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Xuexi Tie
NCAR

L. K. Emmons
National Center for Atmospheric Research

Larry Horowitz
NOAA

Guy Brasseur
Max-Planck Institute of Meteorology

Brian Ridley
NCAR

See next page for additional authors

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Authors

Xuexi Tie, L K. Emmons, Larry Horowitz, Guy Brasseur, Brian Ridley, Elliot Atlas, Craig Stround, Peter Hess, Andrzej Klonecki, Sasha Madronich, R. Talbot, and Jack E. Dibb

Effect of sulfate aerosol on tropospheric NO_x and ozone budgets: Model simulations and TOPSE evidence

Xuexi Tie,¹ Louisa Emmons,¹ Larry Horowitz,² Guy Brasseur,³ Brian Ridley,¹ Elliot Atlas,¹ Craig Stround,¹ Peter Hess,¹ Andrzej Klonecki,¹ Sasha Madronich,¹ Robert Talbot,⁴ and Jack Dibb⁴

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[1] The distributions of NO_x and O₃ are analyzed during TOPSE (Tropospheric Ozone Production about the Spring Equinox). In this study these data are compared with the calculations of a global chemical/transport model (Model for OZone And Related chemical Tracers (MOZART)). Specifically, the effect that hydrolysis of N₂O₅ on sulfate aerosols has on tropospheric NO_x and O₃ budgets is studied. The results show that without this heterogeneous reaction, the model significantly overestimates NO_x concentrations at high latitudes of the Northern Hemisphere (NH) in winter and spring in comparison to the observations during TOPSE; with this reaction, modeled NO_x concentrations are close to the measured values. This comparison provides evidence that the hydrolysis of N₂O₅ on sulfate aerosol plays an important role in controlling the tropospheric NO_x and O₃ budgets. The calculated reduction of NO_x attributed to this reaction is 80 to 90% in winter at high latitudes over North America. Because of the reduction of NO_x, O₃ concentrations are also decreased. The maximum O₃ reduction occurs in spring although the maximum NO_x reduction occurs in winter when photochemical O₃ production is relatively low. The uncertainties related to uptake coefficient and aerosol loading in the model is analyzed. The analysis indicates that the changes in NO_x due to these uncertainties are much smaller than the impact of hydrolysis of N₂O₅ on sulfate aerosol. The effect that hydrolysis of N₂O₅ on global NO_x and O₃ budgets are also assessed by the model. The results suggest that in the Northern Hemisphere, the average NO_x budget decreases 50% due to this reaction in winter and 5% in summer. The average O₃ budget is reduced by 8% in winter and 6% in summer. In the Southern Hemisphere (SH), the sulfate aerosol loading is significantly smaller than in the Northern Hemisphere. As a result, sulfate aerosol has little impact on NO_x and O₃ budgets of the Southern Hemisphere. *INDEX TERMS*: 0305

Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; *KEYWORDS*: tropospheric aerosol, NO_x, ozone

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1. Introduction

[2] Sulfate aerosol plays important roles in the Earth's radiation balance. It can directly affect the Earth's radiative budget by scattering radiation. It also can indirectly influence the radiation budget through its participation in cloud formation. Sulfate aerosol can also have strong interactions with oxidants in the atmosphere through heterogeneous surface reactions. It is well known that the hydrolysis of

N₂O₅ on sulfate aerosol impacts stratospheric nitrogen partitioning by converting reactive nitrogen oxide (NO_x = NO + NO₂) to a longer-lived nitrogen reservoir species, HNO₃. Including this reaction, models produce remarkably better agreement between calculated and observed NO_x concentrations in the stratosphere [Fahey *et al.*, 1993]. Reduction of NO_x due to volcanic eruption is clearly detected by ground based NO₂ measurements [Johnston *et al.*, 1992; Koike *et al.*, 1994]. Modeling calculations also show evidence that NO_x concentrations are significantly reduced when sulfate aerosol concentrations are greatly enhanced after large volcanic eruptions [Hofman and Solomon, 1989; Rodriguez *et al.*, 1991; Brasseur and Granier, 1992; Pitari and Rizi, 1993; Bekki and Pyle, 1994; Tie *et al.*, 1994].

[3] In the troposphere and stratosphere, NO_x is closely related to O₃ chemistry via two separate processes. In the

¹National Center for Atmospheric Research, Boulder, Colorado, USA.

²NOAA/GFDL, Princeton University, Princeton, New Jersey, USA.

³Max-Planck Institute of Meteorology, Hamburg, Germany.

⁴Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham, New Hampshire, USA.

troposphere, O₃ is produced photochemically in the cycling of NO to NO₂, which is facilitated by peroxy radicals formed during oxidation of carbon monoxide, methane, and other volatile organic compounds (VOCs); while in the stratosphere, O₃ is catalytically destroyed by NO_x. Nitrogen oxides are also intricately linked to the hydroxyl radical, OH, another key atmospheric oxidizing species. The reaction between NO₂ and OH leads to the formation of relatively stable nitric acid (HNO₃), which can be removed from the atmosphere by wet and dry deposition and hence provides an important source of nitrogen for the biosphere. NO_x also affects the production of OH. When NO_x changes from low to moderate levels, the oxidation of hydrocarbons results in the production of O₃. Enhanced O₃ results in greater production of OH via O₃ photolysis. Also, since O₃ strongly absorbs the Earth's infrared radiation, knowledge of the regional and global NO_x distribution is important for climate studies.

[4] Several studies suggest that hydrolysis of N₂O₅ on sulfate aerosol can play an important role in tropospheric chemistry. Model studies by *Dentener and Crutzen* [1993] and *Tie et al.* [2001] show that this heterogeneous reaction can reduce the tropospheric NO_x budget up to 50% in the Northern Hemisphere during winter. As a result, O₃ concentrations are reduced by 10 to 20% in the Northern Hemisphere. The direct in-situ measurement of the effect of hydrolysis of N₂O₅ on NO_x and O₃ concentrations is difficult because NO_x and O₃ concentrations are not only impacted by the hydrolysis, but are also affected by other chemical and physical processes such as gas-phase chemistry and transport. A simultaneous measurement of chemical species (N₂O₅, NO_x, and O₃) and sulfate aerosols can provide very useful information in order to verify the model results. However, there have been few observations to compare the global model assessments of the impact of N₂O₅ hydrolysis on tropospheric chemistry.

[5] In this paper, we compare model results to field observations of NO_x, O₃, and sulfate aerosol to demonstrate that the hydrolysis of N₂O₅ on sulfate aerosol has a significant impact on NO_x and O₃ budgets in the troposphere, and we will show that observations of NO_x and O₃ during TOPSE strongly support this conclusion.

[6] The paper is divided into several sections. Section 2 provides a description of the model assessment of the effect of hydrolysis of N₂O₅ on sulfate aerosol on global NO_x and ozone budgets, and comparison to the observations during TOPSE. Section 3 discusses the uncertainties in model calculations and their effect on the conclusions, and section 4 gives a summary of this study.

2. Method and Results

2.1. Model Assessment of Global NO_x and O₃ Budgets Due to N₂O₅ Hydrolysis

[7] The NCAR global chemical transport model (MOZART) is used in this study. The model is a comprehensive tropospheric chemical/transport model, calculating the global distribution of 56 gas-phase chemical species. The nitrogen species in the model include NO_x, HNO₃, N₂O₅, HNO₄, NO₃, and PAN (CH₃CO₃NO₂). Currently, HONO is not included in the MOZART model. The detailed model configurations (version 1) are described in *Brasseur*

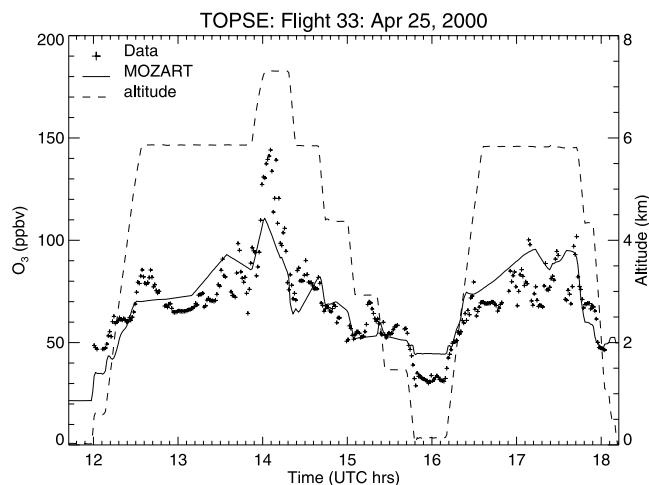


Figure 1. Calculated and measure O₃ concentrations during the TOPSE flight 33 (April 25/2000). The solid dots are the calculations, and the solid line is the measurements. The dashed line is the flight altitude. The hydrolysis of N₂O₅ on sulfate aerosol is included in the model.

et al. [1998]. The calculated climatological distributions of tropospheric chemical species have been validated by comparison to measurements [*Hauglustaine et al.*, 1998]. In this early version of MOZART, the hydrolysis of N₂O₅ is parameterized according to the method suggested by *Muller and Brasseur* [1995]. The results show that the model calculated tropospheric CO, O₃ and NO_x concentrations are generally consistent with the observations, especially in the tropics. The global OH budget is estimated by calculating the CH₄ chemical lifetime. The model estimate of CH₄ lifetime is about 10 years, which is comparable or slightly higher than previous estimations [*Prinn et al.*, 1987; *Tie et al.*, 1992]. In this study, the chemical and transport schemes are updated from the version used by *Brasseur et al.* [1998]. Heterogeneous reactions of N₂O₅ on sulfate aerosols are included, with the sulfate aerosol distribution prescribed based on a sulfate aerosol mass distributions. The sulfate area is then calculated from sulfate aerosol mass loading with an assumption that the mean radius of sulfate aerosols is 0.15 μm [*Tie et al.*, 2001]. The kinetic reaction rates are based on laboratory measurement [*Hu and Abbatt*, 1997]. Advection of tracers is performed using the flux-formatted semi-Lagrangian advection scheme of *Lin and Rood* [1996]. The deep convection scheme developed by *Zhang and McFarlane* [1995] is included in the model. The detailed description of the updated MOZART is described by L. W. Horowitz, et al. (A global simulation of tropospheric ozone and related tracers: Description and evaluation of MOZART, version 2, manuscript in preparation, 2001). The model can be either driven by ECMWF (European Centre for Medium-Range Weather Forecasts) assimilated wind fields or by NCAR- CCM (Community Climate Model) wind fields. For this work, ECMWF assimilated wind fields for 2000 were used as dynamical inputs in the model. The ECMWF fields have a horizontal resolution of 2 degree by 2 degree and 60 levels to 0.1 mb, so that local synoptical scale transport events can be captured in the model during TOPSE flights. Figure 1 shows an example of

the model calculated O₃ during the TOPSE flights. Synoptic events such as stratospheric O₃ intrusions are clearly indicated from the model calculations. More detailed analysis is given by L. K. Emmons et al. (The budget of tropospheric ozone during TOPSE from two CTMs, manuscript submitted to *Journal of Geophysical Research*, 2002).

