JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 106, NO. D3, PAGES 3167-3178, FEBRUARY 16, 2001

Effects of lightning on reactive nitrogen and nitrogen reservoir species in the troposphere

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Abstract. The impact of lightning on tropospheric reactive nitrogen NO_x ($NO + NO_2$) and nitrogen reservoir species (HNO_3, peroxyacetyl nitrate (PAN), N_2O_5, and HNO_4) has been evaluated using a global chemical/transport model. Comparison of calculations made with and without lightning show that lightning has a significant effect on the nitrogen species on a global scale, resulting in significant enhancements of NO_x, HNO_3, and PAN over the no lightning case. Of the nitrogen species, HNO_3 is influenced the most, comprising approximately 60 to 80% of the total increase in the nitrogen species concentration. The increase in PAN accounts for approximately 20 to 30% of the nitrogen enhancement by lightning in the middle troposphere. In the lower troposphere of the tropics, NO_x is rapidly converted into HNO_3 due to the high OH concentration in this region. As a result, the enhancement in NO_x from direct lightning emission is limited primarily to the upper troposphere. The conversion between NO_x and less reactive nitrogen species (PAN and HNO_3) also plays an important role in affecting NO_x, especially over the oceans where lightning activity is low. The model results suggest that recycling of NO_x from the lightning-enhanced PAN and HNO_3 produces 2 to 10 parts per trillion by volume (pptv) increases in NO_x over the oceans in the lower troposphere of the tropics. The enhancement of NO_x over the oceans can partially explain the observations of NO_x (mixing ratios of typically 10-50 pptv) over the tropical oceans, which are characterized by higher concentrations than would be expected from direct transport of NO_x from the continents.

1. Introduction

Ozone is produced in the troposphere by photochemical oxidation of hydrocarbons and CO catalyzed by hydrogen oxide radicals ($HO_x = OH + HO_2$) and nitrogen oxide radicals ($NO_x = NO + NO_2$). Consequently, changes in atmospheric NO_x concentrations can lead to a modification in the rate of ozone production [*Crutzen*, 1970]. NO_x is also intricately linked to the hydroxyl radical. The reaction between HO_2 and NO facilitates OH formation, while the reaction between NO_2 and OH leads to the formation of HNO_3, which is a relatively stable nitrogen reservoir species. As a result, NO_x directly influences the oxidizing capacity of the atmosphere [*World Meteorological Organization (WMO)*, 1995]. NO_x is emitted into the atmosphere from various natural and anthropogenic sources, including fossil fuel combustion, biomass burning, aircraft emission, and lightning [e.g., *Brasseur et al.*, 1996; *Seinfeld and Pandis*, 1998]. The production of NO_x by lightning has been a subject of numerous studies [e.g., *Liaw et al.*, 1990; *Biazar and McNider*, 1995; *Price et al.*, 1997]. Estimates of the global NO_x production by lightning vary considerably [e.g., *Levine*, 1981; *Franzblau and Popp*, 1989; *Nesbitt et al.*, 2000]. In a recent study, it has been suggested that a source strength in excess of 20 Tg N/yr would yield model-calculated mixing ratios of reactive nitrogen in the upper troposphere significantly larger than those typically observed [*Lamarque et al.*, 1996]. However, even the NO_x production in the range of 1-12 Tg N/yr from lightning is still sufficient to allow for a significant difference in the large-scale model-predicted abundance of the reactive nitrogen and in the photochemical formation of ozone in the middle and upper troposphere.

A number of studies have been conducted to investigate the effects of lightning on the tropospheric chemical constituents, especially on NO_x and ozone concentrations [e.g., *Lamarque et al.*, 1996; *Pickering et al.*, 1998]. For example, the model calculation by *Lamarque et al.* [1996] suggests that the NO_x concentration in the southern hemisphere is mostly dominated by the lightning source, while in the northern hemisphere the influence of lightning on NO_x is significant, but less important than in the southern hemisphere. Field experimental data also support that the NO_x concentrations are considerably enhanced when lightning is present [*Ehhalt et al.*, 1992]. Airbone measurements in and near mature thunderstorms show that NO_x is increased by as much as a few ppb from lightning in the upper troposphere on small spatial scales [*Ridley et al.*, 1996; *Huntrieser et al.*, 1998; *Stith et al.*, 1999]. In addition, another recent study has found evidence between the enhancement of NO_x in the upper troposphere and lower stratosphere and lightning activity [*Zhang et al.*, 2000].

The typical lifetime of NO_x increases from a few hours in the planetary boundary layer to a few days in the upper troposphere in summer. Observations over the tropical oceans indicate free troposphere NO_x mixing ratios of typically 10-50 parts per trillion by volume (pptv) [*Carroll and Thompson*, 1995; *Emmons et al.*, 1997] which is higher than would be expected from direct transport of primary NO_x from the continents, indicating that

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Paper number 2000JD900565.
0148-0227/01/2000JD900565$09.00

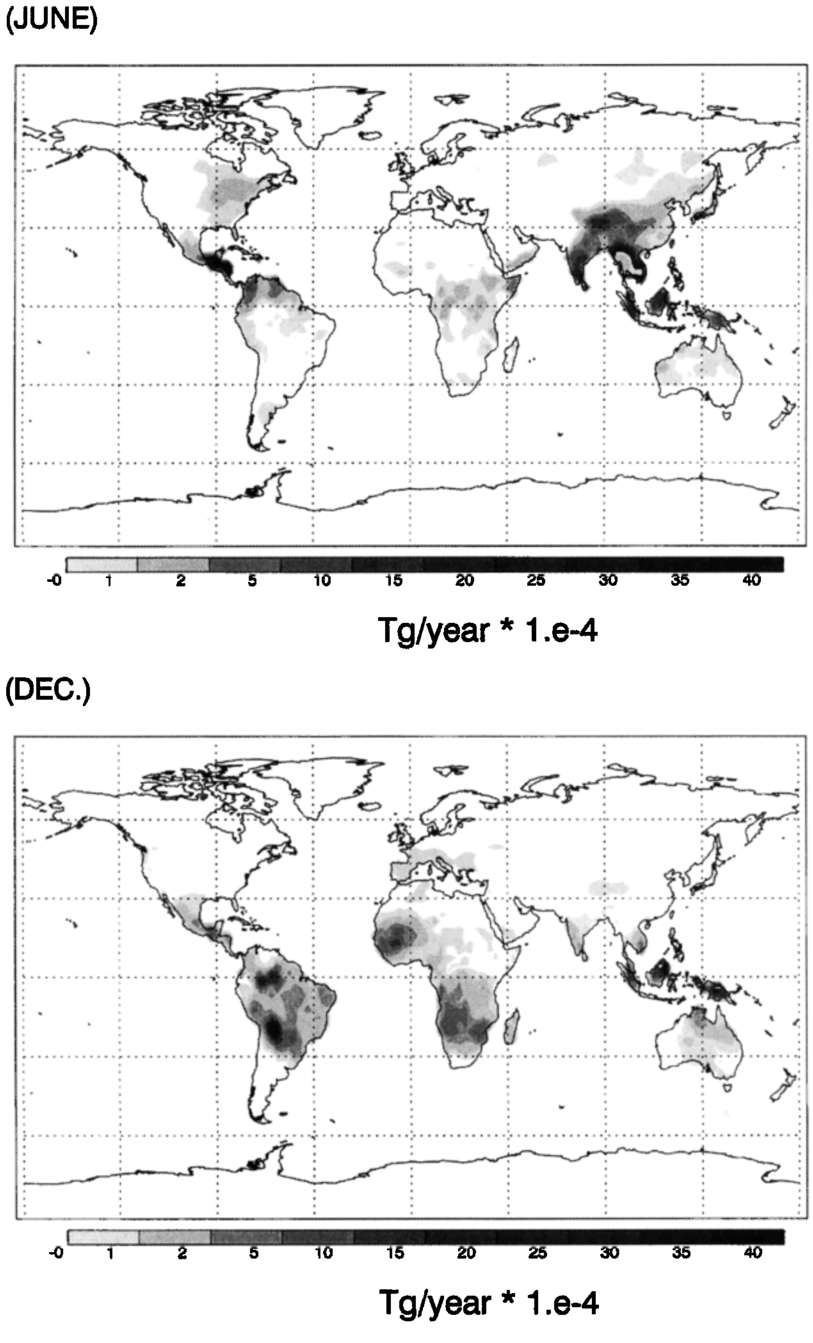

Figure 1. The global horizontal distribution of lightning NO_x emission used in the model for June and December.

