Global inorganic nitrate production mechanisms: comparison of a global model with nitrate isotope observations

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Abstract. The formation of inorganic nitrate is the main sink for nitrogen oxides (NOx = NO + NO2). Due to the importance of NOx for the formation of tropospheric oxidants such as the hydroxyl radical (OH) and ozone, understanding the mechanisms and rates of nitrate formation is paramount for our ability to predict the atmospheric lifetimes of most reduced trace gases in the atmosphere. The oxygen isotopic composition of nitrate (Δ¹⁵O(nitrate)) is determined by the relative importance of NOx sinks and thus can provide an observational constraint for NOx chemistry. Until recently, the ability to utilize Δ¹⁵O(nitrate) observations for this purpose was hindered by our lack of knowledge about the oxygen isotopic composition of ozone (Δ¹⁵O(O3)). Recent and spatially widespread observations of Δ¹⁵O(O3) motivate an updated comparison of modeled and observed Δ¹⁵O(nitrate) and a reassessment of modeled nitrate formation pathways. Model updates based on recent laboratory studies of heterogeneous reactions render dinitrogen pentoxide (N2O5) hydrolysis as important as NO2 + OH (both 41%) for global inorganic nitrate production near the surface (below 1 km altitude). All other nitrate production mechanisms individually represent less than 6% of global nitrate production near the surface but can be dominant locally. Updated reaction rates for aerosol uptake of NO2 result in significant reduction of nitrate and nitrous acid (HONO) formed through this pathway in the model and render NO2 hydrolysis a negligible pathway for nitrate formation globally. Although photolysis of aerosol nitrate may have implications for NOx, HONO, and oxidant abundances, it does not significantly impact the relative importance of nitrate formation pathways. Modeled Δ¹⁵O(nitrate) (28.6 ± 4.5‰) compares well with the average of a global compilation of observations (27.6 ± 5.0‰) when assuming Δ¹⁵O(O3) = 26‰, giving confidence in the model’s representation of the relative importance of ozone versus HOx (= OH + HO2 + RO2) in NOx cycling and nitrate formation on the global scale.

1 Introduction

Nitrogen oxides (NOx = NO + NO2) are a critical ingredient for the formation of tropospheric ozone (O3). Tropospheric ozone is a greenhouse gas, is a major precursor for the hydroxyl radical (OH), and is considered an air pollutant due to its negative impacts on human health. The atmospheric lifetime of NOx is determined by its oxidation to inorganic and organic nitrate. The formation of inorganic nitrate (HNO3(g) and particulate NO3−) is the dominant sink for NOx globally, while formation of organic nitrate may be significant in rural and remote continental locations (Browne and Cohen, 2014). Organic nitrate as a sink for NOx may be becoming more important in regions in North America and Europe where NOx
emissions have declined (Zare et al., 2018). Uncertainties in the rate of oxidation of NO\textsubscript{x} to nitrate have been shown to represent a significant source of uncertainty for ozone and OH formation in models (e.g., Newsome and Evans, 2017), with implications for our understanding of the atmospheric lifetime of species such as methane, whose main sink is reaction with OH.

NO\textsubscript{x} is emitted to the atmosphere primarily as NO by fossil fuel and biomass/biofuel burning, soil microbes, and lightning. Anthropogenic sources from fossil fuel and biofuel burning and from the application of fertilizers to soil for agriculture currently dominate NO\textsubscript{x} sources to the atmosphere (Jaegle et al., 2005). After emission, NO is rapidly oxidized to NO\textsubscript{2} by ozone (O\textsubscript{3}), peroxy (HO\textsubscript{2}) and hydroperoxy radicals (RO\textsubscript{2}), and halogen oxides (e.g., BrO). During the daytime, NO\textsubscript{2} is rapidly photolyzed to NO + O at wavelengths ($\lambda$) < 398 nm. NO\textsubscript{x} cycling between NO and NO\textsubscript{2} proceeds several orders of magnitude faster than oxidation of NO\textsubscript{x} to nitrate during the daytime (Michalski et al., 2003).

Formation of inorganic nitrate is dominated by oxidation of NO\textsubscript{2} by OH during the day and by the hydrolysis of dinitrogen pentoxide (N\textsubscript{2}O\textsubscript{5}) at night (Alexander et al., 2009). Recent implementations of reactive halogen chemistry in models of tropospheric chemistry show that formation of nitrate from the hydrolysis of halogen nitrates (XNO\textsubscript{3}, where X = Br, Cl, or I) is also a sink for NO\textsubscript{x} with implications for tropospheric ozone, OH, reactive halogens, and aerosol formation (Schmidt et al., 2016; Sherwen et al., 2016; Saiz-Lopez et al., 2012; Long et al., 2014; Parrella et al., 2012; von Glasow and Crutzen, 2004; Yang et al., 2005). Other inorganic nitrate formation pathways include hydrogen abstraction of hydrocarbons by the nitrate radical (NO\textsubscript{3}•), heterogeneous reaction of N\textsubscript{2}O\textsubscript{5} with particulate chloride (Cl\textsuperscript{-}), heterogeneous uptake of NO\textsubscript{2} and NO\textsubscript{x}, direct oxidation of NO to HNO\textsubscript{3} by HO\textsubscript{2}, and hydrolysis of organic nitrate (Atkinson, 2000). Inorganic nitrate partitions between the gas (HNO\textsubscript{3}(g)) and particle (NO\textsubscript{3}•) phases, with its relative partitioning dependent upon aerosol abundance, aerosol liquid water content, aerosol chemical composition, and temperature. Inorganic nitrate is lost from the atmosphere through wet or dry deposition to the Earth’s surface with a global lifetime against deposition on the order of 3–4 d (Park et al., 2004).

Formation of inorganic nitrate was thought to be a permanent sink for NO\textsubscript{x} in the troposphere due to the slow photolysis of nitrate compared to deposition. However, laboratory and field studies have shown that NO\textsubscript{3}• adsorbed on surfaces is photolyzed at rates much higher than HNO\textsubscript{3}(g) (Ye et al., 2016). For example, the photolysis of NO\textsubscript{3}• in snow grains on ice sheets has a profound impact on the oxidizing capacity of the polar atmosphere (Domine and Shepson, 2002). More recently, observations of NO\textsubscript{x} and nitrous acid (HONO) provide evidence of photolysis of aerosol NO\textsubscript{3}• in the marine (Reed et al., 2017; Ye et al., 2016) and continental (Ye et al., 2018; Chen et al., 2019) boundary layer, with implications for ozone and OH (Kasibhatla et al., 2018).

Organic nitrates form during reaction of NO\textsubscript{x} and NO\textsubscript{3} with biogenic volatile organic compounds (BVOCs) and their oxidation products (organic peroxy radicals, RO\textsubscript{2}) (Browne and Cohen, 2014; Liang et al., 1998). Products of these reactions include peroxy nitrates (RO\textsubscript{2}NO\textsubscript{3}) and alkyl and multifunctional nitrates (RONO\textsubscript{2}) (O’Brien et al., 1995). Peroxy nitrates are thermally unstable and decompose back to NO\textsubscript{x} on the order of minutes to days at warm temperatures. Decomposition of longer-lived peroxy nitrates such as peroxyacetyl nitrate (PAN) can provide a source of NO\textsubscript{x} to remote environments (Singh et al., 1992). The fate of RONO\textsubscript{2} is uncertain. First-generation RONO\textsubscript{2} is oxidized to form second-generation RONO\textsubscript{2} species with a lifetime of about a week for the first-generation species with ≥ 4 carbon atoms and up to several weeks for species with fewer carbon atoms (e.g., days to weeks for methyl nitrate) (Fisher et al., 2018). Subsequent photolysis and oxidation of second-generation RONO\textsubscript{2} species can lead to the recycling of NO\textsubscript{x} (Müller et al., 2014), although recycling efficiencies are highly uncertain (Horowitz et al., 2007; Paulot et al., 2009). RONO\textsubscript{2} can also partition to the particle phase ($\rho$RONO\textsubscript{2}) contributing to organic aerosol formation (Xu et al., 2015). $\rho$RONO\textsubscript{2} is removed from the atmosphere by deposition to the surface or through hydrolysis to form inorganic nitrate and alcohols (Rindelaub et al., 2015; Jacobs et al., 2014).