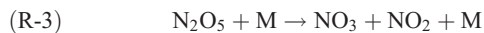
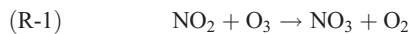
[8] The reaction coefficient of the hydrolysis of N₂O₅ can be written as [Schwartz, 1986];

$$k_{\text{het}} = [r/Dg + 4/(c\gamma)]^{-1} A \times 10^8 \quad (1)$$

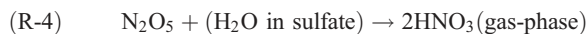
Where $c = [8kT/m]^{1/2}$ (cm/s) is the mean molecular speed of the gas at temperature T, $A(\text{m}^2/\text{cm}^3)$ is the surface area density of the particles, γ is the uptake coefficient, $m(\text{gram})$ is the molecular mass of the gas-phase molecule under consideration, k is the Boltzmann constant, Dg (cm^2/s) is the gas-phase diffusion coefficient and r is the mean radius of the aerosol particles. According to the calculation of *Perry and Green* [1984], Dg is close to $0.1 \text{ cm}^2/\text{s}$. To convert the mass into surface area, we assume aerosols are spherical with a mean radius of $0.15 \text{ }\mu\text{m}$ according to the observation by *Blake and Kato* [1995]. The sulfate surface area is growth with humidity according to an empirical formula suggested by *Shettle and Fenn* [1979]. According to the analysis of *Dentener and Crutzen* [1993], when $\gamma < 0.1$, the term $4/(c\gamma)$ dominates, and Equation (1) can be written as;

$$k_{\text{het}} = (c\gamma)/4 \times A \times 10^8 \quad (2)$$

[9] The effect of the hydrolysis of N₂O₅ on sulfate aerosols on NO_x starts with the following gas-phase reactions:



The ratio of the reaction coefficients of R-2 and R-3 determines the amount of N₂O₅, which is stabilized relative to that which is decomposed. The ratio is strongly temperature dependent. When the temperature is low, N₂O₅ concentration is high, suggesting that during winter it is more favorable for the formation of N₂O₅. When N₂O₅ is available in the atmosphere, hydrolysis of N₂O₅ on sulfate aerosol takes place, i.e.:



The net result from R-1 to R-4 is to generate a chain pathway that converts NO₂ to HNO₃. However, this conversion only occurs during nighttime. During daytime, NO₃ is quickly destroyed by photo-dissociation, and the reaction of R-2 is slowed. The conversion of NO_x to HNO₃ is mainly through the following reaction



Because the daytime conversion of NO₂ to HNO₃ is much slower than the nighttime conversion, as indicated in Figure 2,

R-5 has a small effect on the net loss of NO₂ when the nighttime loss is included. Figure 2 is a schematic of the conversion of NO_x into HNO₃ during nighttime and daytime. During nighttime, the conversion of NO_x into HNO₃ is through a series of chain reactions. The numbers in parentheses show the chemical time constants (hours) of the reaction averaged over the NH below 5 km during winter. The reaction with the slowest rate is the rate limiting step in the chain, which determines the net rate of the conversion. In these reactions (R-1 to R-4), the rate-limiting step is R-1 with a chemical time constant of 26 hours. The time constant for hydrolysis of N₂O₅(R-4) on sulfate is about 2.5 hours (with uptake coefficient $\gamma = 0.1$) which is about 10 times faster than R-1. However, without hydrolysis of N₂O₅, the conversion of NO_x to HNO₃ will be terminated during nighttime. In this case, daytime conversion (R-5) is the only pathway to convert NO₂ to HNO₃. The chemical time constant of R-5 is about 5 times longer than that during nighttime when hydrolysis of N₂O₅ on sulfate is considered. This implies that hydrolysis of N₂O₅ on sulfate provides a very effective conversion of NO_x to HNO₃. However, from the above analysis, the following conditions are required for this conversion: (1) sunlight is low (nighttime or polar night), (2) temperature is low, leading to a low decomposition rate of N₂O₅ by R-3, so that the N₂O₅ concentration is high, and (3) sulfate aerosol surface areas are relatively high, producing a high rate of hydrolysis of N₂O₅. Such conditions are often found in the NH at high latitudes in winter. It is noted that including the hydrolysis of N₂O₅ leads to increase in HNO₃. Generally, the calculated HNO₃ concentration is overestimated by chemical models [Chatfield, 1994; Jacob et al., 1996; Hauglustaine et al., 1998; Wang et al., 1998a, 1998b]. In middle latitudes of the NH, the zonally averaged calculated HNO₃/NO_x ratio is about 5 in summer and 5 to 20 in winter in the lower and middle troposphere, which consistent to other calculations [Chatfield, 1994; Jacob et al., 1996; Wang et al., 1998a, 1998b]. The problem of the overestimation of HNO₃ could be due to several chemical and physical processes. The problem is beyond the scope of this paper, and will not be discussed in this paper.

[10] To provide a global view and to understand the spatial and temporal distributions of the effect of hydrolysis of N₂O₅ on sulfate aerosol (with an uptake coefficient of 0.1 as a standard calculation) on NO_x and O₃ budgets, the model was run with and without R-4. Then the differences between the model runs were analyzed for the impact of R-4 on the global NO_x and O₃ distributions in different seasons. Figure 3 shows the changes in NO_x at surface due to including R-4 in December and in June. The results show that hydrolysis of N₂O₅ on sulfate aerosol has a significant impact on global NO_x distributions. The maximum NO_x reduction due to this reaction occurs at high latitudes in the NH during winter. At latitudes between 50°N and the North Pole, the magnitude of the reduction is about 60 to 90% (corresponding to a few hundred pptv in absolute concentrations), indicating that a significant amount of NO_x is removed by the sulfate aerosol in and near polar night region. During summer, reduction of NO_x due to this reaction is smaller (less than 20 percent in most of the globe) than during winter. In the Southern Hemisphere, the changes in NO_x are small because most anthropogenic sulfur emission occurs in the NH. During summer the effect

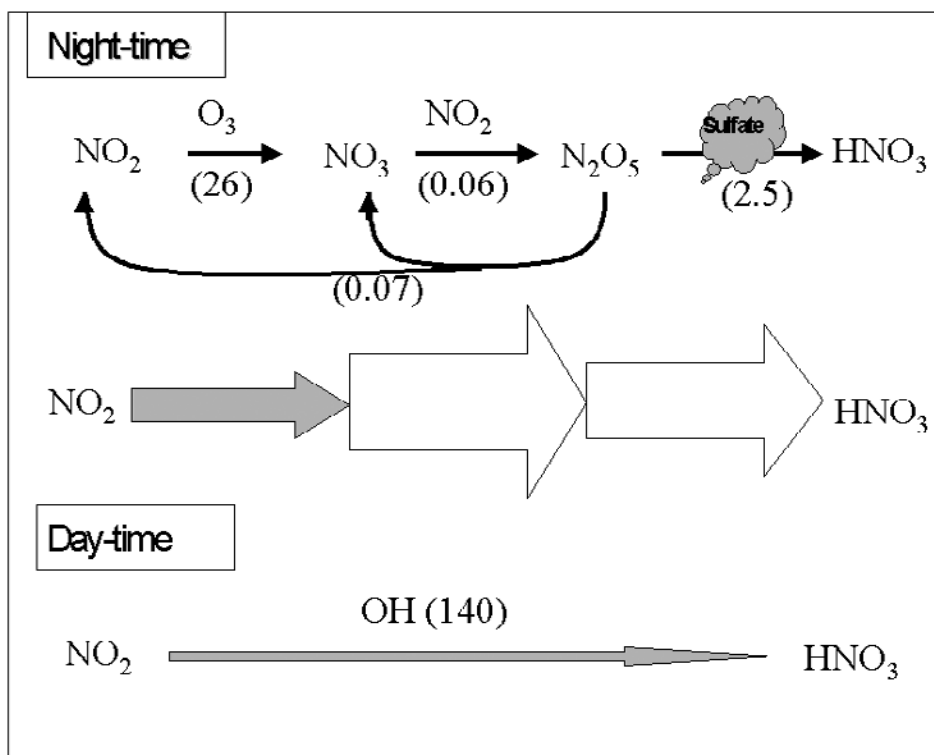


Figure 2. A schematic of the conversion of NO_x into HNO₃ during nighttime and daytime. The numbers in parentheses are the chemical reaction time constants (hours) averaged over the NH below 5 km during winter. The size of the arrows is proportional to the reaction rates.

of R-4 on NO_x concentrations in the SH is negligible. Some regional characters are also noticed. In the polluted regions over North America (in the US and southern Canada), despite the largest changes in absolute concentrations in NO_x (not show), the percentage changes are smaller than the regions in high latitudes near the North Pole because the background NO_x concentrations are very high in the US and southern Canada. In the Southern Hemispheric winter there is a 20 to 30% change in NO_x at 60°S where large amounts of dimethyl sulfide (DMS) are released, and oxidized to form sulfate aerosols [Tie *et al.*, 2001].

