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Lightning-produced NO_2 observed by two ground-based UV-visible spectrometers at Vanscoy, Saskatchewan in August 2004

A. Fraser[1], F. Goutail[2], C. A. McLinden[3], S. M. L. Melo[4], and K. Strong[1]

[1]Department of Physics, University of Toronto, Toronto, Ontario, Canada
[2]Service d'Aéronomie du Centre Nationale de la Recherche Scientifique, Verrières le Buisson, France
[3]Environment Canada, Downsview, Ontario, Canada
[4]Space Science, Canadian Space Agency, Saint-Hubert, Québec, Canada

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Correspondence to: A. Fraser (amery@atmosp.physics.utoronto.ca)

Abstract

Ground-based measurements of ozone and NO_2 slant columns by the SAOZ (Système d'Analyse par Observations Zénithales) and UT-GBS (University of Toronto Ground-Based Spectrometer) instruments during the MANTRA 2004 field campaign are presented herein. During the afternoon of 28 August, a thunderstorm passed over the instruments, which were installed at Vanscoy, Saskatchewan (52° N, 107° W). Enhanced slant columns of ozone and NO_2 were observed by both instruments during the storm, with maximum values of two and 25 times the expected columns, respectively. The enhanced ozone slant columns are primarily due to the longer path traversed by the solar radiation caused by multiple scattering inside the thick cloud layer associated with the thunderstorm. The enhanced NO_2 columns are attributed to NO_x production by lightning. Two different methods are used to separate the NO_2 enhancements into contributions from the longer path length and production by lightning. Combining the observed excess NO_2 with lightning flash data from the Canadian Lightning Detection Network and Environment Canada Doppler radar measurements, the production of NO_2 molecules per lightning flash is determined. Using these two methods, the best estimate of the production rate is found to be $(7.45\pm1.38)\times10^{26}$ molecules NO_2/flash from the UT-GBS and $(6.58\pm1.21)\times10^{26}$ molecules NO_2/flash from SAOZ. These results are consistent with previous estimates which range from 10^{26} molecules NO_2/flash (Noxon, 1976) to $(7\pm3)\times10^{26}$ molecules NO_2/flash (Franzblau and Popp, 1989).

1 Introduction

Active nitrogen oxides (NO_x=NO+NO_2) play an important role in ozone photochemistry, reacting catalytically with ozone in both the troposphere and the stratosphere (Crutzen, 1970). In the upper stratosphere NO_x is one of the dominant sinks of ozone, while in the lower stratosphere, it mitigates ozone loss by converting other ozone-

depleting chemicals (HO_x, BrO_x, and ClO_x) into their reservoir species (McElroy et al., 1992). In the troposphere, in areas of high NO_x concentration, ozone is produced through reactions with volatile organic compounds (VOCs), while in areas of low NO_x concentration, ozone is catalytically destroyed by NO_x. The source of NO_x in the stratosphere is dominated by the transport of N_2O from the troposphere. Sources of NO_x in the troposphere are more numerous, and include ground-based fossil fuel burning (∼24 Tg N/year), biomass burning (∼8 Tg N/year), soil emissions (∼12 Tg N/year), NH_3 oxidation (∼3 Tg N/year), aircraft emissions (∼0.4 Tg N/year), and transport from the stratosphere (≤0.4 Tg N/year) (Price et al., 1997, and references therein). Another source of NO_x in the middle and upper troposphere, with by far the largest uncertainty, is lightning. The large amounts of energy released by lightning flashes can break apart N_2 and O_2 molecules, which then recombine to form NO. This newly formed NO can then react with ozone to form NO_2 (Zel'dovitch and Raizer, 1966). Recent estimates of the global annual production rate due to lightning lie between 2 and 20 Tg N/year (Huntrieser et al., 1998; Price et al., 1997; Bond et al., 2001).

The MANTRA (Middle Atmosphere Nitrogen TRend Assessment) series of balloon campaigns was conducted in Vanscoy, Saskatchewan (52° N, 107° W) in late summer during the reversal of the stratospheric flow, known as turnaround, to measure stratospheric constituents that impact ozone chemistry (Strong et al., 2005). The turnaround condition provides a scenario when the atmosphere is the closest to photochemical equilibrium and dynamics do not have a large influence (Wunch et al., 2005, and references therein). The MANTRA field campaigns were held biennially from 1998 to 2004. As a complement to the balloon measurements, a suite of ground-based instruments were operated throughout each campaign, measuring the day-to-day variability of some of the trace gases of interest. Ozonesondes were also launched regularly throughout each campaign. In 2004, ground-based measurements were accumulated on 43 days, from 3 August to 15 September.

