



## CHANGES IN SURFACE UV SOLAR IRRADIANCE AND OZONE OVER THE BALKANS DURING THE ECLIPSE OF AUGUST 11, 1999

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### ABSTRACT

Intensive measurements of UV solar irradiance, total ozone and surface ozone were carried out during the solar eclipse of 11 August 1999 at Thessaloniki, Greece and Stara Zagora, Bulgaria, located very close to the footprint of the moon's shadow during the solar eclipse with the maximum coverage of the solar disk reaching about 90% and 96% respectively. It is shown that during the eclipse the diffuse component is reduced less compared to the decline of the direct solar irradiance at the shorter wavelengths. A 20-minute oscillation of erythemal UV-B solar irradiance was observed before and after the time of the eclipse maximum under clear skies, indicating a possible 20-minute fluctuation in total ozone presumably caused by the eclipse induced gravity waves. The surface ozone measurements at Thessaloniki display a decrease of around 10-15 ppbv during the solar eclipse. Similarly, ozone profile measurements with a lidar system indicate a decrease of ozone up to 2 km during the solar eclipse. The eclipse offered the opportunity to test our understanding of tropospheric ozone chemistry. The use of a chemical box model suggested that photochemistry can account for a significant portion of the observed surface ozone decrease. © 2001 COSPAR. Published by Elsevier Science Ltd. All rights reserved.

### INTRODUCTION

A solar eclipse being a photolytical perturbation of the atmospheric environment provides an excellent opportunity to investigate the observed changes in solar UV irradiances, in total columnar ozone, in surface ozone or other surface chemical parameters and in meteorological parameters at sites located near the path of the moon's shadow. In the literature there have been several studies that report effects of a solar eclipse on total ozone column (Zerefos et al., 2000 and references therein). Bojkov (1968) reported results from Dobson spectrophotometric observations performed in Sofia, Bulgaria during the solar eclipse of May 1966 and concluded that an increase of 14 D.U. was observed at the maximum phase of the eclipse. In that paper a critical review of total ozone measurements during a solar eclipse is presented and it was emphasized that similar results were also reported in other studies based on Dobson ozone observations. More recently Chakrabarty et al., (1997) reported that total ozone measurements performed with a Dobson spectrophotometer during the solar eclipse of 24 October 1997 over Ahmedabad, India, showed a sharp fall in the ozone column 10 minutes before the maximum obscuration of the sun, followed by a sharp rise 10 minutes after. Mims and Mims (1993) using a portable filter radiometer took observations during the total solar eclipse of July 1991. They reported the occurrence of two ozone minima (down to -7% of the pre-eclipse values) on either side of totality, as well as two maxima (3% higher than the post-eclipse observations) on either side of totality. It should be noted that the majority of

these studies note that conventional photochemical and dynamical processes could not explain the observed fluctuations.

However there are few studies (Fernandez *et al.*, 1993; Mikhalev *et al.*, 1999) investigating the solar-eclipse-induced changes in the spectral solar UV irradiance at the Earth's surface.

There are also few studies discussing the induction of gravity waves in the upper atmosphere during solar eclipse events because the cut off of the UV radiation in the shadowed region reduces the heating of the ozone layer. Chimonas and Hines (1970, 1971) and Fritts and Luo, (1993) have shown that the supersonic movement of the moon's shadow over the earth creates gravity waves, which are formed around the source region and have quasi periods ranging from 20 min to few hours. The existence of these waves has been confirmed by Davis and da Rosa (1970) by a wavelike ionospheric disturbance but, until now, they have not been confirmed in the observed fluctuations in the total ozone column. Such wave-like structures were also inferred from measurements of the vertical column abundance of atmospheric OH (Burnett and Burnett, 1985).

Some other articles discuss the effects of solar eclipse on surface temperature and surface winds (Fernandez *et al.*, 1993b), and on the mesoscale atmospheric circulation over Europe (Gross and Hense, 1999). As far as it concerns the effects of solar eclipse on surface ozone or other chemical components there is limited literature (Srivastava *et al.*, 1982).

