Boundary layer photochemistry during a total solar eclipse

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Abstract
Simultaneous measurements of radiation, photolysis frequencies, O3, CO, OH, PAN and NOx species were carried out in the boundary layer, along with pertinent meteorological parameters, under total solar eclipse conditions. This experiment performed at about 34° solar zenith angle and noon time conditions thus provided a case study about the interactions between radiation and photochemistry under fast “day-night” and “night-day” transitions, at high solar elevation. The results reveal a close correlation of photolysis frequencies \( j_{O_1D} \) and \( j_{NO_2} \) with the UV radiation flux. All three parameters show, due to the decreasing fraction of direct radiation at shorter wavelengths, much weaker cloud shading effects than global solar radiation. NO and OH concentrations decrease to essentially zero during totality. Subsequently, NO and OH concentrations increased almost symmetrically to their decrease preceding totality. The NO/NO\(_2\) ratio was proportional to \( j_{NO_2} \) over 30 min before and after totality indicating that the partitioning of NO\(_x\) species is determined by \( j_{NO_2} \). Simple box model simulations show the effect of reduced solar radiation on the photochemical production of O3 and PAN.

Zusammenfassung
Während der totalen Sonnenfinsternis am 11. August 1999 wurden simultane und kontinuierliche Messungen von O3, CO, OH, PAN und NOx, Strahlung, Photolysefrequenzen und relevanten meteorologischen Parametern durchgeführt. Dieses Experiment, durchgeführt etwa am Mittag, bei 34° Zenithwinkel der Sonne, ermöglichte die Untersuchung der Interaktion von Strahlung und Photochemie für schnelle Tag-Nacht- und Nacht-Tag-Übergänge bei hohem Sonnenstand. Die Ergebnisse zeigen eine enge Korrelation der Photolysefrequenzen \( j_{O_1D} \) und \( j_{NO_2} \) mit dem UV-Strahlungsfluss. Alle drei Parameter zeigen, wegen des abnehmenden Anteils direkter Sonnenstrahlung bei kurzen Wellenlängen, erheblich geringere Abschwächung durch Wolken als die Globalstrahlung. NO und OH gehen während der Verdunkelungsphase auf Null herunter. Danach steigen NO und OH nahezu symmetrisch zum vorherigen Abfall wieder an. Das NO/NO\(_2\)-Verhältnis war 30 min vor bis 30 min nach der Totalität proportional zu \( j_{NO_2} \) und zeigte damit, dass die Partitionierung von NO\(_x\) durch \( j_{NO_2} \) bestimmt wurde. Mit einem einfachen Boxmodell wurde der Effekt der reduzierten Sonnenstrahlung auf die photochemische Produktion von O3 und PAN berechnet.

1 Introduction

On August 11, 1999, a total solar eclipse happened in parts of Europe and Asia. At Freising-Weihenstephan (WHS) (Lat. 48°24′5″N, Long. 11°43′10″E), 30 km NE of Munich, it occurred at 10:37 UT (12:37 CEST), with totality lasting 2.3 minutes, at a solar zenith angle of 34°, enabling us to investigate photochemical processes under fast daylight-to-darkness and darkness-to-daylight transitions. Within BAYSOFI (Bayerische Sonnenfinsternis), an interdisciplinary field campaign focussed on the effects of the total eclipse (see FABIAN et al., this issue), measurements of radiation, photolysis rates, O3, CO, PAN, NOx and meteorological parameters were carried out at WHS. Simultaneously, measurements of OH along with other chemical and meteorological parameters were conducted at the Meteorological Observatory Hohenpeißenberg (MOHp) about 60 km SW of WHS. At MOHp the eclipse reached 99% of totality. For logistic reasons, the OH instrument could...
not be transferred to WHS. Thus for comparison of the MOHp and WHS data, certain restrictions apply.

### 2 Measurements and results

For both WHS and MOHp meteorological and air chemistry data from previous measurement campaigns are documented (FABIAN et al., 1998; RAPPENGLÜCK and FABIAN, 1999). WHS is close to the small town of Freising, whereas MOHp is located on top of the Hohenpeißenberg mountain (1000 m a.s.l.), about 300 m above the surrounding rural terrain. The instruments used are listed in Table 1 within FABIAN et al., 2001.