chemical recycling of NO_x from HNO_3 and peroxyacetyl nitrate (PAN) ($CH_3CO_3NO_2$) could play a major role in maintaining NO_x concentrations over the ocean [*Singh*, 1987]. Also, lightning may play an important role in the NO_x concentrations over the oceans. In the lower troposphere, NO_x released from lightning is rapidly converted into nitrogen reservoir species, such as HNO_3 and PAN. However, some of those reservoir species, especially PAN, can reproduce NO_x through thermal decomposition when the temperature is high. Transport of PAN and regeneration of NO_x can affect the atmospheric photochemistry even in lightning-free regions.

In this paper, we employ a global chemical/transport model, Model for Ozone And Related Chemical Tracers, version 1 (MOZART), to evaluate the effects of lightning on NO_x and especially on their reservoir species (HNO_3, PAN, HNO_4, and N_2O_5). The relative enhancements of, and the interactions among, the reactive nitrogen and nitrogen reservoir species due to lightning are discussed. The enhancement of NO_x in lightning-free regions due to the long-range transport of the nitrogen reservoir species is also investigated.

2. Method and Results

2.1. Model Description

The numerical model used in the present study is a global three-dimensional chemical/transport model (MOZART) developed at the National Center for Atmospheric Research (NCAR) [*Brasseur et al.*, 1998]. The model is a comprehensive tropospheric chemical/transport model, calculating the global distribution of 56 gas-phase chemical species. Version 1 of the model used here is configured with a T42 (2.8° x 2.8°) horizontal resolution and 25 hybrid vertical levels ranging from the surface to 4 mbar. There are four levels in the boundary layer ranging from the surface to 786 mbar. Meteorological information (i.e., winds, temperature, etc.) is provided by the NCAR Community Climate Model (CCM2) every 3 hours on the basis of precalculated results (off-line). The cloud water content and precipitation flux are generated from an early version of the prognostic cloud parameterization described by *Rasch and Kristjansson* [1998]. In the present study, aqueous-phase chemistry in the clouds is not taken into account. However, both in-cloud and below-cloud scavenging in precipitation clouds are considered in this calculation. The rate of scavenging is a function of rainwater tendency and of the effective Henry's law constants. The model time step for chemistry and transport is 20 min. Chemical species are transported by advective [*Rasch and Williamson*, 1991], diffusive [*Holtslag and Boville*, 1993], and convective [*Hack*, 1994] processes. Details on the treatment of the gas-phase chemical mechanisms and transport processes are provided by *Brasseur et al.* [1998].

The global lightning emission is based upon the parameterization method developed by *Price et al.* [1997]. In their study, they present the global and seasonal distributions of lightning-produced NO_x based on the observed distribution of electrical storms and the physical properties of lightning strokes. In the MOZART model the lightning emission is determined using the parameterization based on model-calculated convective cloud heights. Different assumptions have been made regarding the vertical distribution of the NO_x production within the clouds. In this study, we assume for simplicity that the NO_x emission (expressed in mass per unit volume) is distributed uniformly with height below the top of convective clouds and covers the entire grid-cell in which such clouds are present. The total global annual emission of nitrogen oxides is chosen to be 7 Tg N/yr in the present study. The global horizontal distribution of lightning emissions calculated by MOZART is shown in Figure 1. In general, lightning activity depends on the incoming solar radiation and on the geographical distribution of land/ocean surfaces. In MOZART the distribution of lightning is determined by the location and height of convective clouds in CCM2, and therefore observed lightning distributions are not necessarily reproduced. The most intensive lightning activity occurs over land where the surface heating is maximal. Hence the seasonal variation of lightning activity is significant. In June, intensive lightning occurs at low latitudes in the northern hemisphere, while in December the lightning activity occurs primarily at low latitudes in the southern hemisphere. Marine convection, although occurring throughout the year, yields little lightning over the central Atlantic and Pacific [*Nesbitt et al.*, 2000].

In order to calculate the effect of lightning on nitrogen species, a model simulation made without any lightning emissions is compared to the standard simulation. Figure 2 shows a comparison of the NO_x concentrations between the model calculations with and without the lightning source and observations made during the several aircraft field campaigns. The sites of the observations are indicated in Figure 3 and Table 1 and are further described by *Emmons et al.* [2000]. These selected sites represent different levels of lightning activity. Sites 1 and 2 are located in the Pacific, and represent regions of low lightning activity. Sites 3 and 4 are located between two large lightning regions (Africa and South America). Sites 5 and 6 are located on the east coast of Asia where lightning often occurs. Sites 7 to 10 are located in regions of high lightning activity (Africa and South America). Figure 2 shows the significant contribution lightning makes to the NO_x distribution in the large difference between the model simulations with and without lightning. Over land and coastal areas (i.e., locations 5 to 10 in East Asia, Africa, and South America), the inclusion of the lightning NO_x source yields simulated profiles in much better agreement with the observed values. Those results also support our use of 7 Tg N/yr lightning-NO_x production rate. Over the Pacific Ocean (i.e., locations 1 and 2) the simulated NO_x excluding the lightning source shows a small difference from the observation and from the standard model results, suggesting that the influence of NO_x from lightning is quite small in this remote region. However, over the Atlantic Ocean (sites 3 and 4) the calculated NO_x profiles are improved compared to the observations when the lightning NO_x source is taken into account. Since lightning activity occurs primarily over continental areas, this implies possible transport of the nitrogen species derived from lightning-generated NO_x. This question will be addressed later. There is also a suggestion that there is a larger source of NO_x in the upper troposphere than would be expected from a uniform vertical distribution of lightning-NO_x production in the cloud [*Pickering et al.*, 1998]. A sensitivity study in which vertical distribution of the NO_x production within the clouds is distributed in the top four levels of clouds is made in the calculation. The results show a maximum of 900% increase in NO_x concentrations (not shown) in the upper troposphere contrasted to 600% increase with uniformed vertical distribution of lightning-NO_x production in the cloud, indicating that lightning NO_x production directly emitted in the upper troposphere play a significant role in controlling NO_x concentrations in this region.

