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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Lightning-produced NO_2 observed by two ground-based UV-visible spectrometers at Vanscoy, Saskatchewan in August 2004" *by* A. Fraser et al.

A. Fraser et al.

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We thank the reviewer for their helpful comments on our paper. In the following, the reviewer's comments are repeated in italics, followed by our responses.

The paper describes the estimation of the NO2 production by lightning from ground based DOAS observations of NO2 during a heavy thunderstorm. From the measured enhancement of the NO2 absorptions they separate the contribution due to enhanced light paths and attribute the remaining increase to the NO2 production by lightning. From the comparison of the derived NO2 production with simultaneously measured lightning counts, the authors derive the NO2 production per flash. In general, the

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paper presents a nice case study of the effect of lightning on ground based DOAS observations of NO2 (and O3 and O4). Also the ideas to separate the effects of enhanced light paths and the actual NO2 productions are promising and help to improve the quantitative interpretation of DOAS observations under cloudy sky conditions. Nevertheless, I feel that (besides some general errors of the approach, see below), the conclusions are a little bit too ambiguous and the presented accuracies are by far too optimistic. However, taking into account the very large uncertainties of current estimates of NOx production by lightning, the derived results are still valuable, and I think the paper is a good contribution to improve our understanding of the NOx production by lightning. After a few major comments and several minor comments are addressed, I recommend publication in ACP.

Major comments: A) Several assumptions, on which the final conclusions are based, are very optimistic. For example, I have doubts that the derived NO2 production from the measurements is really representative for this (and for other) thunderstorms. A1) The observations cover only a small part of the thunderstorm and already from the temporal variation of the observed NO2 production, it can be concluded that the production is not homogeneous throughout the volume. A2) The separation of the light path effects from the total enhancement is based on (implicit) assumptions on the profile shapes of NO2, O3 and O4 as well as on the height distribution of the light path enhancement. Since for the latter and the concentrations of NO2 and O3 no height profiles are actually known, the estimation of the effect of the light path enhancement on the total enhancement of the NO2 absorption is actually very uncertain. Light path enhancement in different altitudes will have very different effects on all three absorbers. The authors should state which assumption on the profiles they have made. They should also give more details on the uncertainties. (it should be also taken into consideration that besides the uncertainties of the vertical profiles, also the horizontal distribution is not known, but could have a strong effect.) The authors should also state which profiles they have assumed for the AMF calculations. The

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ratio of the AMFs for NO2 and O3 will also strongly depend on the assumptions made for the tropospheric profiles.

The AMFs are calculated using the temperature, pressure, and ozone profiles from an average of all the ozonesondes flown during the MANTRA field campaign. The NO2 profile used in the radiative transfer model is based on climatology. In calculating the path-enhanced AMF in Sect. 5.2, only the cloud-free AMF is used (as well as the observed SCDs), for which we assume no change in the shape of the ozone, NO2, or O4 profile. This results in a derived enhanced AMF, which allows us to calculate how much of the observed NO2 is due to the presence of clouds. We have clarified this on pg. 10071 , lines 19-21 : “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.” And also on pg. 10072 line 3 :“The same profiles were used to initialize the model in both the cloud-free and cloud cases.”

To account for the errors in calculating the AMFs as well as the non-homogeneity in the NO2 field, we attribute an additional 10% error to the VCDs calculated in Sect. 5.3. We have added a comment on this in Sect. 5.3: “No attempt has been made to account for the horizontal variations in the NO2 concentrations. In addition to the errors in the DSCDs, a 10% error is attributed to the VCDs as a result of the uncertainties in calculating the AMF, as well as the non-homogeneity of the NO2 field.”

B) The authors integrate the measured NO2 enhancement over the time. Is this really justified? I guess that the NO2 produced at the beginning will be still present at the end of the period of enhanced NO2 absorptions. If one integrates over the time, is it counted several times?

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As the thunderstorms pass over Vanscoy, so does the lightning-produced NO2. The lifetime of LNOx is several days, and so the decrease in the peak of the NO2 seen in Figs. 5, 7, and 9 is a result of transport, not decay. By integrating over time we are counting the LNO2 produced by different parts of the storm, and not the same LNO2 several times. We have added discussion of this in Section 4.

"As the lifetime of NOx is several days, the decrease in NO2 after the peak is most likely due to transport as the thunderstorm moves over Vanscoy, and not due to the decay of NO2."