The late afternoon of 28 August saw a heavy thunderstorm over Vanscoy, with lightning and thunder observed for three hours. Ozone and NO_2 slant column densities

measured during the storm by two of the ground-based instruments are discussed herein. The observed NO_2 is separated into a contribution from path enhancement due to multiple scattering and production by lightning. The production of NO_2 per lightning flash is also calculated.

2 Instruments

The University of Toronto's Ground-Based Spectrometer (UT-GBS) was assembled in 1998 and has participated in all four MANTRA campaigns (Bassford et al., 2001, 2005; Farahani, 2006). It consists of a triple-grating spectrometer with a thermo-electrically cooled, two-dimensional CCD (charged-coupled device) array detector. Sunlight from the zenith-sky is gathered by a fused silica lens with a two-degree field of view, and focused on a liquid light guide, which minimizes the effects of polarization. Spectra are recorded continuously throughout the day, with varying exposure times to maximize the signal on the CCD. Shortly before the 2004 campaign, the CCD detector began malfunctioning. A replacement was obtained from the manufacturer, a liquid-nitrogen-cooled 1024×128 pixel front-illuminated CCD. Spectra were recorded between 345 and 555 nm, with a resolution of approximately 0.5 nm in the NO_2 region and 1.0 nm in the ozone region. The loaned CCD's sensitivity to UV-Vis radiation was lower than that of the original detector, meaning that longer exposure times were required to maximize the signal, leading to fewer measurements over twilight. A low signal-to-noise ratio was obtained during the MANTRA 2004 campaign due to an error in the data acquisition software, which has since been corrected. Despite these issues, good data was obtained, as seen in the spectral fits shown in Fig. 1.

The SAOZ (Système d'Analyse par Observations Zénithales) instrument was constructed in the late 1980s, and is now deployed in a global network for measurements of stratospheric concentrations of trace gases important to ozone loss (Pommereau and Goutail, 1998). SAOZ records spectra between 270 and 620 nm, with a resolution of 1.0 nm. The detector is an uncooled 1024-pixel linear diode array. SAOZ records

zenith-sky spectra with a 10° field-of-view. Spectra are recorded every thirty minutes throughout the day, and continuously during twilight, defined as when the solar zenith angle (SZA) is between 80° and 95°.

The DOAS technique (e.g., Solomon et al., 1987; Platt, 1994) is used for the analysis of spectra from both instruments with absorption cross-sections of ozone (Burrows et al., 1999), NO_2 (Vandaele et al., 1998), H_2O (Rothman et al., 2003), and O_4 (Greenblatt et al., 1990) fitted using a Marquardt-Levenberg non-linear least-squares technique. Slant column densities (SCDs) of ozone are retrieved between 450 and 550 nm, and NO_2 SCDs are retrieved between 425 and 450 nm. The program WinDOAS, developed by the IASB (Belgian Institute for Space Aeronomy, Fayt and Van Roozendael, 2001), has been used to analyze data from both instruments. A single reference spectrum was chosen for each instrument for the entire campaign (3 September, SZA=44.8°), and the two were selected to be as close as possible in time. Figure 1 shows typical ozone and NO_2 fits from the two instruments, taken during the thunderstorm.

Measurement errors for both instruments are calculated from the root-sum-square of individual sources of error, after Bassford et al. (2005) and references therein. The individual errors are the same for both instruments unless otherwise noted and include random noise on the spectra (2.5% for UT-GBS ozone, 1% for SAOZ ozone, 2% for NO_2), instrument error arising from uncertainty in the dark current, bias, and slit function (2% for the UT-GBS, 1% for SAOZ), pseudo-random errors resulting from unaccounted-for structure in the spectra (1–2% for ozone, 4-6% for NO_2), errors in the absorption cross sections (2.6% for ozone, 5% for NO_2), the temperature dependence of the NO_2 cross-section (≤8%), and the effects of multiple Raman scattering, which acts to fill in absorption features (1% for ozone, 5% for NO_2). The total error for the UT-GBS is 4.6% for ozone and 11.9% for NO_2, while the errors for SAOZ are 3.5% for ozone and 11.8% for NO_2.

3 Thunderstorm observations

Environment Canada (EC) weather observations from nearby Saskatoon (30 km North of Vanscoy) show a thunderstorm occurring between 17:00 and 20:00 LT (SZA 63°–90°). Figure 2 shows the hourly total cloud opacity and cloud base height recorded by Environment Canada. During the thunderstorm, the sky was completely overcast by a thick cloud with a base varying from 750 to 1350 m. EC radar observations from Radisson, Saskatchewan (60 km North-West of Vanscoy) also show thunderstorm and thick cloud activity occurring over Vanscoy. Figure 3 shows the precipitation occurring at an altitude of 1.5 km at 17:00 LT (23:00 UTC, SZA 63°). A cell of heavy rain (pink colour) was observed over Vanscoy (indicated by a red arrow on Fig. 3).

