Lightning-generated NO\textsubscript{X} and its impact on tropospheric ozone production: A three-dimensional modeling study of a Stratosphere-Troposphere Experiment: Radiation, Aerosols and Ozone (STERAO-A) thunderstorm

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Received 28 October 2004; revised 24 February 2005; accepted 25 March 2005; published 22 July 2005.

[1] A three-dimensional cloud-scale chemical transport model has been used to simulate trace gas transport, lightning NO production, and photochemical ozone production in the 12 July 1996 storm observed during the Stratosphere-Troposphere Experiment: Radiation, Aerosols and Ozone (STERAO-A) field experiment. The model is driven by meteorological fields from a nonhydrostatic cloud-resolving model (see Stenchikov et al., 2005). An assumption that both cloud-to-ground and intracloud flashes produce 460 moles NO/flash on average yielded the best comparison with the profile of NO observed in the storm anvil. Scenarios in which the NO production of an intracloud flash was 75 to 100\% of the production of a cloud-to-ground flash best matched the column NO\textsubscript{X} mass computed from observations. Additional ozone production attributable to lightning NO within the storm cloud during the lifetime of the storm was very small (~2 ppbv). However, simulations of the photochemistry over the 24 hours following the storm show that an additional 10 ppbv of ozone production can be attributed to lightning NO production in the upper troposphere. Convective transport of HO\textsubscript{X} precursors led to the generation of a HO\textsubscript{X} plume, which substantially aided the downstream ozone production. Soluble species mixing ratios in the simulated cloud were all within a factor of two of observations.


1. Introduction

[2] The nitrogen oxides NO and NO\textsubscript{2} (known collectively as NO\textsubscript{X}) are important atmospheric trace species owing to their catalytic effects on the production of tropospheric ozone. NO\textsubscript{X} also affects the OH concentration which impacts the oxidizing capacity of the atmosphere. Lightning is an important source of NO\textsubscript{X}, particularly for the upper troposphere [Ridley et al., 1996; DeCaria et al., 2000]. Though lightning accounts for only roughly 15\% of the NO\textsubscript{X} input to the troposphere [Bradshaw et al., 2000], lightning NO\textsubscript{X} is primarily found in the upper troposphere [Pickering et al., 1998] where its lifetime is longer and its ozone producing potential greater [Liu et al., 1987; Pickering et al., 1990] than in the boundary layer, where the majority of NO\textsubscript{X} is added to the atmosphere.

[3] There remains large uncertainty over the total contribution of lightning to the global NO\textsubscript{X} budget, with most studies placing the figure at between 2 and 20 Tg(N) yr\textsuperscript{-1} (see DeCaria et al. [2000] for summary of some recent studies). Several studies published since that of DeCaria et al. [2000] have suggested that the lower portion of this range of values is most likely. Tie et al. [2001] obtained reasonable comparisons between airborne observations of reactive nitrogen species and output of simulations using the MOZART (Model for Ozone and Related Chemical Tracers) with a lightning source of 7 TgN yr\textsuperscript{-1}. Zhang et al. [2003a] have shown that summertime lightning plays a dominant role in controlling middle and upper tropospheric NO\textsubscript{X} and O\textsubscript{3} over the United States with a global source strength of 7 TgN yr\textsuperscript{-1}. On the basis of Harvard
GEOS-CHEM global chemical transport model simulations, Martin et al. [2002] suggest that a value of 6 Tg(N) yr\(^{-1}\) shows the best agreement with observations. Huntrieser et al. [2002] estimate the strength of the lightning source at 3 Tg(N) yr\(^{-1}\) based on detailed analysis of airborne NO\(_x\) measurements of European thunderstorms.

[4] The uncertainty in global lightning NO production stems from two primary sources: the global flash rate and the production of NO per flash. While satellite-based lightning detection has provided useful information concerning the global number of flashes, major uncertainty still remains regarding the NO production per flash or per meter of flash channel length. Huntrieser et al. [2002] estimate a median value of \(2.7 \times 10^{21}\) molecules NO per meter flash length based on aircraft measurements of NO spikes during the EULINOX (European Lightning NO\(_x\) Experiment) field project conducted over central Europe, but the values for individual flashes span over 2 orders of magnitude. Stith et al. [1999] obtain a range of \(2.0 \times 10^{20}\) to \(1.0 \times 10^{22}\) molecules NO per meter flash length based on aircraft measurements for several STERAO-A (Stratosphere-Troposphere Experiment: Radiation, Aerosols, and Ozone) storms. On the basis of an analysis of lightning interferometer and airborne NO\(_x\) data obtained during the 10 July STERAO storm, in combination with NO\(_x\) tracer transport results from a cloud model, Skamarock et al. [2003] calculate a mean NO production of \(1.0 \times 10^{21}\) molecules NO\(_x\) per meter of flash channel. The flashes considered in these analyses of anvil NO\(_x\) predominate predominantly intracloud (IC) flashes. Langford et al. [2004] measured NO\(_x\) column abundances in the core region of a thunderstorm over Boulder, Colorado, and used these data along with radar and cloud-to-ground (CG) flash rates to estimate a mean production of \(5.8 \times 10^{20}\) molecules per CG flash, which is close to the theoretical estimate of Price et al. [1997]. NO production is thought to occur in the hot channel within a flash, and not in electrical coronas [Coppens et al., 1998]. Production within a flash is also believed to be proportional to ambient pressure [Wang et al., 1998]. An open question is the ratio of NO\(_x\) contributed per IC lightning flash to that per CG lightning flash. Recent work [Gallardo and Cooray, 1996; DeCaria et al., 2000; Fehr et al., 2004] has challenged the traditional view [e.g., Price et al., 1997] that an individual IC flash produces much less NO than a CG flash.