The total solar eclipse took place on 11 August 1999 with the moon's shadow tracing a footprint from NW to SE of Europe. The maximum obscuration of the sun disk reached 90% at Thessaloniki. The effects of the solar eclipse on solar UV irradiances, total ozone, surface ozone and meteorological parameters at Thessaloniki and the signature of possible gravity waves using the erythemal solar irradiance measurements are discussed in the present study.

## DATA AND METHODOLOGY

Global and diffuse erythemal irradiances were obtained using two broadband pyranometers UVB-1 from Yankee Environmental Systems (YES), with a 1 min time resolution. Global UV-A irradiance, between 315 and 400 nm was measured with the MS-210A UV-A radiometer from EKO, with the same time resolution. A Kipp and Zonen pyranometer was used to measure the global shortwave radiation (300-3000 nm), with 1 min resolution. The latter measurements were used as an indication of the sun disk coverage or for estimating cloud effects. All measurements were performed under clear-sky conditions. The vertical distribution of ozone and of the relative aerosol backscatter was measured during the eclipse with a Lidar system operating at 289 and 299 nm (Papayannis *et al.*, 1999), with a time resolution of 5 minutes and a vertical resolution of 7.5 m.

Surface ozone measurements along with other chemical measurements ( $\text{NO}_x$ , CO,  $\text{SO}_2$ ) and meteorological measurements (pressure, temperature, wind speed, wind direction and relative humidity) are carried out regularly at several urban stations in the city of Thessaloniki (40.5N / 23E) in order to assess pollution problems. Ozone is measured with UV absorption (O341M analyser) and  $\text{NO}_x$  with chemiluminescence accompanied by  $\text{NO}_2$  conversion using a molybdenum converter (AC30M analyser). At Stara Zagora (42.25°N, 25.37°E) UV spectral measurements were performed with a newly developed spectroradiometer Photon-2 with a spectral resolution 1 nm.

A photochemical box model written in the FACSIMILE code (Curtis and Sweetenham, 1987) was used in this study. The photochemical scheme mainly includes the photolysis reactions of  $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ , HCHO, HONO,  $\text{NO}_3$ ,  $\text{HO}_2\text{NO}_2$ , and  $\text{CH}_3\text{OOH}$  coupled to the CO and  $\text{CH}_4$  oxidation reactions (Ayers *et al.*, 1997, Zanis *et al.*, 1999). All the necessary kinetic data for the calculation of the rate constants for all the bimolecular and termolecular reactions are based on De More *et al.* (1997).

## RESULTS AND DISCUSSION

The partial total eclipse of August 11, 1999 at Thessaloniki (40.5°N, 22.9°E) started at 9:37 UT, reached the maximum obscuration of the solar disk of 88% at 11:05 and finished at 12:29. Figure 1 shows the total, UV-A and erythemal solar irradiances measured during the day of the eclipse at Thessaloniki, normalized to the values measured at the first contact. It is evident from this figure, that there is a

decrease of about 90% in solar irradiance during the eclipse maximum compared to the pre-eclipse values. The decrease is slightly smaller for the total global irradiance compared to the decrease in the UV-A and the erythemal irradiance when comparing measurements at the same site.

