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Observation of enhanced ozone in an electrically active storm over Socorro, NM: Implications for ozone production from corona discharges

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[1] Enhancements in ozone were observed between about 3 and 10 km altitude within an electrically active storm in central New Mexico. Measurements from satellite sensors and ground-based radar show cloud top pressures between 300 and 150 mb in the vicinity of an ozonesonde launched from Socorro, NM, and heavy precipitation with radar reflectivities exceeding 50 dBZ. Data from a lightning mapping array and a surface electric field mill show a large amount of electrical activity within this thunderstorm. The observed ozone enhancements are large (50% above the mean) and could have resulted from a number of possible processes, including the advection of polluted air from the urban environments of El Paso and Juarez, photochemical production by lightning-generated NO_x from aged thunderstorm outflow, downward mixing of stratospheric air, or local production from within the thunderstorm. We find that a large fraction of the ozone enhancement is consistent with local production from corona discharges, either from cloud particles or by corona associated with lightning. The implied global source of ozone from thunderstorm corona discharge is estimated to be 110 Tg O_3 a^{-1} with a range between 40 and 180 Tg O_3 a^{-1}. This value is about 21% as large as the estimated ozone production rate from lightning NO_x, and about 3% as large as the total chemical production rate of tropospheric ozone. Thus while the estimated corona-induced production of ozone may be significant on local scales, it is unlikely to be as important to the global ozone budget as other sources.

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1. Introduction

[2] Ozone is important in maintaining the oxidizing capacity of the troposphere (from the surface to about 12–16 km altitude). Locally, it is one of the most significant contributors to photochemical smog. Globally, tropospheric ozone plays a role in the Earth's thermal balance as the third most important anthropogenic greenhouse gas, with a radiative forcing of 0.35 W m^{-2} [*IPCC*, 2007]. Ozone is produced within the troposphere primarily by photochemical mechanisms involving reactions of hydrocarbons with oxides of nitrogen. It also can be transported into the troposphere from the stratosphere during periods of localized cross-tropopause mass exchange. The range of global estimates for the two main sources of tropospheric ozone are 3000–4600 Tg O_3 a^{-1} for chemical production and 400–1100 Tg O_3 a^{-1} due to transport from the stratosphere [*Jacob*, 1999].

[3] The importance of NO_x ($NO+NO_2$) in the chemical production of tropospheric ozone has motivated a large body of research into the natural and anthropogenic sources of NO_x [*IPCC*, 2001, and references therein]. Lightning was identified early on as a potentially important source of NO_x production [*Tuck*, 1976; *Noxon*, 1976]. As pointed out by *Price et al.* [1997], published estimates for global NO_x production rate from lightning span two orders of magnitude, from 1 Tg N a^{-1} to 100 Tg N a^{-1}, with the most likely value lying between 5 and 20 Tg N a^{-1}. More recent values have tended to favor the low end of this range, and the review by *Schumann and Huntrieser* [2007] now places the best estimate at 5 (+−3) Tg N a^{-1}.

[4] Considerably less has been published on ozone changes associated with thunderstorms. *Orville* [1967] reported a ground-level enhancement of a factor of ten above ambient ozone based on ultraviolet absorption of a lightning flash observed with a slitless spectrograph. *Shlanta and Moore* [1972] measured large transient increases in ozone

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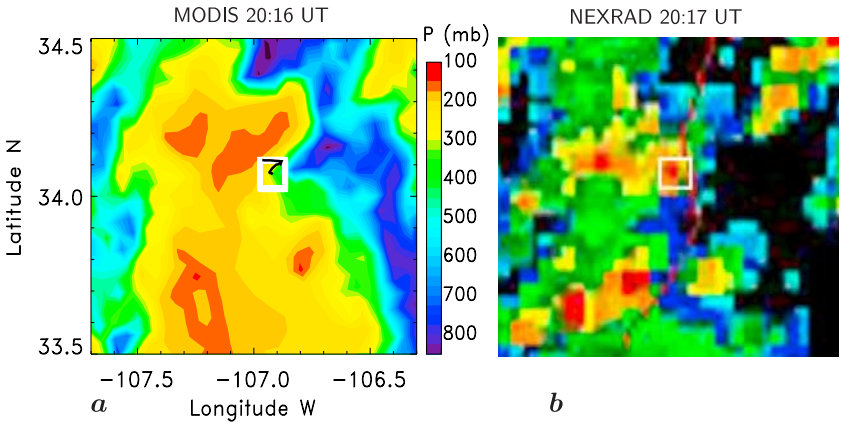

