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Enhanced O_3 and NO_2 in Thunderstorm Clouds: Convection or Production?

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Abstract. Ground based zenith sky measurements of O_3 and NO_2 slant optical thickness (SOT) from a field campaign at the Observatoire de Haute Provence in June 1996 are reported. Differential optical absorption spectroscopy in the 450–497 nm region was used to derive SOT for both species under clear sky, cloudy and thunderstorm conditions. SOT enhancements of 62% for O_3 and up to 320% for NO_2 are found in a thunderstorm cloud. Interpretation of the measurements was carried out using a radiative transfer model. To explain the measurements a mean increase of 38 ppbv of the in-cloud concentration of O_3 has to be assumed. This amount leads to a mean in-cloud concentration of more than 100 ppbv of O_3. The corresponding increase in NO_2 is 3 ppbv, resulting in an in-cloud concentration of 3.2 ppbv. The NO_2 enhancements are in large part explained by lightning processes. In contrast, the enhanced O_3 appears to be induced by intrusion of stratospheric air and possibly ozone production by non-lightning discharge mechanisms.

Introduction

As previous measurements have shown, the slant optical thickness (SOT) increase in the presence of optically thick clouds [Brewer and Kerr, 1973; Van Roozendael *et al.*, 1994; Erle *et al.*, 1995]. The reason is twofold: first, the atmospheric light path is enhanced due to multiple scattering of light by the cloud particles [Kurosu *et al.*, 1997; Pfeilsticker *et al.*, 1998, and references therein]. This leads to larger SOTs, which can be calculated with an appropriate radiative transfer model such as GOMETRAN [Rozanov *et al.*, 1997]. Second, the chemical composition of the in-cloud air is different from cloud free air as a result of transport [Dickerson *et al.*, 1987], photolysis and heterogeneous processes specific to clouds [Lelieveld and Crutzen, 1990], and chemical reactions specific to thunderstorms [Ridley *et al.*, 1994; Price *et al.*, 1997].

Estimates of NO_x production resulting from lightning vary considerably, because measurements are rare and influenced by the inhomogeneity of the clouds (see *Huntrieser et al.* [1998] for a survey of previous studies). The observed mixing ratios vary between less than 2 ppbv and 60 ppbv (e.g., *Drapcho et al.* [1983], *Dickerson et al.* [1987]), all showing enhanced in-cloud mixing ratios compared to measurements in the boundary layer. Absorption measurements show a maximum column of $5.5{\cdot}10^{20}$ molec/m^2 of NO_2 in a thunderstorm [Franzblau and Popp, 1989], and enhancements in the total column by a factor of 10–30 in NO_2 and 1.2 in O_3 during pre-monsoon thunderstorms [Jadhav *et al.*, 1996].

Measurements of O_3 in clouds indicate that both production and loss mechanisms exist. *Dickerson et al.* [1987] measured enhanced mixing ratios inside a cloud compared to the boundary layer value, *Poulida et al.* [1996] measured high O_3 near but not within a thunderstorm anvil. Both attributed this effect to intrusion of stratospheric air. *Hauf et al.* [1995] detected a drop in O_3 on entering the anvil core of a thunderstorm cloud. Similar measurements by *Ridley et al.* [1994] and *Huntrieser et al.* [1998] also showed no systematic increase of in-cloud O_3 concentrations. Sonde measurements carried out by *Shlanta and Moore* [1972] show O_3 values inside a cloud at 6 km that are 2.6 times higher than their pre-storm boundary layer level. They assigned the sources to be point discharges at the ground followed by transport and in-cloud production. In contrast, *Drapcho et al.* [1983] found a correlation between a decrease in O_3 and an increase in NO_2 caused by the production of NO, followed by its reaction with O_3. Recent laboratory studies of arc discharges also indicate a large ratio of NO/NO_2 and minimal O_3 production [Wang *et al.*, 1998].