The oxygen isotopic composition ($\Delta^{17}$O = $\delta^{17}$O – 0.52 × $\delta^{18}$O) of nitrate is determined by the relative importance of oxidants leading to nitrate formation from the oxidation of NO\textsubscript{x} (Michalski et al., 2003). Observations of the oxygen isotopic composition of nitrate ($\Delta^{17}$O(nitrate)) have been used to quantify the relative importance of different nitrate formation pathways and to assess model representation of the chemistry of nitrate formation in the present day (Alexander et al., 2009; Michalski et al., 2003; Costa et al., 2011; Ishino et al., 2017; Morin et al., 2009, 2008, 2007; Savarino et al., 2007, 2013; Kunasek et al., 2008; McCabe et al., 2007; Hastings et al., 2003; Kaiser et al., 2007; Brothers et al., 2008; Ewing et al., 2007) and in the past from nitrate archived in ice cores (Sofen et al., 2014; Alexander et al., 2004; Geng et al., 2014, 2017). Ozone-influenced reactions in NO\textsubscript{x} oxidation lead to high $\Delta^{17}$O(nitrate) values while HO\textsubscript{x}-influenced reactions lead to $\Delta^{18}$O(nitrate) near zero. Oxidation by XO (where X = Br, Cl, or I) leads to $\Delta^{15}$O(nitrate) values similar to reactions with ozone because the oxygen atom in XO is derived from the reaction X + O\textsubscript{3}. Therefore, $\Delta^{17}$O(nitrate) is determined by the relative importance of O\textsubscript{3} + XO versus HO\textsubscript{3} (= OH + HO\textsubscript{2} + RO\textsubscript{2}) in both NO\textsubscript{x} cycling and oxidation to nitrate. Although freshly emitted NO will have $\Delta^{17}$O(NO) = 0%, NO\textsubscript{x} achieves isotopic equilibrium during the daytime due to rapid NO\textsubscript{x} cycling, so that its $\Delta^{17}$O value ($\Delta^{17}$O(NO\textsubscript{x})) is solely determined by the relative abundance of (O\textsubscript{3} + XO) to (HO\textsubscript{2} + RO\textsubscript{2}) (Michalski et al., 2003).
The $\Delta^{17}O$ value of HO$_x$ ($\Delta^{17}O$(HO$_x$)) is near zero due to isotopic exchange of OH with water vapor (Dubey et al., 1997). Previously, observations of the $\Delta^{17}O$ value of ozone ($\Delta^{17}O$(O$_3$)) showed a large range ($6\%$–$54\%$) (Johnston and Thiemens, 1997; Krankowsky et al., 1995), in contrast to laboratory and modeling studies suggesting that the range of $\Delta^{17}O$(O$_3$) in the troposphere should be relatively narrow ($30\%$–$46\%$) (Morton et al., 1990; Thiemens, 1990). The large range of observed $\Delta^{17}O$(O$_3$) values is thought to be due to sampling artifacts (Brenninkmeijer et al., 2003). Uncertainty in the value of $\Delta^{17}O$(O$_3$) has been the largest source of uncertainty in quantification of nitrate formation pathways using observations of $\Delta^{17}O$(nitrate) (Alexander et al., 2009). Previous modeling studies showed good agreement with observations of $\Delta^{17}O$(nitrate) when assuming that the bulk oxygen isotopic composition of ozone ($\Delta^{17}O$(O$_3$)) is equal to $35\%$ (Alexander et al., 2009; Michalski et al., 2003) but varied in their assumption on terminal oxygen atom versus statistical isotopic transfer from O$_3$ to the reactant (NO and NO$_2$). This is an important distinction because it is now known that the $^{17}O$ enrichment in O$_3$ is contained entirely in its terminal oxygen atoms, and it is the terminal oxygen atom that is transferred from O$_3$ (Vicars et al., 2012; Berhanu et al., 2012; Bhattacharya et al., 2008, 2014; Savarino et al., 2008; Michalski and Bhattacharya, 2009), so that the $\Delta^{17}O$ value of the oxygen atom transferred from ozone to the product is $50\%$ larger than the bulk $\Delta^{17}O$(O$_3$) value. Recently, much more extensive observations of $\Delta^{17}O$(O$_3$) using a new technique (Vicars et al., 2012) consistently show $\Delta^{17}O$(O$_3$) = $26\pm1\%$ in diverse locations (Vicars et al., 2012; Ishino et al., 2017; Vicars and Savarino, 2014) and suggest that previous modeling studies are biased low in $\Delta^{17}O$(nitrate) (e.g., Alexander et al., 2009), which would occur if the model underestimated the relative role of ozone in NO$_x$ chemistry. These new observations of $\Delta^{17}O$(O$_3$), combined with improved understanding and hence more comprehensive chemical representation of nitrate formation in models, motivate an updated comparison of observed and modeled $\Delta^{17}O$(nitrate) as an observational constraint for the relative importance of nitrate formation pathways in the atmosphere. Note that laboratory studies show that the magnitude of $\Delta^{17}O$(O$_3$) is dependent on temperature and pressure (Heidenreich and Thiemens, 1986; Thiemens, 1990; Morton et al., 1990). The observations of $\Delta^{17}O$(O$_3$) by Vicars et al. (2012, 2013) were at the surface over a large temperature range but may not reflect the value of $\Delta^{17}O$(O$_3$) at higher altitudes. However, with the exception of lightning, whose emissions are presently several times smaller than NO$_x$ emissions from anthropogenic and biomass burning sources (Murray, 2016), NO$_x$ sources emit at the surface. With a NO$_x$ lifetime relative to its conversion to nitrate on the order of 1 d (Levy et al., 1999), most nitrate formation also occurs near the surface. Here, we examine the relative contribution of each nitrate formation pathway in a global chemical transport model and compare the model with surface observations of $\Delta^{17}O$(nitrate) from around the world.

2 Methods

We use the GEOS-Chem global chemical transport model version 12.0.0 driven by assimilated meteorology from the MERRA-2 reanalysis product with a native resolution of $0.5^\circ\times0.625^\circ$ and 72 vertical levels from the surface up to the 0.01 hPa pressure level. For computational expediency, the horizontal and vertical resolution were downgraded to $4^\circ\times5^\circ$ and 47 vertical levels. GEOS-Chem was originally described in Bey et al. (2001) and includes coupled HO$_x$–NO$_x$–VOC–ozone–halogen–aerosol tropospheric chemistry as described in Sherwen et al. (2016, 2017) and organic nitrate chemistry as described in Fisher et al. (2016). Aerosols interact with gas-phase chemistry through the effect of aerosol extinction on photolysis rates (Martin et al., 2003) and heterogeneous chemistry (Jacob, 2000). The model calculates deposition for both gas species and aerosols (Liu et al., 2001; Zhang et al., 2001; Wang et al., 1998).

Global anthropogenic emissions, including NO$_x$, are from the Community Emissions Data System (CEDS) inventory from 1990 to 2014 CE (Hoey et al., 2018). The CEDS global emissions inventory is overwritten by regional anthropogenic emissions inventories in the US (EPA/NE11), Canada (CAC), Europe (EMEP), and Asia (MIX Li et al., 2017). Global shipping emissions are from the International Comprehensive Ocean-Atmosphere Data Set (ICOADS), which was implemented into GEOS-Chem as described in Lee et al. (2011). NO$_x$ emissions from ships are processed using the PARANOX module described in Vinken et al. (2011) and Holmes et al. (2014) to account for nonlinear, in-plume ozone and HNO$_3$ production. Lightning NO$_x$ emissions match the OTD/LIS satellite climatological observations of lightning flashes as described by Murray et al. (2012). Emissions from open fires are from the Global Fire Emissions Database (GFED4.1). Biogenic soil NO$_x$ emissions are described in Hudman et al. (2012). Aircraft emissions are from the Aviation Emissions Inventory Code (AEIC) (Stettler et al., 2011).