Figure 1. (a) MODIS cloud top pressures observed near 20:16 UT on 15 August 2006. The white square outlines a 10 × 10 km area centered on ozonesonde launch site and the dark curve shows the path of the calculated balloon trajectory up to 30 km altitude. (b) Composite reflectivity measured by KABX Albuquerque NWS radar at 20:17 UT on 15 August 2006. The composite reflectivity image is formed from the strongest returned signal over the range of elevation angles from 0 to 19.5° (essentially the surface to tropopause at the range between KABX and Socorro). The reflectivity scale varies from 5 dBZ (light blue) to 50 dBZ (dark red). The white square outlines the same 10 × 10 km area, and the dark red curve indicates the Rio Grande river valley.

above point discharges (corona) on the ground beneath active thunderstorms. Laboratory studies of hot electrical discharges for simulating lightning have observed large production rates for NO, but the production of O_3 was found to be negligible [*Levine et al.*, 1981; *Franzblau*, 1991]. On the other hand, experiments involving lower currents and colder, coronal-type discharges found the production efficiency for O_3 to be a factor of ten or more larger than for NO [*Peyrous and Lapeyre*, 1982; *Hill et al.*, 1988].

[5] Here, we report measurements of enhanced levels of ozone observed within a thunderstorm during a balloon flight from Socorro, New Mexico, on 15 August 2006. Ancillary data on this storm was provided by infrared satellite sensors, weather radar, a lightning mapping array, and a surface electric field mill. These observations could have consequences for a reevaluation of the impact of lightning on the global budget of ozone in the free troposphere.

2. Balloon Instrumentation

[6] Ozonesondes were flown daily from the campus of New Mexico Institute of Mining and Technology (34.07°E, 106.92°W, 1.45 km ASL) from 1 to 25 August 2006, as part of the INTEX Ozonsonde Network Study, 2006 (IONS-06). The balloon packages consisted of EN-SCI 2Z electrochemical concentration cell (ECC) ozonesondes coupled with Vaisala RS-80 radiosondes for profiles of pressure, temperature and humidity flown with a 1500 gram latex balloon. The ozonesondes were equipped with the V2D radiosonde interface and telemetry data were recorded and analyzed using the strato program (http://cires.colorado.edu/~voemel/strato/strato.html). The software also calculates the ozone mixing ratios from the ECC current, pressure, and temperature using calibration factors determined during preflight preparation of the instrument.

[7] This ozonesonde package has been used extensively for measuring ozone profiles within both the troposphere and the stratosphere. The ozone sensor consists of two platinum electrodes in separate cells of potassium iodide solutions with different concentrations. Ambient air is drawn through one cell and the presence of ozone drives chemical reactions that give rise to a small (microampere) current between the electrodes. A complete description of the ECC ozonesonde is given by *Komhyr et al.* [1995].

[8] The ozonesondes were prepared in accordance with the manufacturer's standard procedure using 1% potassium iodide solutions with a buffer concentration of 1/10 of that specified by EN-SCI to improve instrument time response [*EN-SCI Corporation*, 1996; *Johnson et al.*, 2002]. The characteristic time response of the instrument in the upper troposphere is estimated to be 35 s [*Kalnajs et al.*, 2006] and the accuracy of the instrument is approximately 5% in the midtroposphere [*Brinksma et al.*, 2000]. The surface-level ozone measured by the 15 August flight instrument was in good agreement (+−4 ppbv) with a measurement made by a colocated Thermo Environmental Instruments model 49C UV photometric ozone analyzer.