The measurements presented in this paper have been performed by the Bremen group during the NDSC (Network for the Detection of Stratospheric Change) and SCUVS (Stratospheric Climate using UV/Vis-Spectroscopy) validation campaign at the Observatoire de Haute Provence (OHP), which is located at 44°N, 6°E (see Figure 1) at an altitude of 684 m above sea level. The aim of this work is to analyse the enhancement of the SOTs in O_3 and NO_2, which were measured on June 15th, 1996 at OHP, when convective cumulonimbus clouds developed over the site.

Measurements and Analysis

Detailed information about the validation campaign and the zenith sky spectrometer and DOAS (Differential Optical Absorption Spectroscopy) retrieval algorithm used for this study are given in *Richter et al.* [1995] and *Roscoe et al.* [1998]. Briefly, for each solar zenith angle (SZA) the term

$$(\ln I(\Theta_0,\lambda)/I(\Theta,\lambda)) - \sum_i \sigma_i(\lambda) SCD_i - P(\lambda)$$

is minimised in a least square fit for the selected spectral window. Here, $I(\Theta,\lambda)$ is the radiance measured at SZA Θ and wavelength λ, Θ_0 a reference SZA, σ_i the absorption cross section, $SCD_i = SOT_i/\sigma_i$ the slant column density, and $P(\lambda)$ a polynomial, which is used to differentiate broad

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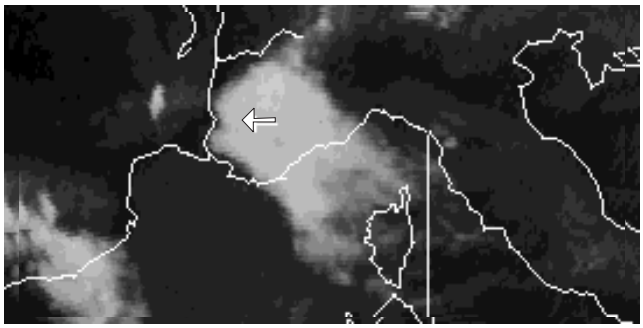

Figure 1. METEOSAT picture (provided by DWD) showing the analysed thunderstorm cloud over part of southern France at 6 pm on 06/15/96. Northern Italy is on the right, Corsica and Sardinia at the bottom. The white arrow marks the location of OHP.

band absorptions and scattering from differential gas absorption structures. The spectral window for both O_3 and NO_2 measurements was 450–497 nm. This was selected after a careful study of potential interferences by other absorbers. Figure 2 shows June 15th measurements for O_4, O_3, and NO_2, as well as the Colour Index (CI), a measure of cloudiness, defined as the ratio of the red to the blue part of a spectrum. A significant enhancement in the SOTs of all trace gases was observed during the thunderstorm. Similar results were obtained on other days, but the relative amounts of the O_4, NO_2 and O_3 enhancements varied from cloud to cloud. As part of the SCUVS project, cloud measurements of several zenith sky instruments at OHP have been compared [Pfeilsticker *et al.*, 1998]. It is important to note, that zenith sky measurements of the type described here under an optically thick cloud yield values averaged over a large volume, and cannot be readily compared to in-situ measurements.

Modelling Calculations simulating the enhancements due to changes in the radiative transfer were performed with GOMETRAN, which is a 1-dimensional full multiple scattering radiative transfer model based on the finite differencing method. It contains a quasi-exact parameterisation for cloud scattering [Kurosu *et al.*, 1997] where the cloud is defined by plane-parallel layers with an altitude dependent droplet spectrum and cloud optical properties derived from Mie theory. For the radiative transfer calculations presented here, balloon borne measurements taken by the CNRS group at Gap, close to the measurement site on the same day (temperature, pressure, O_3) and June 19th (NO_2) were used as profile input.

Determination of cloud parameters On June 15th, convection started at midday inducing the development of clouds over the site as can be seen in Figure 1. METEOSAT data clearly indicate a cumulonimbus system of large horizontal extent covering the measurement site completely at 6 pm, the time selected for detailed analysis. Lightning was observed in the afternoon starting around 4:30 pm. Heavy rain was recorded between 4 and 7 pm. The wind direction was from the south-west, turning north-east in the evening, with frequent changes of direction during the thunderstorm episode.