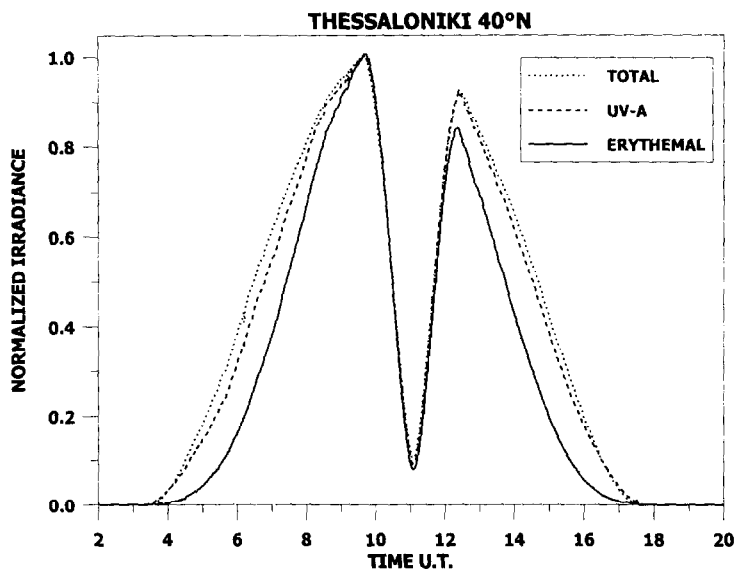


Fig.1. Normalized values of the total , UV and erythemal irradiances measured at Thessaloniki during the solar eclipse of August 11, 1999.

The spectral solar UV measurements of global irradiance performed at Stara Zagora during the eclipse are shown in figure 2. During the maximum phase of the eclipse (96%) the global irradiance at 305 nm shows a rather stronger decrease compared to the ones at 325 and 340 nm, consistent with the measurements at Thessaloniki.

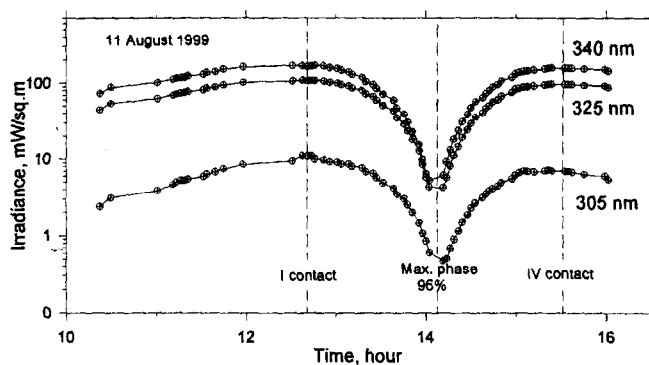


Fig. 2. Measurements of solar UV global irradiance at Stara Zagora, during the solar eclipse of August 11, 1999.

In figure 3 they are shown the global, diffuse and direct components of the erythemal irradiance as measured at Thessaloniki. The direct component is reduced more and the diffuse less during the maximum phase of the eclipse. As discussed by Zerefos et al, (2000) the diffuse irradiance during the eclipse does not follow the decline of the direct irradiance, the latter being directly proportional to the obscuration of the solar disk. A possible explanation for this different behaviour, is that the source of the diffused irradiance does not originate only from the shadowed overhead sky but multiple scattering provides solar photons also from more luminous parts of the sky, coming from different distances from the station.

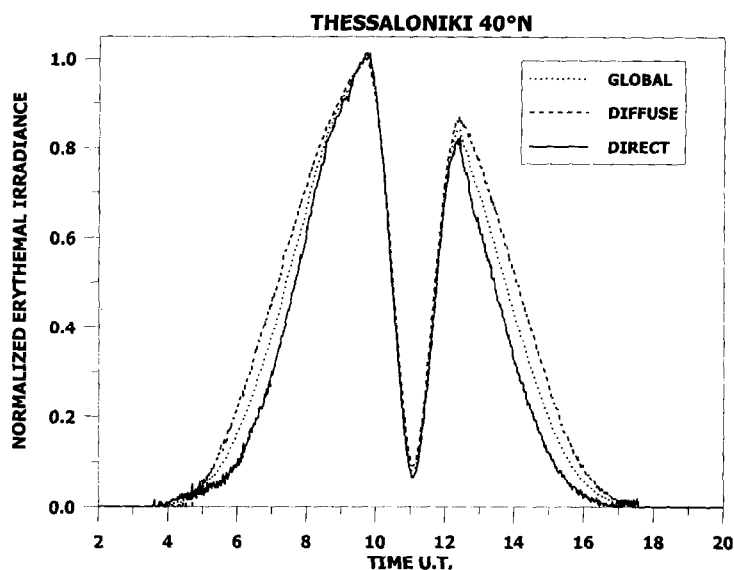


Fig.3. Normalized global, diffuse and direct erythemal irradiance during the solar eclipse of August 11, 1999.

