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Lightning-produced NO₂ observed by two ground-based UV-visible spectrometers at Vanscoy, Saskatchewan in August 2004

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Abstract. Ground-based measurements of ozone and NO₂ differential 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 differential slant columns of ozone and NO₂ were observed by both instruments during the storm, with maximum values of two and 25 times the expected clear sky columns, respectively. The enhanced ozone differential 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 NO₂ columns are partly attributed to NO_x production by lightning. Two new methods are used to separate the NO₂ enhancements into contributions from the longer path length and production by lightning. Combining the observed excess NO₂ with lightning flash data from the Canadian Lightning Detection Network and Environment Canada Doppler radar measurements, the production of NO₂ molecules per lightning flash is determined. Using these two methods, the best estimate of the production rate is found to be $(7.88 \pm 2.52) \times 10^{26}$ molecules NO₂/flash from the UT-GBS and $(6.81 \pm 2.17) \times 10^{26}$ molecules NO₂/flash from SAOZ. These results are consistent with the range of previous estimates reported in the literature.

1 Introduction

Active nitrogen oxides (NO_x=NO+NO₂) play an important role in ozone photochemistry, reacting catalytically with ozone in both the troposphere and the stratosphere (Crutzen, 1970). In the troposphere, NO_x can act as both an ozone source and sink, depending on the concentrations of ozone precursors (CO, CH₄, and volatile organic compounds) and NO_x, as well as the amount of available sunlight. Sources of NO_x in the troposphere are numerous, and include ground-based fossil fuel burning (~24 Tg N/year), biomass burning (~8 Tg N/year), soil emissions (~12 Tg N/year), NH₃ 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 N₂ and O₂ molecules, which then recombine to form NO. This newly formed NO can then react with ozone to form NO₂ (Zel'dovitch and Raizer, 1966). Recent estimates of the global annual production rate due to lightning-produced NO_x lie between 1 and 20 Tg N/year (Huntrieser et al., 2002; Tie et al., 2002; Ridley et al., 2004; Boersma et al., 2005; Beirle et al., 2006; Martin et al., 2007).

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

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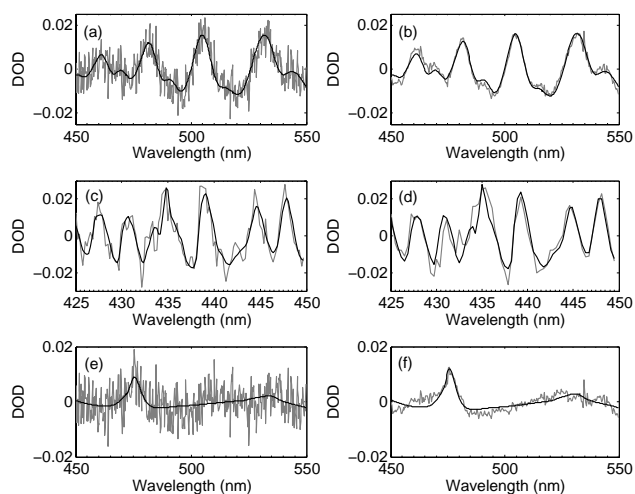


Fig. 1. Typical differential optical depth (DOD) fits for (a) ozone, UT-GBS, (b) ozone, SAOZ, (c) NO₂, UT-GBS, (d) NO₂, SAOZ, (e) O₄, UT-GBS, and (f) O₄, SAOZ. All fits are for spectra recorded in Vanscoy during the thunderstorm, at a SZA of approximately 76° (18:25 LT, 00:25 UTC). In all the figures, the gray line is the data while the black line is the fit to the data.

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 NO₂ differential slant column densities measured during the storm by two of the ground-based instruments are discussed herein. The observed NO₂ is separated into contributions from path enhancement due to multiple scattering and production by lightning. The production of NO₂ per lightning flash is also calculated. Measurements of lightning-produced NO₂ from ground-based UV-Vis instruments are rare. The thunderstorms must pass over or near the instruments, and it can be difficult to estimate the lightning-produced NO_x from the measurements. In addition, if the instrument is located in an area with tropospheric pollution (such as in a large city), the lightning NO₂ enhancement can be difficult to extract from the pollution.