2.2. Changes in the Nitrogen Species Caused by Lightning

Figure 4a shows the calculated zonally averaged changes in the relevant nitrogen species concentration due to lightning, including NO_x ($NO + NO_2$), PAN, HNO_3, N_2O_5, HNO_4, and NO_y (NO_x + PAN + HNO_3 + $2N_2O_5$ + HNO_4 + NO_3) in June. The results indicate that the change in NO_x due to lightning represents less than 30% of the change in the total nitrogen concentrations. However, the change in the NO_x concentration can be large relative to ambient concentrations. Figure 4a shows that a maximum change of the NO_x mixing ratio (300 pptv) is located within a small latitude range (between 30°N and 40°N) in the upper troposphere. In contrast, the increase in NO_y concentration is quite uniformly distributed in both horizontal and vertical directions, with an increase of over 200 pptv from 40°N to 40°S and 2 to 15 km in altitudes. This uniformity is due to the zonally averaged NO_x emissions being fairly uniformed over 40°S-40°N, and NO_y having a long lifetime. The largest increase in the nitrogen species concentration from lightning occurs in the case of HNO_3, with a maximum value of 300 pptv over a large vertical range at 15° to 30°N. The increase in PAN mixing ratio is also significant with a maximum value of 50 pptv. Figure 4 shows that the PAN enhancement is uniformly distributed in the middle and upper troposphere between 0° and 50°N latitudes where intensive lightning occurs. The increases in N_2O_5 and HNO_4 density are less significant than in the case of NO_x, HNO_3, and PAN. Figure 4b shows the calculated percentage increase of NO_x, NO_y, PAN,

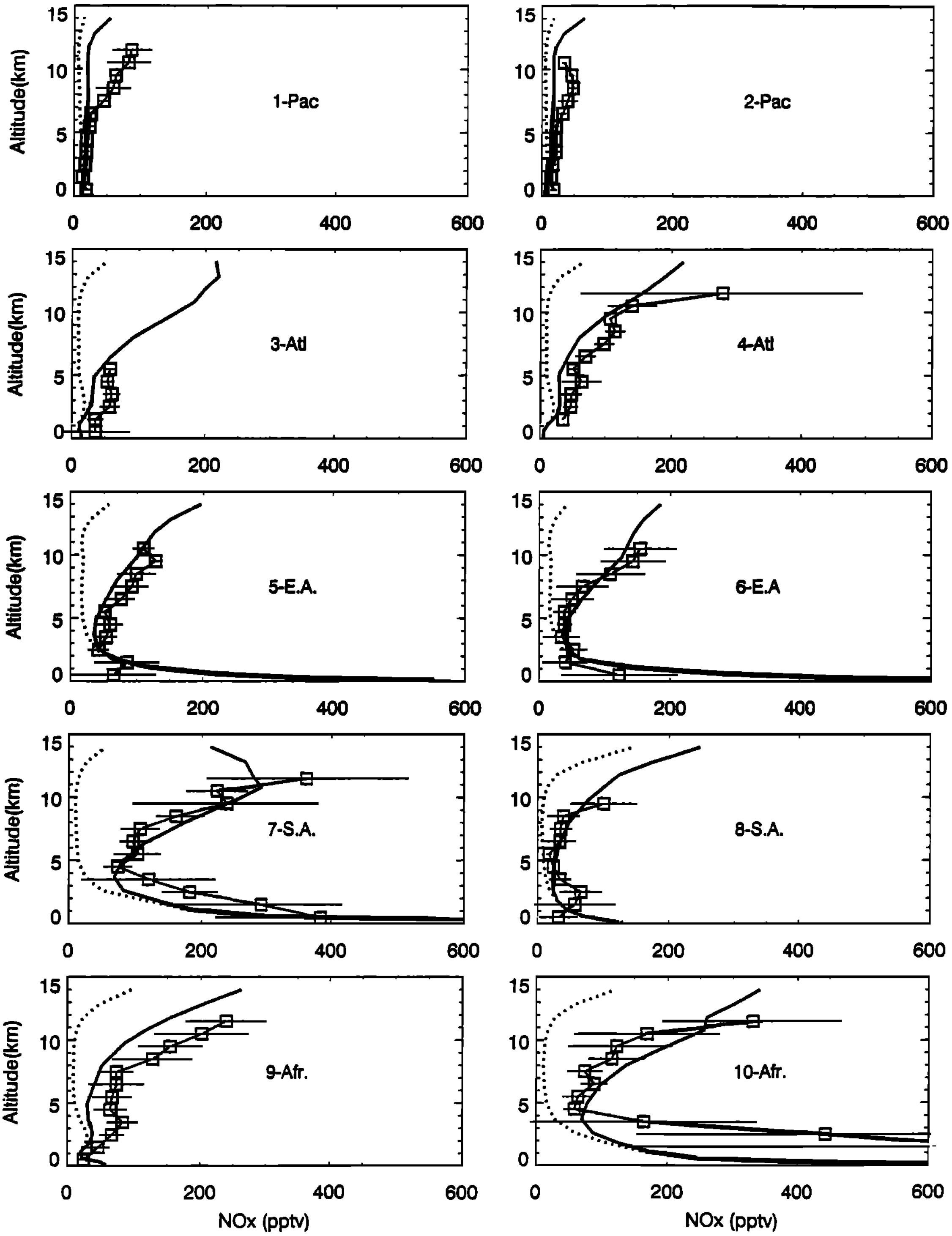

Figure 2. Comparison of NO_x between model simulations with (solid line) and without lightning (dotted line) and observations (squares) in 10 different locations: 1 and 2, Pacific Ocean; 3 and 4, Atlantic Ocean; 5 and 6, East Asia; 7 and 8, Africa; 9 and 10, South America. The locations of the observations are shown in Figure 3.

HNO_3, N_2O_5, and HNO_4 due to lightning. It shows that in the middle and upper troposphere of the tropics, NO_x and NO_y concentrations increase as much as a few hundred percent, indicating that lighting emission of NO_x is a major source of NO_x and NO_y in this region. We also note that although the percentage increase in N_2O_5 is very large (greater than 1000%), the absolute change of N_2O_5 is very small (less than a few pptv, see Figure 4a).

Figure 5 shows the calculated zonally and vertically averaged latitudinal changes in the distributions of NO_y, NO_x, HNO_3, and PAN mixing ratios in June, along with the integrated lightning NO emissions. The enhanced NO_x concentrations are correlated with the lightning emission, but NO_x is also enhanced at latitudes outside the regions of the lightning emissions. This feature will be discussed in more detail in the following section. The changes in NO_y concentrations, however, are broadly distributed over a wide latitude range because of the long chemical lifetime (greater than 20 days) involved. The changes in the latitudinal gradient of HNO_3 and PAN are very similar to that of NO_y, but the HNO_3

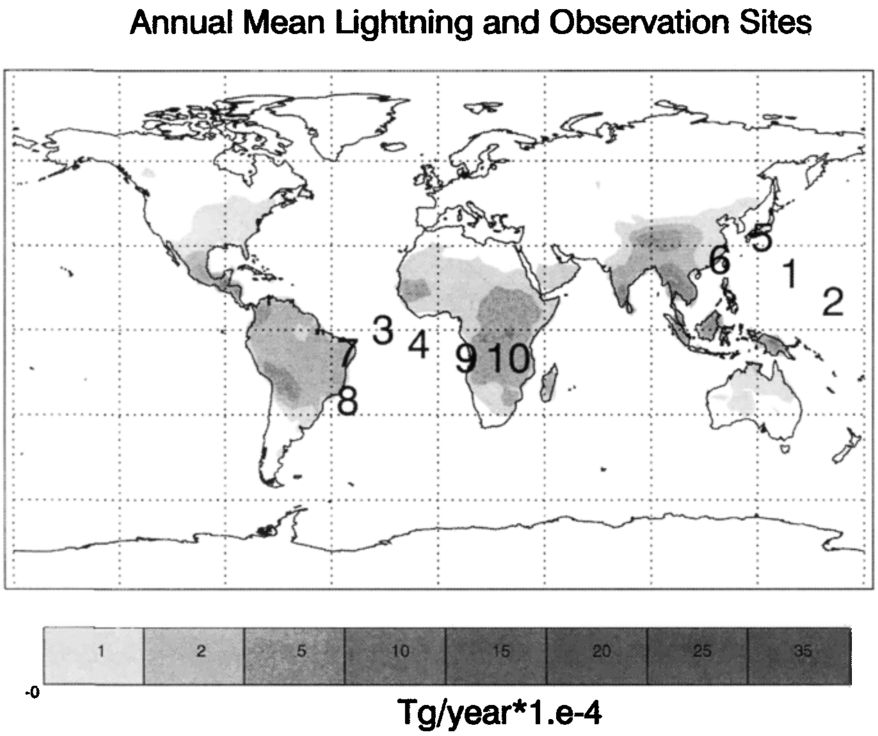

Figure 3. The annually averaged horizontal distribution of lightning NO_x emission and the locations of observation sites (indicated by numbers used for the comparison of NO_y between model simulations and observations.

concentration increase is about 7 times larger than the increase in the PAN density. Note that the lightning activity in June is very intensive between the equator and 50°N, as shown in Figure 5.