The diurnal cycle of the erythemal irradiance was next removed from the 1-min resolution measurements, shown in Figure 1, by applying polynomial fits, taking into account the shape of the eclipse signature. The residual deviations are presented in Figure 4.

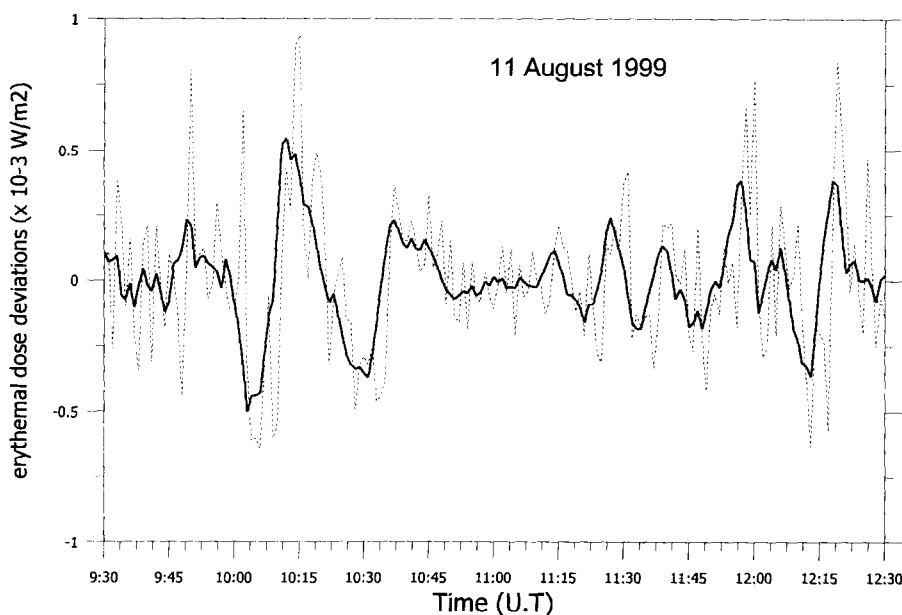


Fig. 4. Erythemal irradiance deviations for 11 August 1999. The bold line is 5-minute running average

These peak-to-peak deviations are about 1% of the erythemal irradiance averaged over the period 9:30 – 12:30 UTC. In these deviations it is evident an oscillation after the eclipse maximum. The power spectral analysis that was performed in order to detect the period and amplitude of possible fluctuations induced by the solar eclipse revealed a significant oscillation with a period of 20 min near the time of the eclipse, which is not evident in the next day's power spectra. This 20 min oscillation is not evident in the corresponding spectral analysis for the UV-A and shortwave irradiance. In an early paper Davis and da

Rosa (1970) found a 20 min oscillation in the columnar electron content, which has been attributed by Chimonas and Hines (1971) to solar eclipse-induced gravity waves. However there is no evidence in the literature, for such a periodicity in total ozone during a solar eclipse. These 1% peak-to-peak deviations of the erythemal irradiance could be eventually attributed to a periodicity in total ozone with a peak-to-peak amplitude of 3 matm-cm. Periodicities induced by a solar eclipse have been reported in certain studies. Mims and Mims (1993) reported fluctuations in total ozone with a period of about 6 min during the solar eclipse of 11 July 1991 using a hand-held TOPS instrument. Moreover Burnett and Burnett (1985) reported a solar eclipse induced oscillation in OH column, having a period of about an hour, which lasted for about two hours. The oscillatory behavior of the solar irradiance during the eclipse could not have been produced by helioseismological modes, because they appear only during the eclipse and because of the difference in the frequencies of the helioseismology waves, which have periods much larger than the observed 20min waves (Gough et al, 1996).