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 NO₂ region (425–450 nm) and 1.0 nm in the ozone region (450–550 nm). The loaned CCD's sensitivity to UV-Vis radiation (~10% quantum efficiency) was lower than that of the original detector (~60% quantum efficiency), 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 (Differential Optical Absorption Spectroscopy) 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), NO₂ (Vandaele et al., 1998), H₂O (Rothman et al., 2003), and O₄ (Greenblatt et al., 1990) fitted using a Marquardt-Levenberg non-linear least-squares technique. Differential slant column densities (DSCDs) of ozone and O₄ are retrieved between 450 and 550 nm, and NO₂ DSCDs are retrieved between 425 and 450 nm. The program WinDOAS, developed by the IASB (Belgian Institute for Space Aeronomy, Fayt and Van Roozendaal, 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, NO₂, and O₄ fits from the two instruments, taken during the thunderstorm at a SZA of approximately 76° (18:25 LT).

Measurement errors for DSCDs measured by 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 NO₂), 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 NO₂), errors in the absorption cross sections (2.6% for ozone, 5% for NO₂), the temperature dependence of the NO₂ cross-section ($\leq 8\%$), and the effects of multiple Raman scattering, which acts to fill in absorption features (1% for ozone, 5% for NO₂). The total error for the UT-GBS is 4.6% for ozone and 11.9% for NO₂, while the errors for SAOZ are 3.5% for ozone and 11.8% for NO₂.

3 Thunderstorm observations

Environment Canada (EC) meteorological observations from nearby Saskatoon (30 km north of Vanscoy) show a thunderstorm occurring between 17:00 and 20:00 LT (23:00 to 02:00 UTC, 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 radar reflectivity at an altitude of 1.5 km at 16:30 LT (22:30 UTC, SZA 59°). Cells of heavy rain and hail (pink colour) was observed over Vanscoy (indicated by a orange arrow on Fig. 3). The maximum radar reflectivity in the 5 km area around Vanscoy is shown in Fig. 2. Further examination of the radar imagery, available at 10-min intervals, shows a series of thunderstorm cells forming to the West of Vanscoy, near the Alberta-Saskatchewan border, and traveling to the East, eventually dissipating to the East of the measurement site. The supplementary movie shows an animation of the radar images between 15:00 and 22:00 LT (21:00 and 04:00 UTC). In total, three cells or remnants of cells passed over Vanscoy. The maximum total area of the three storm cells is $(61 \pm 10) \text{ km}^2$, using the area with reflectivity greater than 40 dBz (MacKee et al., 1999). Vanscoy was upwind of Saskatoon for the duration of the storm, making it unlikely that NO₂ enhancements are due to the upward transport of anthropogenic NO₂.

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°). The total number of flashes observed by the CLDN during the five-hour total lifetime of the thunderstorms that eventually pass over Vanscoy is (524 ± 52) . Only flashes upwind of Vanscoy were counted. The detection efficiency of the

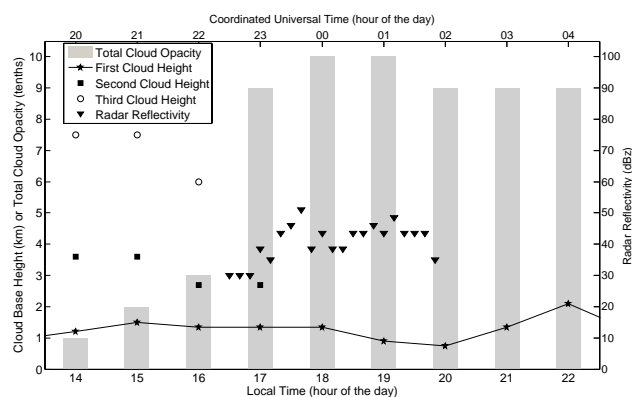


Fig. 2. Cloud base heights (in km) and total cloud opacity (in tenths) recorded by Environment Canada at Saskatoon on 28 August 2004. First, second, and third heights are the base heights of the three layers of cloud. Also shown is the maximum radar reflectivity in the 5 km area around Vanscoy, recorded by the Environment Canada radar in Radisson, Saskatchewan.