Lightning flash data was obtained from the Canadian Lightning Detection Network (CLDN), a series of ground-based detectors that sense lightning using the time-of-arrival of radio pulses generated by lightning (Burrows et al., 2002). Figure 4 shows the lightning detected over the Canadian Prairies for the one-hour period from 17:00 LT to 18:00 LT on 28 August (23:00 UTC to 00:00 UTC, SZA 63° to 72°). In the 50-km radius surrounding Vanscoy (marked by an X on Fig. 4), an average flash rate of 2.87 flashes/min was observed by the CLDN for the duration of the storm. Figure 4 also shows the visible GOES (Geostationary Operational Environmental Satellite) image of the storm, which extends over Saskatchewan and into Alberta and the northern United States.

4 Slant column measurements

Figure 5 shows the ozone, NO_2, and O_4 SCDs measured by both instruments on 28 August. That afternoon, both instruments observed a maximum in all three species centered at a solar zenith angle of 77° (18:31 LT), which is consistent with the occurrence of the thunderstorm. At the ozone maximum, slant column densities measured by both instruments have increased by roughly a factor of two. At the peak of NO_2,

the slant column densities have increased by a factor of 25 as observed by the UT-GBS and 20 as observed by the SAOZ instrument 15 min before the peak. Because SAOZ had not switched to continuous measurements at the peak of the storm, which occurred before twilight, it did not capture the true maximum in NO_2 columns. However, since the NO_2 columns between the two instruments are in agreement throughout the campaign, it can be assumed that had SAOZ been measuring, it would have observed a maximum NO_2 SCD similar to that seen by the UT-GBS.

The increase in ozone is consistent with similar observations of ozone during thick cloud events (Pfeilsticker et al., 1999) and thunderstorms (Winterrath et al., 1999), both in Southern France. The increase in NO_2 is roughly double that seen by Langford et al. (2004) during a Colorado thunderstorm, though less than the 35-fold increase seen by Winterrath et al. (1999). The observed enhancements in both ozone and NO_2 are partly caused by increased path length through the atmosphere. In the case of NO_2, the increase could also be due to lightning-produced NO_x.

There are two processes that combine to increase the path length, or air mass factor (AMF), in the presence of thick clouds, described in detail in Pfeilsticker et al. (1998). Optical paths can be enhanced by multiple reflections between layers of clouds (the "ping-pong" effect) or by photon diffusion inside a thick cloud. Other processes could account for the observed increase of ozone, including transport, in-cloud production, convection, intrusion of stratospheric air, or reaction with NO (Winterrath et al., 1999). One way to verify the influence of multiple scattering is to look at the ratios of ozone and NO_2 to O_4. O_4 concentrations are related to concentrations of oxygen, and hence a maximum in O_4 such as the one observed in Fig. 5 is evidence of multiple scattering through the atmosphere, in this case due to the thick clouds associated with the thunderstorm. The ratios of ozone and NO_2 to O_4 for the afternoon of 28 August are shown in Fig. 6. As seen in Fig. 6a, the O_3 to O_4 ratio is fairly constant until the start of twilight, indicating that the excess ozone is a result of increased scattering through clouds. In the case of NO_2, in Fig. 6b, there is a clear maximum in the ratio at 77°, the peak of the thunderstorm, indicating additional NO_2 in the atmosphere, which is attributed here to

production by lightning.

5 Derivation of lightning-produced NO_2

Two methods have been used to separate the observed enhancement of NO_2 into a portion due to path-enhancement and a portion due to lightning production. These methods are discussed in this section.

5.1 Method one: NO_2 to O_4 ratio

The behaviour of the NO_2/O_4 ratios is fairly consistent between clear-sky days, however it can vary significantly between cloudy days, due to varying cloud cover. It is therefore difficult to predict what the NO_2/O_4 ratio would have been on 28 August if no NO_2 was formed by lightning. However, the ratio generally increases exponentially with solar zenith angle. An exponential fit was made to the observed NO_2/O_4 ratio, omitting the points between 65° and 82°, which correspond to the beginning and end of the observed maximum in the ratio. These fits for both the SAOZ and UT-GBS instruments are shown in Fig. 6b, with the measured value of the ratio used before and after the peak (before 65° and after 82°). From these fitted values of the NO_2/O_4 ratio during the storm, an estimate of the portion of the NO_2 slant column due to enhanced path length can be derived:

$$NO_{2,PE}(SZA) = \left[\frac{NO_2}{O_4}(SZA)\right]_{fit} \times O_{4,meas}(SZA) \quad (1)$$

where $NO_{2,PE}$ is the path-enhanced NO_2, the subscript "fit" indicates the fitted NO_2/O_4 ratio, and $O_{4,meas}$ the measured O_4 column.