[5] The effects of convective transport on the chemistry of the atmosphere can also be significant. By analyzing airborne tracer measurements in the vicinity of a thunderstorm, Dickerson et al. [1987] verified that deep convection can significantly alter the vertical distribution of key chemical species. Pickering et al. [1990] determined that ozone production in the upper troposphere can be enhanced by convective transport of precursor species.

[6] Cloud scale chemical transport models can provide valuable insight into the impact of convection and lightning on tropospheric chemistry [e.g., Pickering et al., 1992, 1996]. Passive tracer transport for the 10 July 1996 STERAO-A storm was calculated by Skamarock et al. [2000] using a three-dimensional (3-D) cloud model. Barth et al. [2001] examined the fate of tracers with various solubilities using the same 3-D cloud model simulation of the 10 July STERAO-A storm. Wang and Prinn [2000] used a cloud model to investigate the impact of vertical transport, cloud-perturbed UV fluxes, soluble species scavenging, and lightning NO\(_x\) on the atmosphere. Zhang et al. [2003b] have developed a 3-D storm electrification model in which IC flashes are explicitly simulated.

[7] The STERAO-A experiment has been summarized by Dye et al. [2000]. DeCaria et al. [2000] used a 2-D cloud model that included a parameterized source of lightning NO\(_x\) to study the production and advection of NO\(_x\) associated with the developing thunderstorm that was observed on 12 July 1996, as part of the STERAO-A field campaign. The 2-D results indicated that IC flashes were significant sources of NO\(_x\), not only collectively, but also on a per-flash basis. In this paper we study the lightning NO\(_x\) production and subsequent ozone production for the same storm using a 3-D cloud-scale chemical transport model (CSCTM), comparing the results with the previous 2-D study. A complete description of the 3-D cloud model simulation of the convection (used to drive the CSCTM described in this paper) is given by Stenchikov et al. [2005]. A detailed description of the observed storm is given by DeCaria et al. [2000].

2. The 3-D Cloud-Scale Chemical Transport Model

[8] The 3-D cloud-scale chemical transport model (CSCTM) is driven with meteorological fields generated by the Goddard Cumulus Ensemble (GCE) model, described fully by Tao and Simpson [1993] and Tao et al. [2001]. Stenchikov et al. [2005] describe the particular version of the model used in these simulations. The horizontal and vertical grids have fixed spacing of 2 km and 500 m, respectively. Advection of chemical species is accomplished using an explicit Van Leer scheme (described by Allen et al. [1991]). Diffusion is handled with an explicit, forward-in-time, centered-in-space finite difference scheme. Transport is calculated “off-line,” with the required fields from the GCE Model saved at intervals of 10 min for use by the CSCTM. A time step of 15 s is used to ensure numerical stability of the advection and diffusion routines.

[9] Chemical production and loss are calculated using a version of the SMVGEAR-II solver [Jacobson, 1995]. Thirty-five chemically active species (NO, NO\(_2\), NO\(_3\), N\(_2\)O, HONO, HNO\(_3\), HO\(_2\)NO\(_2\), O(1D), O(1\(^{3}\)P), OH, O\(_3\), HO\(_2\), H\(_2\)O\(_2\), CO, CH\(_4\), C\(_2\)H\(_6\), C\(_3\)H\(_8\), C\(_6\)H\(_{10}\), HCHO, CH\(_2\)CHO, CH\(_3\)O, CH\(_3\)O\(_2\), CH\(_3\)O\(_2\)NO\(_2\), CH\(_3\)O\(_2\)NO\(_2\), C\(_2\)H\(_4\)O\(_2\), C\(_3\)H\(_6\)O, C\(_3\)H\(_6\)O\(_2\), C\(_2\)H\(_4\)O\(_2\), C\(_2\)H\(_4\)OH, HO\(_2\)H\(_2\)O\(_2\), CH\(_2\)O\(_3\), CH\(_3\)CO\(_3\)NO\(_2\), and H\(_2\) are included, and three additional species (H\(_2\)O, O\(_2\), and N\(_2\)) enter the chemical calculations but their mixing ratios remain unchanged by chemical processes. The chemical mechanism includes 76 gas phase kinetic reactions and 18 photolytic reactions, representing the O\(_3\) – NO\(_x\) – HO\(_x\) – CO system. NO\(_x\) is maintained in equilibrium with other NO\(_x\) species (HNO\(_3\), PAN, H\(_2\)NO\(_2\), HONO, NO\(_3\), N\(_2\)O\(_3\)). Four nonmethane hydrocarbons (ethane, propane, butane, and ethene) are used. The chemistry is updated at 30-s intervals (though SMVGEAR-II itself uses a smaller internal time step based on stiffness). Reaction rates are from DeMore et al. [1997].
Clear sky photolysis rates are calculated using the method of Stamnes et al. [1988], using observed overhead-column ozone amounts measured by an ozonesonde launched from Boulder, Colorado, at 1635 UT 12 July 1996. Enhancement of photolysis rates within clouds (illustrated in Figure 1) is based on the “crudely typical” summertime estimates from Madronich [1987]. Three separate regimes of cloud thickness are considered: very thick (depth > 5 km), thick (5 km > depth > 1 km), and thin (depth < 1 km). For the “very thick” regime, clear-sky photolysis rates are doubled at the top of the cloud, and multiplied by 0.1 at cloud base, with a linear enhancement profile between the top and the bottom. For the “thick” regime the top and bottom enhancements are 1.7 and 0.4, respectively. For thin clouds an enhancement of 1.4 is used throughout the cloud. Above very thick and thick clouds the enhancement factor is held constant at the top of the cloud; the grid cells below the thick clouds all have an enhancement equal to that at the bottom of the cloud. For the “thin” regime, the clear sky enhancement values both above and below the cloud are set to 1.0.