To more closely examine the correlation between lightning emission and the enhancements (in percentages of total nitrogen changes due to lightning) in NO_x, HNO_3, and PAN, we calculate the vertical profiles of the changes of NO_x, PAN, and HNO_3 averaged over three latitudinal bands in June, that is, between 10°S and 90°S (the low lighting activity zone in the winter), 10°S and 60°N (the high lightning activity zone), and 60°N and 90°N (the low lightning activity zone in the summer) as shown in Figure 6. In the region between 10°S and 90°S, most of the enhancement of nitrogen due to lightning is in the form of HNO_3 (about 70 to 80%). The increase in PAN accounts for 20 to 30% of the NO_y enhancement below 10 km. The NO_x enhancement is very small below 5 km and gradually increases to 15% above 10 km. In the latitudinal band between 60°N and 90°N, the situation is very similar to that between 10°S and 90°S. However, in the region between 10°S and 60°N where intensive lightning activity occurs, the enhancement of NO_x is larger in the upper troposphere (30 to 40% increase of the nitrogen concentration). In the lower troposphere the NO_x increase is less than 10%, and most nitrogen enhancement is in the form of HNO_3, which accounts for 80% increase of the nitrogen species.

To understand the relative enhancement of the nitrogen species due to lightning, we calculate the timescales for chemical production and destruction of HNO_3 and PAN in June. The results are shown in Figure 7. The time constant to form HNO_3 and PAN is less than 1 day in the tropical lower troposphere because high OH concentrations are located in this region. The formation of HNO_3 occurs through the direct reaction of NO_2 with OH, and it is expressed by

Table 1. Observations Shown in Figure 2 With Locations Indicated in Figure 3

Location	Campaign	Date	Region	Latitude, Longitude, deg
1	PEM-West A	Sept. 16 to Oct. 21, 1991	Philippine Sea	5-20N, 135-150E
2	PEM-West A	Sept. 16 to Oct. 21, 1991	Pacific_Tropics_W	5S-15N, 155-165E
3	CITE 3	Aug. 22 to Sept. 29, 1989	Natal	5S-5N, 325-335E
4	TRACE-A	Sept. 21 to Oct. 26, 1992	Atlantic_S	20S-0, 340-350E
5	PEM-West A	Sept. 16 to Oct. 21, 1991	Japan_Coast_E	25-40N, 135-150E
6	PEM-West A	Sept. 16 to Oct. 21, 1991	China_Coast_E	20-30N, 115-130E
7	TRACE-A	Sept. 21 to Oct. 26, 1992	Brazil_E	15-5S, 310-320E
8	TRACE-A	Sept. 21 to Oct. 26, 1992	Brazil_Coast	35-25S, 310-320E
9	TRACE-A	Sept. 21 to Oct. 26, 1992	Africa_Coast_W	25-5S, 0-10E
10	TRACE-A	Sept. 21 to Oct. 26, 1992	Africa_S	25-5S, 15-35E

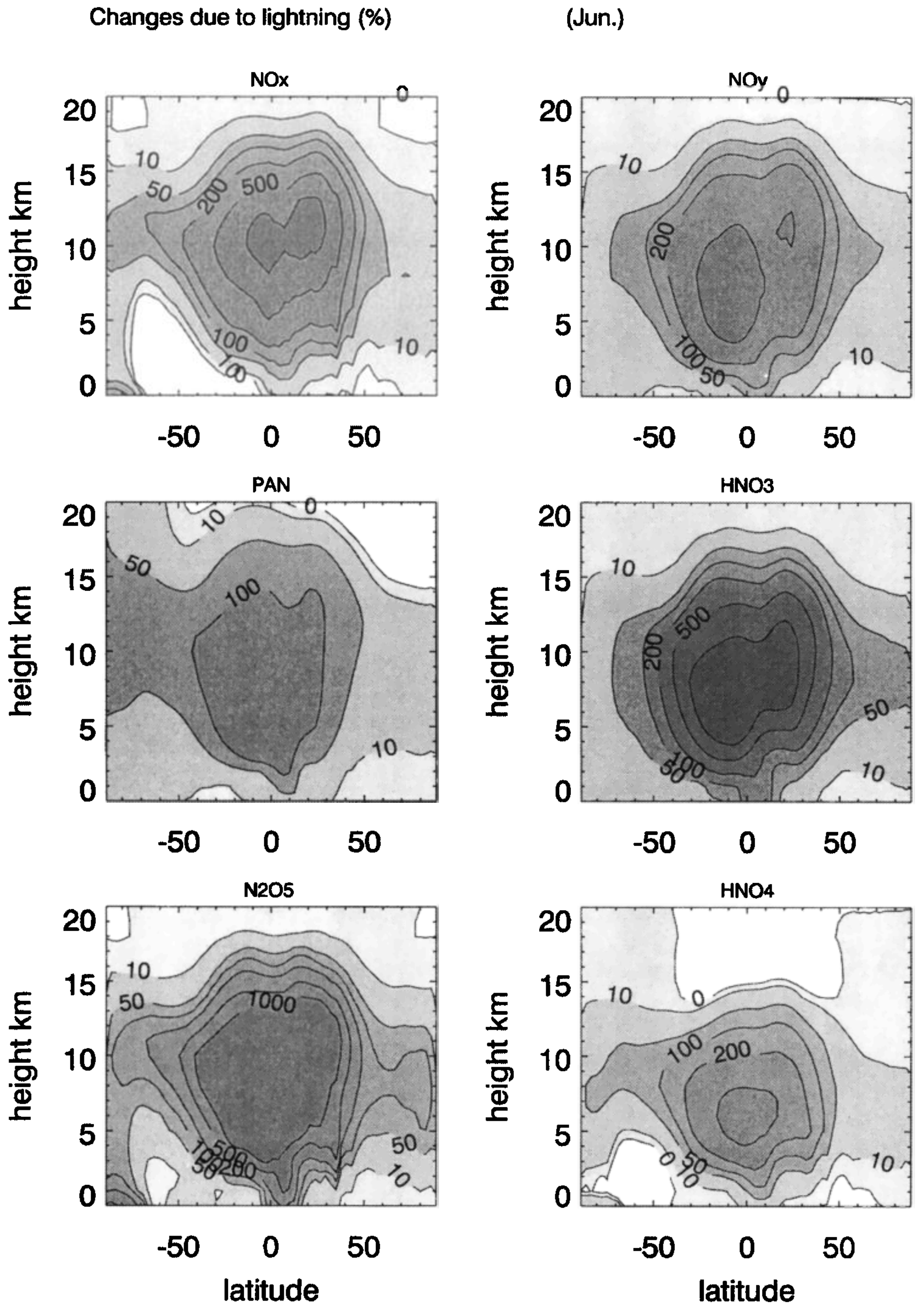

Figure 4a. Zonally averaged changes of nitrogen species from lightning, including NO_x ($NO+NO_2$), PAN, HNO_3, N_2O_5, HNO_4, and NO_y (NO_x + PAN + HNO_3 + $2N_2O_5$ + HNO_4 + NO_3) in June.