3. Results

[9] The ozonesonde was launched at 19:54 UT on 15 August 2006. At that time, an electrically active storm was developing approximately 3 km to the west of the launch site. The balloon package was swept into the storm 3 min after launch at an altitude of about 2 km and horizontal distance about 1 km west of the launch site. Figure 1 shows the distribution of cloud top pressures measured 20 min after launch (the approximate balloon altitude was 10 km at this time) during an overpass of the EOS Aqua satellite. Cloud top pressures were retrieved using spectral radiances near the CO_2 15 μm band from the Moderate Resolution Imaging Spectroradiometer (MODIS) at 5-km spatial resolution [*King et al.*, 2003]. These data show the local storm cell to be part of a larger regional complex of deep

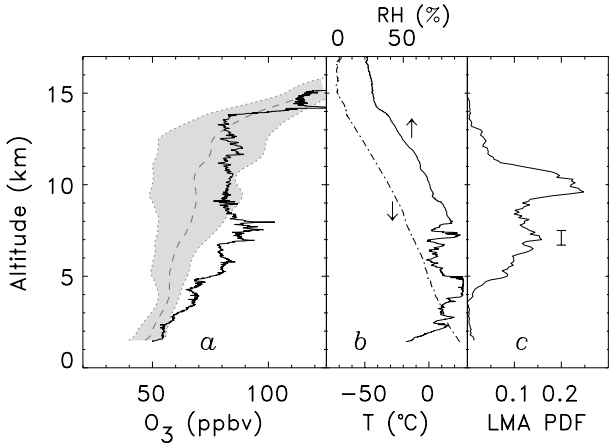

Figure 2. (a) Solid curve shows the ozone mixing ratio measured at Socorro, NM on 15 August. Dashed curve shows the 10-d mean profile of ozone for days surrounding 15 August, along with 1-sigma variations about the mean (shaded region bounded by dotted curves). (b) Vertical profiles of temperature (dash-dotted curve) and relative humidity (solid curve) measured with the Viasala sensor. Arrows refer to the axis used for each profile. (c) Vertical distribution of the frequency of lightning discharges observed by the LMA. The PDF was constructed by vertically binning all events within a 10 × 10 km horizontal area centered on the ozonesonde launch site (the area outlined by the white square in Figure 1). The altitude uncertainty in the lightning PDF profile is 0.5 km, indicated by a vertical error bar in the figure.

convection with cloud top pressures between about 300 and 150 mb (roughly 10 to 14 km altitude). Also shown are radar reflectivities observed at nearly the same time and spatial area as the MODIS cloud data. The radar reflectivities were observed from the Albuquerque National Weather Service (NWS) WSR-88, located about 120 km north of Socorro. The launch site is located at the center of the outlined square in both figures, where the dimensions of the square are 10 × 10 km.

[10] The estimated horizontal projection of the balloon flight is indicated in the left panel of Figure 1, and it shows that the balloon initially drifted northwest, then northeast, and finally due west above the tropopause. The trajectory path was calculated using horizontal winds from the Albuquerque NWS radiosonde sounding from 1200 UT on the same day, along with ascent rates computed from the measured pressure altitude. Ideally, the balloon package would have included a global positioning system (GPS) for determining precise location, and in fact two such packages were flown on 17 and 24 August. On the basis of comparisons between the computed trajectories using Albuquerque winds and the true locations from GPS in these two flights, we conclude that errors in the computed trajectories are in the range of 1–2 km up to about 8 km altitude. Above this height, small differences in wind direction or speed produce larger errors due to higher overall wind speeds. Three of the non-GPS sondes were recovered; all were found between 20 and 40 km to the west-northwest and within 5 to 8 km of the predicted landing locations.

[11] The measured vertical profile of ozone for 15 August is shown in Figure 2, along with a mean ozone profile calculated using 10 flights surrounding the August 15 measurement. The use of a longer averaging period did not change the mean or standard deviation significantly. Large enhancements in ozone were seen on 15 August, up to 30 ppbv or a 50% local enhancement above the mean level, and outside of the range of variability indicated by the standard deviation of the 10-d mean. The largest enhancements were observed between about 3 and 10 km altitude, which corresponds approximately to the region where the balloon package was within clouds. Figure 2 also shows the profiles of temperature and relative humidity from the RS-80. The accuracy of the humidity sensor is questionable at very large humidities or if the sensor becomes wet, therefore it is impossible to use these data to determine precisely where the balloon package entered or exited the cloud. However, a reasonable estimate is a relative humidity threshold of 80%, which places the balloon inside the storm between about 2 and 9 km. Additionally, the balloon ascent rate increased by factors of 2 to 3 above typical buoyant ascent rates of 5 m s^{-1} within the altitude range from 3 to 13 km altitude, indicating that the instrument package was swept into a strong updraft in the convective core of the thunderstorm.