Since the CSCTM is run “off-line” from the cloud model, explicit calculation of liquid phase chemistry is not possible. To account for the wet scavenging of the moderately soluble species (HNO₂, H₂O₂, HCHO, and CH₃OOH) the following scheme is used. The equilibrium gas phase fractions of each species are calculated from the mass of hydrometeors present and Henry’s law coefficients (temperature effects on the Henry’s law coefficients are included). The first time liquid water appears in a grid cell the gas phase mixing ratios of the soluble species are multiplied by the equilibrium gas-phase fraction. At all subsequent time steps for that grid cell the gas-phase production or loss is multiplied by updated values of the equilibrium gas phase fractions, and the result is added to (or subtracted from) the existing gas-phase mixing ratio. Nitric acid (HNO₃) and the nitrate radical (NO₃) are treated differently because of their extreme solubility. At the typical pH values of cloud and rainwater, for any liquid water content greater than 0.001 g m⁻³, virtually all of these species are absorbed into the hydrometeors. Therefore, when liquid hydrometeors are present, the HNO₃ and NO₃ mixing ratios in that grid cell are set to zero. Gases are assumed to be released to the air upon freezing of liquid hydrometeors, and uptake by ice is not included.

Initial profiles of CO, NO, O₃, HCHO, C₂H₆, C₃H₈, C₄H₁₀, C₅H₁₀, H₂O₂, and CH₃OOH were derived from data taken from the NOAA WP-3D aircraft during a spiraling ascent at ~2200 UT in clear air ahead of the convection. There were also measurements of NOₓ, PAN, and PPN which were used to derive estimates for HNO₃ (by subtracting NOₓ, PAN, and PPN from NOₓ). NO₂ was not directly measured, but was inferred from the photostationary state assumption [Leighton, 1961], which assumes that the production of NO₂ via reaction of NO with O₃,

\[ NO + O_3 \rightarrow NO_2 + O_2, \]

is nearly instantaneously balanced by its destruction through photolysis,

\[ NO_2 + hv \rightarrow NO + O. \]

In the free troposphere, and in the boundary layer away from regions of high concentrations of organic peroxy radicals (which can react with NO to form NO₂), the photostationary state assumption is reasonable, and the concentration of NO₂ can be inferred by

\[ [NO_2] \approx \frac{k(1)[NO][O_3]}{J_2}, \]

where \( k(1) \) is the rate coefficient for reaction (1) and \( J_2 \) is the photolysis rate for NO₂.

Rather than start the chemistry in the model “cold” at the beginning of the simulation, a 15-min “spin-up” was performed using a column model with the same chemical reactions as the 3-D model. For OH, typical values of 0.1 pptv in the boundary layer, and 0.01 pptv in the free troposphere were used for initialization; for HO₂ initial values of 1.0 pptv in the boundary layer, and 0.1 pptv in the free troposphere were used, based on work by Seinfeld and Pandis [1998]. The spin-up allows those radical species with unknown concentration to form and adjust their mixing ratios to an equilibrium condition.

3. Lightning NO Parameterization

The scheme used for parameterizing the production and distribution of lightning NOₓ is essentially that of DeCaria et al. [2000], which can be consulted for a detailed derivation. The equation for the change in NO mixing ratio at a given altitude in the storm due to a single lightning flash is

\[ \Delta q_{NO_x}(z) = \frac{KRT(z)f(z)}{A(z)}, \]

where \( R \) is the universal gas constant, \( T(z) \) is the temperature at level \( z \), and \( f(z) \) is the vertical distribution function for...
lightning channel segments, and $A(z)$ is the horizontal area of the storm at level $z$. The term $K$ is

$$K = \frac{N_{\text{total}}}{\int_{z_0}^{z_T} f(z)p(z)dz},$$

where $p(z)$ is the pressure profile, and $z_0$ and $z_T$ are the lower and upper altitudes for the lightning. $N_{\text{total}}$ is the estimated number of moles of NO generated over the entire length and duration of the lightning flash.

[15] On the basis of lightning channel data presented by MacGorman and Rust [1998], the CG flash segments are assumed to have a Gaussian vertical distribution given as

$$f(z) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(z - \mu)^2}{2\sigma^2}\right),$$

where $\mu$ is the altitude of the maximum negative charge density, and $\sigma$ is chosen such that greater than 99% of the lightning channel segments lie between the ground and the storm top. For CG flashes, $\mu$ was chosen as the altitude of the $-15^\circ C$ isotherm, a reasonable proxy for where the maximum negative charge is located [Houze, 1993]. For IC flashes, two Gaussian distributions were superimposed to achieve a bimodal distribution. The lower mode was at the altitude of the $-15^\circ C$ isotherm, while the altitude of the upper mode was set at $-45^\circ C$. Figure 2 shows examples of the CG and IC vertical channel segment distributions used in the model.

[16] MacGorman and Rust [1998] point out that based on numerous studies mapping lightning channels with respect to radar reflectivity [e.g., Mazur and Rust, 1983; Mazur et al., 1986; Proctor, 1983; Ray et al., 1987; Rutledge and MacGorman, 1988; Shao and Krehbiel, 1996; Taylor et al., 1984], most lightning channels correspond to areas of reflectivity $>20$ dBZ, except those channels very near the top of the cloud. Therefore $A(z)$ is defined as the area within the storm enclosed by the 20-dBZ isoecho.