$$OH + NO_2 \rightarrow HNO_3 \,. \tag{1}$$

For PAN, however, the situation is somewhat different. The formation of PAN is through a chemical chain reaction, initiated by the oxidation of hydrocarbons, for example, propene (C_3H_6)

$$C_3H_6 + O_3 \rightarrow CH_3CHO + \text{products} \tag{2}$$
$$C_3H_6 + OH + O_2 \rightarrow C_3H_6OHO_2 \tag{3}$$
$$C_3H_6OHO_2 + NO \rightarrow CH_3CHO + \text{products} \tag{4}$$
$$CH_3CHO + OH + O_2 \rightarrow CH_3CO_3 + H_2O \tag{5}$$
$$CH_3CHO + NO_3 \rightarrow CH_3CO_3 + HNO_3 \tag{6}$$
$$CH_3CO_3 + NO_2 + M \rightarrow PAN + M. \tag{7}$$

The destruction rate of HNO_3, however, is relatively slow with a lifetime of approximately 20 to 30 days in the tropics, and even larger at high latitudes during the winter. Because the photochemical rate of destruction of HNO_3 is much slower than its production rate, especially in the tropics, the cycling of NO_x through the chemical destruction of HNO_3 is slow, that is,

$$HNO_3 + h\nu \rightarrow OH + NO_2 \tag{8}$$
$$HNO_3 + OH \rightarrow NO_3 + H_2O \tag{9}$$

and HNO_3 will primarily be removed from the atmosphere by wet and dry deposition, representing a major role for the sink of NO_x

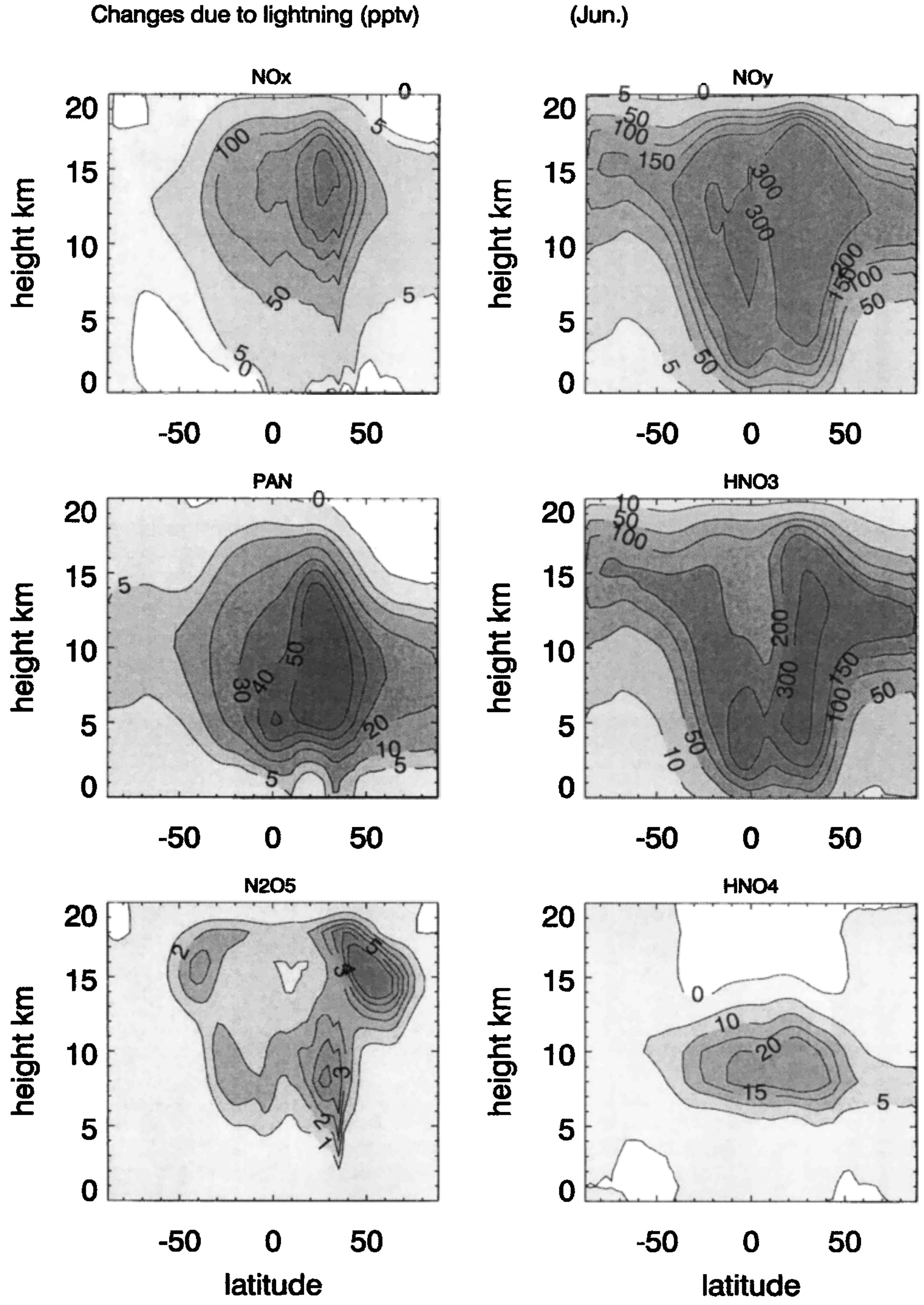

Figure 4b. Same as Figure 4a, except changes in percent.

[*Brasseur et al.*, 1998]. Furthermore, the chemical lifetime of HNO_3 is often longer than the transport time constant along longitude (approximate 1-2 weeks). As a result, the enhancement in HNO_3 from lightning is almost uniform with longitude which will be discussed further below. The conversion of NO_x to HNO_3 has several possible consequences. First, the enhancement in NO_x due to lightning is not significant below 5 km, as depicted in Figures 4 and 6. Second, a significant enhancement of NO_x by lightning can occur in the upper troposphere, as shown by satellite measurements [*Zhang et al.*, 2000]. Third, the slow destruction of HNO_3 allows for its transport over long distances away from lightning source regions, resulting in a large scale enhancement in NO_y over the globe as shown in Figures 4 and 5. Fourth, since the conversion of HNO_3 to NO_2 (reaction (8)) is slow, the enhancement of HNO_3 in regions far from lighting activity will not produce a large increase in the NO_x concentrations.