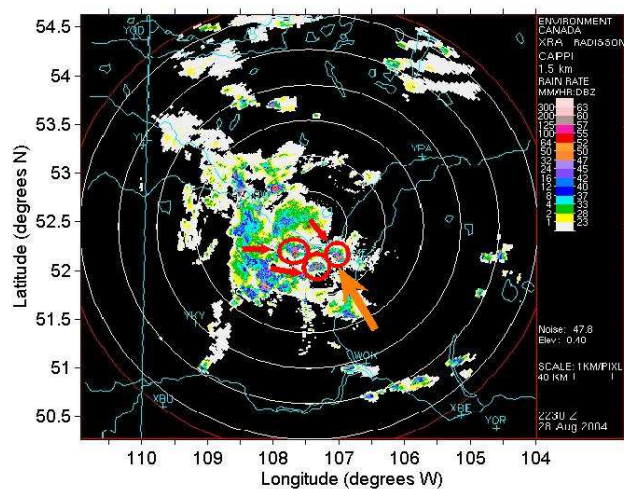


Fig. 3. Precipitation rate at 16:30 LT (22:30 UTC, SZA 59°) calculated from the Environment Canada radar measurements in Radisson, Saskatchewan on 28 August 2004. Vanscoy is indicated by the large orange arrow. The three red circles indicate the three thunderstorms that pass over Vanscoy. The three smaller red arrows indicate the direction in which the storm is moving. An animation of the radar images between 15:00 and 22:00 LT (21:00 and 04:00 UTC) is available as a supplement.

CLDN is approximately 85–90% for cloud-to-ground (CG) flashes and only 1–4% for intra-cloud flashes (IC), due to the lower amounts of energy released during the latter (Burrows et al., 2002). Approximately 94.4% of the observed flashes were cloud-to-ground. Correcting these 494 flashes for the detection efficiency of the CLDN yields (565 ± 59) total flashes. Due to the large uncertainties introduced in

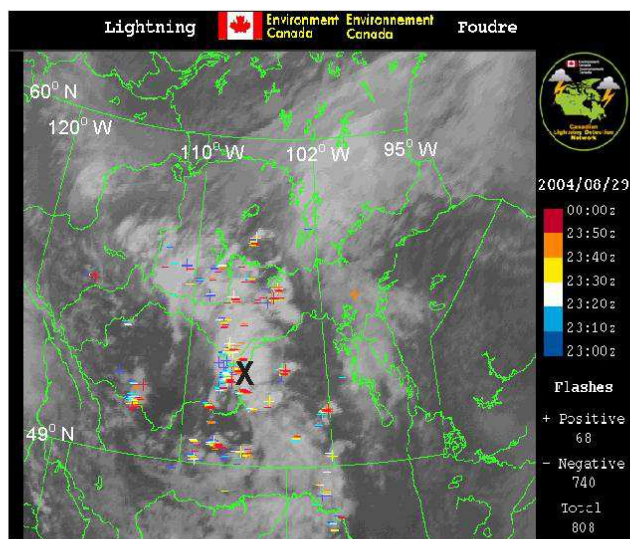


Fig. 4. Lightning flash data for the one-hour period beginning 28 August at 17:00 LT (23:00 UTC, SZA 63°) in Vanscoy (X) from the Canadian Lightning Detection Network (CLDN) superimposed on a visible GOES image taken at 17:00 LT. Each plus (+) and minus (−) represents an individual lightning flash.

correcting for the intra-cloud flashes, no correction is applied to the remaining (30±3) flashes. 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 Differential slant column measurements

Figure 5 shows the ozone, NO₂, and O₄ DSCDs, as well as the intensities measured by both instruments on 28 August. Intensities are calculated by dividing the intensity at 450 nm (the peak of the spectrum) by the exposure time of the measurement. The resulting intensity per time measurements (in counts per second) are referenced to the intensity per time at SZA=60° in the morning. That afternoon, both instruments observed a maximum in all three species centered on a solar zenith angle of 77° (18:31 LT), which is consistent with the occurrence of the thunderstorm. The measured intensities during the thunderstorms fall by roughly 95% of the morning intensities. At the ozone maximum, differential slant column densities measured by both instruments have increased by roughly a factor of two compared to the morning values. At the peak of NO₂, the differential 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 NO₂ columns. However, since the NO₂ 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 NO₂ DSCD similar to that seen by the UT-GBS. As the lifetime of NO_x is several days, the decrease in NO₂ after the peak is most likely due to advection of less NO₂ rich air masses as the thunderstorm moved over Vanscoy, and is not due to the decay of NO₂.