The cloud condensation level was estimated to be 2.2 km, assuming an adiabatic rise of air from the ground. Cloud top height was inferred from the cloud top temperature observed by METEOSAT. The cloud particle profile, which is shown in Figure 3, was derived from GOMETRAN simulations of the SOT of the chemically inert O_4 (proportional to $[O_2]^2$) by matching the model results for a cumulonimbus cloud to the observed SOT of O_4.

Determination of NO_2 and O_3 in-cloud mixing ratios The cloud parameters, that reproduce the observed O_4 amount, yield SOTs for NO_2 and O_3 which are significantly different from the measured quantities. Therefore the chemical composition of the cloud air mass must have changed. Table 1 shows the values for clear sky conditions and the measured and calculated amounts for the cloudy situation.

The model fit of the measurements is performed by variation of the assumed mixing ratios until the observed O_3 and NO_2 SOTs are obtained. Two cases were evaluated for this purpose: the first, where changes were limited to taking place within the cloud (case I), results in values of about 3.20 ppbv and 115 ppbv for NO_2 and O_3, respectively. For the second case, a constant mixing ratio is assumed from the ground to the top of the cloud (case II). This results in values of about 3.15 ppbv and 109 ppbv, i.e., not significantly different from case I. For NO_2, two alternative vertical profiles (IIb+c) were investigated, which also reproduced the observed SOT (see Figure 3). Profile IIb corresponds to the case when the NO/NO_2 ratio is determined by a photostationary state, involving NO_2 photolysis and the reaction of NO with O_3. In this calculation, actinic fluxes calculated by GOMETRAN for this particular cloud and sonde measured O_3 and T profiles have been used. For this case, a 38% decrease of the NO_2 mixing ratio from cloud bottom to cloud top was derived for a constant NO_x mixing ratio inside the cloud, resulting in an enhancement in the NO_2 column of $4.3{\cdot}10^{20}$ molec NO_2/m^2. The IIc case has a cloud bottom to cloud top ratio of 10 in NO_2, which could represent the upwelling of highly polluted air masses from the boundary layer. Even for this extreme situation, the vertical column of NO_2 is only 4% higher than in the case of the constant

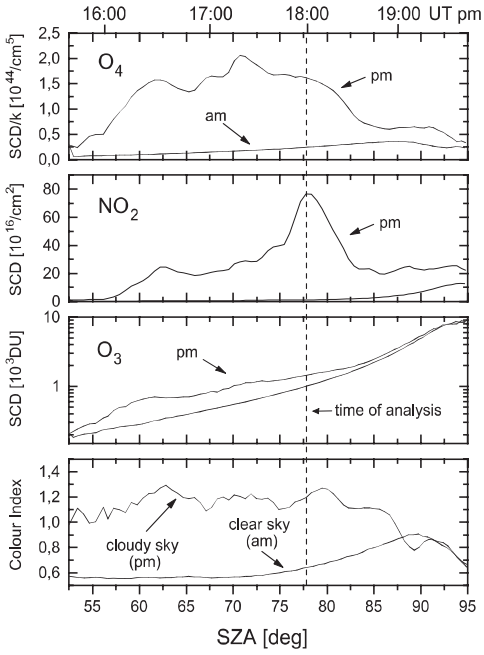

Figure 2. The time development of the observed SCDs of various trace gases and the CI (see text for definition). The evening values during the cloudy period are clearly enhanced. Note the logarithmic scale for O_3. The dashed line indicates the time of analysis.

profile. This demonstrates that the shape of the vertical profile within the cloud has only a small influence on the integrated trace gas column. In a series of sensitivity tests, the mixing ratios obtained for O_3 and NO_2 were shown to be relatively insensitive to cloud vertical position. For example, a vertical shift of $\pm$500 m results in changes of less than 2.0% in O_3 and less than 2.5% in NO_2.