In the lower atmosphere the destruction of PAN is mainly due to its thermal decomposition,

$$PAN + M \rightarrow CH_3CO_3 + NO_2 + M \qquad (10)$$

which is rapid when temperature is high. As shown by Figure 7, the production of PAN is relatively fast in the tropical lower troposphere, with a time constant of about 1 day. The destruction rate of PAN is strongly dependent on altitude. In the lower troposphere the decomposition of PAN is very fast because of the

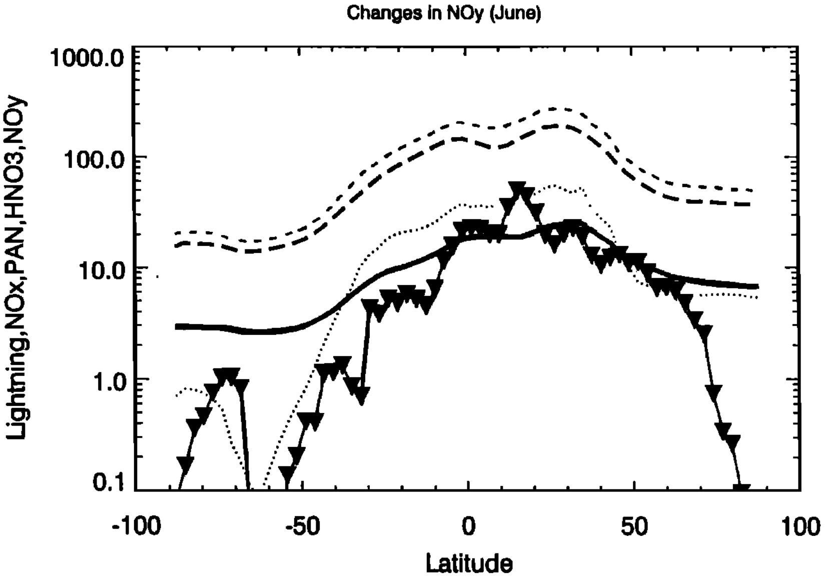

Figure 5. Calculated zonally and vertically averaged latitudinal changes (pptv) in the distributions of NO_y (short-dashed line), NO_x (dotted line), HNO_3 (long-dashed line), and PAN (solid line) in June. Also shown in this figure for comparison is the zonally averaged latitudinal lightning emissions (10^{-4} Tg/yr) (triangles).

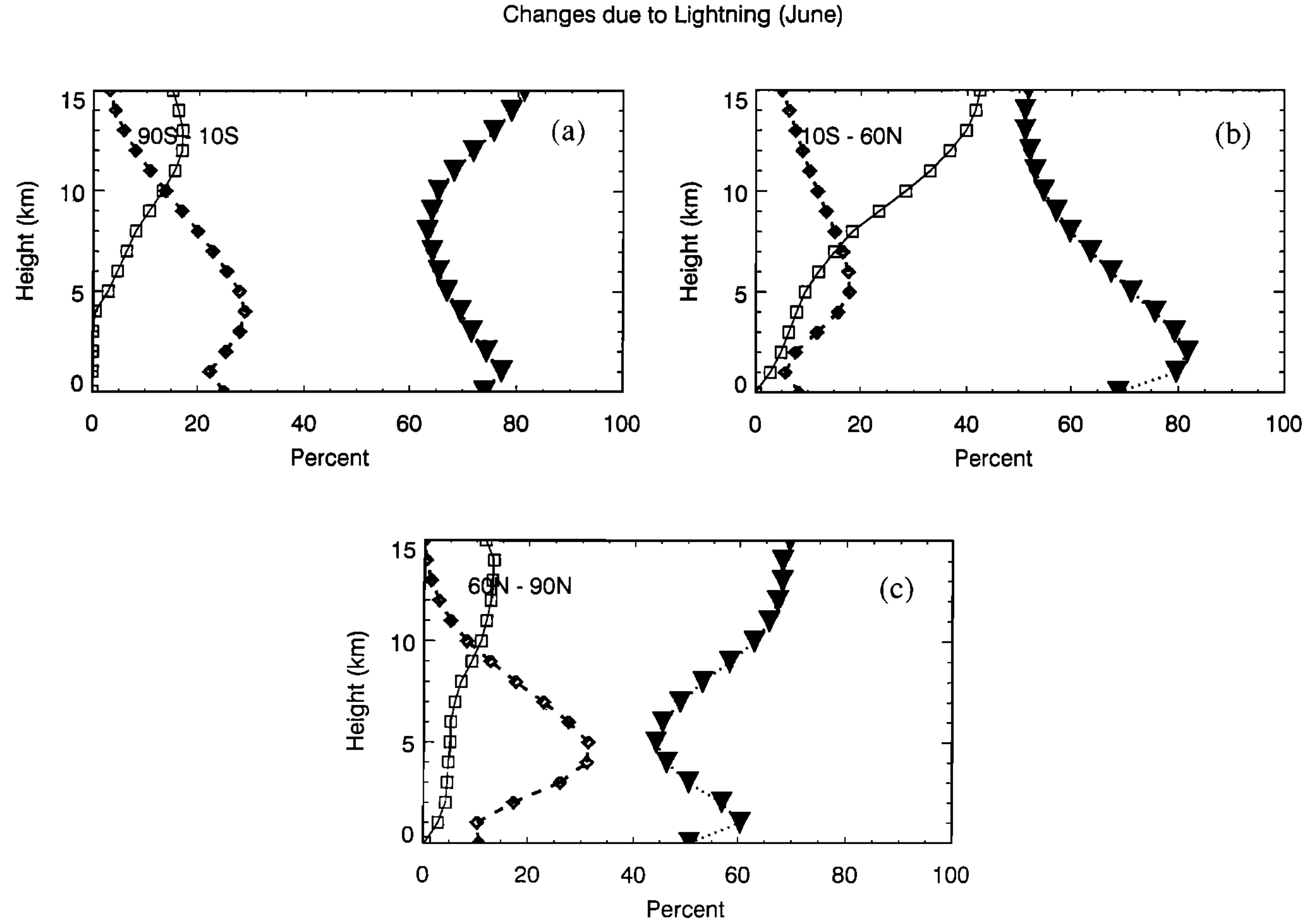

Figure 6. Averaged vertical profiles of the changes (in percentages of total nitrogen changes due to lightning) of NO_x (squares), PAN (diamonds), and HNO_3 (triangles) in three latitudinal bands: (top) between 10°S and 90°S, (middle) between 10°S and 60°N, and (bottom) between 60°N and 90°N.