[17] The CG flash rate was determined using data from the National Lightning Detection Network™ (NLDN). The IC flash rate was computed by subtracting the CG flash rate from the total flash rate determined from the VHF interferometer operated by the French Office Nationale d’Etudes et de Recherches Aerospatiales (ONERA), counting only those flashes with durations greater than 100 ms. The NO from lightning was introduced into the model at 3-min intervals. Figure 3 shows the time series of CG and IC lightning flash rates for the period from 2000 to 2400 UT (1300–1700 LST). Lightning activity did not begin until ~2100 UT, with 188 CG and 2121 IC flashes recorded during the subsequent 3 hours. The IC flash rate may possibly have a low bias, especially during the early portion of the storm when it was located on the edge of the interferometer network. However, the bulk of the IC activity occurred after 2200 UT when the storm position allowed better flash detection. NO production from a CG flash ($P_{CG}$) was calculated from the mean peak current reported by the

Figure 2. Examples of representative vertical distribution functions for (a) CG and (b) IC flashes used in the lightning NO$_x$ algorithm. Note that the ground surface is at about 1.5 km MSL in the region of interest.

Figure 3. (a) Time series of observed CG and IC lightning flash rates for the period of simulation. Units are flashes min$^{-1}$ averaged over 3-min intervals. (b) Time series of ratio of IC to CG flash rates.
NLDN during the storm, using the method of Price et al. [1997], resulting in a value of $P_{CG} = 460$ mole flash$^{-1}$ (details from DeCaria et al. [2000]).

[18] The NO production from IC flashes suffers from even greater uncertainty than does that for CG flashes. The 2-D model results for this storm indicated a ratio of $P_{IC}/P_{CG}$ greater than or approximately equal to 0.5. For the 3-D study, values of $P_{IC}$ equal to 0.1, 0.5, 0.75, 1.0 and 1.5 times $P_{CG}$ were used in several sensitivity tests in our model simulations, and the results were compared with NO observed in the anvil.

4. Results

[19] DeCaria et al. [2000] have described the synoptic conditions and evolution of the 12 July STERAO-A storm. The convective system began as group of cells in southeastern Wyoming, which strengthened and organized into a linear structure between 2141 and 2212 UT. By 2258 UT the storm had evolved into a four-cell rectangular structure which reached the Colorado border by 2304 UT. The northeastern cell evolved into a single intense cell by 0113 UT on 13 July. This cell may have acquired supercell characteristics for a brief period. A 4-hour simulation of this convective system using the 3-D GCE model is described by Stenchikov et al. [2005]. The model reproduced the linear and four-cell structures quite well, but transitioned the southeastern cell into an intense cell rather than the northeastern one. The overall time evolution of the storm and speed of propagation are very similar to the observations. The 12 July STERAO-A storm was similar to the 10 July event simulated by Skamarock et al. [2000] in that both storms were configured as multicellular lines in their initial stages. However, the 12 July storm experienced an intermediate four-cell quadrilateral structure, which the 10 July storm did not attain. In the later stages the 10 July storm transitioned to a well-developed supercell, but the 12 July event only very marginally achieved supercell status.

[20] The CSCTM simulation was run for 4 hours (starting at 2030 UT), driven by the GCE model output. The lightning parameterization was not started until after a 30-min spin-up period, in order to allow the simulated convection to develop into the size and strength of the observed electrified storm before injecting lightning-produced NO. The CSCTM results were compared with data taken from the University of North Dakota's Cessna Citation II aircraft, which performed a spiraling ascent through the anvil shortly after 2300 UT. These data were taken approximately 2 hours after

![Figure 4. Box (thick solid line) over which vertical profiles of CO, NOx, and other species are averaged, shown in relation to the model-computed zero dBZ radar reflectivity contour at an altitude of 9.5 km MSL. The smaller dotted contours represent 50 dBZ and show the cores of the convective cells.](image-url)
the first lightning flash was observed, which corresponds to the model simulation fields at $t = 150$ min.

Analysis of the aircraft track with respect to the convective cells showed the center of the aircraft’s spiral located approximately 55 to 60 km east and 20 km north of the southeastern cell. Rather than pick a specific profile from the model domain, horizontally averaged profiles of chemical species were used for comparison with the aircraft data. These averages were performed within a 42 km square box shown in Figure 4.

4.1. Transport Only

Figure 5 shows the initial profiles of CO, NO$_x$, and O$_3$ from the model simulation. These profiles were derived from WP-3D and Citation measurements outside the storm and from the Boulder, Colorado, ozonesonde profile (see DeCaria et al. [2000] for details). The model was first run in a “transport only” mode (i.e., no active chemical reactions and no lightning source of NO). Figure 6a shows the comparison of the model profile of CO mixing ratio at $t = 150$ min compared with the aircraft observations in the storm anvil. The brackets are a measure of the variability of the 441 individual model profiles that comprise the average profile. The close agreement establishes the model’s ability to represent convective transport. The agreement with the measured profile is better in this 3-D simulation than was obtained in the 2-D simulation reported by DeCaria et al. [2000]. The mean absolute difference between model and measurements over the 9–11 km layer of maximum anvil CO was 3 ppbv for the 3-D simulation versus 5 ppbv for the 2-D model run. Maximum increases of 35–40 ppbv CO above the initial condition at 11 km in the anvil are noted and can be attributed to convective transport. Stenchikov et al. [2005] note that the maximum vertical velocity in this storm was $\sim 20$ m s$^{-1}$, whereas it was $\sim 30$ m s$^{-1}$ in the 10 July STERAO-A case. As would be expected, a larger (45–50 ppbv) maximum increase in CO at $\sim 11$ km due to convective transport was estimated for the 10 July storm [Skamarock et al., 2000]. The comparison for O$_3$ is shown in Figure 6b. The model average profile is lower than the observations, though the observations are within the range of variability of the individual model profiles that make up the average profile. It is possible that the initial condition data from the Boulder ozonesonde contained lower mixing ratios in the upper troposphere than was actually the case in the vicinity of where the storm developed.