The resulting NO_2 slant columns are shown in Fig. 7a. The difference between the observed NO_2 slant column and the slant column calculated from the interpolated NO_2/O_4 ratio is the amount of NO_2 attributed to production by lightning, shown in Fig. 7b. Values from both instruments are similar.

5.2 Method two: derived air mass factors

A second method of deriving the amount of NO_2 caused by path enhancement is to use the measurements of ozone to derive the enhanced air mass factor, or path length, for ozone and NO_2. Generally, measured slant column densities of both ozone and NO_2 are related to the air mass factor by:

$$\mathrm{SCD(SZA)} = \mathrm{VCD} \times \mathrm{AMF(SZA)} - \mathrm{RCD} \quad (2)$$

where VCD is the vertical column density, RCD is the reference column density, the amount of absorber in the reference spectrum used in the DOAS analysis, and SZA is the solar zenith angle. With no path enhancement, the afternoon ozone SCDs would follow the same trend as the morning SCDs, increasing with SZA. Assuming no change in the VCD, the path-enhanced SCD′ will be related to the enhanced AMF′ by:

$$\mathrm{SCD'(SZA)} = \mathrm{VCD} \times \mathrm{AMF'(SZA)} - \mathrm{RCD} \quad (3)$$

where the primes indicate path-enhancement. The enhanced AMF′ can be found by combining these two equations:

$$\mathrm{AMF'(SZA)} = \mathrm{AMF(SZA)} \frac{\mathrm{SCD'(SZA)} + \mathrm{RCD}}{\mathrm{SCD(SZA)} + \mathrm{RCD}} \quad (4)$$

The enhanced AMF′ is an upper limit on the AMF, and assumes that all of the excess ozone is due to multiple scattering in and between clouds. This assumption is justified by the behaviour of the ozone to O_4 ratio shown in Fig. 6a. The non-path-enhanced AMF was found using a radiative transfer model (McLinden et al., 2002) initialized with temperature, pressure, and ozone profiles taken from the average of all ozonesondes launched during the campaign. The RCDs for ozone and NO_2 were found from Langley plots, of SCD versus AMF, for the morning of 28 August. Measured ozone slant columns from the morning and afternoon were used as SCD and SCD′, respectively, in Eq. (4). Figure 8a shows the enhanced ozone AMF′ for both instruments, derived

using Eq. (4), as well as the AMF calculated with the radiative transfer model assuming no clouds and assuming a thick cumulus cloud near the surface, of optical depth 70, extending between 1 and 5 km (Bassford et al., 2001).

The air mass factors for ozone and NO_2 differ since they are retrieved in different wavelength regions. In the radiative transfer model, the ozone AMF is calculated at 500 nm, while the NO_2 AMF is calculated at 425 nm. The AMFs for the two species are affected by the cloud differently. Figure 8b shows the ratio of the NO_2 AMF to the O_3 AMF for the cloudless and thick cloud calculations. This ratio is a maximum for the cloud-free scenario. Without more detailed observations of the clouds, it is difficult to predict what the ratio of the AMFs would have been during the storm, and even more difficult to quantify how it would change with SZA. Given this, a maximum NO_2 AMF can be found by assuming there are no clouds during the storm. Although this assumption is certainly false, it allows a calculation of an upper limit on the NO_2 due to path enhancement, and a lower limit on the NO_2 produced by lightning. Taking this cloud-free ratio, estimated NO_2 (AMF′)s are found from:

$$\mathrm{AMF'_{NO_2}(SZA)} = \mathrm{AMF'_{O_3}(SZA)} \frac{\mathrm{AMF_{NO_2}(SZA)}}{\mathrm{AMF_{O_3}(SZA)}} \quad (5)$$

Figure 8c shows this estimated NO_2 AMF for each instrument, as well as the calculated AMFs for the cloudless and cloudy scenarios.

Figure 7a shows the resulting upper limit for NO_2 SCDs due to path enhancement calculated from Eq. (4). The NO_2 slant columns measured in the morning were used as SCDs, increased to account for the expected increase due to the diurnal variation of NO_2. The upper limit of NO_2 from both SAOZ and UT-GBS is similar. Prior to 67°, the upper limit exceeds the measured NO_2 SCD, an indication that an assumption made in calculating the NO_2 AMFs is incorrect – either there is additional ozone produced or transported into the optical path, or the ratio of the air mass factors is smaller than assumed, as expected given Fig. 8b. At SZAs between 75° and 85°, this maximum NO_2 is exceeded by the NO_2 found using the NO_2 to O_4 ratio method. This is perhaps an

indication that the interpolated NO_2 to O_4 ratio is too large in this region, a result of the difficulty in predicting the NO_2/O_4 ratio. However, since both methods result in similar amounts of NO_2 due to path-enhancement they can be believed to be approximately correct.