[11] O₃ is produced in the troposphere by oxidation of hydrocarbons and CO, catalyzed by HO_x and NO_x. As a result, the large reduction in NO_x due to hydrolysis of N₂O₅ on sulfate aerosol will lead to changes in tropospheric O₃ concentrations. Figure 4 shows the calculated surface O₃ reductions in winter (December) and in summer (June) due to R-4. It shows that O₃ concentrations are significantly reduced in the NH. The maximum O₃ reduction (20%) occurs at midlatitudes during winter. The O₃ reduction at high latitudes is smaller than at midlatitudes even though the decrease in NO_x at high latitudes is largest. This is a result of OH concentrations being lower at high latitudes than at midlatitudes during winter, leading to a lower ozone production in this region. During summer at high latitudes in the NH, although the NO_x reduction is much smaller than during winter, the reduction of O₃ concentrations occurs with a similar magnitude (10%) compared to that during winter. This is a result of the strong seasonality of OH, i.e., mean OH in the NH is normally 3 times higher in summer

than in winter [Tie *et al.*, 1992]. Because O₃ production in the troposphere depends on the rate of the reactions of OH with CO, CH₄, and VOC as well as the rate of NO₂ photolysis, the combination of the higher OH concentrations and stronger NO₂ photolysis produces a relative higher O₃ reduction in this region due to the impact of hydrolysis of N₂O₅. In the SH, the reduction in O₃ concentrations is not significant. Some regional characters are also noticed. In some polluted regions such as in the eastern US, the NO_x concentrations are very high. The reduction of NO_x due to hydrolysis of N₂O₅ produces relatively smaller changes in O₃ due to the fact that the NO_x and O₃ relationship is non-linearly correlated and complicated as suggested by Sillman *et al.* [1990].

[12] Figures 5a and 5b show the zonally averaged changes in NO_x, O₃, and OH in June and December due to R-4, in percent and in mixing ratio respectively. The upper panels of Figure 5a show the percentage changes in NO_x. It shows that NO_x reduction has very strong latitudinal and altitudinal variations. The NO_x reduction is well confined in the NH, with a maximum of 80 to 90% reduction at 60°N in the lower troposphere in December, and a very sharp gradient in the reduction takes place between 50°N and the equator. In the tropical region, the reduction is negligible. In the SH, the maximum reduction is about 10% in high latitudes in June as result of the high DMS emission in this region. The altitudinal distribution of the reduction reveals that the reduction is highest in the lower troposphere, and it rapidly decreases with altitude. At 15 km, the reduction decreases to 20%, suggesting that the greatest

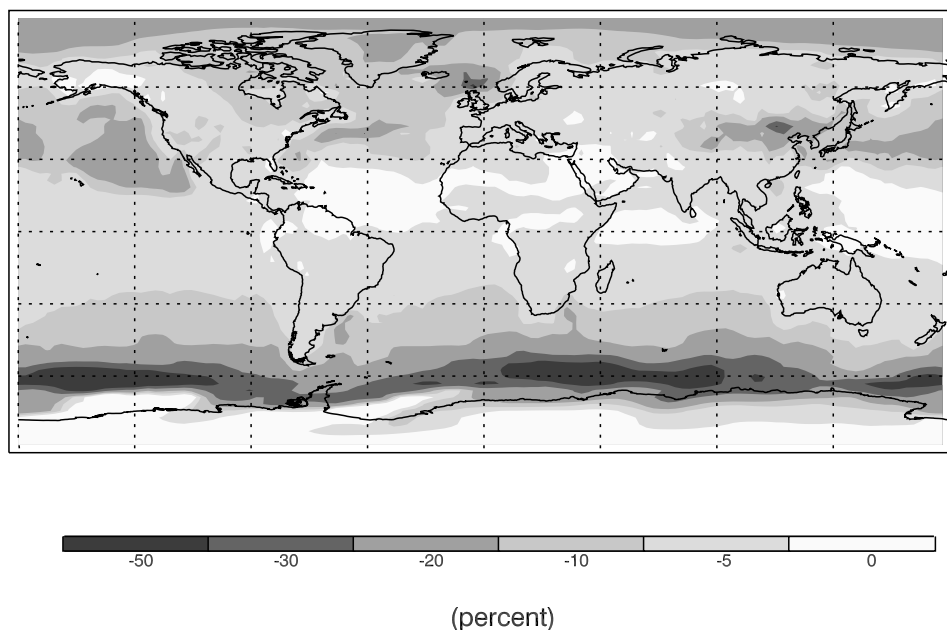
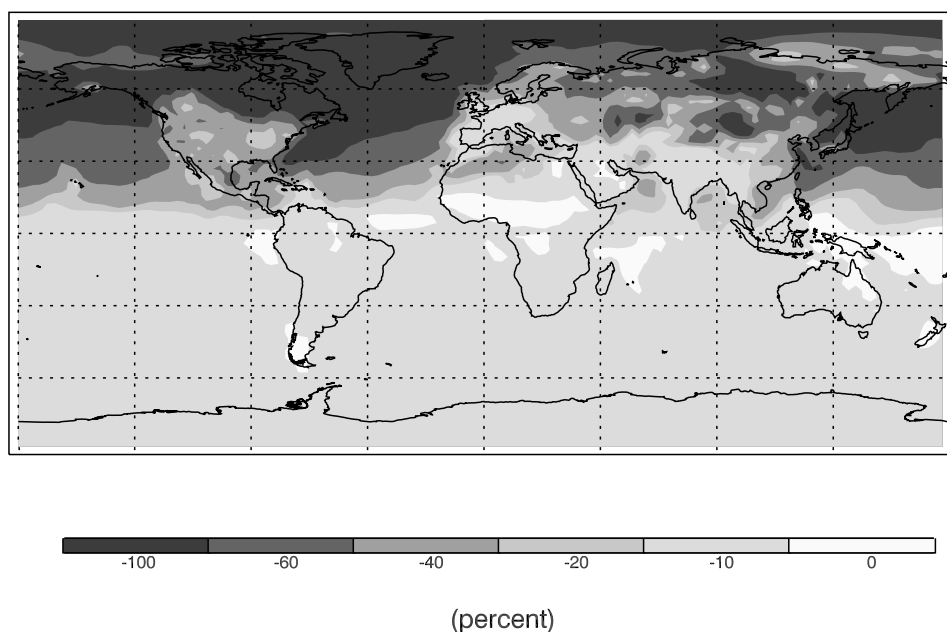
NO_x reduction in JuneNO_x Reduction in Dec.

Figure 3. Calculated changes (percent) due to hydrolysis of N₂O₅ on sulfate aerosol ($\gamma = 0.1$) for NO_x concentrations at the surface in December (top) and in June (bottom).

NO_x reduction is well confined in the lower troposphere, consistent with the location of most of the sulfate aerosols [Tie *et al.*, 2001]. We note that the maximum absolute changes in the NH are near the surface (see Figure 5b). However, the percentage change is located between 2 and 6 km (see Figure 5a) due to the fact that the background values are the highest at the surface.

[13] The middle panels of Figure 5a show the changes of O₃. The O₃ reduction is limited to the NH, with a

maximum of 10% reduction between 50°N and the North Pole in December, and 8 to 10% in June. A very sharp latitudinal gradient of the reduction takes place between midlatitudes and the equator. Except in this transition region, the reduction is relatively small in the SH. Between 50°N and the North Pole the chemical lifetime of O₃ is relatively long, and O₃ concentrations in these regions are well mixed. The reduction of O₃ is also confined to the lower to middle troposphere, with a maximum reduction of

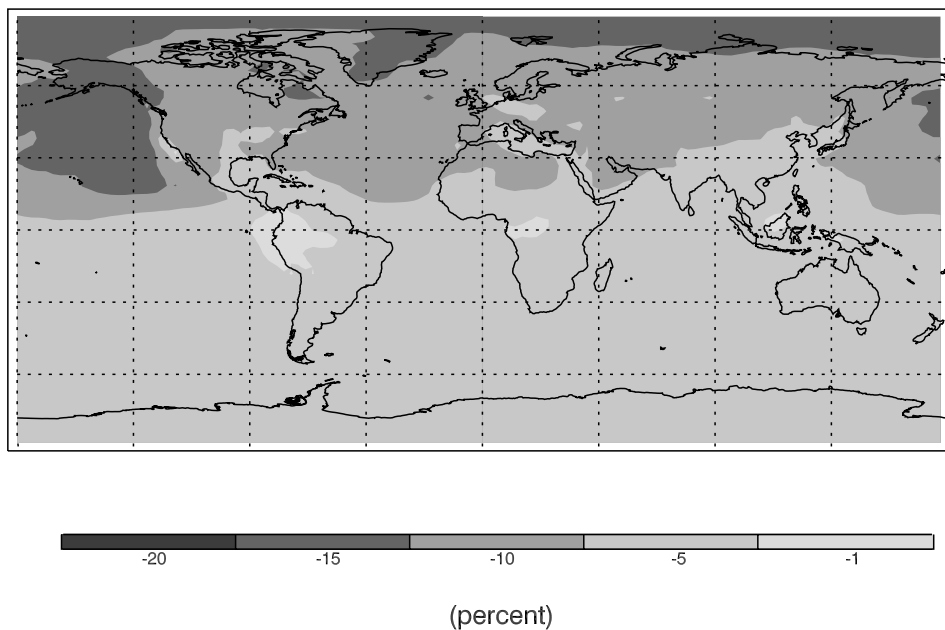
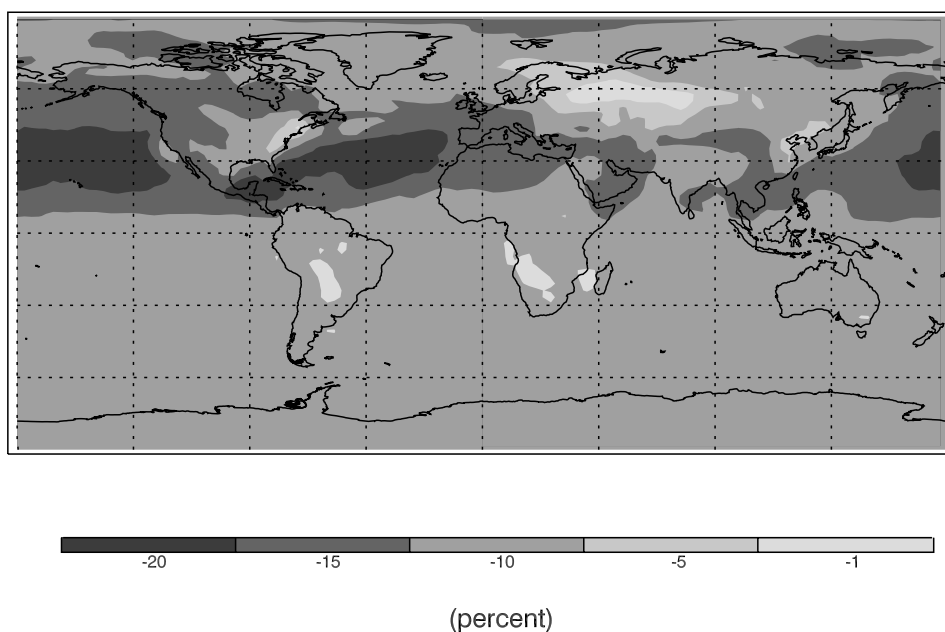
O₃ reduction in JuneO₃ Reduction in Dec.