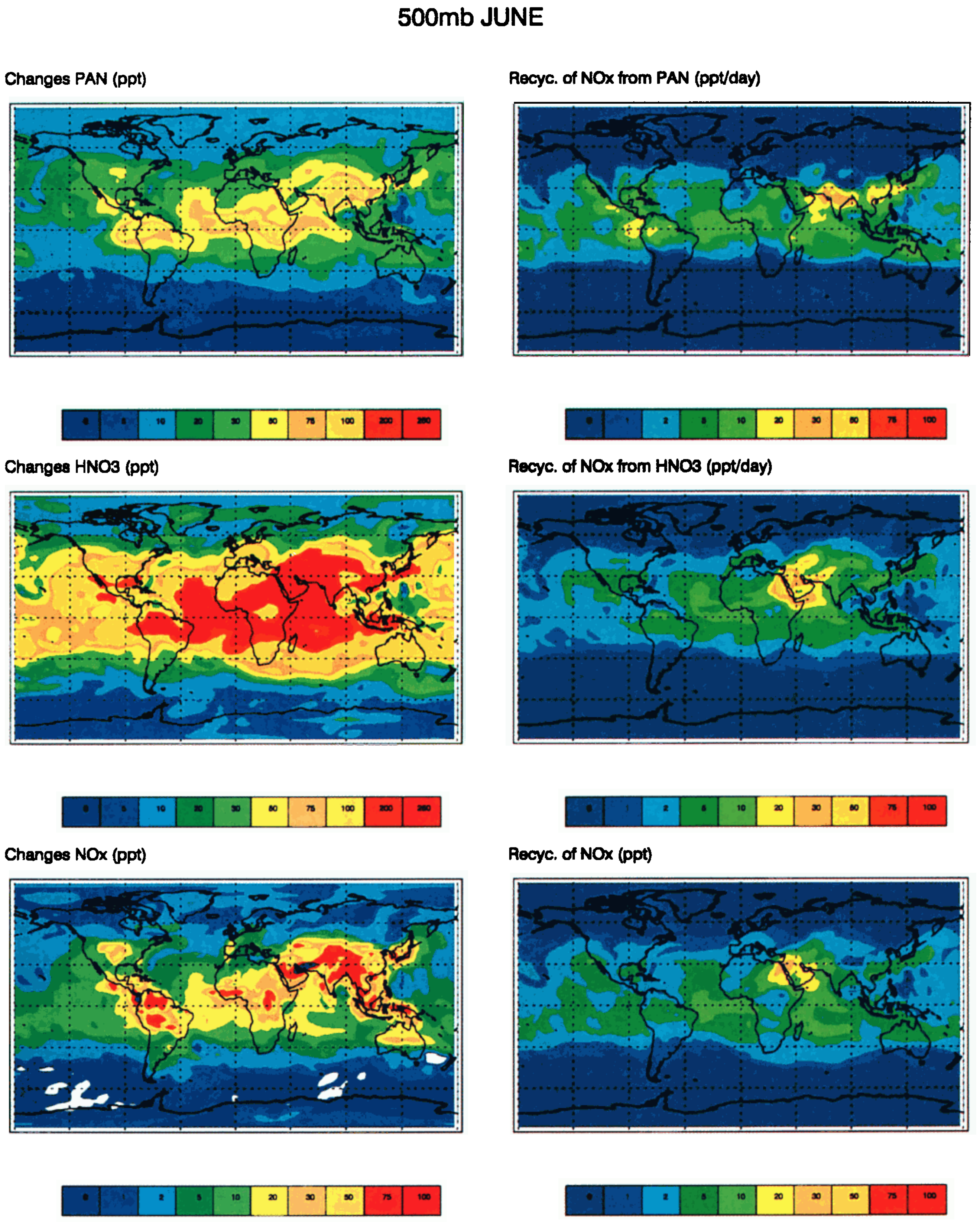

Plate 1. (left) Calculated lightning enhancements of PAN, HNO_3, and NO_x as well as (right) the rate of the recycling of NO_x from lightning-enhanced PAN and HNO_3, and total NO_x recycled ($R\mathrm{NO}_t$) at 500 mbar in June.

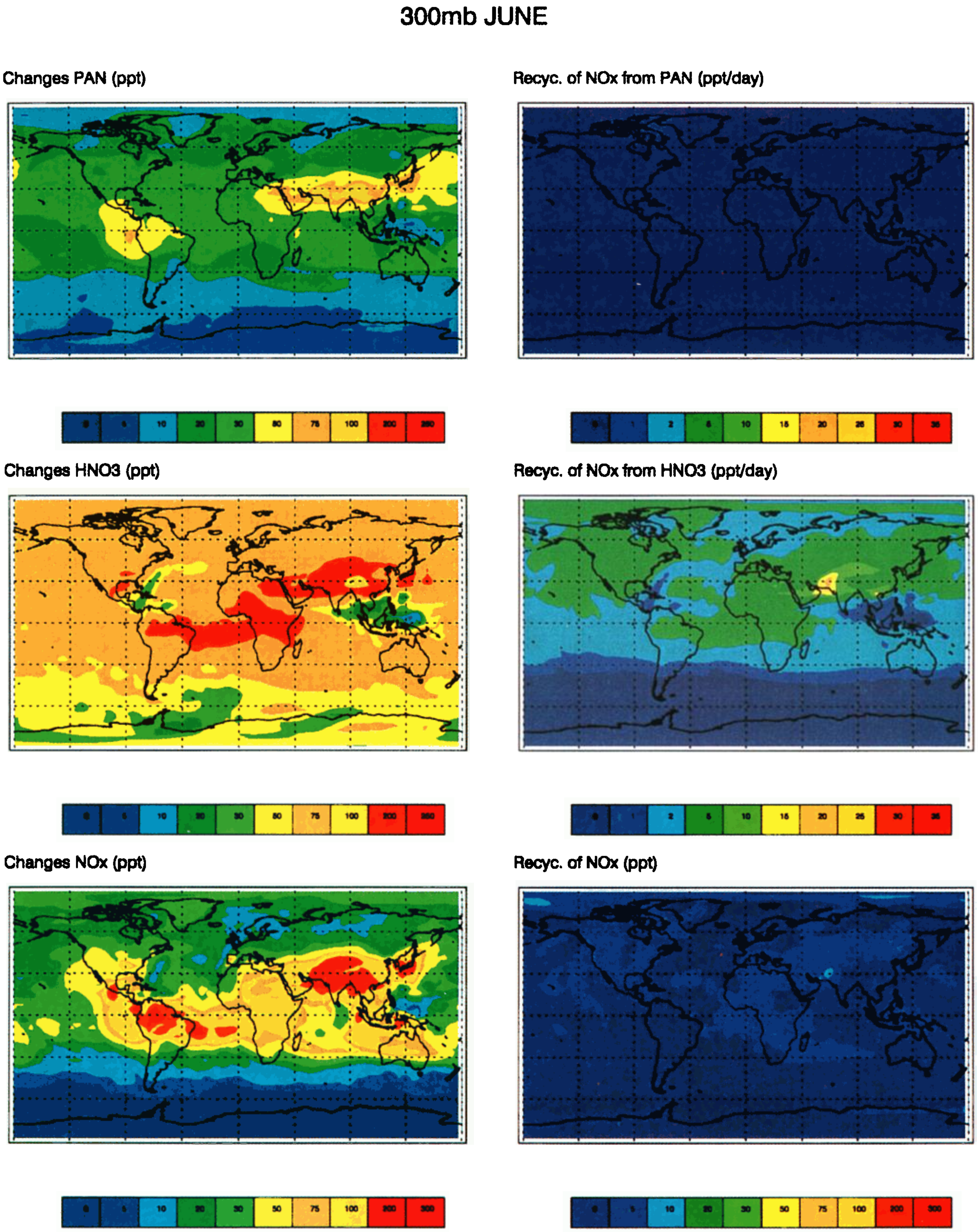

Plate 2. Same as Plate 1 except at 300 mbar.