Discussion

Three possible sources for the observed O_3 and NO_2 enhancements were studied: convective transport of polluted air masses, stratospheric intrusion, and lightning induced production.

Convection A longer time-series of measurements taken at OHP indicates that enhancements in NO_2 column are often associated with tropospheric pollution (*J.-P. Pommereau, private communication*). On June 15th, southwesterly winds transported air from the direction of Marseille towards the measurement site. To explain the enhancements observed at OHP, a Marseille plume having 3.8 ppbv of NO_2 at 2 pm is required. Measurements in the boundary layer at Cadarache, approx. 32 km S-SW of OHP have lower early afternoon values. In the late afternoon, when Cadarache was also influenced by lightning, high values of up to 10 ppbv were observed. In summary, convection may have contributed but cannot explain all of the observed increase in NO_2 column.

Assuming advection as the source of O_3 in the cloud, a boundary layer air parcel with a mixing ratio of 110 ppbv is required. An O_3 sounding, which was launched at Gap at 9 am on the 15th, shows a mixing ratio of 42 ppbv O_3 at 590 m. On the 17th, when the meteorological situation was similar to that on the 15th, a value of 63 ppbv O_3 was measured around 6 pm. Values of 110 ppbv are usually not encountered in the afternoon, as the Cadarache data

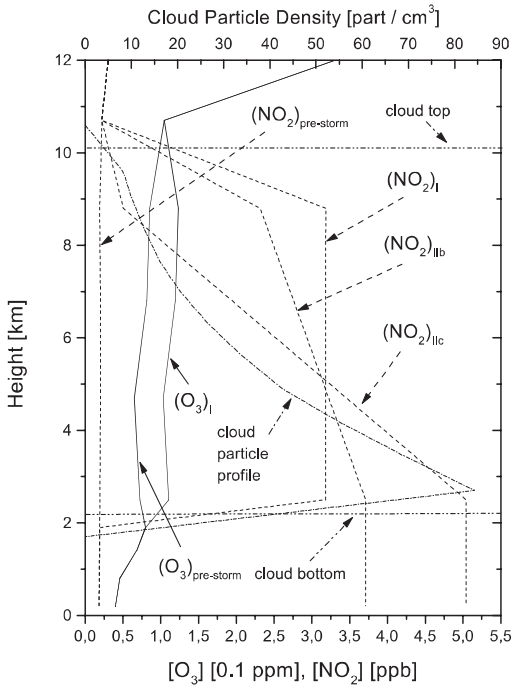

Figure 3. Trace gas profiles: pre-storm and modified to reproduce the observed cloud effect (labeled according to the different cases described in the text) and vertical profile of the cloud particle density.

Table 1. Observed (clear sky (AM) and cloudy sky (PM)) and modelled (cloudy sky) SOTs for 06/15/96. The diurnal change in stratospheric NO_2 has been taken into account by applying a factor of 1.4 to the AM NO_2 column. The calculated values are given for a cumulonimbus cloud between 2.2 and 10.1 km, and the original trace gas profiles as described in the text. All SOTs are given for 77.8° SZA and 477 nm.

SOT	clear sky	cloudy	model
O_4	0.025	0.111	0.111
O_3	0.023	0.037	0.032
NO_2	0.007	0.220	0.022

confirm. Overall, it is unlikely that convection is responsible for the majority of the observed increase in O_3.

Stratospheric intrusion Transport of air parcels from the stratosphere into the cloud anvil has been identified as a source of high concentrations of O_3 measured in cloud top regions by several authors [Dickerson *et al.*, 1987; Poulida *et al.*, 1996]. and can explain part of the observed enhancement in O_3 columns. For NO_2, the same mechanism can be ruled out as a result of its small mixing ratios in the lower stratosphere.