Fig. 1 shows pertinent information on the meteorological conditions before, during and after the total solar eclipse at the Weihenstephan site. Both during morning and afternoon of August 11, cloudy conditions prevailed, with large fluctuations of the global radiation $G$. With the onset of the eclipse (first contact at 09:17 UT) the cloud cover diminished. Cloud sections obscured the sun between 09:45 and 09:55 UT, but from 10:00 onwards, towards totality and during the first phase of reappearance sun, cumulus clouds vanished leaving only some altostratus clouds allowing to observe the event. Clouds reappeared after 11:10 UT. During the final phase of the eclipse the wind velocity dropped from 5 m/s to 2 m/s, and temperatures decreased by about 3 K. This temperature drop was derived taking into account the diurnal temperature variation. It can be seen directly from the measurements shown in Fig. 5 of FABIAN et al., 2001.

The photolysis frequencies $j_{O_1D}$ and $j_{NO_2}$ and the UV radiation flux are closely correlated, showing the same temporal structure as $G$ due to cloud effects (Fig. 2). The magnitude of the cloud effect decreases towards shorter wavelengths due to the decreasing portion of direct radiation and is lower for the actinic flux than for the irradiance (KOEPEKE et al., 2001). Thus, while $G$ was reduced by about 70% from its cloudless level, the corresponding reductions in UV radiation and $j_{O_1D}$ were about 50% and 30–40%, respectively. During totality all observed radiation quantities were below the instrument detection limits. With $G$ close to zero, the radiation budget (not shown) became negative, similar to nighttime conditions.

Fig. 3 shows the temporal behaviour of the chemical species of interest, along with the UV radiation changes. With about 100 ppb of CO and 5 ppb of NOx, the pollution level was moderate. O₃ fluctuated between 30 and 40 ppb, showing a sudden increase by about 10 ppb during totality. Measured NO and NO₂ agreed such that their sum matched measured NOₓ well. As NO became zero NOₓ showed almost the same values, indicating that NOₓ was composed of NO₂ only during totality. It should be noted that for measuring NO a high-sensitivity chemiluminescence instrument with a very low detection limit of only 3 pptv was used (Table 1 of FABIAN et al., 2001). With this instrument the zero signal due to interferences of chemiluminescence reactions with trace

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**Table 1**: Mixing ratios (ppb) of some important species used to initialize the photochemical box model.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mixing ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>3.5</td>
</tr>
<tr>
<td>NO</td>
<td>1.0</td>
</tr>
<tr>
<td>PAN</td>
<td>0.1</td>
</tr>
<tr>
<td>O₃</td>
<td>30</td>
</tr>
<tr>
<td>HONO</td>
<td>0.4</td>
</tr>
<tr>
<td>HNO₃</td>
<td>0.2</td>
</tr>
<tr>
<td>CO</td>
<td>110</td>
</tr>
<tr>
<td>CH₄</td>
<td>1800</td>
</tr>
<tr>
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<td>1.40</td>
</tr>
<tr>
<td>Propane</td>
<td>1.00</td>
</tr>
<tr>
<td>n-Butane/i-Butane</td>
<td>0.14</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.11</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.30</td>
</tr>
<tr>
<td>Xylene</td>
<td>0.12</td>
</tr>
<tr>
<td>Isoprene</td>
<td>0.30</td>
</tr>
</tbody>
</table>

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**Figure 1**: Meterological measurements obtained at WHS. This presentation also includes the global radiation as calculated for the WHS site based on astronomical data.

**Figure 2**: Measurements of $j_{NO_2}$, $j_{O_1D}$ and UV-radiation at WHS.
Figure 3: Air chemistry data obtained at WHS.

Figure 4: Diurnal variations of the OH and H$_2$SO$_4$ concentrations and the ozone photolysis frequency $j_{O(1D)}$ measured at Hohenpeißenberg (MOHp) on August 11, 1999.

Gases other than NO is largely reduced by using a zeroing chamber which can be inserted into the sample gas flow. Inside the zeroing volume NO is completely oxidized to NO$_2$, and cross-chemiluminescence reactions can be determined during this time in the main reaction chamber. Thereby, the partitioning between NO and NO$_2$ as a function of $j_{NO_2}$ could be measured during BAYSOFI over the entire period of the solar eclipse.