To compare the model simulated NO$_x$ with observations measured from the Cessna Citation II in the anvil of the storm, the NO measurements needed to be converted into values of NO$_x$ by estimating the amount of NO$_2$ present using the photostationary state approximation. The photolysis rate for NO$_2$ can be readily calculated under clear sky conditions, but within the anvil the photolysis rate can either be increased or decreased depending on the optical depth of the cloud and the solar zenith angle [Kelley et al., 1995]. The ratio $J_{\text{anvil}}/J_{\text{clear sky}}$ will be somewhere in the range of 0.5 to 4.0 [Madronich, 1987]. Therefore a single value of NO$_x$ mixing ratio is not plotted, but instead, the likely range of the mixing ratio is plotted. The comparison of passive nonlightning NO$_x$ in the anvil of the simulated storm compared with aircraft observations is shown in Figure 6c. The large difference between this version of
the model (which has no lightning) and observations is due to the generation of NO\textsubscript{x} by lightning.

4.2. Inclusion of Lightning Generated NO\textsubscript{x} With Transport

[24] Figure 7 shows the comparison of the model NO\textsubscript{x} profile in the anvil with the aircraft observations for PCG = 460 mole flash\textsuperscript{-1} and several different values of PIC. Including a source of NO\textsubscript{x} from lightning in the model gives much better agreement with the observed NO\textsubscript{x} profile in the anvil of the storm. The results suggest that production efficiency of NO\textsubscript{x} by an IC flash is significant, and on the order of that from a CG flash. The best comparison in terms of the amplitude and altitude of the NO\textsubscript{x} plume in the anvil is achieved using a PIC value that equals that for PCG (Figure 7c); in terms of column NO\textsubscript{x} mass (see Table 1), the best results are for PIC to be in the range of 75 to 100% of that for PCG. In this case (PIC = 0.75 PCG), IC lightning contributed 73% of the total NO\textsubscript{x} mass in the anvil column. CG lightning contributed only 10% of the column NO\textsubscript{x} mass, while the remaining 17% came from either pre-existing upper tropospheric NO\textsubscript{x} or that transported from the boundary layer. Skamarock et al. [2003] reported that somewhat over 60% of the observed NO\textsubscript{x} flux out of the

Table 1. Tests of Lightning NO Production Scenarios

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Anvil Column NO\textsubscript{x}, 7–11.2 km, (\mu g(N) m^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observations</td>
<td>370–550</td>
</tr>
<tr>
<td>Model: transport only (no lightning)</td>
<td>70–90</td>
</tr>
<tr>
<td>Model: (P_{CG} = 460) mole flash\textsuperscript{-1}; (P_{IC} = 46) mole flash\textsuperscript{-1}</td>
<td>130–230</td>
</tr>
<tr>
<td>Model: (P_{CG} = 460) mole flash\textsuperscript{-1}; (P_{IC} = 230) mole flash\textsuperscript{-1}</td>
<td>240–490</td>
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<tr>
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<td>310–660</td>
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<tr>
<td>Model: (P_{CG} = 460) mole flash\textsuperscript{-1}; (P_{IC} = 460) mole flash\textsuperscript{-1}</td>
<td>370–820</td>
</tr>
<tr>
<td>Model: (P_{CG} = 460) mole flash\textsuperscript{-1}; (P_{IC} = 690) mole flash\textsuperscript{-1}</td>
<td>510–1150</td>
</tr>
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</table>
anvil of the 10 July STERAO-A storm was produced by lightning.

4.3. Results From Inclusion of Chemistry

[25] The previous results were all generated with a model that does not include chemical reactions occurring within the thunderstorm. To explore the significance of chemical reactions, we ran the transport and lightning model coupled to the chemical solver discussed in section 2. The results shown below are for the lightning scenario of PIC = 0.75 PCG. The three main questions of interest were as follows. (1) How will the inclusion of chemical reactions affect the resultant NOx distribution in the anvil? (2) How will the inclusion of chemical reactions affect the resultant O3 distribution in the anvil? (3) Will the lightning NOx significantly impact the distribution of O3 on the timescale of the convection? These questions are addressed in the following sections.

4.3.1. Effect of Including Chemical Reactions on the O3 and NOx Profiles

[26] Figure 8 compares the averaged profiles of O3 in the anvil region from the transport only simulation, and from the full CSCTM simulation (without lightning). The anvil thickness in the center of the averaging box was 5 km, the borderline between the “thick” and “very thick” regions for the photolysis enhancement parameterization. The profiles are very similar; however, the inclusion of chemical reactions does result in a minimal increase in O3 (less than 1 ppbv) throughout much of the free troposphere over the course of 150 min. The increase in the boundary layer is more pronounced, with up to 3 ppbv more ozone in the profile that included chemical reactions. This is due to the greater concentrations of ozone precursors such as NOx and hydrocarbons in the boundary layer versus the free troposphere. During the course of the simulation with chemistry, NOx is converted to reservoir species. Instantaneous rate calculations show that in the boundary layer regions the primary loss pathway for NOx was formation of PAN, with formation of HNO3 ranking second in importance. In the middle and upper troposphere, conversion to HO2NO2 and HNO3 dominate. At 8 km the net conversion of NOx to reservoir species was ~30 pptv over the 4-hour simulation.