[12] It is possible that the ozonesonde ingested liquid water or ice during ascent through the thunderstorm region, however there is no indication that this adversely affected the measurement. The 15 August ozone profile returns to mean values above the storm area, suggesting that the solution strength was unaffected by ingested water. Furthermore, on two subsequent attempts to launch ozonesondes into thunderstorms, the balloon packages passed through regions of dense cloud and precipitation (but not within areas of lightning) and these profiles did not show anomalous ozone readings.

[13] As discussed previously, the 15 August storm was electrically active and numerous cloud-to-ground lightning strikes occurred near the site after the balloon was launched. Figure 2 includes the vertical profile of the probability density function (PDF) for electrical discharges within a 10 × 10 km horizontal area centered on the launch site and observed during the time interval of the flight. The 10 × 10-km area used to compute this PDF was chosen to broadly coincide with the area of precipitation (Figure 1) associated with the storm cell that impacted the 15 August flight. This area also defines the approximate range for the tropospheric portion of the balloon's trajectory. The temperature profile (Figure 2) shows the tropopause height to be near 15 km altitude, which is a typical value at this location during the month of August.

[14] The times and locations of the electrical discharges were determined using the New Mexico Tech Lightning Mapping Array (LMA). The LMA records the time of arrival of peak power of impulsive VHF radiation at 63 MHz from lightning at multiple stations in successive 10-us time windows. The impulsive nature of these events arises from the intermittent nature of negatively charged breakdown of air, thus the LMA can detect both cloud-to-ground and intracloud lightning. The peaks of these radiation bursts are time-tagged by each LMA station at a rate of up to 10^5 s^{-1}, from which the location and time of the associated events can be found

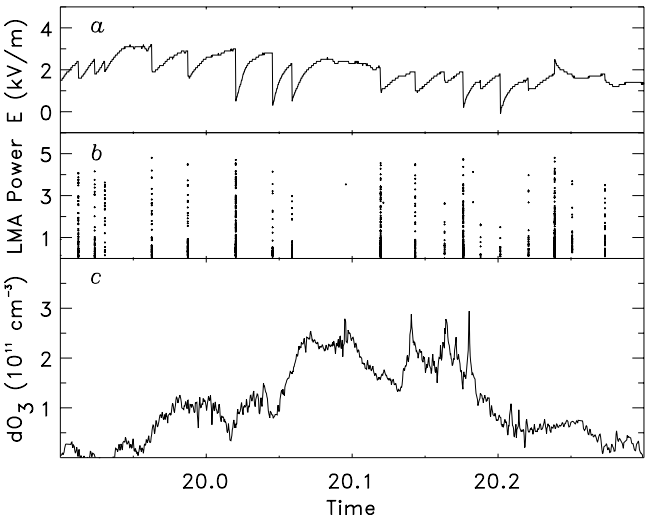

Figure 3. (a) Time history (in hours UT) of the electric field at the surface for 15 August, measured by a field mill located about 300 m from the ozonesonde launch site. Horizontal axis is universal time in hours. (b) Corresponding time series of lightning discharges detected by the LMA plotted as a function of source power in dB. (c) Time series of ozone enhancement based on the difference between measured ozone and the 10-d mean from Figure 2. The ozonesonde was launched at 19.89 h, and the approximate range of altitudes over the time period shown was 1.5–11.5 km.