Next the effect of the eclipse to the local photochemical activity was investigated. The observed surface ozone concentrations at the urban station of Eptapirgio in Thessaloniki during the day of eclipse are illustrated in Figure 5. An ozone decrease of 10-15 ppbv during the eclipse is clearly indicated. This observed ozone decrease during eclipse may be related to photochemical processes. Two different model runs were carried out with a chemical box model in order to evaluate the contribution solely from photochemistry on the observed surface ozone values at the urban station of Eptapirgio. The two model runs differ only on the level of the  $\text{NO}_x$  constraints. The first model run (model A) uses the original quarterly average values of NO and  $\text{NO}_2$  measured at Eptapirgio. The mean level of  $\text{NO}_x$  measured at Eptapirgio was about 28 ppbv, which is typical for an urban site. The modelled diurnal ozone cycle (model A), shown in Figure 5, indicates a clear decrease of ozone at the same time of the eclipse which is progressing more or less proportionally to the rate of decrease of the solar radiation. The amplitude of the modelled ozone decrease (model A) is 3 times larger than the amplitude of the measured ozone decrease as seen in Figure 5. The second model run model B uses a constant level of  $\text{NO}_x$  of 3 ppbv over the day. The ozone calculated with model B is also plotted in Figure 5. The calculated ozone decrease with model B during the eclipse is almost 2 times bigger than the observed ozone decrease. However, there are a few facts that should be considered with caution in order to explain partially the differences between the modelled and observed ozone decrease during the solar eclipse.

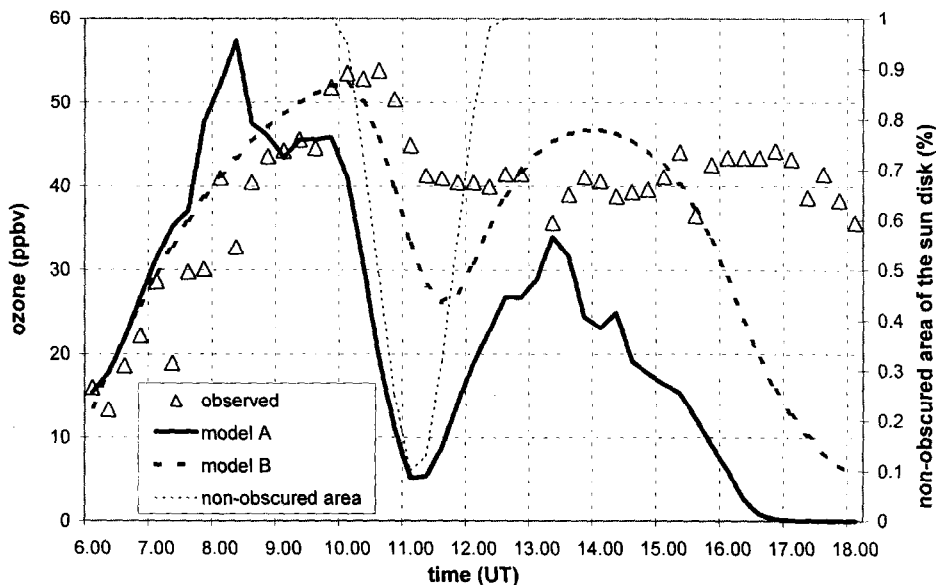


Fig. 5. 15-minute surface ozone means at Eptapirgio, Thessaloniki, for the day of the eclipse 11 August 1999. The percentage coverage of the solar disk during the eclipse is indicated by the dashed curve. Ozone calculated with different models during the day of eclipse is shown. Model A (thick solid line) uses  $\text{NO}_x$  measured at Eptapirgio. Model B (thick dashed line) uses  $\text{NO}_x=3$  ppbv.

The first fact is related to interference on the  $\text{NO}_x$  measurements. Thus the real  $\text{NO}_x$  level can be much lower at Eptapirgio than measured when taking into account the interference of  $\text{NO}_y$  on  $\text{NO}_2$  measurements (molybdenum converter), and also that the  $\text{NO}$  measurements from 8:00 to 20:00 UT were very close at the detection limit of the instrument.