Lightning and discharge induced production Mechanisms for the production of O_3 and NO_2 involving discharge processes have been discussed by *Griffing*, 1977. As the dissociation energy of O_2 is lower than that of N_2, molecular nitrogen only dissociates as a result of lightning flashes, whereas oxygen may also be dissociated by non-lightning discharge processes. Although lightning itself does not appear to produce O_3 [Wang *et al.*, 1998], processes such as coronal, or silent discharges are potential sources [Bhetanabhotla et al., 1985]. O_3 production is therefore likely to occur prior to lightning in an electrically active cloud. Comparing the time development of the SOTs, two observations can be made: first, the maxima in O_3 and NO_2 do not coincide. O_3 peaks before NO_2, in agreement with the measurements of *Jadhav et al.* [1996]. Second, at approximately 78° SZA, a strong enhancement in NO_2 occurs, that is not observed in O_3. Convection of polluted air masses is an unlikely explanation of this effect.

Thunderstorm properties and the magnitude of lightning induced NO_2 production have been calculated according to the method of *Price et al.* [1997], using the measured temperature profile and our derived cloud properties as input data. As a result of the large uncertainty obtained when applying statistical data to a particular cloud, these calculations only yield order of magnitude estimates. For our conditions, this results in a statistical frequency of 2.1 flashes per minute, a NO_x production rate of $6.7 \cdot 10^{26}$ molec/cloud-to-ground lightning (CG) and a proportion of CG of 42%. The NO_x production for CG and intra-cloud lightning is calculated to be $6.8 \cdot 10^{26}$ molec/min. This results in a total production of $6.1 \cdot 10^{28}$ molec NO_x or a column of $6.9 \cdot 10^{20}$ molec NO_x/m^2 at 6 pm. Assuming a ratio of 0.86 for the vertical columns of NO_2/NO_x, as calculated assuming photostationary state (case IIb), a value of $5.9 \cdot 10^{20}$ molec NO_2/m^2 results. The enhancement in the vertical column of NO_2 from the ground to the cloud top, as derived from GOMETRAN calculations, is $4.3 \cdot 10^{20}$ molec NO_2/m^2. The two values are

of the same order of magnitude, but, as values of the NO_x production rate found in the literature cover a wide range [Biazar and McNider, 1995], this agreement might nevertheless be fortuitous. In conclusion, a significant contribution to the overall NO_2 content in the cloud appears to result from lightning discharge.

According to *Griffing* [1977], $3{\cdot}10^{26}$ molec O_3/flash are produced. This value results in an enhancement of the vertical column of O_3 between ground and cloud top of $6.2{\cdot}10^{20}$ molec O_3/m^2. According to *Jadhav et al.* [1996], lightning yields no more than 2–3% of the total O_3 produced in a thunderstorm cloud. This implies that a total O_3 column for the OHP cloud would be $2–3{\cdot}10^{22}$ molec/m^2. The measured excess O_3 vertical column at 6 pm on the 15th of June 1996 was $5.1{\cdot}10^{21}$ molec O_3/m^2. Both the temporal behaviour and this estimate indicate that O_3 might be produced by non-lightning discharges in the cloud. However, intrusion of stratospheric air could equally well explain the observed enhancement.

Summary

Zenith sky measurements of enhanced NO_2 and O_3 SOTs in a thunderstorm cloud have been analysed using the radiative transfer model GOMETRAN. Mixing ratios in the thunderstorm of more than 100 ppbv O_3 and 3 ppbv NO_2 were derived. Neglecting changes in the in-cloud chemistry, three mechanisms are likely to account for these enhancements: convective transport from the boundary layer, stratospheric intrusion, and discharge induced production. The differences in the temporal behaviour of O_3 and NO_2 indicate that the observed enhancements of the two molecules have different origins. For NO_2, lightning is the most likely source for the majority of the enhanced NO_2 observed at 6 pm. A smaller contribution may in addition result from the convection of polluted air. For O_3, intrusion of stratospheric air and possibly O_3 production by non-lightning discharge processes appear to be the most likely explanation of the observed in-cloud amount and its temporal behaviour. This study has used ground based DOAS measurements to detect in-cloud trace gas composition. It appears a promising approach for the study of lightning and related processes in clouds.

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