6 NO_2 flash production rate

The difference between the measured NO_2 SCD and the derived path-enhanced NO_2 in Fig. 7a is the minimum amount of NO_2 produced by lightning, which is shown in Fig. 7b. Using the ratio method, the amount of excess NO_2, found by integrating under the curves between 60° and 85° for method one in Fig. 7b is $(1.28\pm0.20)\times10^{18}$ molecules NO_2/cm^2 for the UT-GBS and $(1.13\pm0.18)\times10^{18}$ molecules NO_2/cm^2 for SAOZ. The error estimates on the total excess NO_2 are the root-sum-square of the SCD error discussed in Sect. 2 and the estimated integration error (10%). From Fig. 3, the size of the heavy-precipitation cell is $(30\pm3)\,km^2$. Using the average flash rate during the storm from the CLDN (2.87 flashes/min), the storm-averaged NO_2 production per flash of lightning can be calculated from:

$$NO_2 \text{ produced} = \frac{E \times A}{F \times D} \tag{6}$$

where E is the excess NO_2 measured by the instrument, A is the area of the storm, F is the lightning flash rate, and D is the duration of the storm (three hours) (Noxon, 1976). The production amounts from this method are $(7.45\pm1.38)\times10^{26}$ molecules NO_2/flash from the UT-GBS and $(6.58\pm1.21)\times10^{26}$ molecules NO_2/flash from SAOZ. The values derived from both instruments agree within error bars.

Using the air mass factor method, the UT-GBS observed $(1.18\pm0.83)\times10^{18}$ excess molecules NO_2/cm^2 and SAOZ observed $(1.06\pm0.16)\times10^{17}$ excess molecules NO_2/cm^2. The minimum production amounts are found to be $(6.83\pm1.26)\times10^{26}$ molecules NO_2/flash from the UT-GBS, and $(6.18\pm1.14)\times10^{26}$ molecules NO_2/flash

from SAOZ. Again, the two instruments agree within their combined error bars. The values from the two methods are also in agreement for the two instruments. However, it should be noted that the values calculated are slightly different quantities. The values found using the air mass factor method of limiting the NO_2 due to lightning production are minimum values for the amount of NO_2 production by lightning, whereas the values found using the NO_2 to O_4 ratio are best estimates of the actual NO_2 production rate.

Noxon (1976) estimated an order of magnitude value of 10^{26} molecules NO_2/flash based on DOAS slant column measurements of NO_2 made during a thunderstorm in Colorado. Franzblau and Popp (1989) derived a rate of $(7\pm3)\times10^{26}$ molecules NO_2/flash using a similar method in New Mexico. Langford et al. (2004) measured $(5.8\pm2.9)\times10^{26}$ molecules NO_2/flash from a zenith-viewing UV-Visible spectrometer. All the values derived here are in agreement within the combined error bars of these previously published values.

The detection efficiency of the CLDN is approximately 85–90% for cloud-to-ground flashes and only 1–4% for cloud-to-cloud flashes, due to the lower amounts of energy released during the latter (Burrows et al., 2002). The majority (90%) of lightning-produced NO_2 is produced by the more energetic cloud-to-ground flashes (Price et al., 1997). No correction has been made to the flash frequency observed by the CLDN. Taking the detection efficiency into account would slightly increase the flash rate, and therefore decrease the calculated NO_2 production value.

7 Conclusions

Elevated columns of ozone and NO_2 were observed by both SAOZ and UT-GBS during a thunderstorm that occurred the afternoon of 28 August 2004 in Vanscoy, Saskatchewan during the 2004 MANTRA campaign. In the case of ozone, the enhancement is most likely due to increased path length in and between clouds. In the case of NO_2 the enhancement is due to increased path length and the production of NO_x by lightning. The amount of excess NO_2 due to lightning has been calculated, us-

ing two methods to estimate the excess NO_2 due to path enhancement within the cloud. Lightning flash data from the CLDN and radar data from a nearby Environment Canada radar station were used to determine the amount of NO_2 produced per lightning flash. The production values in the range of ($6.18–7.45\times10^{26}$) molecules NO_2/flash calculated from both instruments agree with each other, and are also in agreement with previously published values.