Chemical processes leading to nitrate formation in GEOS-Chem have expanded since the previous work of Alexander et al. (2009). Figure 1 summarizes the formation of inorganic nitrate in the current model. In the model, NO is oxidized by O$_3$, HO$_2$, RO$_2$, and halogen oxides (XO = BrO, ClO, IO, and HOCl) to form NO$_2$. The reaction of NO + HO$_2$ can also form HNO$_3$ directly, although the branching ratio for this pathway is $<1\%$ (Butkovskaya et al., 2005). NO$_2$ can form HNO$_3$ directly from its reaction with OH and through hydrolysis on aerosol surfaces. NO$_2$ can react with XO to form halogen nitrates (BrNO$_3$, ClNO$_3$, and INO$_3$), which can then form HNO$_3$ upon hydrolysis (as described in Sherwen et al., 2016). NO$_2$ can also react with O$_3$ to form NO$_3$, which can
then react with NO₂, hydrocarbons (HC), and the biogenic VOC monoterpenes (MTN) and isoprene (ISOP). Reaction of NO₃ with NO₂ forms N₂O₅, which can subsequently hydrolyze or react with Cl⁻ in aerosol to form HNO₃. Reaction of NO₃ with HC forms HNO₃ via hydrogen abstraction. Reactions of NO₃ are only important at night due to its short lifetime against photolysis. Formation of organic nitrate (RONO₂) was recently updated in the model as described in Fisher et al. (2016). Reaction of NO₃ with MTN and ISOP can form RONO₂. RONO₂ also forms from the reaction of NO with RO₂ derived from OH oxidation of BVOCs. RONO₂ hydrolyzes to form HNO₃ on a timescale of 1 h. Inorganic nitrate partitions between the gas (HNO₃(g)) and particle (NO₃⁻) phase according to local thermodynamic equilibrium as calculated in the ISORROPIA-II aerosol thermodynamic module (Fountoukis and Nenes, 2007). HNO₃(g) and NO₃⁻ are mainly lost from the atmosphere via wet and dry deposition to the surface.

In the standard model, hydrolysis of N₂O₅, NO₁ (γN₂O₅ = 1 × 10⁻³), and NO₂ (γNO₂ = 1 × 10⁻⁴) occurs on aerosol surfaces only. Uptake and hydrolysis of N₂O₅ on aerosol surfaces depend on the chemical composition of aerosols, temperature, and humidity as described in Evans and Jacob (2005). Recently, Holmes et al. (2019) updated the reaction probabilities of the NO₂ and NO₃ heterogeneous reactions in the model to depend on aerosol chemical composition and relative humidity. Holmes et al. (2019) also updated the N₂O₅ reaction probability to additionally depend on the H₂O and NO₃⁻ concentrations in aerosol (Bertram and Thornton, 2009). In addition to these updates for hydrolysis on aerosol, Holmes et al. (2019) included the uptake and hydrolysis of N₂O₅, NO₂, and NO₃ in cloud water and ice limited by cloud entrainment rates. We incorporate these updates from Holmes et al. (2019) into the cloud chemistry model to examine the impacts on global nitrate production mechanisms. We consider the cloud chemistry model as state of the science, and as such we focus on the results of this particular simulation. Additional model sensitivity studies are also performed and examined relative to the standard model simulation, which represents a more common representation of nitrate chemistry in atmospheric chemistry models. These additional sensitivity simulations are described in Sect. 4.

Δ¹⁷O(nitrate) is calculated in the model using monthly mean, local chemical production rates rather than by treating different isotopic combinations of nitrate as separate tracers that can be transported in the model. Alexander et al. (2009) transported four nitrate tracers, one each for nitrate production by NO₂ + OH, N₂O₅ hydrolysis, NO₃ + HC, and nitrate originating from its formation in the stratosphere. Since Δ¹⁷O(NO₃) was not transported in the Alexander et al. (2009) model, it was calculated using local production rates, so effectively only one-third of the Δ¹⁷O(nitrate) was transported in Alexander et al. (2009). Accurately accounting for transport of Δ¹⁷O(nitrate) in the model would require transporting all individual isotopic combinations of the primary reactant (NO), the final product (nitrate), and each reaction intermediate (e.g., N₂O₅), which we do not do here due to the large computational costs. Thus, the model results shown here represent Δ¹⁷O(nitrate) from local NO₃ recycling and nitrate production. This may lead to model biases, particularly in remote regions such as polar regions in wintertime when most nitrate is likely transported from lower latitudes or the stratosphere. This should make less of a difference in polluted regions where most nitrate is formed locally or for example in polar regions in summer when photochemical recycling of nitrate in the snowpack represents a significant local source of NO₃ at the surface (Domine and Shepson, 2002). Although lack of transport of the isotope tracers adds uncertainty to direct comparison of the model with observations at any particular location, this approach will reflect the full range of possible modeled Δ¹⁷O(nitrate) values for the current chemical mechanism, which can then be compared to the range of observed Δ¹⁷O(nitrate) values around the globe.

Figure 1. Simplified HNO₃ formation in the model. Numbers show the global annual-mean percent contribution to NO₂ and HNO₃ formation in the troposphere below 1 km for the cloud chemistry (standard) simulation. Red indicates reactions leading to high Δ¹⁷O values, and blue indicates reactions leading to low Δ¹⁷O values. H₂O = HO₂ + RO₂; X = Br + Cl + I; HC: hydrocarbons; MTN: monoterpenes; ISOP: isoprene.
Table 1. Calculated $\Delta^{17}$O(nitrate) in the model for each nitrate production pathway ($X = \text{Br}, \text{Cl}, \text{and} \ I$; HC: hydrocarbon; MTN: monoterpenes; ISOP: isoprene; $\Delta^{17}$O(O$_2$) = 39‰). $A$ is defined in Eq. (1).

<table>
<thead>
<tr>
<th>Nitrate formation pathway</th>
<th>$\Delta^{17}$O(nitrate)</th>
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<tbody>
<tr>
<td>Gas-phase reactions</td>
<td></td>
</tr>
<tr>
<td>R1 NO$_2$ + OH</td>
<td>$\frac{2}{3}A\Delta^{17}$O(O$_2$)</td>
</tr>
<tr>
<td>R2 NO$_3$ + HC</td>
<td>$(2/3 + 1/3)\Delta^{17}$O(O$_2$)</td>
</tr>
<tr>
<td>R3 NO + HO$_2$</td>
<td>$1/3\Delta^{17}$O(O$_2$)</td>
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<tr>
<td>Aerosol uptake from the gas phase followed by hydrolysis</td>
<td></td>
</tr>
<tr>
<td>R4 N$_2$O$_5$ + H$_2$O(aq)</td>
<td>$(2/3 + 1/3)\Delta^{17}$O(O$_2$)</td>
</tr>
<tr>
<td>R5 N$_2$O$_5$ + Cl$^-$(aq)</td>
<td>$(2/3 + 1/3)\Delta^{17}$O(O$_2$)</td>
</tr>
<tr>
<td>R6 XNO$_2$ + H$_2$O(aq)</td>
<td>$(2/3 + 1/3)\Delta^{17}$O(O$_2$)</td>
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<tr>
<td>R7 NO$_2$ + H$_2$O(aq)</td>
<td>$(2/3 + 1/3)\Delta^{17}$O(O$_2$)</td>
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<tr>
<td>R8 NO$_3$ + H$_2$O(aq)</td>
<td>$(2/3 + 1/3)\Delta^{17}$O(O$_2$)</td>
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<tr>
<td>R9 RONO$_2$ + H$_2$O(aq)</td>
<td>$1/3\Delta^{17}$O(O$_2$)</td>
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<tr>
<td>(where RONO$_2$ is from NO + RO$_2$)</td>
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<tr>
<td>R10 RONO$_2$ + H$_2$O(aq)</td>
<td>$(2/3 + 1/3)\Delta^{17}$O(O$_2$)</td>
</tr>
<tr>
<td>(where RONO$_2$ is from NO$_3$ + MTN/ISOP)</td>
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The $\Delta^{17}$O(nitrate) value of nitrate produced from each production pathway is calculated as shown in Table 1. The value of $A$ in Table 1 represents the relative importance of the oxidation pathways of NO to NO$_2$ where the oxygen atom transferred comes from ozone (NO + O$_3$ and NO + XO):