Figure 4. Same as Figure 3 except for O₃.

10% below 6 km, decreasing with altitude to a reduction of 2% above 10 km.

[14] The lower panels of Figure 5a show the percentage changes of OH. The reduction of OH is correlated with the O₃ reduction, suggesting that the reduction of O₃ concentrations produces the reduction of OH concentrations. In the NH, the largest OH reduction is located in 50°N in the lower troposphere in December with a maximum of 30 to 40% reduction. Despite the largest reduction of the absolute changes in June (see Figure 5b), the percentage changes

in OH are smaller in June than in December because the background values are higher in summer than in winter. In the SH, the reduction of OH is very small. The reduction of OH is also confined to the lower to middle troposphere. Above 10 km the reduction of OH is very small.

[15] Figure 6 shows seasonal and latitudinal variations of the reduction of column NO_x and O₃ due to R-4. A strong seasonal variation is shown in NO_x and O₃ reduction, especially at middle and high latitudes in the NH. However, there is about a 2–3 month lag between the maximum

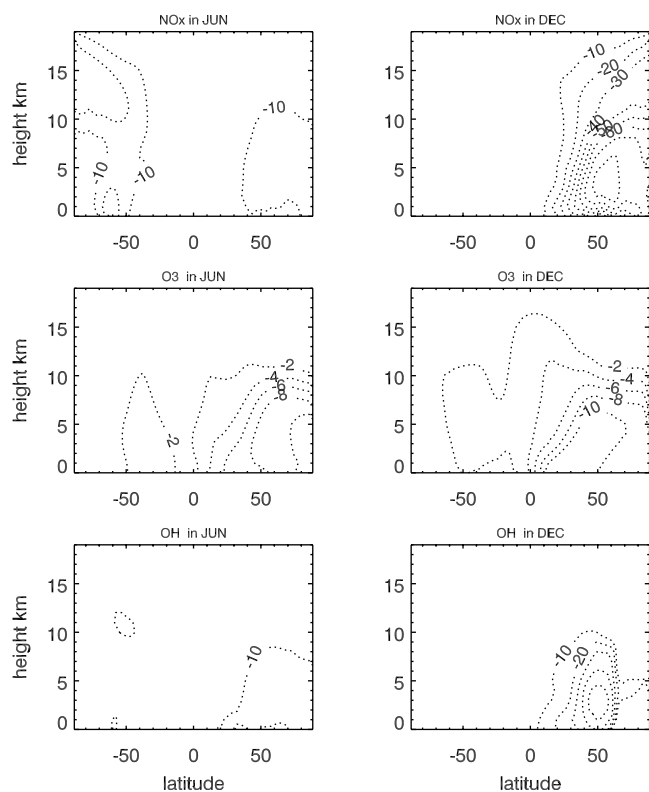


Figure 5a. Calculated zonally averaged changes (%) due to hydrolysis of N₂O₅ on sulfate aerosols for NO_x (upper panels), O₃ (middle panels), and OH (lower panels) in June and December.

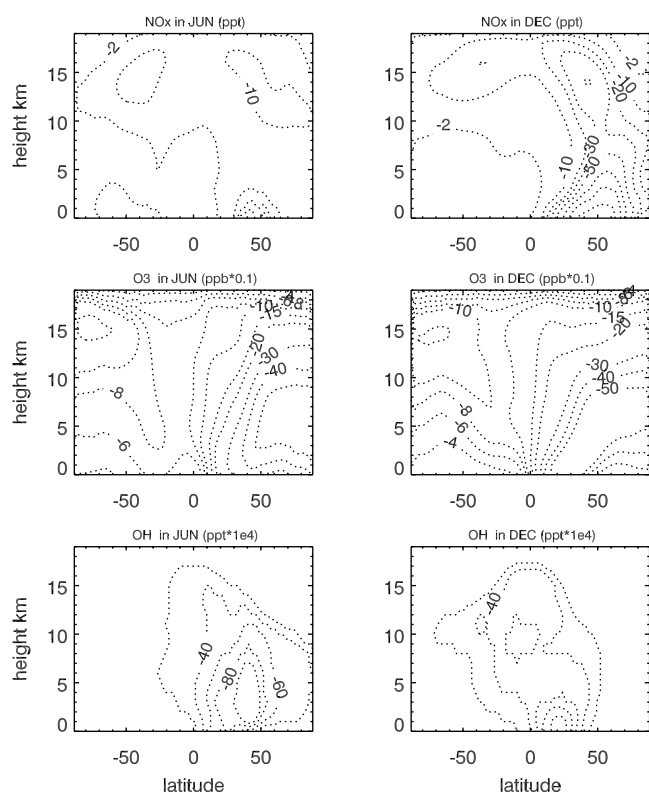


Figure 5b. Same as Figure 5a except for changes in mixing ratio.

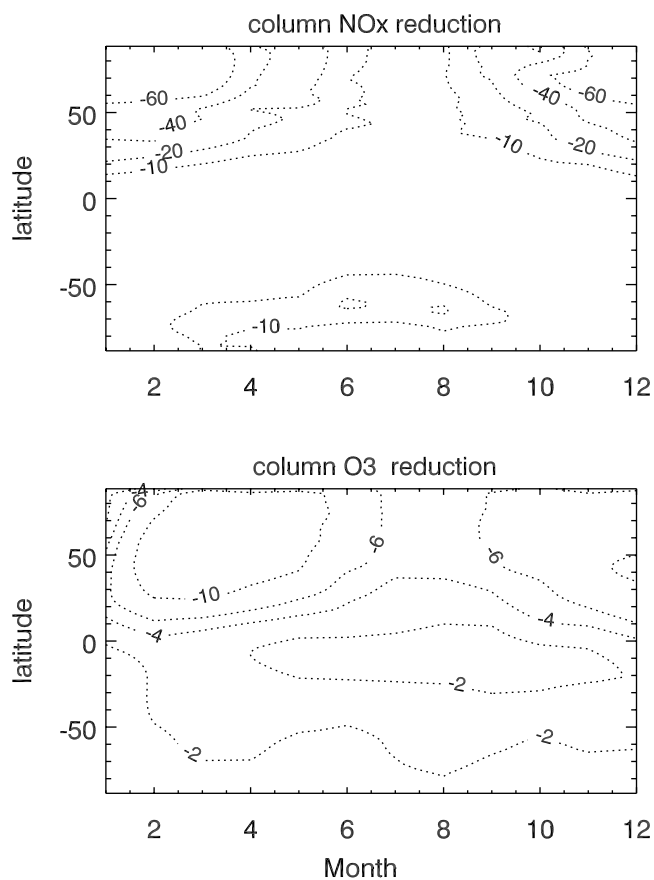


Figure 6. Calculated latitudinal-seasonal reductions in tropospheric column NO_x (top) and O₃ (bottom) due to hydrolysis of N₂O₅ on sulfate aerosol.

reduction of O₃ and NO_x. This is because the maximum NO_x reduction occurs in winter when OH is low. Because OH is a key species for catalytically producing O₃, the low OH concentrations in winter have little impact on O₃ concentrations even though the NO_x reduction is at a maximum. In early spring, however, the reduction of NO_x is still high, and OH concentrations increase, leading to a maximum in O₃ reduction. In the northern high latitude, the reduction of NO_x is at a maximum between November and March with 60% reduction, and is at a minimum in August with less than 10% reduction. The reduction of O₃ is at a maximum between February and May with 10% reduction, and is at a minimum in August with less than 6% reduction.