4.3.2. Impact of Lightning NOx on the O3 Profile

[27] The inclusion of lightning NOx had very little impact on the ozone profile in the anvil during the lifetime of the storm. Figure 9a displays the anvil-averaged ozone profiles

![Figure 8](image1.png)

**Figure 8.** Model profiles of ozone (averaged over the box in Figure 4) at 150 min for the simulations with (dashed line) and without (solid line) chemical reactions.

![Figure 9](image2.png)

**Figure 9.** Model profiles of (a) ozone (averaged over the box in Figure 4) at 150 min for the simulations without (solid line) and with (dashed line) lightning, and (b) HOx from the simulations without (solid line) and with (dashed line) lightning. The initial HOx profile is shown by the dotted line.
with and without lightning. The curves are nearly identical through most of the column, differing significantly only in the region between 8 and 12 km MSL where the lightning NO\textsubscript{x} has enhanced the photochemical O\textsubscript{3} production rate and increased O\textsubscript{3} mixing ratios by up to 2 ppbv over the 150 min of the simulation. This region corresponds to the maximum in NO\textsubscript{x} concentrations; however, there is also a significant NO\textsubscript{x} plume below 8 km which did not lead to enhanced ozone. This is explained by viewing the HO\textsubscript{x} (OH + HO\textsubscript{2}) profile (Figure 9b), which shows that the region of enhanced ozone corresponds closely with the HO\textsubscript{x} plume in the anvil, and illustrates the importance of HO\textsubscript{x} on ozone production. (The difference in HO\textsubscript{x} profiles for the simulations with and without lightning is discussed in section 4.3.3).

That the lightning NO\textsubscript{x} lead to such small ozone enhancements over the 4-hour simulation of the active storm is not surprising. Lightning NO\textsubscript{x} can certainly lead to enhanced ozone production downstream in the thunderstorm outflow as shown by Pickering et al. [1990, 1996]. However, this process occurs on a timescale longer than that of an individual thunderstorm (see section 4.3.4). Aircraft observations for this storm and others [e.g., Luke et al., 1992; Ridley et al., 1996] show little evidence for short-term photochemical enhancement of ozone within thunderstorms.

**4.3.3. Effects of Convection and Lightning on the HO\textsubscript{x} Profile**

The initial HO\textsubscript{x} profile, along with the profiles of HO\textsubscript{x} from the simulations with and without lightning, has been shown previously in Figure 9b. The role of convection is evident in the maximum of HO\textsubscript{x} in the anvil, between 8 and 12 km MSL. This maximum is a reflection of the importance of convective transport of HO\textsubscript{x} precursors into the upper troposphere as has been discussed by Jaegle et al. [1997] and Prather and Jacob [1997], for example. Convection pumps large quantities of water vapor into the otherwise relatively dry upper troposphere, and combined with the enhanced production of O(1D) from ozone photolysis in and above the anvil, leads to enhanced production of OH via the reaction

\[
\text{H}_2\text{O} + \text{O}(^1\text{D}) \rightarrow \text{OH} + \text{OH}.
\]

Other important HO\textsubscript{x} precursors that are transported into the upper troposphere are H\textsubscript{2}O\textsubscript{2}, CH\textsubscript{3}OOH, and HCHO. Figure 10 shows the profiles of H\textsubscript{2}O\textsubscript{2} and CH\textsubscript{3}OOH from the averaging box in the model for the initial conditions and after convective transport. Enhancement of these two species by factors of 3 and 5, respectively, is noted at 10 km, the altitude where the mixing ratios of these species peak in the convective outflow. The convective enhancement extends from 9 to 13 km for H\textsubscript{2}O\textsubscript{2} and 8 to 13 km for CH\textsubscript{3}OOH. Our results for CH\textsubscript{3}OOH (Figure 10) agree with the Barth et al. [2001] 10 July STERAO-A model simulations, which imply that this species is readily transported to the upper troposphere. HCHO is also enhanced by a factor of 3 at 10 km, and for water vapor the increase is a factor of 2. An additional precursor which was not included in the current chemistry mechanism is acetone, CH\textsubscript{3}C(O)CH\textsubscript{3}. Recent work [Arnold et al., 2004] has shown that temperature-dependent quantum yields for acetone produce photolysis rates that lead to a ~250-day acetone lifetime in the midlatitude upper troposphere. Therefore the acetone contribution to HO\textsubscript{x} for the timescales considered here would be minimal.

The inclusion of lightning NO\textsubscript{x} has a dramatic impact on the HO\textsubscript{x} profile. The abundance of NO from lightning results in a reduction of the HO\textsubscript{2}/OH ratio (Figure 11) through the NO + HO\textsubscript{2} and NO\textsubscript{2} + HO\textsubscript{2} reactions, as well

![Figure 10. Vertical profiles of (a) H\textsubscript{2}O\textsubscript{2} and (b) CH\textsubscript{3}OOH averaged over the box in Figure 4 at 150 min. Profiles from the model simulation without (with) lightning NO production are shown with solid lines (dashed lines). The initial peroxide profiles are shown with dotted lines.](image-url)
as in enhanced loss of OH via production of HNO₃, and to a lesser extent, HONO. This results in the HOₓ maxima with lightning being only 75% of that without lightning. Inclusion of lightning NOₓ also reduces the mixing ratios of the peroxides in the convective outflow (Figure 10). The anvil-averaged HO₂/OH ratio reduction with inclusion of lightning NOₓ is substantial. Over the course of the simulation the ratio at 10.5 km declines from ~48 to 15 as lightning NOₓ is added to the anvil.