$$A = \frac{k_{O_3+NO}[O_3] + k_{XO+NO}[XO]}{k_{O_3+NO}[O_3] + k_{XO+NO}[XO] + k_{HO_2+NO}[HO_2] + k_{RO_2+NO}[RO_2]}.$$  \hspace{1cm} (1)

In Eq. (1), $k$ represents the local reaction rate constant for each of the four reactions, XO = BrO, ClO, IO, and IO$_2$; and we assume $\Delta^{17}$O(XO) is equal to the $\Delta^{17}$O value of the terminal oxygen atoms of ozone, as described in more detail below. This effectively assumes that the other oxidation pathways (NO + HO$_2$ and NO + RO$_2$) yield $\Delta^{17}$O(NO$_x$) = 0‰. Although HO$_2$ may have a small $^{17}$O enrichment on the order of 1‰ to 2‰ (Savarino and Thiemens, 1999b), the assumption that this pathway yields $\Delta^{17}$O(NO$_x$) = 0‰ simplifies the calculation and leads to negligible differences in calculated $\Delta^{17}$O(nitrate) (Michalski et al., 2003). This approach assumes that NO$_x$ cycling is in a photochemical steady state, which only occurs during the daytime. $A$ is calculated in the model as the 24 h average NO$_2$ production rate rather than the daytime average only. As was shown in Alexander et al. (2009), rapid daytime NO$_x$ cycling dominates the calculated 24 h averaged $A$ value, leading to negligible differences in calculated $\Delta^{17}$O(nitrate) for 24 h averaged values versus daytime averaged values.

NO$_x$ formed during the day will retain its daytime $\Delta^{17}$O(NO$_x$) signature throughout the night due to lack of NO$_2$ photolysis (Morin et al., 2011), suggesting similar $A$ values for the nighttime reactions (R2, R4, R5, R8, and R10 in Table 1). However, NO emitted at night will not undergo photochemical recycling, initially suggesting that NO will retain its emitted $\Delta^{17}$O(NO) value of 0‰ prior to sunrise. Thus, any NO emitted at night and oxidized to NO$_2$ before sunrise will result in $\Delta^{17}$O(NO$_2$) equal to one-half of the $\Delta^{17}$O value of the oxidant, since only one of the two oxygen atoms of NO$_2$ will originate from the oxidant. Since HO$_x$ abundance is low at night, ozone will be the dominant oxidant. Thus, NO both emitted and oxidized to NO$_2$ at night will lead to $A_{night} = 0.5$ (half of the O atoms of NO$_2$ originate from O$_3$). Although isotopic exchange between NO + NO$_2$ (Sharma et al., 1970) and NO$_2$ and NO$_3$ via thermal dissociation of N$_2$O$_2$ (Connell and Johnston, 1979) will tend to increase $\Delta^{17}$O(NO) above its emitted value of 0‰, the bulk $\Delta^{17}$O value of the NO$_x$ plus NO$_3$ system will be lower at night than during the daytime due to the absence of photochemical cycling at night (Michalski et al., 2014; Morin et al., 2011). Since the atmospheric lifetime of NO$_x$ near the surface against nighttime oxidation to nitrate (R2 + R4 + R5) is typically greater than 24 h (Fig. S1 in the Supplement), most nitrate formed during the nighttime will form from NO$_x$ that reached photochemical equilibrium during the previous day. Thus, we use values of $A$ calculated as the 24 h average NO$_2$ production rate for calculating the $\Delta^{17}$O(nitrate) value of all nitrate production pathways, including those that can occur at night. Using 24 h averaged $A$ values may lead to an overestimate of $\Delta^{17}$O(nitrate) in locations with more rapid nighttime nitrate formation rates such as in China and India (Fig. S1). However, even in these locations the lifetime of NO$_x$ against nighttime oxidation is greater than 12 h, suggesting that over half of nitrate formation at night occurs from the oxidation of NO$_x$ that reached photochemical equilibrium during the daytime. When comparing modeled
\( \Delta^{17}O(\text{nitrate}) \) with observations, we add error bars to model values in these locations (Beijing and Mt. Lulin, Taiwan) that reflect the range of possible \( A \) values for nighttime nitrate formation, with the high end \( (A_{\text{high}}) \) reflecting 24 h average \( A \) values and the low end assuming that half of nitrate formation occurs from oxidation of NO\(_2\), that reached photochemical equilibrium during the daytime \( (A_{\text{low}} = 0.5A + 0.5A_{\text{night}}, \text{where } A_{\text{night}} = 0.5) \).

\( \Delta^{17}O(\text{nitrate}) \) for total nitrate is calculated in the model according to

\[
\Delta^{17}O(\text{nitrate}) = \sum_{R=R1}^{R10} f_R \Delta^{17}O(\text{nitrate})_R,
\]

where \( f_R \) represents the fractional importance of each nitrate production pathway (R1–R10 in Table 1) relative to total nitrate production, and \( \Delta^{17}O(\text{nitrate})_R \) is the \( \Delta^{17}O(\text{nitrate}) \) value for each reaction as described in Table 1. To calculate \( \Delta^{17}O(\text{nitrate}) \), we assume that the mean \( \Delta^{17}O \) value of the ozone molecule \( (\Delta^{17}O(\text{O}_3)) \) is equal to 26 ‰ based on recent observations (Vicars et al., 2012; Ishino et al., 2017; Vicars and Savarino, 2014) and that it is the terminal oxygen atom that is transferred to the oxidation product during chemical reactions (Savarino et al., 2008; Berhanu et al., 2012). Thus, we assume that the \( \Delta^{17}O \) value of the oxygen atom transferred from \( \text{O}_3 \) \( (\Delta^{17}O(\text{O}_3^3)) = 1.5 \times \Delta^{17}O(\text{O}_3) \), as in previous work (e.g., Morin et al., 2011), where \( \Delta^{17}O(\text{O}_3^3) \) represents the \( \Delta^{17}O \) value of the terminal oxygen atoms in ozone. Assuming that \( \Delta^{17}O(\text{O}_3) = 26 \text{‰} \) based on recent observations, this leads to \( \Delta^{17}O(\text{O}_3^3) = 39 \text{‰} \).