C) The derived lightning production of NO2 is presented as NO2 SCD. However, what is really needed to quantify the total amount of NO2, is the VCD (vertical column density). The authors would have to correct their SCDs by an appropriate AMF (for multiple scattering inside the clouds). Like for the above point, here assumptions on the profiles of NO2 and the light path enhancements have to be made and an error has to be estimated. In any case, assuming that effective light path enhancement has taken place, the NO2 VCD should be expected to be systematically smaller than the NO2 SCD. This would have direct consequences for the derived NO2 production rate. I also recommend to state clearly which quantities are presented and discussed. In Fig. 7b, e.g. 'residual NO2 SCD' should be written. Quantities like 'amount' or 'value' should be avoided and replaced by more precise expressions.

We have added a new section (Sect. 5.3: Conversion to Vertical Column Densities) and new figure (Figure 9) to address this comment. We have scaled the residual SCDs derived using the ratio and AMF methods of calculating the path-enhancement using the enhanced AMF' calculated using the AMF method (using new Equation 6, derived from Equations 2 and 3). This has the effect of making the final VCDs attributed to lightning not entirely independent of one another. We have clarified

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'amount' and 'value' to refer to slant columns in Sect. 5 and vertical columns in Sect. 6. We have changed the label in Fig. 7(b) to 'Residual NO2 SCD'. We have also estimated a 10% error in the VCDs derived in Sect. 5.3.

D) To derive finally the NOx production by lightning one has to make some assumptions on the NO2/NOx ratio. This ratio depends in particular on the actinic flux and temperature, thus depending strongly on altitude. Again, assumptions on the NO2 profile become important. What are the assumptions the authors make?

We have chosen only to report NO2 production to avoid introducing the uncertainties of converting NO2 to NOx.

Minor comments e) page 10065, line 14: As far as I know the lightning production is given as NOx. The authors should clearly state this here. They should shortly discuss how the NO2 production is related to the NOx production.

The values reported here are calculated from the lightning-produced NOx, but are generally given in Tg N. We have clarified this sentence to read: "Recent estimates of the global annual production rate due to lightning-produced NOx lie between 1 and 20 Tg N/year."

f) page 100066, line 14: What is the NO2 region and the O3 region? Please indicate wavelength ranges.

This is stated on page 10067 lines 8-9, but we have added this information on page 10066 line 16-17.

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“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).”

Which settings are used for the analysis of O4?

O4 was retrieved in the ozone region. This has been added to the second paragraph of pg. 10067.

“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.”

g) page 100066, line 15: How large is the sensitivity (quantum efficiency) of the old and new detector?

We have reworded this section to include this information. Pg. 10066 lines 17-19 have been changed to read: “The loaned CCD’s sensitivity to UV-Vis radiation ($\backsim$ 10% quantum efficiency) was lower than that of the original detector ($\backsim$ 60% quantum efficiency), meaning that longer exposure times were required to maximize the signal, leading to fewer measurements over twilight.”

h) page 100066, line 27: For an uncooled detector I would expect that the influence of the dark current can become important, especially during the presence of a heavy thunderstorm when the measured intensity is low. Please comment on this.

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The SAOZ detector is uncooled and the influence of dark current is taken into account by recording a “dark current” spectrum after each solar spectrum in exactly the same conditions as the actual spectrum: using the same exposure time, the same number of accumulated spectra, and the same detector temperature. In the presence of a heavy thunderstorm, the SAOZ detector is receiving less light. Compared to spectra recorded on the previous day at similar SZA, the measured intensity has been reduced by a factor of 7 but the time of exposure has been correspondingly increased by a factor of 7.

i) page 100068, line 25: It might be interesting to mention here that this finding is consistent with those of Erle et al., 1995 and Wagner et al., 1998.

We agree, and have added these references to page 100069, line 9.

j) page 100069, line 9: It might be interesting to mention here that this finding is consistent with those of Wagner et al., 1998.

We agree, and have added this reference.

k) page 100069, line 22: It might be interesting to include the reference of Greenblatt et al., 1990. Greenblatt G. D., J.J. Orlando, J.B. Burkholder, and A.R. Ravishankara, Absorption measurements of oxygen between 330 and 1140 nm, J. Geophys. Res., 95, 18577-18582, 1990.

This reference is given in Sect. 2, pg. 10067, line 7. We have also added more discussion of O4 in Sect. 4.

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"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)."

l) page 100070, line 9: The ratio will be strongly dependent on the vertical profile of NO2 and the light path enhancement. Please mention here.