### 4.3.4. Comparison of Other Species With Measurements

[31] Though the main focus of this study was lightning NOₓ production and the resulting ozone photochemistry, the fates of other key species were also of interest. The WP-3D aircraft flew primarily outside the cloud from 2033 to 0230 UT but made two passes through the cloud between 0100 and 0200 UT. This time interval is 0.5 to 1.5 hours after the 4-hour model simulation ended at 0030 UT. However, these are the only in-cloud measurements of formaldehyde and total peroxides available. In addition, measurements of NOₓ, PAN, PPN, and NO were used along with calculated NO₂ (described previously) to obtain an estimate for HNO₃ in the cloud. Table 2 shows the maximum, minimum, and mean observed mixing ratios of HCHO, total peroxides, and HNO₃ for the two anvil penetration periods along with the maximum, minimum, and mean mixing ratios within the model-simulated cloud at the appropriate level in the vertical. Since the WP-3D anvil penetrations occurred approximately an hour after the end of the model simulation, the model results presented are for the last model time at which a substantial cloud existed in the model output (210 min), corresponding to approximately 2400 UT. The range of HCHO mixing ratios observed in both anvil penetrations is larger than the range of values found in the model. It appears that, in general, that the model underestimated HCHO. Both the maximum and minimum total peroxide mixing ratios from the model exceeded those in the observations. The estimate of HNO₃ in the cloud agrees well with the model. The maximum and minimum HNO₃ mixing ratios from the model represent very nearly the range of values found in the observations. It appears that the wet scavenging parameterization is performing well for HNO₃, but may have removed too much HCHO and an insufficient amount of peroxides. However, all model values are within a factor of 2 of those observed.

### 4.4. Downstream Ozone Production

[32] The chemical transport model could not be used to directly assess the impact of the lightning NOₓ on downstream ozone production. This is because of the limited size of the model domain, which could not contain the storm over a 24-hour simulation. Instead, a chemistry only model was used to estimate upper tropospheric ozone production. This model is nothing more than the chemical transport model with advection turned off, so that the chemical plume remains stationary within the model domain, but the domain is considered to be moving downstream with the atmospheric flow. However, owing to vertical wind shear, the resulting ozone production cannot be considered to occur in a single column. The anvil is assumed to have dissipated so that clear sky photolysis rates can be used. Isotropic eddy diffusion is included to allow dilution of the chemical plume. In the chemical transport model the isotropic eddy diffusion coefficients were input from the cloud model. These values can be quite large near the top of the thunderstorm (on the order of 200 m² s⁻¹), and are not expected to be representative of the upper troposphere downstream of the convection. Away from convection, eddy diffusion coefficients from the cloud model were on the order of 5 m² s⁻¹ near the surface, and negligible in the upper troposphere, which is consistent with theory [Chamberlain and Hunten, 1987]. Therefore an eddy diffusion coefficient of 5 m² s⁻¹ was used at the surface (1.5 km MSL) and was assumed to decay exponentially in the vertical [Chamberlain and Hunten, 1987] with an e-folding scale of 4 km. This reduces the diffusion coefficient to a value of 0.22 m² s⁻¹ at 14 km MSL. The lack of advection and reduced eddy diffusion coefficients allowed a much longer time step of 15 min to be used during this portion of the simulation.

[33] The chemistry-only model was initialized with the chemical fields from the output of the CSCTM (with

### Table 2. Model to Measurement Comparison for Soluble Species

<table>
<thead>
<tr>
<th>Altitude, km</th>
<th>Species</th>
<th>Observed, ppbv</th>
<th>Simulated, ppbv</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Maximum</td>
<td>Mean</td>
</tr>
<tr>
<td>6.7</td>
<td>HCHO</td>
<td>1.01</td>
<td>0.75</td>
</tr>
<tr>
<td>6.7</td>
<td>peroxides*</td>
<td>1.56</td>
<td>1.11</td>
</tr>
<tr>
<td>6.7</td>
<td>HNO₃</td>
<td>0.41</td>
<td>0.18</td>
</tr>
<tr>
<td>8.0</td>
<td>HCHO</td>
<td>0.99</td>
<td>0.65</td>
</tr>
</tbody>
</table>

*Total peroxide measurement is (H₂O₂ + 0.65 × higher peroxides) and at these altitudes is approximated by (H₂O₂ + 0.65 CH₃OOH) in the model output.
chemistry turned on) at 180 min, using the water vapor field from the cloud model at the same time (180 min was chosen because after this time the simulated convection rapidly dissipated). The model was then integrated forward for 24 hours. Two simulations were run, one initialized with the chemical fields from the CSCTM with lightning and one initialized with the fields without lightning. Ozone from the latter simulation was subtracted from the former to yield the

Figure 12. (a) Vertical profile of $\Delta P(O_3)$ from lightning NO$_x$, averaged over the box in Figure 4. Solid line is average, while brackets show minimum and maximum. (b) Same as in Figure 12a but for entire model domain.