[*Rison et al.*, 1999; *Thomas et al.*, 2004]. Given the configuration of the array stations at that time and general location of the storm, we estimate the plan-position uncertainty of the sources to be about 300 m and the altitude uncertainty to be 500 m. This plan-position uncertainty has little impact on the PDF based on a relatively larger averaging area; the altitude uncertainty in the PDF is taken to be 0.5 km. Most of the discharges occurred within an altitude range between about 4 and 11 km, corresponding primarily to intracloud lightning in addition to charge draining channels of cloud-to-ground lightning.

[15] An enhancement in the observed concentration of ozone, dO_3, was calculated from the difference between the 15 August measurement and the 10-day mean. This is plotted as a function of time in Figure 3. Also shown are the corresponding time series of lightning discharges observed by the LMA, and the time series of electric field measured at the ground using an E-100 field mill located on the New Mexico Tech Golf Course. The E-100 uses a grounded, rotating conducting shutter above stainless steel electrodes to determine the field strength, which is proportional to the periodically induced charge on the electrodes [*Winn*, 1993]. This particular instrument was located about 300 m from the balloon launch site. During the time interval between the balloon launch and the balloon package passing above 11 km altitude, the ozone enhancements varied from 0.5 to 3×10^{11} cm^{-3}, while the E-100 recorded electric fields in excess of 2 kV m^{-1} and the LMA detected about 15 significant lightning discharges within a 10×10 km area.

4. Discussion

[16] The unusually high ozone observed on 15 August could be explained by a number of possibilities: (1) the lofting and horizontal advection of highly polluted air from urban environments, (2) photochemical production of ozone by lightning-generated NO_x from aged thunderstorm outflow, (3) downward mixing of stratospheric air caused by overshooting deep convection, and (4) local production initiated by the 15 August storm.

[17] Three-day back trajectories show that air parcels at 600 and 400 mb over Socorro on 15 August were advected from the south, within the influence of El Paso, Texas and Juarez, Mexico urban plumes (J. C. Witte, personal communication, 2006). However, similar back trajectories were calculated for 8 other days during the campaign and none of the Socorro flights on these days showed comparable enhancements in ozone. It would seem that the influence of pollution advection from the south, although occurring over Socorro nearly one-third of the time during IONS-06, is likely to be too small to explain the elevated ozone amounts observed on 15 August.

[18] As indicated in Figure 1, there were numerous storms in the vicinity of Socorro on 15 August, and GOES images also confirm the onset of convection in New Mexico up to 2 h prior to the balloon flight and in the days preceding 15 August. It is possible that lightning-generated NO_x from these earlier thunderstorms led to photochemical production of ozone in the middle and upper troposphere, with subsequent advection over Socorro [*Cooper et al.*, 2007]. It should be noted that the high rate of lightning activity in the sampled storm would have produced NO_x as well, although consideration of the short timescales involved (timescales for photochemical ozone production are on the order of hours rather than minutes) and reduced actinic fluxes within the storm cloud make it highly unlikely that the high ozone amounts were related to NO_x generated from within this storm.

[19] Simulations using the FLEXPART Lagrangian particle dispersion model do show an impact from aged thunderstorm outflow on regional NO_x levels above New Mexico during most of the IONS-06 campaign (O. R. Cooper, personal communication, 2007), and it is likely that much of the Socorro ozone data includes the effect of photochemical production via NO_x from aged (up to 10 d in the FLEXPART simulations) thunderstorm outflow. Calculated NO_x levels in the middle troposphere on 15 August were not large, however, (less than 1 ppbv, and smaller than on many other flight days) so that the background ozone should have been considerably less than the observed level of 80–90 ppbv. Furthermore, the ozonesonde was within the storm updraft in the middle troposphere as evidenced by the balloon ascent rate data. We would therefore expect that much of the sampled air had originated near the boundary layer beneath the cloud, and ozone mixing ratios would be close to the surface value – around 50 ppbv (Figure 2).