The increase in ozone is consistent with similar observations of ozone during thick cloud events in England, France, Sweden, and in the tropical Atlantic (Erle et al., 1995; Wagner et al., 1998; Pfeilsticker et al., 1999; Winterrath et al., 1999). The increase in NO₂ 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 ozone and part of the enhancements in NO₂ are caused by an increased path length through the atmosphere. In the case of NO₂, the increase is also partly 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 NO₂ to O₄. O₄ concentrations are related to concentrations of oxygen, and, in the absence of an increase in the oxygen vertical column, are expected to be constant (e.g., Wagner et al., 2002). Hence a maximum in O₄ 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. O₄ SCD measurements are an established method of inferring the path length through the atmosphere in the presence of clouds (Erle et al., 1995; Wagner et al., 1998, 2002). The ratios of ozone and NO₂ to O₄ for the afternoon of 28 August are shown in Fig. 6. As seen in Fig. 6a, the O₃ to O₄ 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 NO₂, in Fig. 6b, there is a clear maximum in the ratio at 77°, indicating additional NO₂ in the atmosphere, which is attributed here to production by lightning.

5 Derivation of lightning-produced NO₂

Two new methods have been used to separate the observed enhancement of the differential slant column of NO₂ into a portion due to path-enhancement and a portion due to lightning production. These methods are discussed in Sects. 5.1 and 5.2. The lightning-produced SCD is then converted into a vertical column amount in Sect. 5.3.

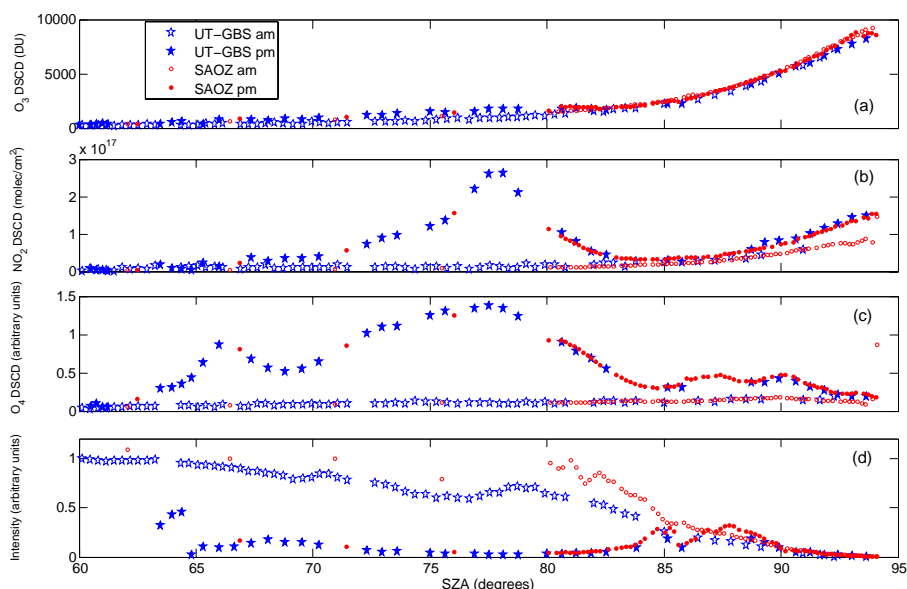


Fig. 5. (a) Ozone, (b) NO₂, and (c) O₄ differential slant column densities, and (d) intensities measured by UT-GBS and SAOZ in Vanscoy on 28 August 2004. Intensities are calculated by dividing the intensity at 450 nm by the exposure time of the measurement and are referenced to the intensity (in counts per second) at SZA=60° in the morning.