Figure 13. (a) Change in net ozone production due to lightning NO$_x$, $\Delta P(O_3)$, versus lightning NO$_x$ at altitude of 10.5 km MSL. (b) Total ozone production, P(O$_3$), versus total NO$_x$ (including lightning) for the same altitude. In each panel, 5860 points are plotted.
were removed prior to this subtraction. Figure 12a shows two runs due to photochemical production during the storm and from lightning NO\textsubscript{x} ozone production anywhere in the domain also occurred at cloud-influenced regions), and shows that the maximum ozone production anywhere in the domain also occurred at 10.5 km MSL and had a value of 13 ppbv d\textsuperscript{-1}. Therefore the region of the model anvil corresponding to the location of the Citation spiral appears to be representative of the peak anvil outflow.

Another interesting way of analyzing these data is to plot \(\Delta P(O_3)\) versus lightning NO\textsubscript{x} for each grid cell at a given model level. Figure 13a displays such a plot for an altitude of 10.5 km MSL. Only those grid cells having a non-zero lightning NO\textsubscript{x} are plotted (a total of 5860 cells). This figure shows that \(\Delta P(O_3)\) is highly correlated with lightning NO\textsubscript{x}. It also shows that \(\Delta P(O_3)\) varies approximately in a linear fashion up to a lightning NO\textsubscript{x} mixing ratio of about 300 pptv, after which production begins to increase less rapidly. It is likely that this decrease in slope indicates that net ozone production rate is approaching the maximum possible at this altitude, solar zenith angle, and HO\textsubscript{x} concentration, similar to that shown in a number of other model studies [e.g., Brasseur et al., 1996]. Total ozone production from both NO\textsubscript{x} transported from the boundary layer and from lightning NO\textsubscript{x} at an altitude of 10.5 km (Figure 13b) reached 15 ppbv d\textsuperscript{-1}. The value of \(\Delta P(O_3)\) obtained using the 3-D simulation is larger than that obtained from the 2-D runs (7 ppbv d\textsuperscript{-1}), primarily because of the differing manner in which important radicals such as HO\textsubscript{x} and organic peroxy radicals were initialized. In the 2-D simulation, there was no initial “spin-up” and evolution of the chemistry. Organic peroxy radicals were initially of zero concentration, and the initial concentrations of OH and HO\textsubscript{2} were only estimates from model runs done on other convective events. In the 3-D simulation, HO\textsubscript{x} and other important radicals were initially initialized and the more accurate simulation of transport is likely due to differences in the way some species were initialized. In the 2-D simulation, HO\textsubscript{x} and other important radicals were initially “spun-up” to representative values, and then allowed to further adjust and evolve as the convection developed, giving a more representative picture of the chemistry for use in the 24-hour ozone production simulations. In addition, a more accurate, less-diffusive advection scheme was used in the 3-D simulation, producing more realistic mixing ratios of ozone precursors.

5. Summary and Conclusion

A 3-D cloud scale chemical transport model has been used to simulate the chemical characteristics of the 12 July storm observed during the STERAO-A field project in order to estimate convective transport of a variety of chemical species, lightning NO\textsubscript{x} production, and the impact on tropospheric ozone. The model replicated the observed convective enhancement of CO in the anvil. The enhancement was smaller in this storm than in the 10 July STERAO-A case due to somewhat weaker vertical velocities. Assuming that both IC and CG flashes produce 460 moles NO/flash yields the best reproduction of the observed mixing ratios and shape of the anvil NO\textsubscript{x} plume. This production scenario, along with \(P_{CG} = 460\) moles NO/flash and \(P_{IC} = 345\) moles NO/flash produce results which compare most favorably with the column NO\textsubscript{x} mass calculated from observations. These results suggest that NO\textsubscript{x} production by an IC flash is on the order of production by a CG flash. DeCaria et al. [2000] estimated a \(P_{IC}/P_{CG}\) ratio between 0.5 and 1 and CG production between 200 and 500 moles NO/flash using a 2-D model simulation of the same storm which is consistent with the results of the 3-D simulation presented here.

The inclusion of chemical reactions between species in the model resulted in a small increase in ozone mixing ratios of less than 1 ppbv throughout the free troposphere over the first 150 min of the simulation with a larger 3 ppbv increase in the boundary layer. Including lightning NO\textsubscript{x} production had only a small effect on ozone during the storm’s lifetime, producing a 2 ppbv increase between 8 and 12 km MSL by 150 min into the simulation. The reason for this enhancement was the presence of NO\textsubscript{x} and HO\textsubscript{x} plumes in this altitude region. The HO\textsubscript{x} profile was strongly influenced by convective transport of precursors H\textsubscript{2}O\textsubscript{2}, CH\textsubscript{3}OOH, HCHO, and water vapor. The inclusion of lightning NO production in the model led to a sharp decline in the anvil-average HO\textsubscript{x}/OH ratio during the storm. Wet scavenging of soluble species was well represented in the model.

Downstream ozone production was estimated using a chemistry-only version of the model. Lightning NO\textsubscript{x} production resulted in an average ozone enhancement of 10 ppbv/day at 10.5 km MSL (peak enhancement altitude) which is greater than the upper tropospheric enhancement of 7 ppbv estimated by DeCaria et al. [2000]. The difference is likely due to differences in the way some species were initialized and the more accurate simulation of transport within the storm in the 3-D simulation presented here.

Acknowledgments. This research was sponsored under National Science Foundation grant ATM9913236. We acknowledge the following individuals who provided observational data: NCAR scientists James Dye, Brian Ridley, Karsten Baumann, Frank Flocke, and Al Fried; NOAA Aeronomy Lab scientists David Parrish, Tom Ryerson, Jim Roberts, Paul Goldan, and Tom Johnson; and Pierre Laroche of ONERA.

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