The decrease of NO$_x$, from about 5 ppb before 09:45 to 3 ppb during the eclipse, accompanied by a similar decrease of CO, is due to almost complete cessation of local NO$_x$ sources, mostly automobiles, because of drivers watching the eclipse. Two distinct spikes of NO$_x$ and CO at 10:05 and 10:20 UT originate from taxicabs carrying visitors to the measuring site. When the sun started reappearing, at about 10:50 UT, people started driving, and NO$_x$ and CO levels rose again. PAN shows moderate levels of about 140 ppt. The peak of 170 ppt during totality is difficult to reconcile with the other data. Similarly, the 10 ppb O$_3$ increase during totality cannot be explained based on the NO$_x$ behaviour alone, as 3 to 4 ppb of NO$_x$ is not sufficient to account for about 10 ppb of O$_3$ titration. Certainly, these peaks are no artefacts, since O$_3$ and PAN were measured independently with different instruments (see Table 1 of FABIAN et al., 2001). Thus it appears that the O$_3$ and PAN peaks observed during totality are due to advection. Based on our own measurements, vertical transport is unlikely, as the wind velocity is decreasing during the event, while the wind direction remains fairly constant. Furthermore, the simultaneous PAN increase, by about 30 percent similar to that of O$_3$, makes downward mixing very unlikely. Downward mixing can nearly be excluded from the measurements by WINKLER et al. (2001) and FOKEN et al. (2001) who found, during the solar eclipse, decreasing winds up to 50 m in altitude and a tendency towards stabilization and decreasing vertical extent of the mixing layer. Thus horizontal advection remains as the most likely cause.

Meteorological and chemical parameters were also measured at the MOHp site (WINKLER et al., 2001). Fig. 4 shows OH concentrations and $j_{O(1D)}$at MOHp. With the exception of a few short-term interruptions in the OH measurements due to intermittent rain showers, decreasing OH levels could well be resolved during the eclipse. Overall, following the statistical interpretation by EHHALT and ROHRER (2000), 74% of the OH variation could be explained by variations in solar UV with O3 photolysis most likely being the predominant source of OH. NO$_x$ levels were mostly low (around 1 ppb) but increased to 2–4 ppb between 12:30–13:30 UT (not shown). At the same time, OH levels decreased significantly because of both lower $j_{O(1D)}$ and enhanced removal of OH by reaction with NO$_2$. With partially cloudy conditions at MOHp maximum $j_{O(1D)}$ levels (1.45 x 10$^{-5}$ s$^{-1}$, measured at 12:33 UT) were lower than at WHS.

Gaseous H$_2$SO$_4$, a major precursor for atmospheric sub-micrometer particles, was also measured with the CIMS instrument (BERRESHEIM et al., 2000) and showed a diurnal variation very similar to that of OH (Fig. 4), but no correlation with SO$_2$. Fig. 4 also shows both measured and calculated H$_2$SO$_4$ concentrations. The major source of gaseous sulphuric acid in the atmosphere is oxidation of SO$_2$ by OH, its major sink is diffusive deposition onto aerosol particles. With respect to the latter process the average atmospheric lifetime of H$_2$SO$_4$ (corresponding to 1/kaw, see equation below)
was calculated to be 3–4 min. The sink rate was determined from the measured particle size distribution (3–800 nm) based on the DAHNEKE interpolation formula for vapour diffusion, and particle sizes being adjusted to ambient relative humidity. See BIRMIL et al. (2000) for more information on the aerosol measurements and balance calculations. The above time scale is typical for the lifetime of H$_2$SO$_4$ in the continental background atmosphere. With OH levels rapidly declining during the eclipse, H$_2$SO$_4$ concentrations also decreased rapidly. Assuming steady-state conditions between H$_2$SO$_4$ production and loss rates a simple balance equation was used to calculate H$_2$SO$_4$ levels based on measured SO$_2$, OH, and aerosol number concentrations:

$$\frac{k[SO_2][OH]}{k_{aw}} = [H_2SO_4]$$

where the numerator on the left hand side represents the production term with $k = 8.5 \times 10^{-13}$ cm$^3$ molec$^{-1}$ s$^{-1}$ (DE-MORE et al., 1997) and kaw in the denominator represents the pseudo-first-order depositional rate constant. The results show values which were mostly somewhat lower than the measured H$_2$SO$_4$ levels. This difference could be due to errors in the measurements and/or an overestimate of the (dry) depositional loss of H$_2$SO$_4$ to aerosol particles.