5.1 Method one: NO₂ to O₄ ratio

The behaviour of the NO₂/O₄ ratio is fairly consistent between clear-sky days, however it can vary significantly between cloudy days, due to varying cloud cover. This ratio is also strongly dependent on the vertical profiles of both species. It is therefore difficult to predict what the NO₂/O₄ ratio would have been on 28 August if no NO₂ was formed by lightning. However, on other days of the campaign, the ratio increases exponentially with solar zenith angle. Two independent exponential fits were made to the observed NO₂/O₄ ratios for the SAOZ and the UT-GBS, 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 instruments are shown in Fig. 6b, along with the measured value of the ratio, which is used before and after the peak (before 65° and after 82°). From these fitted values of the NO₂/O₄ ratio during the storm, an estimate of the portion of the NO₂ differential slant column due to enhanced path length can be derived:

$$\text{NO}_{2,\text{PE}}(\text{SZA}) = \left[\frac{\text{NO}_2}{\text{O}_4}(\text{SZA}) \right]_{\text{fit}} \times \text{O}_{4,\text{meas}}(\text{SZA}) \quad (1)$$

where NO_{2,PE} is the path-enhanced NO₂, the subscript “fit” indicates the fitted NO₂/O₄ ratio, and O_{4,meas} the measured O₄ column. This relationship is only valid if the vertical profiles of O₄ and NO₂ do not change. To find the portion of the observed enhanced NO₂ DSCD that is due to path-enhancement, the assumption is made that the vertical profile does not change. Any change in profile is therefore at-

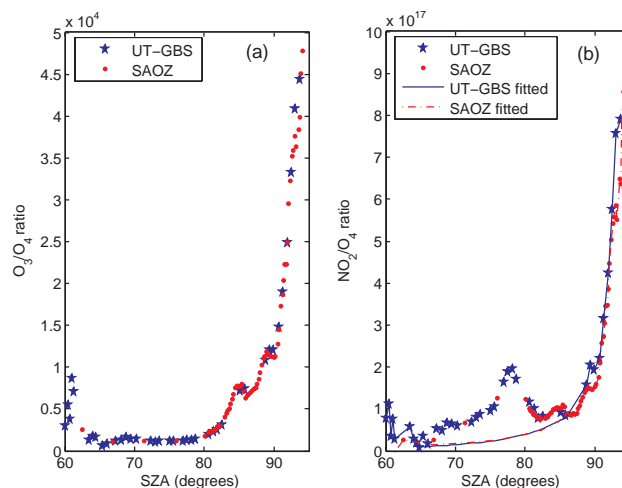


Fig. 6. (a) Measured O₃/O₄ ratios, and (b) measured and fitted NO₂/O₄ ratios for the afternoon of 28 August in Vanscoy. The measured value of the ratio is plotted before and after the peak (before 65° and after 82°) in the NO₂/O₄ ratio (see text).

tributed to the lightning-produced NO₂. The resulting NO₂ differential slant columns are shown in Fig. 7a. The difference between the observed NO₂ differential slant column and the differential slant column calculated from the interpolated NO₂/O₄ ratio is the slant column of NO₂ attributed to production by lightning, shown in Fig. 7b. The results from both instruments are similar.

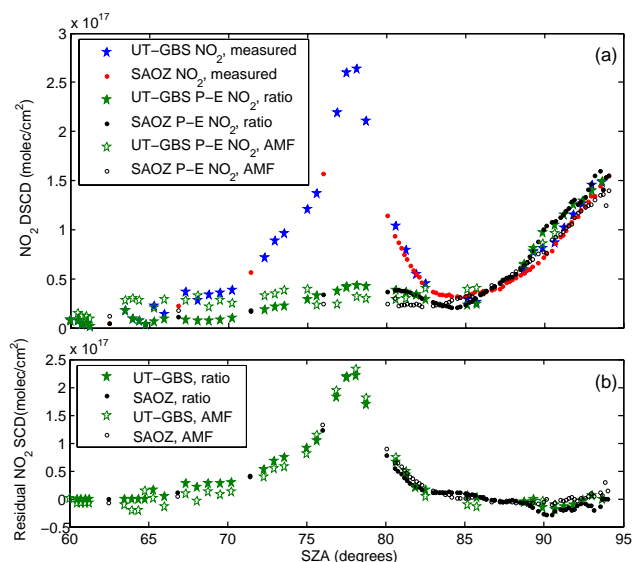


Fig. 7. (a) Measured total NO₂ DSCDs as well as the derived contribution from path-enhancement (P-E) for methods one (ratios to O₄) and two (derived AMFs) discussed in the text. (b) Residual NO₂ SCDs attributed to lightning.