[16] To better understand the spatial and temporal changes of NO_x due to hydrolysis of N₂O₅, Figure 7 shows the zonally averaged time constant to convert NO_x to HNO₃ due to R-5, R-4, and R-1 in June and December. It shows that the rate of OH reacting with NO₂ (R-5 in upper panels) is higher in the tropics than in high latitudes, and is higher in summer than in winter. The rate of hydrolysis of N₂O₅ (R-4 in middle panels) is higher in the NH than in the SH with a maximum in northern middle latitudes of the lower troposphere due to higher sulfate aerosol concentrations. However, the seasonal variability of R-4 is relatively small. The rate of NO₂ reacting with O₃ (R-1 in lower panels) is also higher in the NH than in the SH with a maximum in northern middle latitudes of the lower troposphere due to

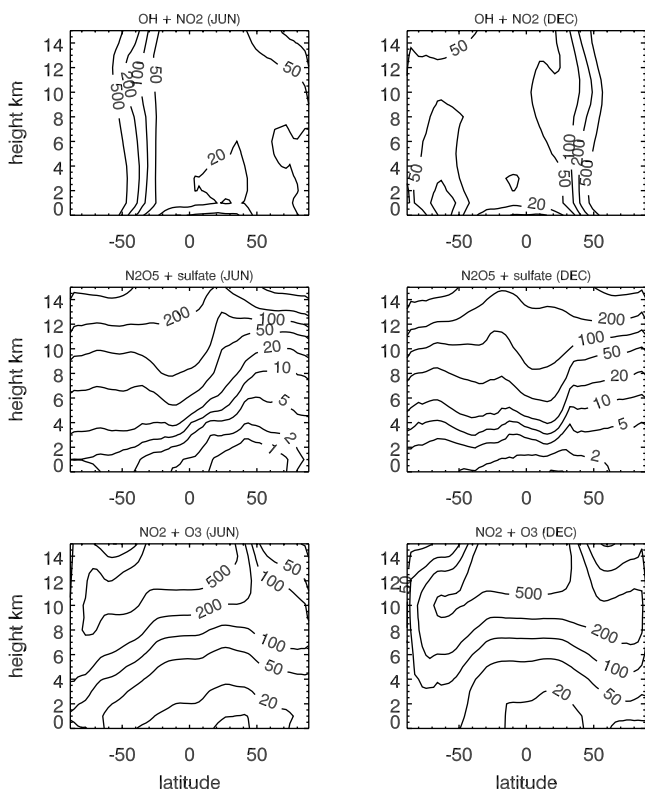


Figure 7. Calculated zonally-averaged chemical time constants of NO_x (hours) due to the chemical reaction of OH + NO₂ (upper panels), the hydrolysis of N₂O₅ on sulfate aerosol (middle panels), and the chemical reaction of NO₂ + O₃ in June and December.

higher O₃ concentrations. Among the reactions, the reaction R-1 is slower than the reaction R-4, indicating that the reaction R-1 is the rate limiting reaction to destroy NO₂ due to hydrolysis of N₂O₅. Comparing the time constants of R-1 and R-5, we see that the hydrolysis provides a fast NO_x chemical destruction in high latitudes during winter in the lower and middle troposphere, especially at high latitudes during winter. However, in the tropics, the reaction of R-1 is normally slower than the reaction R-5. Thus, the hydrolysis plays an insignificant role in destroying NO_x in the tropics.

[17] To provide a hemispheric view of the effect of hydrolysis of N₂O₅ on sulfate aerosol on NO_x and O₃ budgets, we calculate the average changes in NO_x and O₃ in the Northern and the Southern Hemispheres during winter and summer (see Figure 8). Figure 8 show that the globally averaged reduction of NO_x has a very strong seasonal variation, with a reduction of 38 and 6% in December and June, respectively. More of the reduction occurs in the NH than in the SH. In the NH, the reduction of NO_x is 47 and 7% during winter and summer, respectively. While in the SH, the reduction of NO_x is 3 and 5% during December and June, respectively. Despite the strong seasonal variation of the reduction of NO_x, the globally averaged reduction of O₃ has a weak seasonal variation, with 6 and 4% during December and June, respectively. However, in December the O₃ reduction shows a large hemispheric asymmetry, with 8 and 2% in the NH and the SH, respectively. We also note that at the present, the model

tends to overestimated HNO₃ concentrations, and adding the hydrolysis of N₂O₅ tend to further increase in HNO₃ concentrations. Because the overestimation of the HNO₃ is often found by other chemical models [Chatfield, 1994; Wang *et al.*, 1998], there are may be some chemical and physical processes which are mistreated in models.

2.2. Comparison to the Results During TOPSE

[18] The TOPSE experiment took place from February to May 2000 in a series of 7 round trip missions from Colorado to northern latitudes [Atlas *et al.*, 2002]. The experiment covered a latitude range from 40°N to near the North Pole, and from 30 to 8000 meters in altitude. The experiment measured O₃, NO_x, sulfate aerosol and other trace gases which provides a unique characterization of the temporal and spatial distribution of these species to evaluate the effect of hydrolysis of N₂O₅ on sulfate aerosol on NO_x and O₃ concentrations in the free troposphere. Furthermore, the measurements are located in the region where the model indicates the hydrolysis of N₂O₅ will have the maximum impact on NO_x and O₃.

[19] To compare the model results and observations, the model results were interpolated to the TOPSE flight tracks. Averages for each of the 7 missions were then computed for

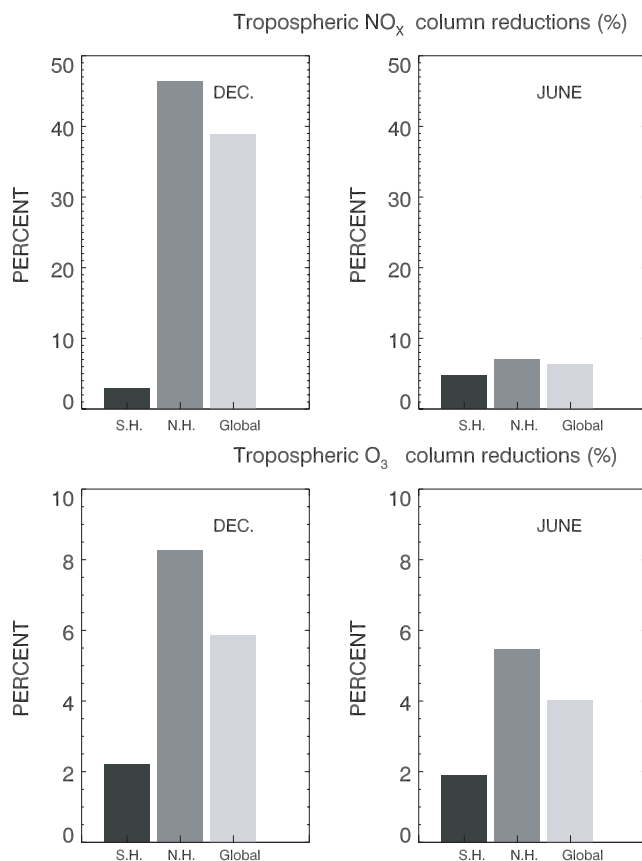


Figure 8. Calculated reductions in NO_x (top) and O₃ (bottom) budgets due to hydrolysis of N₂O₅ on sulfate aerosol in December and in June, respectively. The black bars are the averaged reductions in the SH; the light-black bars are the averaged reductions in the NH; and the gray bars are the averaged reductions for the globe.

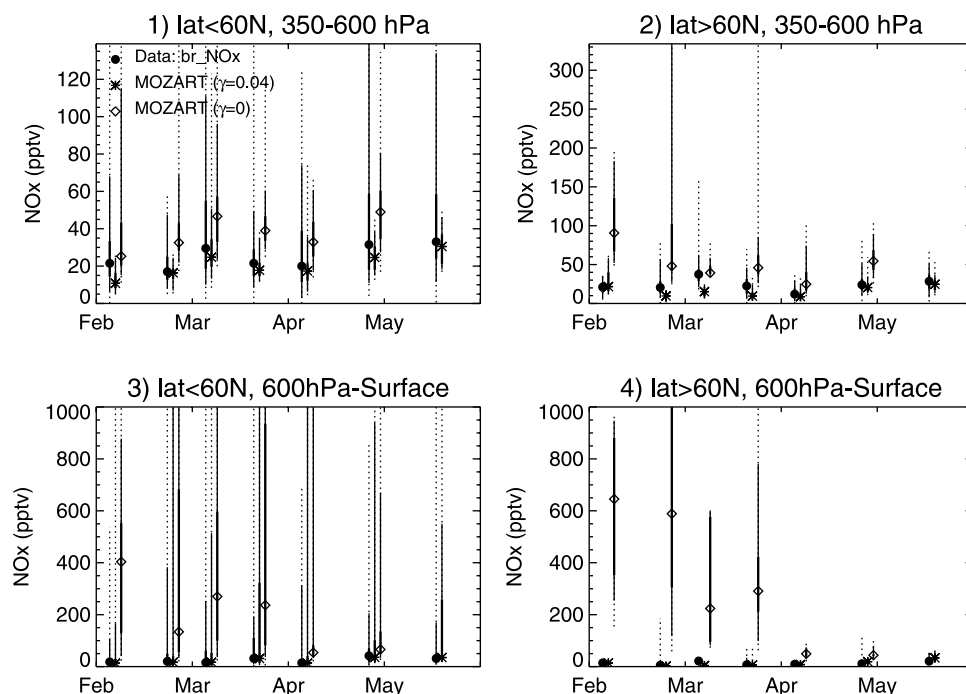


Figure 9a. Comparison of the calculated to the observed NO_x concentrations (pptv) during TOPSE in the following 4 different regions; (1) latitudes <60°N between surface and 600 hPa, (2) latitudes >60°N between surface and 600 hPa, (3) latitudes <60°N between 600 and 300 hPa, and (4) latitudes >60°N between 600 and 300 hPa. The data are averaged for each flight. The black dots are the measured NO_x concentrations; the asterisks are the calculated values with hydrolysis of N₂O₅ on sulfate aerosol ($\gamma = 0.04$); and the diamonds are the calculated values without hydrolysis of N₂O₅ on sulfate aerosol. The symbols indicate the median values, with thick lines between 25% and 75% of the data, thin lines 5% and 95% and dashed lines between extrema.