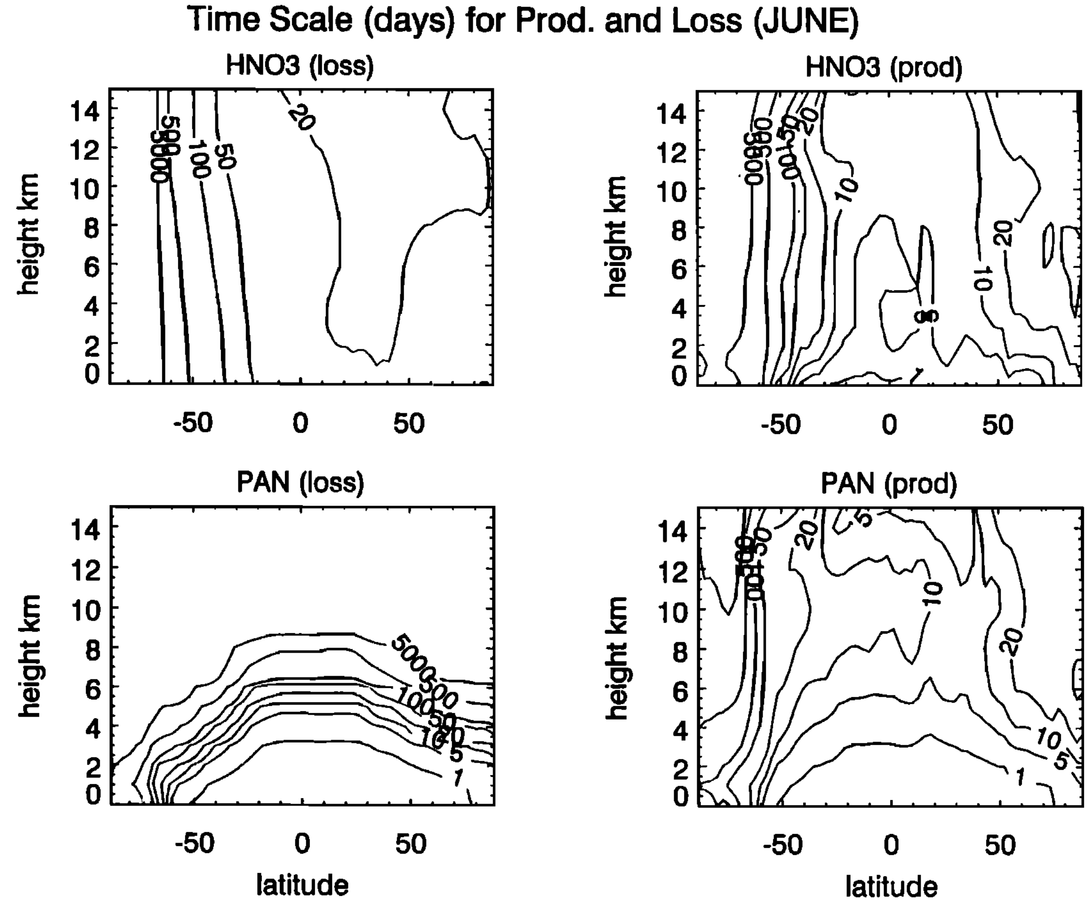

Figure 7. Timescales for chemical production and destruction of HNO_3 and PAN in June.

warmer temperature in this region, corresponding to a chemical lifetime of less than 1 day. In the middle and upper troposphere the chemical lifetime of PAN is long, so that this compound is very stable above 5 km. As a result, the longitudinal distribution of PAN is quite uniform in the upper troposphere.

2.3. Recycling of NO_x From HNO_3 and PAN

The formation and destruction of nitrogen reservoirs such as PAN and HNO_3 have important implications for the NO_x enhancement associated with lightning activities in the following ways. First, as indicated above, significant amounts of NO_x released by lightning are converted to these stable reservoirs (see Figure 4). Because of their slow destruction, HNO_3 and PAN are transported over long distances away from lightning regions in the middle and upper troposphere. In the lower troposphere the fast decomposition of PAN regenerates NO_x. As a result, the enhancement of NO_x from lightning is not only limited to the lightning source regions. To quantitatively analyze the recycling of NO_x from lightning, we calculate the following quantities;

$$P_1(NO_x) = J_2[\Delta HNO_3] + k_3\,[OH][\Delta HNO_3]$$
$$P_2(NO_x) = k_{10}[\Delta PAN]$$
$$L(NO_x) = k_9[CH_3CO_3] + k_1[OH]$$
$$RNO_x = [P_1(NO_x)+P_2(NO_x)]/L(NO_x),$$

where $P_1(NO_x)$ is the production rate of NO_x from the lightning-enhanced HNO_3 (ΔHNO_3), $P_2(NO_x)$ is the corresponding quantity from the lightning-enhanced PAN (ΔPAN), $L(NO_x)$ represents the chemical loss of NO_x, and RNO_x is the NO_x concentration due to the recycling of ΔHNO_3 and ΔPAN.

Plate 1 shows the enhancements of PAN(ΔPAN), HNO_3(ΔHNO_3), and NO_x(ΔNO_x) at 500 mbar in June. With a chemical lifetime of approximately 20 to 50 days for HNO_3 and approximately 5 to 10 days for PAN at 500 mbar in the tropics (see Figure 7), the enhanced HNO_3 and PAN concentrations from lightning are distributed uniformly in the tropics, in response to long-range transport of these slow reacting compounds. The enhancement of NO_x is located primarily in the regions where lightning activity is strong. However, significant NO_x enhancement (10 to 20 pptv) is found over the oceans in regions where lightning activity is very small (see Figure 1). The enhancements of NO_x over the tropical oceans can result from two processes: (1) The lightning-enhanced NO_x in the continents being transported over the oceans, and (2) NO_x being recycled from the lightning-enhanced PAN and HNO_3. The rates of production rate of NO_x resulting from ΔPAN and ΔHNO_3 as well as the concentrations increase of NO_x (RNO_x), calculated by the model, are shown in Plate 1 (right panels). This indicates that the NO_x production from ΔPAN corresponds to approximately 2 to 20 pptv/d and from ΔHNO_3 to approximately 2 to 10 pptv/d over the oceans. The recycling of NO_x from both the lightning-enhanced HNO_3 and PAN produces 10 to 20 pptv NO_x increases over the tropical oceans. A comparison of RNO_x with ΔNO_x shows that the recycling of NO_x contributes approximately 50% of the lightning enhancement of NO_x over the oceans at 500 mbar.

In the upper troposphere (300 mbar) the lifetime of NO_x is approximately 10 days (see Figure 7). The enhancement of NO_x from lightning is transported from the continents over the oceans, producing a maximum increase of 250 pptv in the NO_x mixing ratio over the oceans (see left panels of Plate 2). Because at this altitude the recycling of NO_x from PAN and HNO_3 is very small (see right panels of Plate 2), the large increase in NO_x is mainly due to the direct release of NO_x from lightning (fresh NO_x). However, in the lower troposphere, where the chemical lifetime of PAN drops less than 1 day (see Figure 7), the recycling of NO_x from ΔPAN becomes the dominant process, and produces 2 to 10 pptv over the oceans (not shown). This enhancement of NO_x over the oceans can partially explain the NO_x mixing ratio of typically 10-50 pptv observed over the tropical oceans [*Carroll and Thompson*, 1995].

3. Summary

Our model calculations reveal that the concentrations of all nitrogen species are significantly affected by lightning emissions of NO. In most cases the enhancement in the nitrogen species occurs most importantly as an increase in HNO_3, accounting for 70 to 80% of the increase in total nitrogen. The chemical conversion of NO_x to HNO_3 occurs rapidly in the lower troposphere of the tropics. As a result, the enhancement of NO_x from direct lightning emission is confined mainly to the upper troposphere. The conversion between NO_x and less reactive nitrogen species (PAN and HNO_3) also plays an important role in affecting NO_x, especially in the free troposphere far away from lightning sources. The model results suggest that the recycling of NO_x from the enhanced PAN and HNO_3 produces 2 to 10 pptv increases in NO_x over the tropical oceans. In the middle troposphere (500 mbar), it contributes approximately 50% of the increase of NO_x from lightning.

Acknowledgments. The authors are grateful to Anne Smith, Andy Weinheimer, and two anonymous reviewers for useful comments on the manuscript. The work of X. Tie and G. Brasseur was partially supported by the DOE Atmospheric Chemistry Program under contract DE-AI05-98ER62579. R. Zhang and W. Lei were supported by the NASA New Investigator Program. The National Center for Atmospheric Research is operated by the University Corporation for Atmospheric Research under the sponsorship of the National Science Foundation.

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(Received May 17, 2000; revised August 24, 2000; accepted September 5, 2000.)