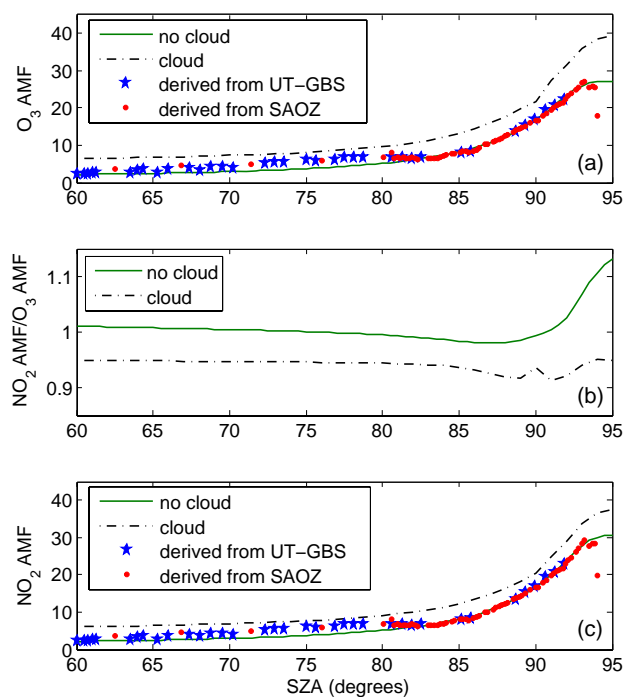


Fig. 8. (a) Ozone air mass factors calculated for the case of no clouds and for a cloud of OD=70 from 1–10 km using a radiative transfer model, and derived from the measurements using Eq. (4). (b) Ratio of NO₂ to ozone AMFs using the radiative transfer model. (c) Same as (a), but for NO₂ and using Eq. (5).

5.2 Method two: derived air mass factors

A second method of deriving the slant column of NO₂ caused by path enhancement is to use the measurements of ozone to derive the enhanced air mass factor, or path length, for ozone and NO₂. Generally, measured differential slant column densities of both ozone and NO₂ are related to the air mass factor by:

$$\text{DSCD}(\text{SZA}) = \text{VCD} \times \text{AMF}(\text{SZA}) - \text{RCD} \quad (2)$$

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 DSCDs would follow the same trend as the morning DSCDs, increasing with SZA. Assuming no change in the VCD, the path-enhanced DSCD' will be related to the enhanced AMF' by:

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

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

$$\text{AMF}'(\text{SZA}) = \text{AMF}(\text{SZA}) \frac{\text{DSCD}'(\text{SZA}) + \text{RCD}}{\text{DSCD}(\text{SZA}) + \text{RCD}} \quad (4)$$

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 O₄ 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 and a climatological NO₂ profile. The RCDs for ozone and NO₂ were found from Langley plots, of DSCD versus AMF, for the morning of 28 August. Measured ozone differential slant columns from the morning and afternoon were used as DSCD and DSCD', 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 10 km (e.g. Bassford et al., 2001). The same profiles were used to initialize the model in both the cloud-free and cloud cases.

The air mass factors for ozone and NO₂ differ since they are retrieved in different wavelength regions. In the radiative transfer model, the ozone AMF is calculated at 500 nm, while the NO₂ 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 NO₂ AMF to the O₃ AMF for the cloudless and thick cloud model calculations. This ratio is a maximum for the cloud-free scenario. Without more detailed observations of the clouds and vertical profiles of

the two species, 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 NO₂ AMF can be found by assuming there are no clouds during the storm. Although this assumption is certainly false, it allows the calculation of an upper limit on the NO₂ due to path enhancement, and a lower limit on the NO₂ produced by lightning. Taking this cloud-free ratio, the estimated NO₂ AMF' is found from:

$$\text{AMF}'_{\text{NO}_2}(\text{SZA}) = \text{AMF}'_{\text{O}_3}(\text{SZA}) \frac{\text{AMF}_{\text{NO}_2}(\text{SZA})}{\text{AMF}_{\text{O}_3}(\text{SZA})} \quad (5)$$

Figure 8c shows this estimated NO₂ AMF for each instrument, as well as the calculated AMFs for the cloudless and cloudy scenarios.