observations and model results. The data were divided into the following four regions: (1) latitudes <60°N between 600 and 300 hPa, (2) latitudes >60°N between 600 and 300 hPa, (3) latitudes <60°N between surface and 600 hPa, and (4) latitudes >60°N between surface and 600 hPa. Comparison of the 2 model runs with and without N₂O₅ hydrolysis and observations (Figure 9a) shows that there is clear evidence that hydrolysis of N₂O₅ has an important effect on NO_x concentrations during TOPSE. With the hydrolysis of N₂O₅, the calculated NO_x concentrations are generally consistent with the measured values. However, without hydrolysis of N₂O₅, the model calculation significantly overestimates observed NO_x concentrations, especially in region 4 in winter (600 pptv by the model via 20 pptv by the measurement). Furthermore, discrepancies between measured and modeled NO_x concentrations have some interesting spatial and seasonal characteristics. For example, in the regions where sulfate aerosol is high (at lower altitudes, in regions 1 and 2), the discrepancies are higher than the regions where sulfate aerosol is low (at higher altitudes, in regions 3 and 4). There is also a strong seasonal variation in which the overestimation of observed NO_x reaches a maximum during winter and early spring, and then significantly decreases during late spring. These spatial and seasonal variabilities are consistent with the model assessment shown in section 2.1. Figure 9b shows the calculated ratio of NO_x/NO_y during the TOPSE flights with and without hydrolysis of N₂O₅ along

with the observed ratio. Because the model is generally overestimated NO_y, the calculated ratio has a systemic bias and tend to be lower than the observed ratio. A sensitivity study (not shown) suggests that increase the washout of HNO₃ can significantly reduce the concentrations of NO_y. With the hydrolysis, the calculated NO_x/NO_y ratio is generally overestimated by a factor of 2–10 in comparison to the TOPSE observation. However, without hydrolysis of N₂O₅, the calculated NO_x/NO_y ratio is very high in the lower troposphere during winter when hydrolysis of N₂O₅ plays an important role in controlling NO_x concentrations, suggesting that despite the bias of the lower NO_x/NO_y ratio in the calculation, the calculated NO_x concentration is still too high in comparison to the TOPSE observation. In the upper troposphere, however, the effect of hydrolysis is small. The change of the ratio of NO_x/NO_y due to the hydrolysis varies within the range of the calculated bias, showing even somewhat improvements in the calculated NO_x/NO_y ratio. In these regions (northern middle to high latitudes in the upper troposphere), we cannot see the improvement in modeled NO_x concentrations and NO_x/NO_y ratio with hydrolysis of N₂O₅ before a further improvement of modeled NO_x/NO_y ratio is made.

[20] During TOPSE the observed O₃ concentrations also show evidence that hydrolysis of N₂O₅ has an important effect on O₃ concentrations in spring. Figure 10 shows that the simulated O₃ concentrations are generally in agreement

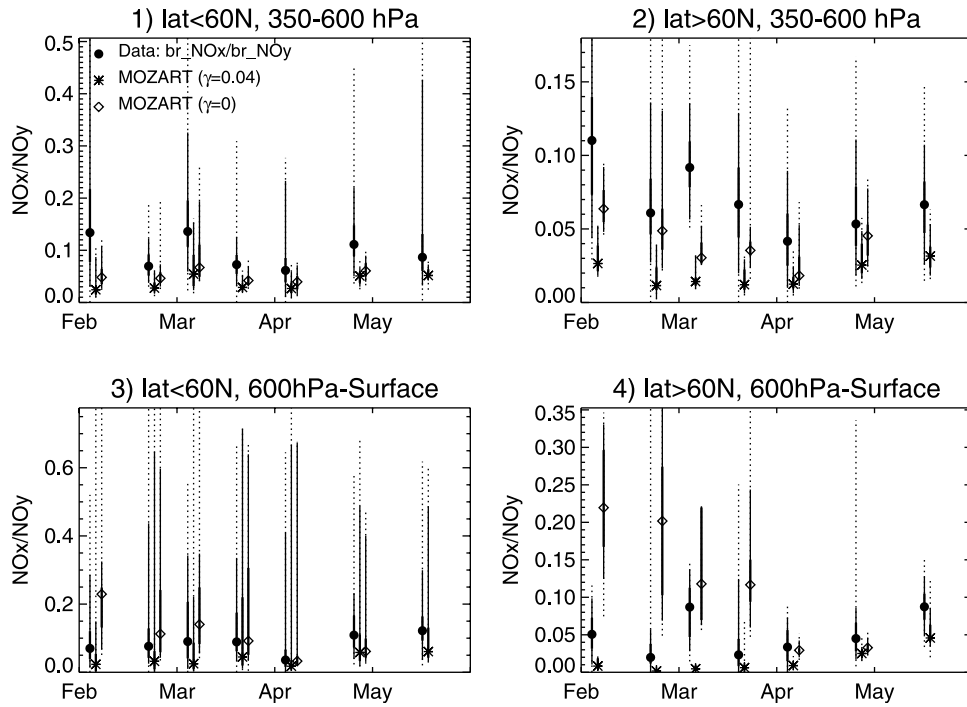


Figure 9b. Same as Figure 9a except for NO_x/NO_y.

with the observed O₃ concentrations when R-4 is included. However, a large discrepancy is found between the measurement and model calculation when R-4 is not included. The discrepancy has a very strong seasonal variability. For example, O₃ is significantly overestimated in the lower troposphere in spring with a maximum discrepancy of 40 ppbv. In winter, however, the discrepancies are very small (less than 10 ppbv). The seasonality of the discrepancy

is consistent with the model assessment shown in section 2.1. The cause of this seasonal variation is discussed in section 2.1. The statistics of the difference between the modeled O₃ and the observed O₃ during TOPSE is ranged from +1% to -6% (Emmons et al., submitted manuscript, 2002). Thus, the calculated large O₃ discrepancy (20 ppbv) without hydrolysis of N₂O₅ suggests that the overestimated O₃ is mainly due to the hydrolysis.

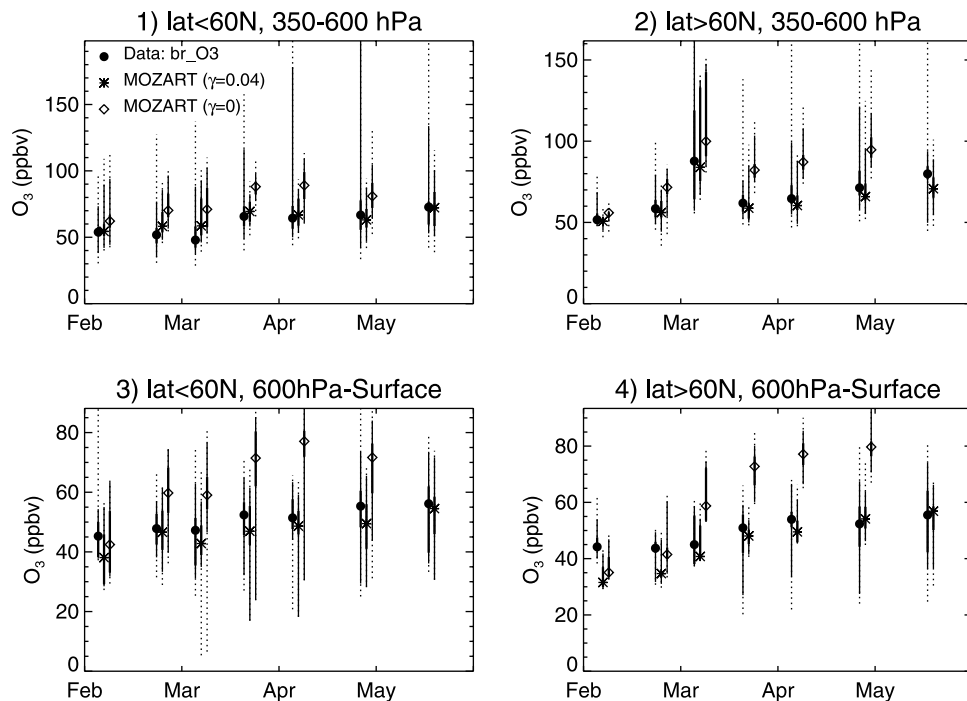


Figure 10. Same as Figure 9a except for O₃.

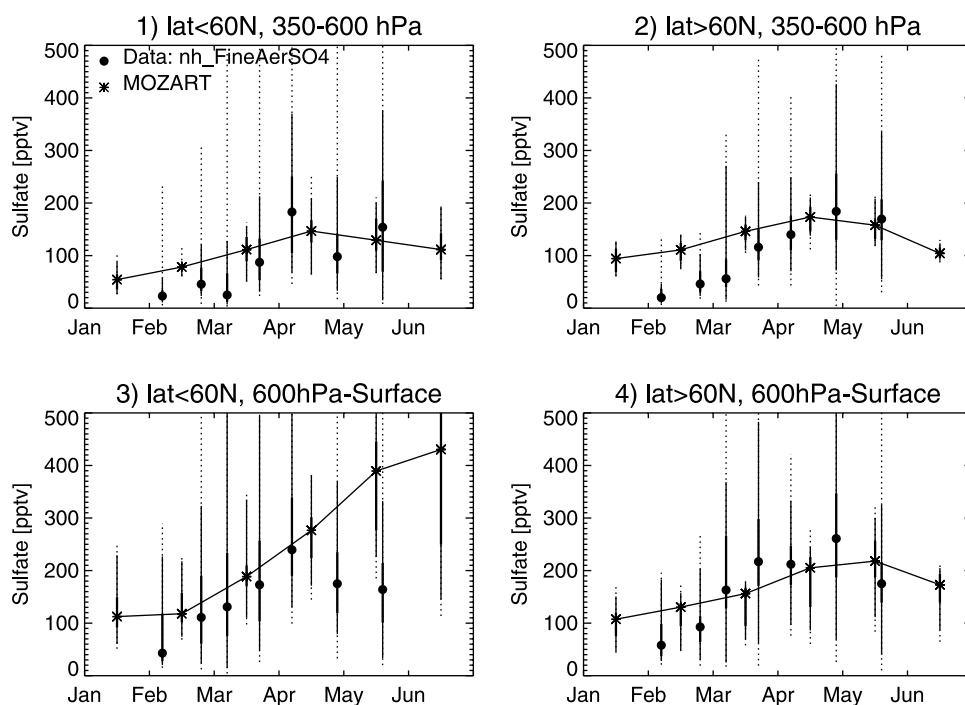


Figure 11. Comparison of the calculated to the observed sulfate aerosol concentrations (pptv) during TOPSE in the following 4 different regions as in Figure 7. The black dots are the measured sulfate aerosol concentrations, and the asterisks with solid line are the calculated values.