We have added a comment on this: "This ratio is also strongly dependent on the vertical profiles of both species."

m) page 100070, line 10: Is there an explanation for the exponential dependence? Or is this just a best fit?

For other days of the campaign, we found an exponential increase to be the best fit to the NO2/O4 ratio. We have reworded line 10 -11 to clarify this: "However, on other days of the campaign, the ratio increases exponentially with solar zenith angle."

n) equation 1: This assumption is only valid if the vertical profile of NO2 and the light path enhancement do not change.

We have added some discussion to address this point: "This relationship is only valid

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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 of NO2 does not change. Any change in profile is therefore attributed to the lightning-produced NO2."

o) page 10072, line 4: To my knowledge, the wavelength dependence of the AMF becomes very important only for large solar zenith angles. However, the AMF is much more dependent on the assumed profile, in particular in the troposphere. Which tropospheric profiles of NO2 and O3 were assumed for the AMF calculations?

The O3 tropospheric profile was taken from the average of all the ozonesondes launched during the campaign, while the NO2 tropospheric profile was taken from climatology. As the AMF is used to find the portion of the DSCD that is due to path-enhancement, we assume that there is no change in the tropospheric profile of either species.

p) page 10072, line 8: Especially this ratio will strongly depend on the assumed profiles.

We have added a comment on this: "Without more detailed observations of the clouds and vertical profiles of the two species, it is difficult to predict what the ratio of AMFs would have been during the storm, and even more difficult to quantify how it would change with SZA."

q) page 10072, line 21: How was the increase determined? How strong is the increase?

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A straight line fit was made to the ratio of the NO2 SCDs observed in the afternoon to those observed in the morning, excluding the values in the peak of the NO2. (NO2(pm)/NO2(am)) This fitted ratio was then applied to the morning SCDs to increase them to what would have been observed in the afternoon without the thunderstorm. This amounted to a maximum increase of roughly 60% at a SZA of 90 degrees. We have clarified this in the paper: “The increase was calculated using a linear fit to the ratio of the NO2 observed in the afternoon to that observed in the morning, excluding the DSCDs measured during the thunderstorm.”

r) page 10073, line 9: The curve in Fig. 7 shows the NO2 SCD. For the determination of the amount of lightning produced NO2, however, the VCD has to be used. In particular, one has to make some assumptions on the light path enhancement (depends on assumed profiles).

As mentioned in response to comment (C), a new section (5.3) has been added to address this comment. The calculated AMF’ in Sect. 5.2 was used to calculate VCDs.

s) page 10073, line 9: Why do the authors integrate over time? The lifetime of NO2 is long enough to let the NO2 accumulate during the thunderstorm. What do the authors assume for the lifetime of NO2?

This is addressed in our response to comment (B).

t) page 10073, lines 19-25: I think the true errors are by far larger than stated here. I think, however, that this is not a great pity, taking into account the high uncertainties of current estimates of lightning produced NOx.

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We have added an estimate of 10% error to the NO2 VCDs calculated in Sect. 5.3. The total error in the NO2 production rate is now roughly 27% for both instruments.

u) Fig. 1: Please show also fit results for O4

We have added O4 fits for both instruments to Fig. 1 and changed the caption accordingly.

v) Fig. 2: In which units is 'cloud opacity' given?

Cloud opacity is given in tenths. We have added this to the figure caption.

w) Fig. 5: It would be very interesting to show also the observed (average) intensity here. The largest optical thickness of the cloud (giving largest light path enhancement) should be related to the lowest intensity (see e.g. Wagner et al., 1998).

Since both instruments adjust their exposure times to maximise the signal on their detectors, the intensity does not change by much during the thunderstorms.

x) Fig. 5: How is the RCD for O4 derived?

O4 RCDs are not derived. Figure 5 shows differential slant column densities. We have changed SCD to DSCD throughout the paper to avoid this confusion.

y) Fig. 8: How realistic are the assumptions of the radiative transfer modelling? I am a

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little bit puzzled by the low upper edge of the cloud (only 5km). Again, here the measured intensity could help to justify the model assumptions.

We have re-calculated the cloudy AMF using a cloud extending from 1 km (cloud base from Fig. 2) up to 10 km (as calculated from the radar imagery). This has been changed in Fig. 8. It should be noted that the cloudy AMF is shown only for discussion, and is not used in any calculations.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 10063, 2006.