Figure 7a shows the resulting upper limit for NO₂ DSCDs due to path enhancement calculated from Eq. (4). The NO₂ differential slant columns measured in the morning were used as DSCDs, increased to account for the expected increase due to the diurnal variation of NO₂. The increase was calculated using a linear fit to the ratio of the NO₂ DSCDs observed in the afternoon to those observed in the morning, excluding the DSCDs measured during the thunderstorm. The upper limit of NO₂ DSCDs from both SAOZ and UT-GBS is similar. Prior to 67°, the upper limit exceeds the measured NO₂ DSCD, an indication that an assumption made in calculating the NO₂ 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 NO₂ is exceeded by the NO₂ found using the NO₂ to O₄ ratio method. This is perhaps an indication that the interpolated NO₂ to O₄ ratio is too large in this region, a result of the difficulty in predicting the NO₂/O₄ ratio. However, since both methods result in similar differential slant columns of NO₂ due to path-enhancement they can be believed to be approximately correct.

5.3 Conversion to vertical column densities

The difference between the measured NO₂ DSCD and the derived path-enhanced NO₂ in Fig. 7a is the amount of NO₂ produced by lightning, which is shown in Fig. 7b. However, these residuals are slant columns: the above methods have calculated the path-enhanced NO₂ assuming no change in the vertical column. Lightning produces NO₂ beneath the cloud through cloud-to-ground flashes, which is transported into the cloud through the strong vertical updrafts present during thunderstorms. NO₂ is also produced within the cloud by intra-cloud flashes (Fehr et al., 2004). Therefore the path length through the lightning-produced NO₂ will also be increased by multiple scattering within the cloud. To convert the derived lightning-produced NO₂ SCDs found in Sects. 5.1 and 5.2 into VCDs, the AMF' calculated in

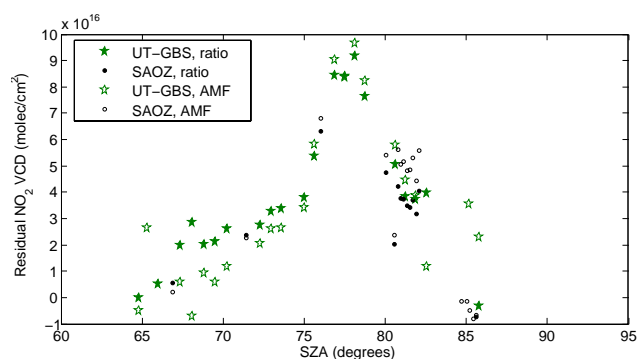


Fig. 9. Lightning-produced NO₂ VCDs calculated from the residual NO₂ in Fig. 7b and Eq. (6).

Sect. 5.2 is used, as well as Eq. (2) and (3), resulting in the following equation:

$$\text{VCD} = \frac{\text{DSCD}'(\text{SZA}) - \text{DSCD}(\text{SZA})}{\text{AMF}'(\text{SZA}) - \text{AMF}(\text{SZA})} \quad (6)$$

This has the result of the two methods no longer being independent. The resulting VCDs, shown in Fig. 9, are attributed to lightning. Only values between 64° and 86° are shown, as the differences in both the numerator and denominator of Eq. (6) are small, due to the fact the slant column of lightning-produced NO₂ is small or non-existent before and after the thunderstorm passes over Vanscoy. Since the AMF' is a maximum of the enhanced AMF, the VCDs are a minimum amount of NO₂ produced by lightning. No attempt has been made to account for horizontal variations in the NO₂ concentrations. In addition, it has been implicitly assumed that the transport of NO₂ produced by lightning outside the thunderstorm cells is approximately balanced by the transport of NO₂ from other thunderstorms into the cells. Although this assumption is most likely false, the assumptions involved in calculating a correction term for the effects of transport would introduce further error into the NO₂ VCD. Instead, a 20% error is attributed to the VCDs in addition to the errors in the DSCDs as a result of these processes, and the uncertainties in calculating the AMF.