### 3 Results and discussion

Figure 1 shows the relative importance of the different oxidation pathways of NO to NO\(_2\) and nitrate formation below 1 km altitude in the model for the cloud chemistry simulation, with equivalent values for the standard simulation shown in parentheses. We focus on model results near the surface (below 1 km) because these can be compared to observations; currently only surface observations of \( \Delta^{17}O(\text{nitrate}) \) are available. We note that two observation data sets – from Bermuda (Hastings et al., 2003) and Princeton, NJ (Kaiser et al., 2007) – are rainwater samples and thus may represent nitrate formed aloft. However, since cloud water peaks on average near 1 km altitude in the MERRA2 meteorology used to drive GEOS-Chem, our model sampling strategy should capture the majority of the influence of clouds on the chemistry of nitrate formation. The dominant oxidant of NO to NO\(_2\) is \( \text{O}_3 \) (84 ‰–85 ‰). Much of the remaining oxidation occurs due to the reaction with peroxy radicals (HO\(_2\) and RO\(_2\)). Oxidation of NO to NO\(_2\) by XO is minor (1 ‰) and occurs over the oceans because the main source of tropospheric reactive halogen is from sea salt aerosol and sea water (Chen et al., 2017; Sherwen et al., 2016; Wang et al., 2019) (Fig. 2). In the model, the global annual-mean lifetime of NO\(_x\) in the troposphere against oxidation to nitrate is about 1 d; about 50% of this loss is from the reaction of NO\(_2\) + OH. NO\(_4\) loss from N\(_2\)O\(_5\) becomes more important near the surface where aerosol surface area is relatively high. The global annual-mean lifetime of nitrate in the troposphere against wet and dry deposition to the surface is about 3 d.

For both the cloud chemistry and standard simulations, the two most important nitrate formation pathways are NO\(_2\) + OH (41 ‰–42 ‰) and N\(_2\)O\(_5\) hydrolysis (28 ‰–41 ‰), the latter of which is dominant over the mid- to high northern continental latitudes during winter, where both NO\(_x\) emissions and aerosol abundances are relatively large (Figs. 1 and 3). The cloud chemistry simulation results in an equal importance of nitrate formation via NO\(_2\) + OH and N\(_2\)O\(_5\) hydrolysis (both 41 ‰) due to increases in the rate of N\(_2\)O\(_5\) uptake in clouds and decreases in the importance of NO\(_2\) hydrolysis, which can compete with N\(_2\)O\(_5\) formation at night. In the standard model, NO\(_2\) hydrolysis represents an important nitrate production mechanism (12 ‰), but it is negligible in the cloud chemistry simulation due to the reduction in the reaction probability (from \( \gamma_{\text{NO}_2} = 10^{-4} \) to \( \gamma_{\text{NO}_2} = 10^{-8} \) in the model, which is supported by laboratory studies (Burkholder et al., 2015; Crowley et al., 2010; Tan et al., 2016). The formation of HNO\(_3\) from the hydrolysis of RONO\(_2\) formed from both daytime (NO + RO\(_2\)) and nighttime (NO\(_3\) + MTN/ISOP) reactions represents 6% of total global nitrate formation (Fig. 1) and is dominant over Amazonia (Fig. 3). RONO\(_2\) hydrolysis represents up to 20% of inorganic nitrate formation in the southeastern US (Fig. 3). This is similar to Fisher et al. (2016), who estimated that formation of RONO\(_2\) accounts for up to 20% of NO\(_x\) loss in this region during summer, with RONO\(_2\) hydrolysis representing 60% of RONO\(_2\) loss. Globally, the formation of in-
organic nitrate from the hydrolysis of RONO$_2$ is dominated by RONO$_2$ formation from the daytime reactions (3%–6%), while the formation of RONO$_2$ from nighttime reactions represents up to 3%. The relative importance of nighttime and daytime RONO$_2$ formation is expressed as a range because precursors to RONO$_2$ that formed from monoterpenes can form from both daytime and nighttime reactions, and these precursors are not separately diagnosed in the model output. HNO$_3$ formation from NO$_3$ + HC and the hydrolysis of XNO$_3$ is small globally (5%–6%). Although XNO$_3$ hydrolysis is the dominant nitrate formation pathway over the remote oceans (Fig. 3), its contribution to total global nitrate production is relatively small due to small local NO$_3$ sources in these regions.

Figures 4–6 show modeled $\Delta^{17}$O(nitrate) for the cloud chemistry simulation (the standard simulation is shown in Figs. S2–S4). Figure 4 shows modeled annual-mean $\Delta^{17}$O(nitrate) below 1 km altitude ($\Delta^{17}$O(NO$_2$) is shown in Fig. S5). The model predicts an annual-mean range of $\Delta^{17}$O(nitrate) = 4‰–33‰ near the surface. The lowest values are over Amazonia due to the dominance of RONO$_2$ hydrolysis, and the highest values are over the midlatitude oceans due to the dominance of XNO$_3$ hydrolysis (Figs. 3 and 4).

Figure 5 compares the model with a global compilation of $\Delta^{17}$O(nitrate) observations from around the world. Observations included in Fig. 5 include locations where there is enough data to calculate monthly means (McCabe et al., 2006; Kunasek et al., 2008; Hastings et al., 2003; Kaiser et al., 2007; Michalski et al., 2003; Guha et al., 2017; Savarino et al., 2013, 2007; Ishino et al., 2017; Alexander et al., 2009; He et al., 2018b; Fibiger et al., 2013; Wang et al., 2014). Figure 6 compares the seasonality in modeled $\Delta^{17}$O(nitrate) to the observations where samples were collected over the course of approximately 1 year (McCabe et al., 2006; Kunasek et al., 2008; Kaiser et al., 2007; Michalski et al., 2003; Guha et al., 2017; Savarino et al., 2013, 2007; Ishino et al., 2017; Alexander et al., 2009). In contrast to Alexander et al. (2009), the model does not significantly underestimate the $\Delta^{17}$O(nitrate) observations when assuming a bulk ozone isotopic composition ($\Delta^{17}$O(O$_3$)) on the order of 25‰ (see Fig. 2d in Alexander et al., 2009). The increase in modeled $\Delta^{17}$O(nitrate) is due to increased importance of O$_3$ in NO$_x$ cycling (85% below 1 km) compared to Alexander et al. (2009) (80% below 1 km altitude), as well as an increase in the number and fractional importance of nitrate formation pathways that yield relatively high values of $\Delta^{17}$O(nitrate) (red pathways in Fig. 1). Although XO species themselves are only a minor NO oxidation pathway (1%), the addition of reactive halogen chemistry in the model has
altered the relative abundance of O₃ and HO₃ (Sherwen et al., 2016) in such a way as to increase the modeled \( \Delta^{17}O(\text{NO}_3) \).

The Alexander et al. (2009) study used GEOS-Chem v8-01-01, which included tropospheric nitrate formation from the NO + OH, N₂O₅ + H₂O, and NO₃ + HC pathways only. An increased importance of N₂O₅ hydrolysis (R4) and additional nitrate formation pathways that yield relatively high values of \( \Delta^{17}O(\text{nitrato}) \) (R5, R6, R8, and R10) in the present study also explain the increase in modeled \( \Delta^{17}O(\text{nitrato}) \) relative to Alexander et al. (2009). An increase in the average \( A \) value from 0.80 to 0.85 would tend to increase the calculated \( \Delta^{17}O(\text{nitrato}) \) on the order of 2 \( \%e \) (0.05 \( \times \Delta^{17}O(O_3^+) \)), suggesting that the increase in the relative importance of the terminal reactions R4, R5, R6, R8, and R10 explains the majority of the difference between the results presented here compared to Alexander et al. (2009). Assuming a value of 35 \( \%e \) for bulk \( \Delta^{17}O(O_3) \) in the model that did not include reactive halogen chemistry or heterogeneous reactions in cloud water produced good agreement between models and observed \( \Delta^{17}O(\text{nitrato}) \) in Alexander et al. (2009); however, in the current version of the model this bulk isotopic assumption leads to a model overestimate at nearly all locations (Fig. S6). The cloud chemistry model somewhat better agreement with the observations (\( R^2 = 0.51 \) in Fig. 5) compared to the standard model (\( R^2 = 0.48 \) in Fig. S3). Improved agreement with the observations occurs in the mid- to high latitudes (Figs. 6 and S4) and is due to addition of N₂O₅ hydrolysis in clouds (Figs. 3 and S6).