[20] On the other hand, some of the measured ozone could have originated from the stratosphere as discussed by *Winterrath et al.* [1999]. They observed a 62% enhancement

in the slant optical thickness due to ozone within a thunderstorm cloud, and tentatively attributed the high ozone column to the intrusion of stratospheric air into the cloud anvil. *Poulida et al.* [1996] observed a cross-tropopause mixing event above a midlatitude mesoscale convective complex. They measured stratospheric values of ozone and carbon monoxide at altitudes near the height of the undisturbed tropopause (between 10.5 and 11 km) and beneath a cumulonimbus anvil that had penetrated into the stratosphere. The Socorro ozone profile does contain a sharp ozone maximum at 14 km altitude (just below the tropopause) that bears a strong resemblance to the one highlighted by *Poulida et al.* [1996] in their Figure 3c, and it could be speculated that the balloon passed through a layer of stratospheric air that was mixed down to 14 km altitude by convection. At lower altitudes in this storm, it seems more unlikely that the broader ozone enhancement seen in the middle troposphere and within the updraft region was from the stratosphere. If this were the case, then the sampled air would have to have been transported down from 15 km to at least 3 km altitude by previous downdrafts, and then entrained into the convective updrafts of the storm.

[21] Another possibility raised by *Winterrath et al.* [1999] was local production of ozone within the storm by corona discharge. These discharges might have occurred on cloud water droplets or ice particles in the presence of high fields, as first postulated by *Shlanta and Moore* [1972], or from corona within streamer filaments and corona envelopes surrounding numerous leader channels associated with lightning [*Griffing*, 1977; *Coppens et al.*, 1998]. As noted in the Introduction, laboratory measurements have established that the direct production of ozone by hot channel lightning is negligible, but that colder corona discharge is an effective means of producing of O_3. A number of experiments have quantified the production of ozone as a function of energy dissipation by corona discharge [e.g., *Peyrous and Lapeyre*, 1982; *Akishev et al.*, 1993; *Simek and Clupek*, 2002]. It is well established that negative current corona produces more ozone than positive current corona per unit energy, with yields for negative corona that range between 2.8 and 4.0×10^{17} molecules O_3 J^{-1} [*Hill et al.*, 1988; *Akishev et al.*, 1993].

[22] It appears likely that corona currents from water droplets or ice crystals can occur within highly electrified thunderstorms. *Griffiths and Latham* [1974] measured corona currents from ice particles at field strengths in the range of 400 to 500 kV m^{-1} at temperatures down to -18°C, and *Petersen et al.* [2006] observed corona from ice crystals down to temperatures of -38°C with similar threshold fields on the order of 500 kV m^{-1}. *Moore et al.* [2000] measured steady corona currents from lightning rods with tip radii between 0.01 and 0.50 mm when ambient field strengths were in the range of 25 to 80 kV m^{-1} (values often found within electrified storms [*Marshall and Stolzenburg*, 2001]). *Standler and Winn* [1979] observed significant corona currents from the tips of trees under thunderstorms when ambient surface fields were as low as 8 kV m^{-1}. Further evidence for the possible coronal production of ozone is provided by observations of elevated levels of N_2O within thunderstorms [*Levine and Shaw*, 1983] and increases in O_3 and N_2O due to corona underneath thunderstorms [*Brandvold et al.*, 1996]. Similar to O_3, the production of N_2O by corona discharge is significant (on the order of 10^{17} molecules N_2O J^{-1} [*Hill et al.*, 1988]), whereas the direct production of N_2O in the hot channel of lightning is negligible.

[23] The only prior balloon-borne measurement of elevated ozone inside an electrical storm was obtained by *Shlanta and Moore* [1972], when a tethered balloon experiment broke free over Langmuir Laboratory and drifted for about 30 min at 6 km altitude. They measured sustained levels of ozone about 2.6 times larger than the prestorm surface mixing ratio. Our results are consistent but somewhat lower, with enhancement factors of 1.2 to 1.5. Short-term ozone enhancements have also been observed from aircraft flights within thunderstorms by *Clarke and Griffing* [1985], *Zahn et al.* [2002], and *Ridley et al.* [2006]. *Zahn et al.* [2002] and *Ridley et al.* [2006] both point out the possibility for artificial production of ozone from corona on metal inlet tubes of aircraft instruments. On the other hand, *Zahn et al.* attributed one observation of a broad plume of elevated ozone to corona discharge by cloud particles.