Photochemical box model calculations were performed to simulate the variations of species of interest for WHS conditions. The model is a simplified zero-dimensional version of a Lagrangian 1-D model (STOHL et al., 1996; WOTAWA et al., 1998), employing an updated RADM scheme (STOCKWELL and KLEY, 1994). Two free-running (i.e. species concentrations were not nudged towards observed data after initialization) simulations were made. Both were initialized at 9:00 UT with mixing ratios either measured or assumed to be typical for the prevailing conditions at WHS as given in Table 1. No emissions or deposition were assumed to occur during the simulation period. The first run was driven by temperature, relative humidity, ambient pressure and $j_{NO_2}$ (photolysis frequencies of other species were scaled to $j_{NO_2}$ using solar zenith angles) as measured at WHS. For the second simulation measured photolysis frequencies were modified in order to represent identical atmospheric conditions but without reduction of the solar flux due to the eclipse, preserving variations in photolysis frequencies caused by variability in cloud cover. Photolysis frequencies for no eclipse conditions (ne) were determined using the measurements (e) according to:

$$j_{NO_2\text{--e}} = \frac{j_{NO_2\text{--e}}}{R_{900nnm}}$$  \hspace{1cm} (R1)

$$j_{O_3(D)\text{--e}} = \frac{j_{O_3(D)\text{--e}}}{R_{510nm}}$$  \hspace{1cm} (R2)

$R$, the ratio between the extraterrestrial radiation with the sun covered by the moon and the extraterrestrial radiation without coverage, is calculated taking into account the effect of spectrally dependent limb darkening (KOEPKE et al., 2001). During about 15 minutes centered around totality, the uncertainty in photolysis frequencies, modified following equations R1 and R2, is high. Therefore data points exceeding a 30% error derived by Gaussian error propagation, were replaced by constant values of 1.52 \times 10^{-5} s$^{-1}$ for $j_{O_3(D)}$ and 5.2 \times 10^{-5} s$^{-1}$ for $j_{NO_2}$, representing average conditions of the time intervals before and after totality (KOEPKE et al., 2001). For this second simulation, temperatures were assumed to be higher than the observed ones. A maximum temperature increase of 3.5 K was assumed to occur 45 minutes after totality, and no increase was applied 30 minutes before and two hours after totality. However, the model results were only moderately sensitive to these temperature modifications.

Both simulations were run for six hours. Despite simplifications and the fact that this episode was dominated by strong advection, our results show the principle effects on tropospheric photochemistry caused by the eclipse (Fig. 5). With the eclipse, a net O$_3$ production of 6 ppb until 12:00 UT and 11 ppb until 15:00 UT is estimated, while with the eclipse being eliminated, the production was 10 ppb and 16 ppb, respectively. Most of the difference in O$_3$ production occurred during the eclipse at high solar zenith angles. However, even after the eclipse, O$_3$ production rates were somewhat higher in the second case due to the more active noon-time
chemistry. Net PAN production was also higher without the eclipse (0.85 ppb) than with the eclipse (0.71 ppb).

Differences for PAN were smaller than for O$_3$. Photochemical box model simulations suggest a 4 ppb reduction in net O$_3$ production until the end of the eclipse and 5 ppb until the afternoon. Both measurements and model simulations show that the partitioning of NO$_x$ between NO and NO$_2$ was determined almost exclusively by the variations in $j_{NO_2}$. Besides illustrating a case study on the interaction between radiation and photochemistry under fast day-night and night-day transitions at high noontime solar elevations, our experiment shows interesting aspects of temporarily almost vanishing and later reappearing local emissions, at quite moderate overall pollution levels, in agreement with our overall understanding of atmospheric processes. The O$_3$ and PAN peaks observed almost simultaneously during totality can only partly be explained by photochemistry, because neither NO$_x$ titration of O$_3$ nor change of thermal decay of PAN can account for the 30 percent increase of both species. As downward mixing can be ruled out, horizontal advection remains as the most likely cause of this interesting effect.

### 3 Concluding remarks

The reduced solar radiation during the eclipse significantly affected the photochemical production of PAN and O$_3$. Photochemical box model simulations suggest a 4 ppb reduction in net O$_3$ production until the end of the eclipse and 5 ppb until the afternoon. Both measurements and model simulations show that the partitioning of NO$_x$ between NO and NO$_2$ was determined almost exclusively by the variations in $j_{NO_2}$. Besides illustrating a case study on the interaction between radiation and photochemistry under fast day-night and night-day transitions at high noontime solar elevations, our experiment shows interesting aspects of temporarily almost vanishing and later reappearing local emissions, at quite moderate overall pollution levels, in agreement with our overall understanding of atmospheric processes. The O$_3$ and PAN peaks observed almost simultaneously during totality can only partly be explained by photochemistry, because neither NO$_x$ titration of O$_3$ nor change of thermal decay of PAN can account for the 30 percent increase of both species. As downward mixing can be ruled out, horizontal advection remains as the most likely cause of this interesting effect.

### Acknowledgments

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### References


![Figure 6: The NO/NO$_2$ ratio as a function of $j_{NO_2}$ during 10:15–10:45 UT. Measurements displayed as thick line/full circles and model results displayed as dashed line/open circles.](image-url)


