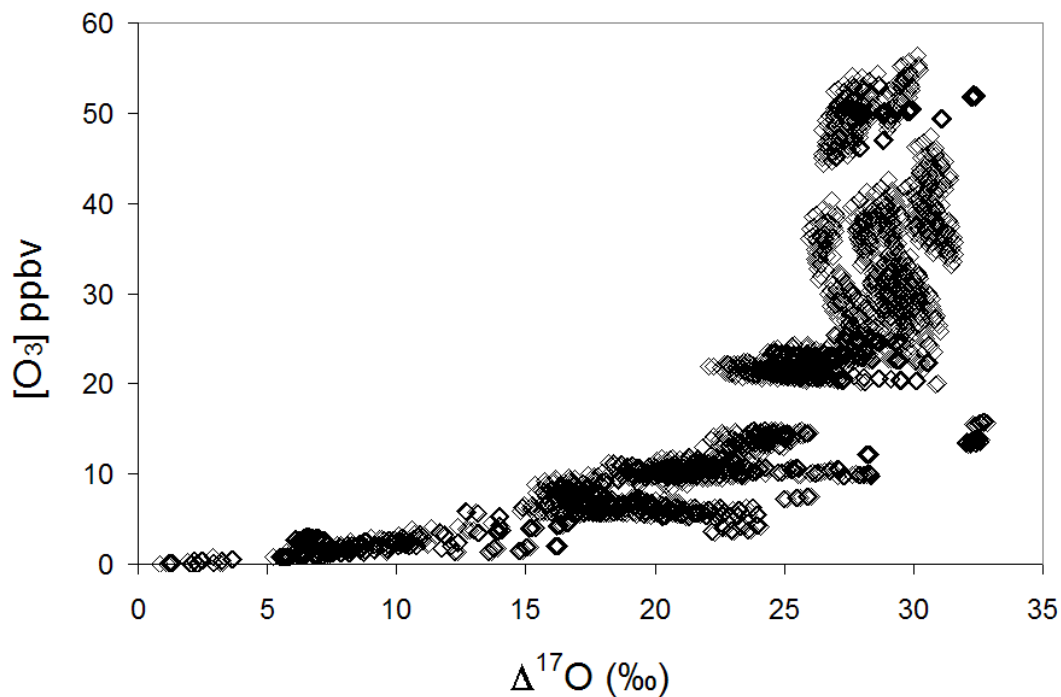**Fig. 9.** Magnitude and range of $NO_{3\ atm}^-$ $\Delta^{17}O$ values as a function of initial NO mixing ratios.

Fig. 10. $NO_{3\ atm}^-$ $\Delta^{17}O$ values as a function of ending simulated O_3 mixing ratios (initialized at 50, 20, 10, and 1 ppbv).