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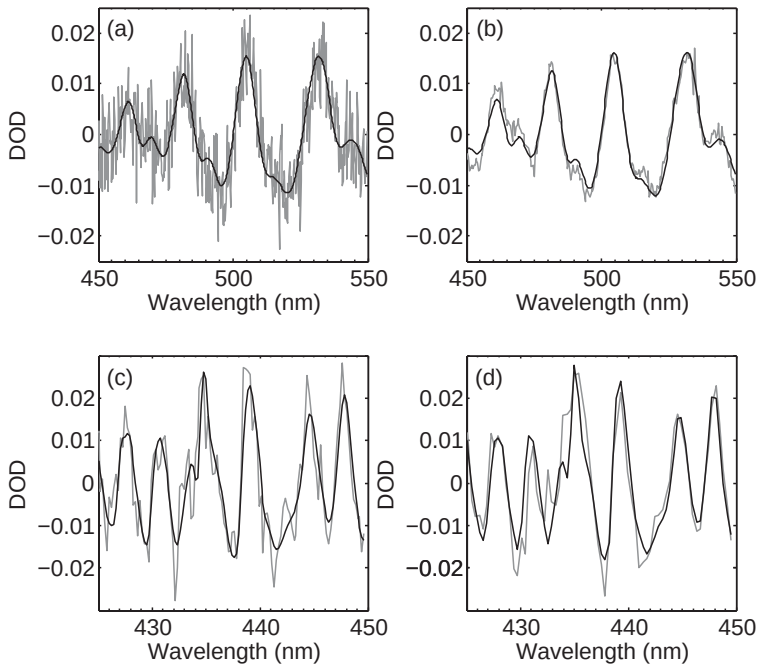

Fig. 1. Typical differential optical depth (DOD) fits for **(a)** ozone, UT-GBS, **(b)** ozone, SAOZ, **(c)** NO_2, UT-GBS, and **(d)** NO_2, SAOZ. All fits are for spectra taken during the thunderstorm, at a SZA of approximately 76° (18:25 LT). In all fits, the grey line is the data while the black line is the fit to the data.

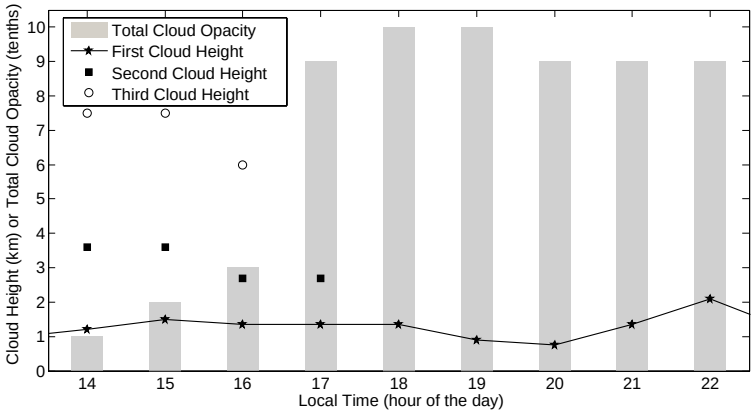

Fig. 2. Cloud base heights and total cloud opacity recorded by Environment Canada at Saskatoon on 28 August 2004.

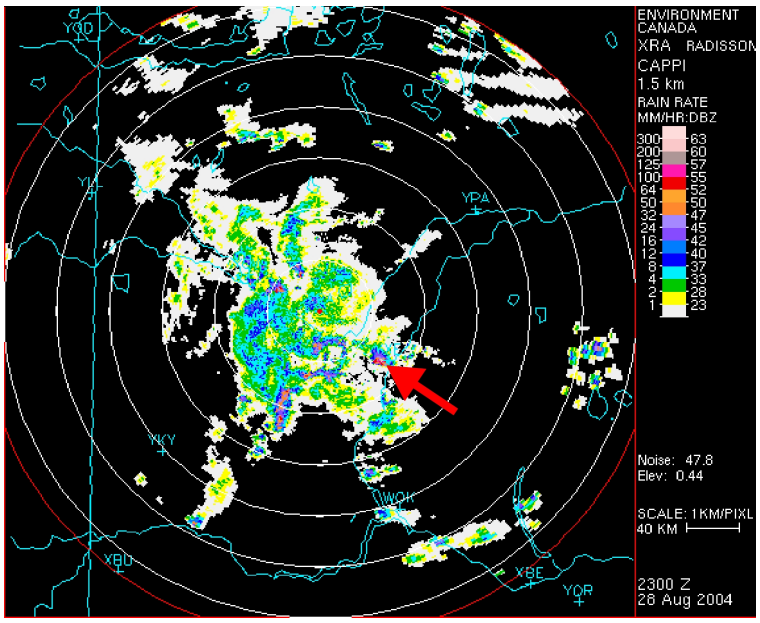

Fig. 3. Precipitation rate at 17:00 LT (23:00 UTC, SZA 63°) observed by the Environment Canada radar in Radisson, Saskatchewan on 28 August. Vanscoy is indicated by the red arrow.