The mean \( \Delta^{17}O(\text{nitrato}) \) value of the observations (27.7 ± 5.0 \( \%e \)) shown in Fig. 5 is not significantly different from the modeled values at the location of the observations (28.6 ± 4.5 \( \%e \)); however, the range of \( \Delta^{17}O(\text{nitrato}) \) values of the observations (10.9 \( \%e \)–40.6 \( \%e \)) is larger than in the model (19.6 \( \%e \)–37.6 \( \%e \)). As previously noted in Savarino et al. (2007), the maximum observed \( \Delta^{17}O(\text{nitrato}) \) value (40.6 \( \%e \)) is not possible given our isotopic assumption for the terminal oxygen atom of ozone (\( \Delta^{17}O(O_3^+) = 39 \%e \)); however, it is theoretically possible given the approximately 2 \( \%e \) uncertainty in observed \( \Delta^{17}O(O_3^+) \). A value of \( \Delta^{17}O(\text{nitrato}) = 41 \%e \) is possible if \( \Delta^{17}O(O_3^+) = 41 \%e \) and all oxygen atoms of nitrate originate from ozone (\( A = 1 \) and all nitrate forms from R2 and/or R5). Although this may be possible for nitrate formed locally in the Antarctic winter due to little to no sunlight, lack of local NO₃ sources during Antarctic winter makes it unlikely that all nitrate observed in Antarctica forms locally. Long-range transport from lower latitudes and/or the stratosphere likely contributes to nitrate observed in Antarctica during winter (Lee et al., 2014). Observed \( \Delta^{17}O(\text{nitrato}) > 39 \%e \) (in Antarctica) has been suggested to be due to transport of nitrate from the stratosphere (Savarino et al., 2007), as stratospheric O₃ is expected to have a higher \( \Delta^{17}O(O_3) \) value than ozone produced in the troposphere (Krankowsky et al., 2000; Mauersberger et al., 2001; Lyons, 2001). Indeed, the model underestimates the observations at Dumont d’Urville (DDU) and the South Pole (both in Antarctica) during winter and spring (Fig. 6), where and when the stratospheric contribution is expected to be most important (Savarino et al., 2007). The model underestimate in Antarctica may also be due to model underestimates of the BrO column (Chen et al., 2017) and ozone abundance (Sherwen et al., 2016) in the southern high latitudes. The largest model overestimates occur at Mt. Lulin, Taiwan (Figs. 5 and 6). Based on nitrogen isotope observations (\( \delta^{15}N \)), nitrate at Mt. Lulin is thought to be influenced by anthropogenic nitrate emitted in polluted areas of mainland China and transported to Mt. Lulin rather than local nitrate production (Guha et al., 2017). However, observations of \( \Delta^{17}O(\text{nitrato}) \) in autumn and winter in Beijing suggest much higher values (30.6 ± 1.8 \( \%e \)) than was measured at Mt. Lulin (15 ± 30 \( \%e \) in winter). A potential reason for the model overestimate of the observed values at Mt. Lulin could be qualitatively explained by transport of nitrate formed in the free troposphere to this high-altitude location, where the high-\( \Delta^{17}O(\text{nitrato}) \)-producing pathways (R4–R8) should be negligible due to minimal aerosol surface area for heterogeneous chemistry. Low \( \Delta^{17}O(\text{nitrato}) \) values from nitrate formed at higher altitudes and transported to Mt. Lulin would not be accounted for in the model since the isotopes are not transported. The model compares better to the midlatitude locations close to pollution sources (La Jolla and Princeton), although the model overestimates wintertime \( \Delta^{17}O(\text{nitrato}) \) in Princeton, NJ, USA, by up to 6 \( \%e \) and underestimates wintertime \( \Delta^{17}O(\text{nitrato}) \) in La Jolla, CA, USA, by up to 4 \( \%e \). The model overestimate at Princeton during winter could be due to the fact that these are precipitation samples and not ambient aerosol samples, and thus may reflect nitrate formed at altitudes higher than we are sampling in the model. The underestimate at La Jolla, CA, could be due to underestimates in reactive chlorine chemistry in the model, which would tend to increase \( \Delta^{17}O(\text{nitrato}) \) by increasing nitrate formation by the hydrolysis of halogen nitrates (R6) in this coastal location. The model underestimates the \( \Delta^{17}O(\text{nitrato}) \) observations at Cabo Verde in late summer/early autumn by up to 6 \( \%e \) (Savarino et al., 2013). Comparison with results from the steady-state model employed in Savarino et al. (2013) suggests that the low bias could be due to an underestimate of nitrate formation via NO₃ + DMS (R2). The steady-state model in Savarino et al. (2013) agreed with observations when R2 represented about one-third of total nitrate formation. The model results presented here have R2 representing about 15 \% of total nitrate formation in this season. An underestimate of the relative importance of R2 could result from a model underestimate of atmospheric DMS abundances.
Figure 5. Comparison of monthly-mean modeled (cloud chemistry) and observed $\Delta^{17}$O(nitrate) at locations where there are enough observations to calculate a monthly mean. References for the observations are in the text. The error bars represent different assumptions for calculated modeled $A$ values for nighttime reactions as described in the text. Error bars for Beijing and Mt. Lulin reflect the range of possible modeled $A$ values for nighttime reactions as described in the text. The $y = x$ (solid line) and $y = 2x$ and $y = 0.5x$ (dashed) are shown.

Figure 6. Comparison of monthly-mean modeled (cloud chemistry) and observed $\Delta^{17}$O(nitrate). Error bars for model results from Mt. Lulin reflect the range of possible modeled $A$ values for nighttime reactions as described in the text. Error bars for the observations reflect the analytical uncertainty in the measurements, except for two data points in June for Summit which reflect the standard deviation of $\Delta^{17}$O(nitrate) from multiple measurements during that month.

4 Model uncertainties

The uncertainty in the two most important nitrate formation pathways, NO$_2$ + OH and N$_2$O$_5$ hydrolysis, and their impacts on NO$_x$ and oxidant budgets have been examined and discussed elsewhere (Macintyre and Evans, 2010; Newsome and Evans, 2017; Holmes et al., 2019). The impacts of the formation and hydrolysis of halogen nitrates on global NO$_x$ and oxidant budgets have also been previously examined (Sherwen et al., 2016). Here we focus on three additional processes using a set of model sensitivity studies. First, we examine the importance of the third most important nitrate production pathway on the global scale as predicted by the standard model, NO$_2$ aerosol uptake and hydrolysis, and its implications for the global NO$_x$, nitrate, and oxidant budgets. Second, we examine the role of changing anthropogenic NO$_x$ emissions over a 15-year period (2000 to 2015) on the relative importance of the formation of inorganic nitrate from the hydrolysis of organic nitrates. Finally, we examine the role of aerosol nitrate photolysis on the relative importance of different nitrate formation pathways. The impact of aerosol nitrate photolysis on NO$_x$ and oxidant budgets has been examined in detail elsewhere (Kasibhatla et al., 2018).

4.1 Heterogeneous uptake and hydrolysis of NO$_2$

Heterogeneous uptake of NO$_2$ to form HNO$_3$ and HONO is the third most important nitrate formation pathway in the standard model on the global scale (Fig. 1). The reaction probability ($\gamma_{\text{NO}_2}$) measured in laboratory studies ranges between $10^{-8}$ and $10^{-4}$ depending on aerosol chemical composition (Lee and Tang, 1988; Crowley et al., 2010; Gutzwiller et al., 2002; Yabushita et al., 2009; Abbatt and Waschewsky, 1998; Burkholder et al., 2015; Bröske et al., 2003; Li et al., 2018a; Xu et al., 2018). A value of $\gamma_{\text{NO}_2} = 10^{-4}$ is used in the standard model, which is at the high end of the reported range. A molar yield of 0.5 for both HNO$_3$ and HONO formation is assumed in the model based on laboratory studies and hypothesized reaction mechanisms (Finlayson-Pitts et al., 2003; Jenkin et al., 1988; Ramazan et al., 2004; Yabushita et al., 2009). However, both the reaction rate and mechanism of this reaction and its dependence on chemical composition and pH are still not well understood (Spataro and Ianniello, 2014).