[21] From the above comparison between the model calculations and the measurements during TOPSE, there is a clear indication that N₂O₅ hydrolysis on sulfate aerosols plays a very important role in controlling NO_x and O₃ budgets in the NH troposphere during winter and spring. The effect on seasonal, latitudinal, and altitudinal patterns are consistent with the model assessments, confirming that this observed evidence is solid and significant. However, as expected, there are uncertainties in the model calculation. To further confirm this conclusion, uncertainties related to the calculations of hydrolysis of N₂O₅ on sulfate aerosol in the model will be analyzed in the following section.

2.3. Uncertainty Analysis

[22] There are uncertainties in the model in estimating the effect of the hydrolysis of N₂O₅ on NO_x and O₃ concentrations. The major uncertainties are related to the predicted aerosol loadings and the measured heterogeneous uptake coefficient γ indicated in Equation (2). From Equation (2), we see that the reaction coefficient k_{het} is a linear product of uptake coefficient γ and sulfate surface area A . Uncertainties in γ and A will produce the uncertainties in the reaction coefficient k_{het} , and thus in the model calculation of the effect of R-4 on NO_x concentrations.

[23] The reaction of N₂O₅ on sulfate aerosol, which produces HNO₃, has been measured by several groups who have found values of γ ranging from 0.02 to 0.10 [Van Doren *et al.*, 1991; Hanson and Ravishankara, 1992; Fried *et al.*, 1994; George *et al.*, 1994; Hanson and Lovejoy, 1994; Zhang *et al.*, 1995; Robinson *et al.*, 1997]. The lowest uptake coefficient is observed by George *et al.* [1994], who report values decreasing from 0.03 to 0.013 with increasing temperature. Hu and Abbatt [1997] measured the uptake

coefficient at various atmospheric conditions. Their measurement shows that the uptake coefficient varies from 0.01 to 0.1 depending on air temperature, humidity, and aerosol composition. When temperature and humidity values are close to tropospheric conditions, the reaction coefficient is measured between 0.017 and 0.06. However, when humidity and temperature are very low (stratospheric condition), the reaction coefficient is around 0.1 which is the value widely used in stratospheric models [Hofman and Solomon, 1989; Rodriguez *et al.*, 1991; Tie *et al.*, 1994].

[24] The model predicted sulfate aerosol has been analyzed by Tie *et al.* [2001]. The simulated global sulfate aerosol distributions are generally in agreement with measurements. The calculated vertical profiles of sulfate aerosols agree well with the observations over North America. During TOPSE sulfate aerosol concentrations were measured and compared with the model results (see Figure 11). Figure 11 shows that the modeled sulfate aerosol is generally consistent with the measured values. Specifically, the seasonal variability is shown in both the model and observation, i.e. the concentrations of sulfate aerosol are higher in spring than in winter. As analyzed by Tie *et al.* [2001], during winter, the chemical conversion of SO₂ to sulfate is low (low OH and H₂O₂ concentrations), and the boundary layer ventilation is weak, leading to high SO₂ and low sulfate concentrations. The differences between modeled and observed sulfate aerosol concentrations are generally within a factor of 2. The ratio of 2 in mass concentrations (volume) is about the ratio of 1.6 in surface area.

[25] As shown in Equation 2, the reaction coefficient of R-4 is the product of aerosol surface area and uptake coefficient, i.e. $k_{\text{het}} \propto (A\gamma)$. Thus, to change the reaction coefficient, we can either change the uptake coefficient or

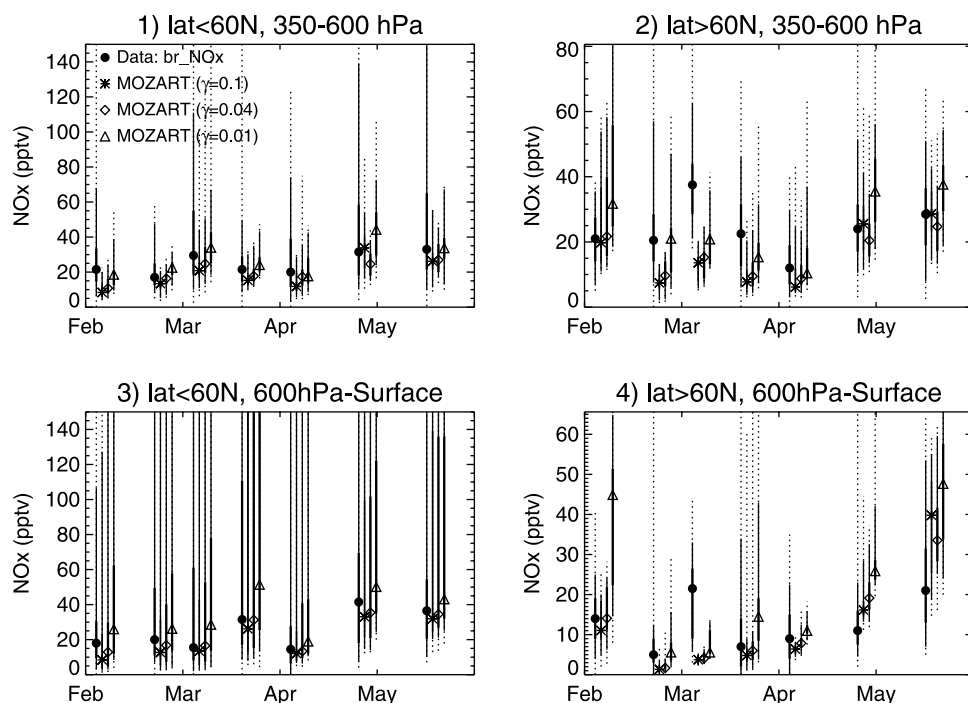


Figure 12. Comparison of the calculated to the observed NO_x concentrations (pptv) during TOPSE in the following 4 different regions as in Figure 7. The black dots are the measured NO_x concentrations; the asterisks are the calculated values with hydrolysis of N₂O₅ at sulfate aerosol ($\gamma = 0.1$); the diamonds are the calculated values with hydrolysis of N₂O₅ at sulfate aerosol ($\gamma = 0.04$); and the triangles are the calculated values with hydrolysis of N₂O₅ at sulfate aerosol ($\gamma = 0.01$). The symbols indicate the median values, with thick lines between 25% and 75% of the data, thin lines 5% and 95% and dashed lines between extrema.

the aerosol loadings. To reveal the impact of the uncertainties related to uptake coefficient and aerosol loadings on the model calculation, several model runs were made with the following conditions; (1) uptake coefficient = 0.1 which is the upper limit of the coefficient, (2) uptake coefficient = 0.04 which is the middle value of the coefficient, and (3) uptake coefficient = 0.01 which is the lower limit of the coefficient. As we described, the changes of the uptake coefficient can be also considered as changes in aerosol loading while the uptake coefficient is a constant. In this case, the aerosol loading is changed by a factor of 10 from condition (1) to condition (3), which fully covers the differences between the model calculation and the measurement shown in Figure 11. As indicated in Figure 2, with an upper value of uptake coefficient ($\gamma = 0.1$), the reaction of R-4 is about 11 times faster than the reaction of R-1, so that R-1 is the determining rate for the conversion of NO₂ to HNO₃. As a result, a further increase in the uptake coefficient or aerosol loading will not change the net conversion from NO₂ to HNO₃ because the conversion is limited by the slower rate of R-1. However, a further decrease in the rate of R-4 to the value that is comparable to the rate of R-1 can reduce the net conversion from NO₂ to HNO₃. As indicated in Figure 12, between the conditions (1) and (2), which imply that either uptake coefficient or aerosol loading is reduced by 4 times, the calculated NO_x concentrations change slightly, indicating that with a reduction of 4 times in reaction coefficient of R-4, the conversion is still limited by the reaction of R-1. However, between the conditions (1) and (3) which imply

that the reaction coefficient of R-4 is reduced by 10 times, the calculated NO_x concentrations change, indicating that in this case the rate of R-4 is comparable to the rate of R-1, and the conversion from NO₂ to HNO₃ is reduced due to the decrease in hydrolysis of N₂O₅. A similar situation is also shown in the calculated O₃ concentrations (see Figure 13). The averaged NO_x and O₃ concentrations with different rates for the hydrolysis of N₂O₅ on sulfate aerosol during March TOPSE flights are summarized in Table 1. It clearly indicates that hydrolysis of N₂O₅ has a significant impact on NO_x and O₃ concentrations during TOPSE. The uncertainties related to reaction coefficient have much smaller effects than the hydrolysis itself.