The second fact is related to advection of air-masses from the relatively unpolluted sector of the sea. According to the meteorological situation prior and during the time of the eclipse, the flow was from westerly-southwesterly directions implying air flow from the sea (Gulf of Thermaikos) which is a relatively unpolluted sector. The wind speeds measured with radiosondes at Macedonia Airport at the coast of Thessaloniki were around 3 to 5 m/s within the Planetary Boundary Layer, thus implying transport of air masses within a range of 10 km to 20 km away from the coast in 1 hour. If taking into account the horizontal transport from the Gulf of Thermaikos, the ozone measured at Eptapirgio may not reflect the ozone maintained *in-situ* at Eptapirgio from the respective local  $\text{NO}_x$  level, but preferably reflects ozone transported from the relatively unpolluted sector of the sea and possibly chemically controlled in an air-mass with much lower  $\text{NO}_x$  level (Zanis *et al.*, 2001). Of course, this is only possible, when it takes longer time (i.e. several hours) to reach a new equilibrium, and the PSS (Photostationary Steady State) reactions are not the main reactions.

The third fact is related to downward mixing during the solar eclipse. The vertical gradient of the "raw" range-corrected lidar signals  $\text{SL}$  ( $(d/dr) \text{SL}$ ) is illustrated in figure 6. As discussed in previous publications (Papayannis *et al.*, 1998) the quantity  $(d/dr) \text{SL}$  provides a mathematical representation of the boundaries between dirtier (higher aerosol content) and cleaner (lower aerosol content). The positive gradients of  $\text{SL}$  correspond to increasing backscatter with height, while the negative gradients correspond to decreasing backscatter with height. The time evolution of the vertical gradient of the lidar signal reveals a layer of higher aerosol content between 500 and 900 m asl indicating possibly the entrainment zone above the well mixed atmospheric boundary layer. It should be mentioned that the radiosonde data taken at Thessaloniki airport indicated a mixing height of around 500 m asl at 12:00 UT. The height of this aerosol layer increases with time from 9:00 UT to 11:00 UT following possibly the thermal expansion of mixing layer due to convective transport. However after the maximum of the sun coverage during the solar eclipse, this layer starts subsiding due to radiative cooling of the mixing layer. A change of  $-4^\circ\text{C}$  was recorded in the surface temperature during the eclipse. This aerosol layer subsided by almost 100 – 150 m in one hour during the eclipse due to radiative cooling of the mixing layer (e.g. the surface temperature decreased by 4 degrees Celsius) indicating subsidence velocities of around 3-4 cm/s above the PBL. This process may have an impact on the surface ozone at Eptapirgio located at 199 m a.s.l. by transporting higher ozone concentrations from the lower part of the free troposphere (above 500 m a.s.l.) and thus masking part of the surface photochemical ozone decrease.

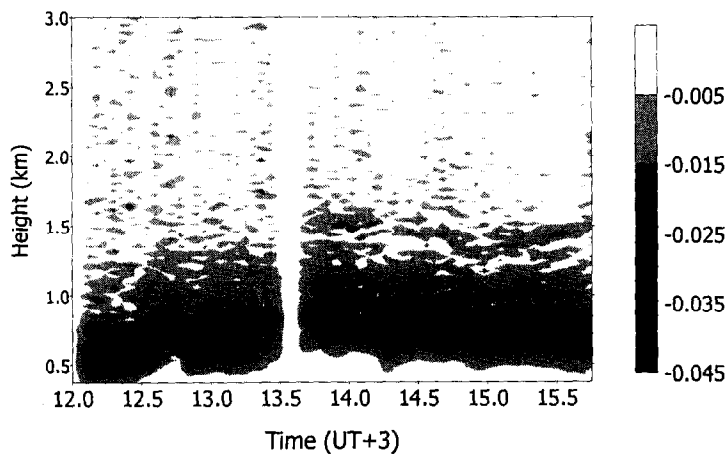


Fig. 6. The vertical distribution of the slope of the backscattered signal at 299 nm (arbitrary units)