The cloud chemistry simulation uses a reaction probability formulation for aerosol uptake of NO$_2$ ($\gamma_{\text{NO}_2}$) that depends on aerosol chemical composition, ranging from ($\gamma_{\text{NO}_2}$) = $10^{-8}$ for dust to ($\gamma_{\text{NO}_2}$) = $10^{-4}$ for black carbon based on recent laboratory studies (Holmes et al., 2019).
Figure 7. Modeled annual-mean HONO (a, c, e) and fine-mode nitrate (b, d, f) concentrations below 1 km altitude in the standard simulation (a, b) with $\gamma_{\text{NO}_2} = 10^{-4}$ for NO$_2$ hydrolysis. Absolute (c, d) and relative (e, f) change in concentrations below 1 km altitude between the standard model and the model simulation with $\gamma_{\text{NO}_2} = 10^{-7}$. Negative numbers represent a decrease relative to the standard simulation.

The updated NO$_2$ reaction probability results in a negligible (< 1 %) importance of this reaction for nitrate formation, compared to a 12 % contribution in the standard model. The cloud chemistry simulation significantly increases the fractional importance of N$_2$O$_5$ hydrolysis (from 28 % to 41 %, globally below 1 km altitude) compared to the standard simulation, in part due to decreased competition from NO$_2$ hydrolysis and in part due to increased N$_2$O$_5$ hydrolysis in clouds. To evaluate the relative importance of competition from NO$_2$ hydrolysis and the addition of N$_2$O$_5$ hydrolysis in clouds, we perform a model sensitivity study that is the same as the standard simulation but decreases the reaction probability of NO$_2$ hydrolysis from N$_2$O$_5 = 10^{-4}$ to N$_2$O$_5 = 10^{-7}$, resulting in a reduction of HONO below 1 km altitude by up to 100 % over the continents, with relatively small (up to 1 ppb) changes in nitrate concentrations (Fig. 7). The reduction in the rate of heterogeneous NO$_2$ uptake leads to reductions in OH where this reaction was most important in the model (over China and Europe) due to reductions in HONO but leads to increases in OH elsewhere due to increases in ozone (by up to a few ppb) resulting from small increases in the NO$_x$ lifetime due to a reduction in the NO$_x$ sink (Fig. 8). Similar changes in HONO are seen when comparing the standard and cloud chemistry simulation (not shown). Increased importance of N$_2$O$_5$ hydrolysis in both the cloud chemistry simulation and the simulation without cloud chemistry but with a reduced reaction probability for NO$_2$ hydrolysis increases modeled annual-mean $\Delta^{17}$O(nitrate) by up to 3 ‰ in China, where this reaction is most important. This improves model agreement with monthly-mean observations of $\Delta^{17}$O(nitrate) in Beijing (He et al., 2018a) (Figs. 5 and S3).
Figure 8. Same as Fig. 7 except for OH (a, c, e) and ozone (b, d, f).

Figure 9. Absolute (a, b, c) and relative (d, e, f) change in HONO (a, d), OH (b, e), and ozone (c, f) concentrations below 1 km altitude between the standard model and the model simulation with an acidity-dependent yield from NO₂ hydrolysis. Positive numbers represent an increase relative to the standard simulation.
The product yields of NO₂ hydrolysis are also uncertain. Jenkin et al. (1988) proposed the formation of a water complex, NO₂·H₂O, leading to the production of HONO and HNO₃. Finlayson-Pitts et al. (2003) and Ramazan et al. (2004) proposed the formation of the dimer N₂O₅ on the surface, followed by isomerization to form NO⁺NO₃⁻. Reaction of NO⁺NO₃⁻ with H₂O results in the formation of HONO and HNO₃. Laboratory experiments by Yabushita et al. (2009) suggested that dissolved anions catalyzed the dissolution of NO₂ to form a radical intermediate XNO₂⁻ (where X = Cl, Br, or I) at the surface followed by reaction with NO₂(g) to form HONO and NO₃⁻. These experiments described above were performed at NO₂ concentrations much higher than exist in the atmosphere (10–100 ppm) (Yabushita et al., 2009; Finlayson-Pitts et al., 2003; Ramazan et al., 2004). A laboratory study utilizing isotopically labeled water to investigate the reaction mechanism suggested that the formation of HONO resulted from the reaction between adsorbed NO₂ and H⁺, while the formation of HNO₃ resulted from the reaction between adsorbed NO₂ and OH⁻, and did not involve the N₂O₅ intermediate (Gustafsson et al., 2009). Results from Gustafsson et al. (2009) suggest an acidity-dependent yield of HONO and HNO₃, favoring HONO at low pH values. A recent study in the northeastern US during winter found that modeled nitrate abundance was overestimated using a molar yield of 0.5 for HONO and HNO₃, and the model better matched the observations of NO₂ and nitrate when assuming a molar yield of 1.0 for HONO (Jaeglé et al., 2018). Particles were acidic (pH < 2) during this measurement campaign (Guo et al., 2017; Shah et al., 2018), which may favor HONO production over HNO₃.

We examine the potential importance of this acidity-dependent yield by implementing a pH-dependent product yield in two separate sensitivity simulations, first using an NO₂ aerosol uptake reaction probability of γ = 10⁻⁴ as in the standard simulation and second with γNO₂ = 10⁻⁷. The acidity-dependent yield for HONO and HNO₃ formation is based on the laboratory study by Gustafsson et al. (2009). We use aerosol pH calculated from ISORROPRIA II (Fountoukis and Nenes, 2007) to calculate the concentration of H⁺ and OH⁻ in aerosol water. The yield of HONO (γHONO) from heterogeneous uptake of NO₂ on aerosol surfaces is calculated according to Eq. (3):

\[
\gamma_{\text{HONO}} = \frac{[\text{H}^+] + [\text{OH}^-]}{[\text{H}^+] + [\text{OH}^-]},
\]

where [H⁺] and [OH⁻] are in units of M. The yield of HNO₃ from this reaction is equal to (1 − γHONO). Eq. (3) yields values of γHONO near unity for aerosol pH values less than 6, decreasing rapidly to zero between pH values of 6 and 8 (Fig. S8). Calculated aerosol pH values are typically < 6 in the model except in remote regions far from NOₓ sources (Fig. S9), favoring the product HONO.

The acidity-dependent yield implemented in the standard simulation with γNO₂ = 10⁻⁴ increases HONO concentrations by up to 1 ppbv in China, where this reaction is most important (Fig. 9). Fractional increases in HONO exceed 100 % in remote locations (Fig. 9). Increased HONO leads to increases in OH on the order of 10 %–20 % in most locations below 1 km altitude, while ozone concentrations increase in most locations by up to several ppbv (Fig. 9). The exception is the southern high latitudes, likely due to decreased formation and thus transport of nitrate to remote locations. The impact on NOₓ and nitrate budgets is relatively minor. The global annual-mean NOₓ burden near the surface (below 1 km) increases slightly (+2 %) as a result of the decreased rate of conversion of NO₂ to nitrate; the change to the global tropospheric burden is negligible. Annual-mean surface nitrate concentrations show small decreases up to 1 ppbv in China, where this reaction is most important in the model; impacts on nitrate concentrations over a shorter time period may be more significant (Jaeglé et al., 2018). The fraction of HNO₃ formed from NO₂ + OH (49 %) increases due to increases in OH from the HONO source. The fraction of HNO₃ formation from the uptake and hydrolysis of N₂O₅ also increases (from 28 % to 32 %) due to reductions in the nighttime source of nitrate from NO₂ hydrolysis. The calculated mean Δ¹⁷O(nitrate) at the location of the observations shown in Fig. 5 (27.9 ± 5.0 ‰) is not significantly impacted due to compensating effects from changes in both high- and low-producing Δ¹⁷O(nitrate) values. Modeled monthly-mean Δ¹⁷O(nitrate) in China, where NO₂ hydrolysis is most important, decreases by 0.9 ‰ to 1.9 ‰ and is biased low by 1.8 ‰ to 3.4 ‰.