6 NO₂ flash production rate

Taking the lightning-produced VCDs derived in Sect. 5.3, the amount of NO₂ produced per CG flash can be calculated. Using the ratio method, the amount of excess NO₂ VCD, found by integrating under the curves between 64° and 86° for method one in Fig. 9 is $(7.30 \pm 1.35) \times 10^{17}$ molecules NO₂/cm² for the UT-GBS and $(6.31 \pm 1.16) \times 10^{17}$ molecules NO₂/cm² for SAOZ. The error estimates on the total excess NO₂ are the root-sum-square of the DSCD error discussed in Sect. 2, the estimated errors in the methods used to obtain

the lightning-produced NO₂ VCD (20%) and the estimated integration error (10%). From Sect. 3, the size of the heavy-precipitation cell is $(61 \pm 10) \text{ km}^2$. Using the corrected number of CG lightning flashes during the storm from the CLDN (565 ± 59 flashes), the storm-averaged NO₂ production per CG flash of lightning can be calculated from:

$$\text{NO}_2 \text{ produced} = \frac{E \times A}{F} \quad (7)$$

where E is the residual NO₂ VCD derived from measurements, A is the area of the storm, and F is the number of lightning flashes (Noxon, 1976). The production amounts from this method are $(7.88 \pm 2.52) \times 10^{26}$ molecules NO₂/CG flash from the UT-GBS and $(6.81 \pm 2.17) \times 10^{26}$ molecules NO₂/CG flash from SAOZ. The values derived from both instruments agree within error bars.

Using the air mass factor method, the UT-GBS observed $(6.49 \pm 1.20) \times 10^{17}$ excess molecules NO₂/cm² and SAOZ observed $(5.96 \pm 1.10) \times 10^{17}$ excess molecules NO₂/cm². The minimum production amounts are found to be $(7.01 \pm 2.23) \times 10^{26}$ molecules NO₂/CG flash from the UT-GBS, and $(6.43 \pm 2.05) \times 10^{26}$ molecules NO₂/CG 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 NO₂ due to lightning production are minimum values for the amount of NO₂ production by lightning, whereas the values found using the NO₂ to O₄ ratio are best estimates of the actual NO₂ production rate. For both methods, the production amounts calculated from the SAOZ measurements are lower. This is a result of SAOZ not measuring during the peak of NO₂ as observed by the UT-GBS.

Noxon (1976) estimated an order of magnitude value of 10^{26} molecules NO₂/CG flash based on DOAS differential slant column measurements of NO₂ made during a thunderstorm in Colorado. Franzblau and Popp (1989) derived a rate of $(7 \pm 3) \times 10^{26}$ molecules NO₂/CG flash using a similar method in New Mexico. Langford et al. (2004) measured $(5.8 \pm 2.9) \times 10^{26}$ molecules NO₂/CG flash from a zenith-viewing UV-Visible spectrometer. All the values derived in this work are in agreement within the combined error bars of these previously published values.

Ridley et al. (2005) suggest that the production of NO from intra-cloud flashes is of the same order of magnitude as from cloud-to-ground flashes. No correction has been made to the flash frequency observed by the CLDN to account for intra-cloud flashes, and these flashes are not considered when applying Eq. (7). As a result, the NO₂ flash production amounts derived here, and the previously reported values cited above, are for CG flashes only. If the IC flashes are considered, the flash production amounts decrease significantly: in the thunderstorms studied here, 30 flashes were detected. Assuming the 1–4% detection efficiency, this trans-

lates into 750–3000 IC flashes. Taking these flashes into account, the range of the NO₂ produced per flash would be $(1.01\text{--}1.24) \times 10^{26}$ for 3000 IC flashes and $(2.70\text{--}3.30) \times 10^{26}$ for 750 IC flashes.

7 Conclusions

Elevated columns of ozone and NO₂ were observed by both SAOZ and UT-GBS ground-based UV-visible spectrometers during a thunderstorm that occurred during 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 NO₂, the enhancement is due to increased path length and the production of NO_x by lightning. The amount of NO₂ due to lightning has been calculated, using two methods to estimate the excess NO₂ 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 NO₂ produced per lightning flash. The production values in the range of $(6.43\text{--}7.88 \times 10^{26})$ molecules NO₂/CG flash calculated from both instruments agree with each other, and are also in agreement with previously published values. If IC flashes are considered as well, this rate becomes $(1.01\text{--}3.30) \times 10^{26}$ molecules NO₂/flash, the large range of estimates being primarily due to the relative insensitivity of the CLDN to intra-cloud flashes. Error estimates for the production amounts are approximately 32% of the derived values, due to the difficulties in accurately representing the area of the NO₂ producing thunderstorms, the transport of NO₂ into and out of the measured air masses, and the separation of the observed NO₂ into contributions from lightning and path-enhancement.

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