The ozone profile measurements over Thessaloniki during the solar eclipse, shown in figure 7 indicate also a clear ozone decrease up to 2 km in agreement with the observed surface ozone decrease. The lowest ozone values in the DIAL profiles are observed at 12:09 UT when compared to the ozone profiles of 11:10 UT (maximum of the solar eclipse) indicating a lag-time between the maximum of the eclipse and the maximum of the induced ozone decrease. This is also clear from the surface ozone measurements (figure 5) which also indicate maximum ozone decrease around 12:00 UT.

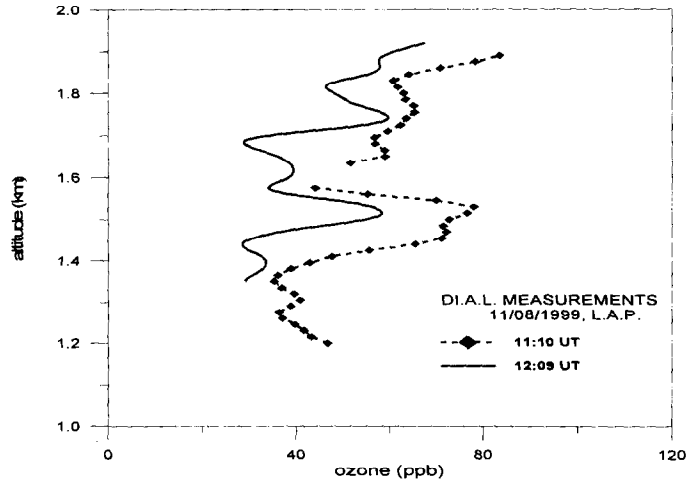


Fig. 7. The vertical distribution of ozone as derived from the Lidar measurements over Thessaloniki during 11 August 1999.

## CONCLUSIONS

The main results of the present work can be summarized as follows:

There is a decrease of about 90% of the total and the erythemal solar irradiance during the eclipse maximum compared to the non-eclipse case (same zenith angle, clear skies) at Thessaloniki

As the eclipse progresses, and moving to the shorter wavelengths, the diffuse irradiance is declining at slower rates compared to the rates of declining of the direct irradiance, which are directly proportional to the rate of obscuration of the solar disk. A possible explanation for this difference is that the diffuse irradiance is contributed from multiple scattering originating also from parts of the sky that are shadowed less than the observation at the measuring site. The phenomenon is more pronounced at the shorter UV wavelengths less than 320 nm and almost vanishes at longer than 400 nm wavelengths.

Power spectrum analysis applied to the residual data series of the global erythemal irradiance, has shown a significant oscillation with a period of about 20min during the eclipse, which is not evident in the next day's measurements (Zerefos et al, 2000). This wave could be attributed to an induced fluctuation in total ozone from the gravity wave produced in the ozone layer by the shock wave of the moon's shadow, moving at supersonic speed.

The surface ozone measurements at Thessaloniki displayed reductions of around 10-15 ppbv, which roughly paralleled the course of the eclipse. The model results suggest that the  $\text{NO}_x$  levels measured at Thessaloniki predict an ozone decrease during the eclipse 3 times higher than the observed ozone decrease. The model run with relatively lower  $\text{NO}_x$  reveal a better agreement with the observed ozone implying possibly a photochemical effect on surface ozone in an air mass transported from the relatively unpolluted sector of the sea. It is suggested that solely photochemistry can account to a significant amount for the observed surface ozone decrease during the eclipse but transport effects mask part of the photochemical effect of eclipse on surface ozone. Lidar ozone profile measurements over Thessaloniki revealed also ozone decreases during the solar eclipse up to 2 km in agreement with the surface ozone decreases, both paralleling the phase of the sun's obscuration.

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