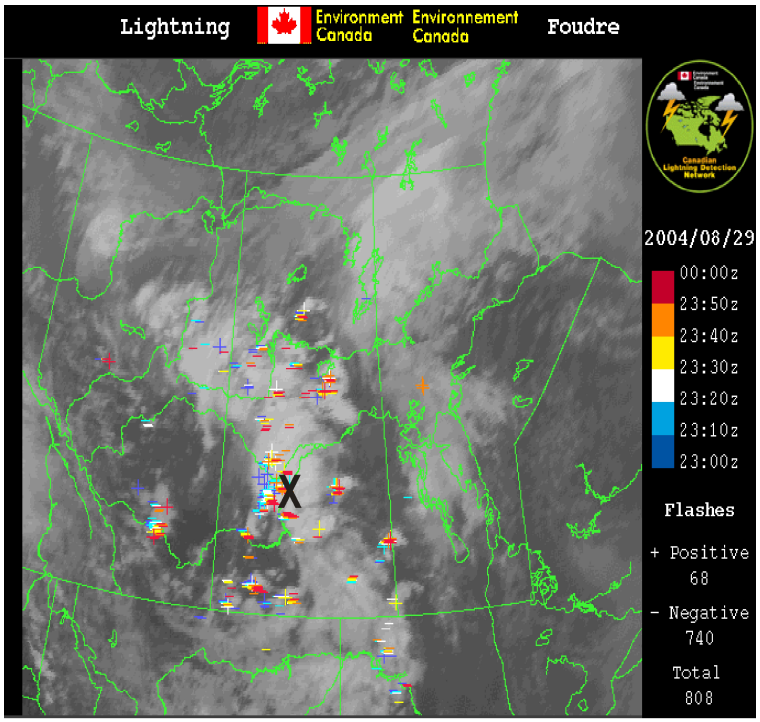

Fig. 4. Lightning flash data for the one hour period beginning 28 August at 17:00 LT (23:00 UTC, SZA 63°) in Vanscoy (X) from the Canadian Lightning Detection Network (CLDN). Each plus (+) and minus (−) represents an individual lightning flash.

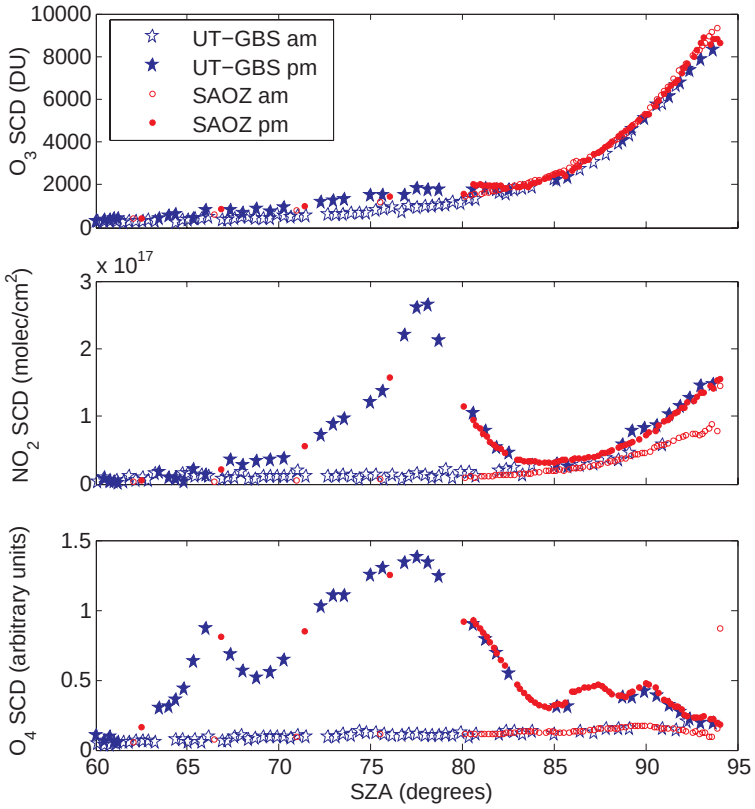

Fig. 5. Ozone, NO_2, and O_4 slant column densities measured by UT-GBS and SAOZ on 28 August 2004.