[24] Using lightning discharges detected by the LMA as a proxy for the amount of corona discharge, we can make a rough estimate for the amount of ozone produced per lightning discharge within this storm,

$$P(O_3) = \overline{dO}_3 \times \frac{\Delta Z \cdot A}{N_L}$$

where $\overline{dO}_3$ is the mean ozone enhancement within a cylindrical storm volume of height ΔZ and cross-sectional area A, and N_L is the number of lightning flashes. The area impacted by enhanced ozone in the 15 August thunderstorm is likely to be smaller than the extent of the storm defined by the area of heavy precipitation from the radar reflectivity or by the electrical activity recorded by the LMA. Attempts were made on two other launches to obtain ozone soundings inside electrically active storms. While both flights took place within 5 km of these storms, neither one penetrated the central updraft region and no significant ozone enhancements were observed. It thus seems reasonable to assume that the elevated ozone observed on 15 August was confined to a horizontal area of diameter 5 km at most. Assuming a mean enhancement dO_3 of 1.5×10^{11} cm^{-3} (Figure 3) within a cylindrical area of diameter 5 km and extending over a 7-km altitude range (Figure 2), we estimate a total storm enhancement of about 2×10^{28} molecules O_3. The number of significant flashes observed from this cell up to the time of the measurement was about 20, which gives an average $P(O_3)$ of 1×10^{27} molecules O_3 per flash. Given the large uncertainty in the mean ozone enhancement (+−30%), and even larger uncertainties in the volume of the enhancement (+20%, −100%), the estimated range of this figure is between 0.35 and 1.6×10^{27} molecules O_3 per flash.

[25] It should be pointed out that a similar production magnitude can be obtained from energy considerations, independent of the observations presented here. The mean energy dissipated in a lightning discharge is estimated to be between 10^9 J and 10^{10} J per flash [*Rakov and Uman*, 2003], and *Cooray* [1997] calculated that up to 50% of the energy dissipation in lightning can be attributed to leader stages, primarily corona. Using 4×10^{17} molecules O_3 J^{-1}

for the ozone production as a function of dissipated energy [*Hill et al.*, 1988] we thus estimate between 0.2 and 2.0×10^{27} molecules O_3 per flash based solely on lightning-associated corona and the energy dissipated in this process.

[26] Assuming a global flash rate of 44 s^{-1} for both intracloud and cloud-to-ground lightning [*Rakov and Uman*, 2003] and that the relationship between lightning frequency and thunderstorm corona is approximately constant, an extrapolation of 110 Tg O_3 a^{-1} is obtained for the global ozone production rate from corona within thunderstorms. The estimated range of this value is between 40 and 180 Tg O_3 a^{-1}. *Schumann and Huntrieser* [2007] reviewed laboratory measurements and global flash rates to infer a comparable source value of 40 Tg O_3 a^{-1} from lightning and corona. In addition, their best estimate of the lightning-NO_x production rate was 5 (+−3) Tg N a^{-1}. Assuming a photochemical production of 30 O_3 molecules per NO_x consumed [*Lin et al.*, 1988] the corresponding ozone yield from lightning-NO_x could lie between 205 and 820 Tg O_3 a^{-1}. Comparison of these latter values with our estimates of 40–180 Tg O_3 a^{-1} indicates that the corona-induced source postulated here could range between 5% and 88% as large as the expected global production of ozone from lightning NO_x, with a best-estimate contribution of 21%. If the total tropospheric ozone production rate from all source is assumed to be 3800 Tg O_3 a^{-1} [*Jacob*, 1999], then this corona production estimate amounts to about 3% of the global source strength.

5. Conclusion

[27] Measurements of elevated ozone within a highly electrified thunderstorm suggest that a significant amount of ozone may have been produced by corona discharge within the storm. An extrapolation to the global scale suggests that the source of ozone from corona discharge within thunderstorms is likely not negligible, but that it is smaller than the estimated source of ozone resulting from lightning-generated NO_x (about 21% as large), and may account for roughly 3% of the total photochemical production of tropospheric ozone. It will be highly desirable to obtain additional measurements of ozone within the cores of thunderstorms, and inside regions of large electric fields and lightning, in order to more accurately quantify this potential source of ozone to the free troposphere.

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