Using a combination of both the low reaction probability (γ = 10⁻⁷) and the acidity-dependent yield gives similar results to using γ = 10⁻⁴ and assuming a molar yield of 0.5 for HONO and HNO₃ (not shown). In other words, including a pH-dependent product yield rather than a yield of 0.5
4.2 Hydrolysis of organic nitrates (RONO₂)

Anthropogenic NOₓ emissions have been increasing in China and decreasing in the US and Europe (Richter et al., 2005; Hoesly et al., 2018), with implications for the relative importance of inorganic and organic nitrate formation as a sink for NOₓ (Zare et al., 2018). To examine the impacts of recent changes in anthropogenic NOₓ emissions for nitrate formation pathways, we run the standard model using the year 2000 emissions and meteorology after a 1-year model spin-up and compare the results to the standard model simulation run in the year 2015. This time period encompasses significant changes in anthropogenic NOₓ emissions in the US, Europe, and China and encompasses most of the time period of the observations shown in Figs. 5 and 6. Total global anthropogenic emissions of NOₓ are slightly lower in the year 2000 simulation (30 Tg N yr⁻¹) compared to the year 2015 simulation (31 Tg N yr⁻¹) due to decreases in North America and Europe, counteracted by increases in Asia (Fig. S10). This leads to increases of less than 10% in the annual-mean, fractional importance of the source of nitrate from the hydrolysis of organic nitrates in the US and corresponding decreases of less than 10% over China (Fig. 10). Relatively small changes (<10%) in nitrate formation pathways yield small changes (<2%) in modeled annual-mean Δ¹⁷O(nitrate) between the year 2000 and 2015; differences in Δ¹⁷O(nitrate) over shorter time periods may be larger. Changes in the formation of nitrate from the hydrolysis of RONO₂ remain unchanged globally, as increases in the US and Europe and decreases in China counteract one another.

4.3 Photolysis of aerosol nitrate

Observations have demonstrated that aerosol nitrate can be photolyzed at rates much faster than HNO₃(g) (Reed et al., 2017; Ye et al., 2016); however, the magnitude of the photolytic rate constant is uncertain. We examine the implications of this process for global nitrate formation pathways by implementing the photolysis of aerosol nitrate as described in Kasibhatla et al. (2018) into the standard model simulation, scaling the photolytic rate constant for both fine- and coarse-mode aerosol nitrate to a factor of 25 times higher than that for HNO₃(g) (Kasibhatla et al., 2018; Romer et al., 2018), with a molar yield of 0.67 for HONO and 0.33 for NO₂ production. The global annual-mean NOₓ burden near the surface (below 1 km) increases slightly (+2%) as a result of the photolytic recycling of nitrate to NOₓ, similar to Kasibhatla et al. (2018). Aerosol nitrate photolysis results in only small impacts on the relative importance of nitrate formation pathways (<2%), likely due to simultaneous increases in O₃ and OH (Kasibhatla et al., 2018), which in turn yields small impacts on calculated Δ¹⁷O(nitrate) at the location of the observations shown in Fig. 5 (27.9±5.0‰). Nitrate photolysis itself has minimal impact on Δ¹⁷O(nitrate) because it is a mass-dependent process (McCabe et al., 2005).

5 Conclusions

Observations of Δ¹⁷O(nitrate) can be used to help quantify the relative importance of different nitrate formation pathways. Interpretation of Δ¹⁷O(nitrate) requires knowledge of Δ¹⁷O(O₃). Previous modeling studies showed good agreement between observed and modeled Δ¹⁷O(nitrate) when assuming a bulk oxygen isotopic composition of ozone (Δ¹⁷O(O₃)) of 35‰ based on laboratory and modeling studies (Morton et al., 1990; Thiemens, 1990; Lyons, 2001). However, recent and spatially widespread observations of Δ¹⁷O(O₃) have consistently shown Δ¹⁷O(O₃) = 26±1‰, suggesting that models are underestimating the role of ozone relative to HOₓ in NOₓ chemistry. We utilize a global compilation of observations of Δ¹⁷O(nitrate) to assess the representation of nitrate formation in a global chemical transport model (GEOS-Chem), assuming that the bulk oxygen isotopic composition of ozone (Δ¹⁷O(O₃)) = 26‰. The modeled Δ¹⁷O(nitrate) is roughly consistent with observations, with a mean modeled and observed Δ¹⁷O(nitrate) of (28.6±4.5‰) and (27.6±5.0‰), respectively, at the locations of the observations. Improved agreement between modeled and observed Δ¹⁷O(nitrate) is due to increased importance of ozone versus HO₂ and RO₂ in NOₓ cycling and an increase in the number and importance of nitrate production pathways that yield high Δ¹⁷O(nitrate) values. The former may be due to implementation of tropospheric reactive halogen chemistry in the model, which impacts ozone and HOₓ abundances. The latter is due mainly to increases in the relative importance of N₂O₅ hydrolysis, with the hydrolysis of halogen nitrates also playing an important role in remote regions.

The main nitrate formation pathways in the model below 1 km altitude are from NO₂ + OH and N₂O₅ hydrolysis (both 41%). The relative importance of global nitrate formation from the hydrolysis of halogen nitrates and hydrogen-abstraction reactions involving the nitrate radical (NO₃) is of similar magnitude (~5%). The formation of nitrate from the hydrolysis of organic nitrate has increased slightly in the US and decreased in China (changes <10%) due to changing NOₓ emissions from the year 2000 to 2015, although the global mean fractional importance (6%) remains unchanged as the regional changes counteract one another. Nitrate formation via heterogeneous NO₂ and NO₃ uptake and NO₂ + HO₂ are negligible (<2%). Although aerosol nitrate photolysis has important implications for O₃ and OH, the impacts on nitrate formation pathways are small.

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The model parameterization for heterogeneous uptake of NO\textsubscript{2} has significant impacts on HONO and oxidants (OH and ozone) in the model. HONO production from this reaction has been suggested to be an important source of OH in Chinese haze due to high NO\textsubscript{2} and aerosol abundances (Hendrick et al., 2014; Tong et al., 2016; Wang et al., 2017), with implications for the gas-phase formation of sulfate aerosol from the oxidation of sulfur dioxide by OH (Shao et al., 2019; Li et al., 2018b). More recent laboratory studies suggest that the reaction probability of NO\textsubscript{2} on aerosols is lower than that previously used in the model. Using an NO\textsubscript{2} reaction probability formulation that depends on the chemical composition of aerosols as described in Holmes et al. (2019) renders this reaction negligible for nitrate formation and has significant implications for modeled HONO, ozone, and OH. Although uncertainty also exists in the relative yield of nitrate and HONO from this reaction, the impacts of this assumption are negligible when we use these updated NO\textsubscript{2} reaction probabilities. Observations of $\Delta^{17}$O(nitrate) in Chinese haze events during winter (He et al., 2018b) may help to quantify the importance of this nitrate production pathway in a region where the model predicts it is significant.

Data availability. The GEOS-Chem model is available at: https://doi.org/10.5281/zenodo.1343547 (last access: 10 August 2018).

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/acp-20-3859-2020-supplement.

Author contributions. BA designed the study and performed the model simulations and calculations. All other authors provided model code and contributed to writing and analysis.

Competing interests. The authors declare that they have no conflict of interest.

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