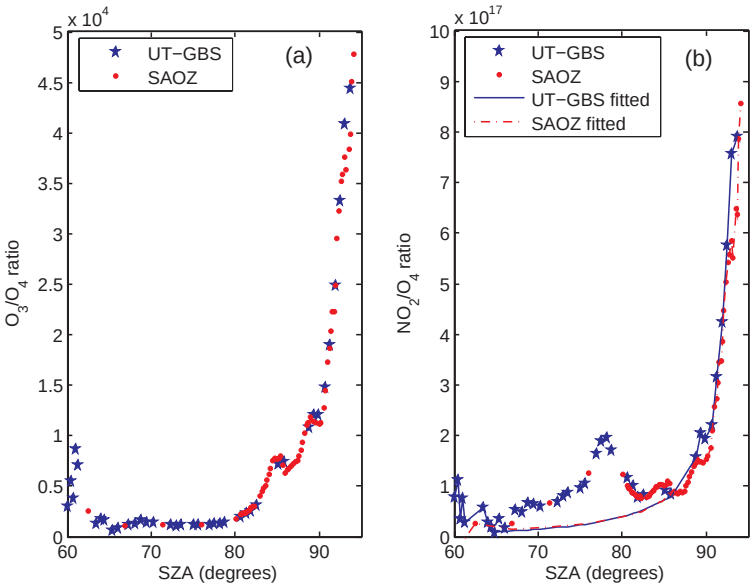

Fig. 6. (a) Measured O_3/O_4 ratios, and **(b)** measured and fitted NO_2/O_4 ratios for 28 August. The measured value of the ratio is plotted before and after the peak (before 65° and after 82°) in the NO_2/O_4 ratio (see text).

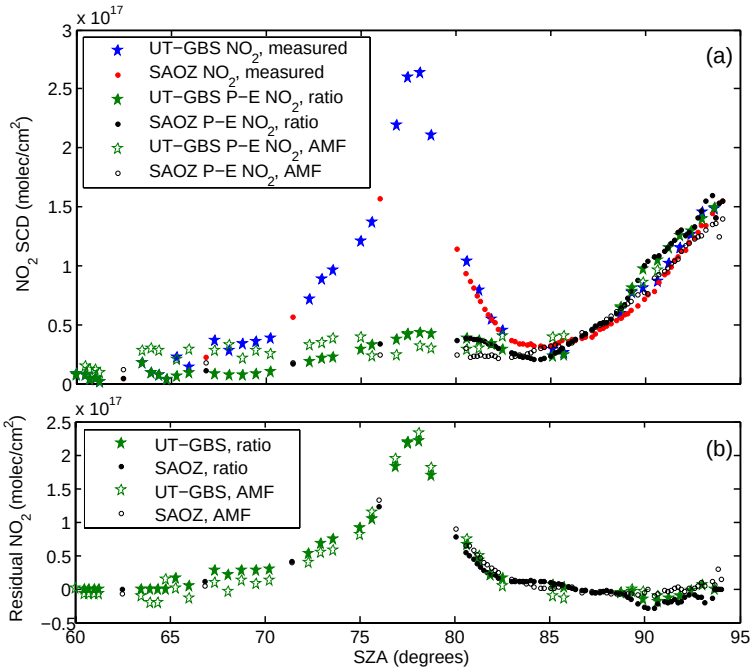

Fig. 7. **(a)** Measured total NO_2 SCDs as well as the derived contribution from path-enhancement (P-E) for methods one (ratios to O_4) and two (derived AMFs) discussed in the text. **(b)** Residual NO_2 SCDs attributed to lightning.

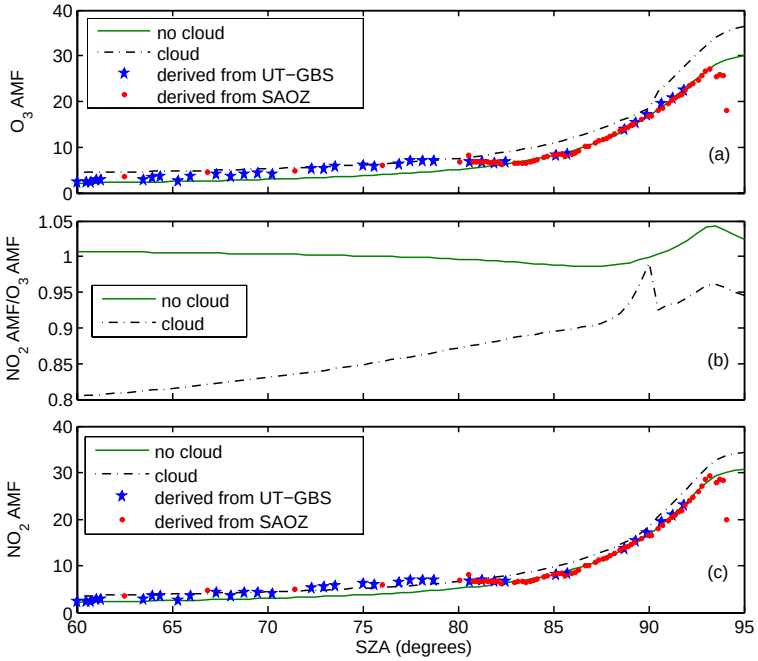

Fig. 8. **(a)** Ozone air mass factors calculated for the case of no clouds and for a cloud of OD=70 from 1–5 km using a radiative transfer model, and derived from the measurements using Eq. (4). **(b)** Ratio of NO_2 to ozone AMFs using the radiative transfer model. **(c)** Same as (a), but for NO_2 and using Eq. (5).