[26] To better understand the saturation effect of hydrolysis of N₂O₅ on NO_x concentrations in the troposphere, we show in Figure 14 the changes in NO_x as a function of aerosol surface area. The calculations were made with a photochemical box model which included a highly detailed description for the photo-oxidation of hydrocarbons (C1–C8) in the presence of HO_x and NO_x [Madronich and Calvert, 1989]. The chemistry was recently updated to the recommendations of Demore *et al.* [1997] and Atkinson [1997]. The model was run over representative diurnal profiles with photolysis rate coefficients calculated using Tropospheric Ultraviolet (TUV) radiation code [Madronich, 1989]. Several cases were modeled for different altitudes (1–3 km vs. 6–8 km), latitudes (40–50°N vs. 58–85°N) and months (February and May). For each case, the box model was initialized with measured median values derived

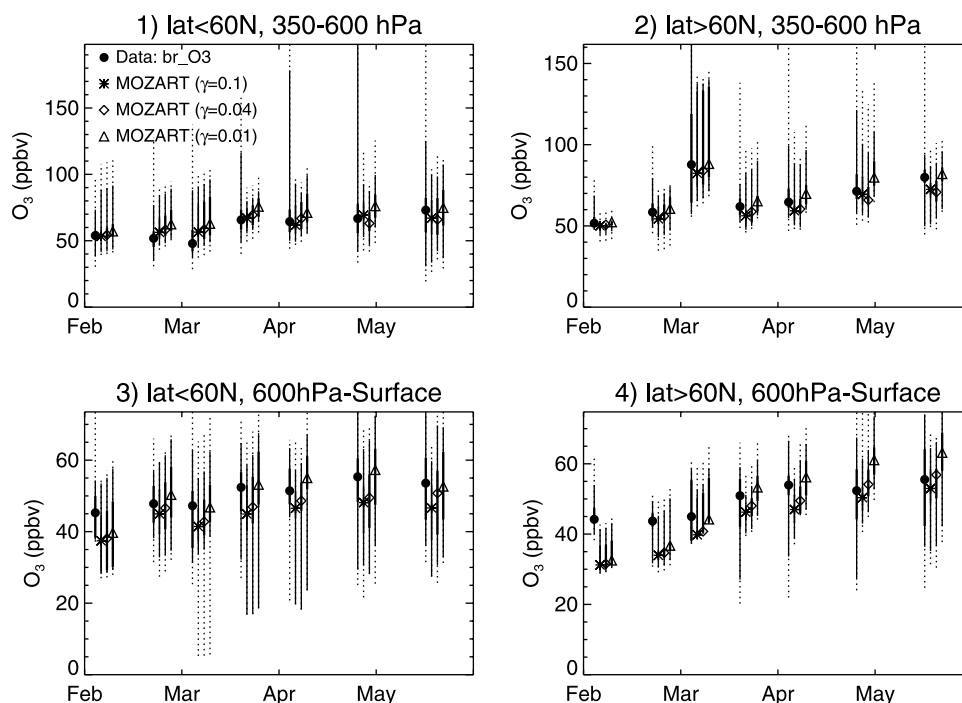


Figure 13. Same as Figure 12 except for O₃.

from the TOPSE aircraft data archive (with the exception of NO_x which was initialized at 600 pptv for all cases). The model was run unconstrained over 6 diurnal cycles with a constant N₂O₅ uptake coefficient of 0.1. For each case, runs with varying surface areas were performed so that the point of saturation could be studied. In high latitudes (58–85°N) of the lower troposphere (1–3 km) in winter (February), hydrolysis of N₂O₅ had the greatest effect on NO_x concentrations. When hydrolysis was included in the model, the NO_x concentrations decreased rapidly with increases in surface areas. More than an 80% reduction in NO_x was modeled when the sulfate area was above 10 μm²/cm³. A saturation point was reached at 10 μm²/cm³. In high latitudes of the middle to high troposphere (6–8 km) in winter, the effect of hydrolysis of N₂O₅ on NO_x concentrations was smaller than in the lower troposphere. About 40% reduction in NO_x was produced when the surface area was above 10 μm²/cm³. Again, a saturation point was reached at 10 μm²/cm³. In middle latitudes (40–50°N) of the lower troposphere in winter, the effect of hydrolysis of N₂O₅ on NO_x concentrations was smaller than in the high latitudes. About 40% reduction in NO_x was modeled when the sulfate area was above 50 μm²/cm³. A saturation point was reached when the surface area was above 50 μm²/cm³. In spring (May), the effect of hydrolysis of N₂O₅ on NO_x concentrations was very small. The saturation point is basically the point when the reaction of NO₂ with O₃ (R-3) and the hydrolysis (R-4) are competitive. As a result, saturation depends on sulfate surface areas as well as O₃ and NO₂ concentrations. When O₃ and NO₂ concentrations are high, such as in middle latitudes of North America, saturation is reached with a higher sulfate surface area than in high latitudes. Modeled sulfate surface areas range between 10 to 30 μm²/cm³ in high latitudes and more than 50 μm²/cm³ in middle latitudes in the NH [Tie *et al.*, 2001]. Thus,

saturation is normally reached during TOPSE. For example, in high latitudes in winter, if the surface area changes from 30 μm²/cm³ to 10 μm²/cm³, only small changes in NO_x concentrations will result.

[27] From the above analysis, we see that within the uncertainty range of the reaction coefficient, the model calculated NO_x and O₃ concentrations change moderately. However, such changes are much smaller than the differences between the model runs with and without R-4 (see Figures 9a, 9b, and 12). Within some uncertainties in the uptake coefficient or aerosol loading, the TOPSE comparison provides strong evidence that hydrolysis of N₂O₅ plays an important role in controlling NO_x and O₃ budgets.

3. Summary

[28] A comprehensive global chemical/transport/aerosol model (MOZART) is used to study the impact of hydrolysis

Table 1. Measured and Calculated NO_x and O₃ During TOPSE in March

	lat < 60N 350–600 hPa	lat > 60N 350–600 hPa	lat < 60N 600 hPa-Surf	lat > 60N 600 hPa-Surf
<i>NO_x(pptv)</i>				
Obs.	24.5	25.0	23.0	8.5
γ = 0.0	40.3	44.6	244.6	272.3
γ = 0.04	20.1	9.9	22.8	5.8
γ = 0.10	16.8	8.3	18.3	4.5
<i>O₃(ppbv)</i>				
Obs.	59.1	63.1	50.5	50.3
γ = 0.0	83.6	84.5	65.8	72.1
γ = 0.04	65.6	60.4	45.3	47.9
γ = 0.10	62.9	58.2	43.4	46.2
Obs.	59.1	63.1	50.5	50.3

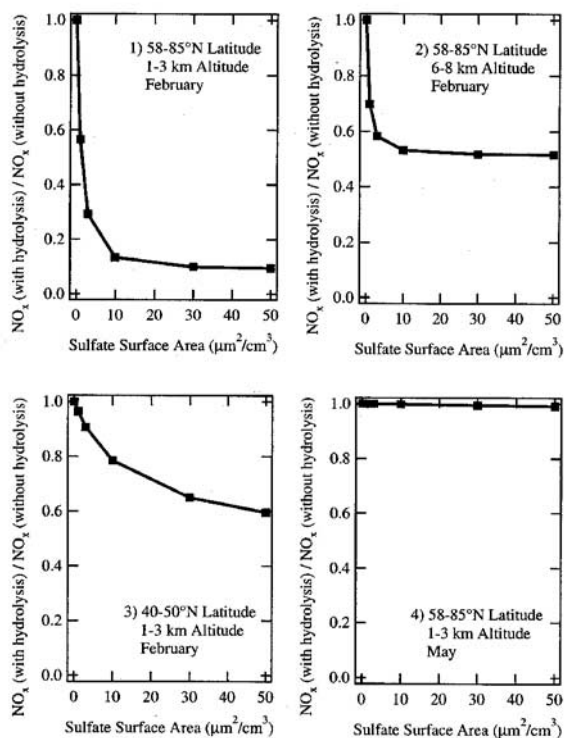


Figure 14. NO_x changes for different sulfate surface areas calculated with a chemical box model for different conditions; (1) in high latitudes (58–85°N) at 1–3 km in February, (2) in high latitudes (58–85°N) at 6–8 km in February, (3) in middle latitudes (40–50°N) at 1–3 km in February, and (4) in high latitudes (58–85°N) at 1–3 km in May. An uptake coefficient for N₂O₅ hydrolysis of 0.1 was used for all simulations.

of N₂O₅ on sulfate aerosol on NO_x and O₃ budgets. To study this impact, the MOZART model was run for different conditions (with and without the hydrolysis of N₂O₅). The model calculation shows that the globally averaged reduction of NO_x due to the heterogeneous reaction on sulfate aerosols has a strong seasonal variation, with a reduction of 38 and 6% during December and June, respectively. Much more of the reduction occurs in the NH than in the SH. In the NH, the reduction of NO_x is 47 and 7% during December and June, respectively. While in the SH, the reduction of NO_x is 3 and 5% during December and June, respectively. Despite the strong seasonal variation of the reduction of NO_x, the globally averaged reduction of O₃ has a weak seasonal variation, with 6 and 4% during December and June, respectively. However, in December the O₃ reduction shows a large hemispheric asymmetry, with 8 and 2% in the NH and the SH, respectively. The model results also reveal that the maximum impact of hydrolysis of N₂O₅ on sulfate aerosol on NO_x occurs at high latitudes of the NH during winter. Because the TOPSE experiment was designed to investigate the chemical and dynamic evolution of tropospheric chemical composition over the middle to high latitude continental North America during the winter/spring transition, it provided valuable data to study the impact of hydrolysis of N₂O₅ at sulfate aerosol on NO_x and

O₃ budgets at high latitudes of the NH. The calculated results are compared with field measurements (TOPSE), and this comparison shows clear evidence that the hydrolysis of N₂O₅ on sulfate aerosol plays an important role in controlling tropospheric NO_x and O₃ budgets at high latitudes of the Northern Hemisphere in winter and spring. The calculations indicate that without this heterogeneous reaction, the model calculated NO_x concentrations are very high (300 to 600 pptv) at high latitudes of the NH in winter and early spring, which is much higher than the measured values during TOPSE (below 20 pptv). With the hydrolysis reaction, modeled NO_x concentrations are close to the measured values. Several model runs using different values of the reaction coefficient of hydrolysis of N₂O₅ are conducted to study the effect of uncertainties in the model on the calculated NO_x concentrations. The analysis indicates that the changes in NO_x due to model uncertainties are much smaller than the impact of hydrolysis of N₂O₅ on sulfate aerosol.

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- E. Atlas, L. Emmons, P. Hess, A. Klonecki, S. Madronich, B. Ridley, C. Stroud, and X. Tie, National Center for Atmospheric Research, 1850 Table Mesa Drive, Boulder, CO 80307, USA. (xxtie@ucar.edu)
- L. Horowitz, NOAA/GFDL, Princeton University, POB 308, Princeton, NJ 08542, USA.
- G. Brasseur, Max-Planck Inst Meteorologie, Bundesstrasse 55, Hamburg, 20146 Germany.
- J. Dibb and R. Talbot, Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Morse Hall, 39 College Road, Durham, NH 03824, USA.