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Photochemical Activity Over the Eastern Mediterranean Under Variable Environmental Conditions

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Abstract. - The present paper presents some of the results from the EU-funded Photochemical Activity and solar Ultraviolet Radiation (PAUR) and Photochemical Activity and solar Ultraviolet Radiation Modulation Factors (PAUR II) projects that are relevant to the photochemistry of the Eastern Mediterranean under variable conditions. Compared to S-SW flows, northern flows result in higher ozone values above the PBL. Usually during N flow the aerosol optical depth is also lower, thus resulting in higher NO_2 photodissociation rates. In one case of northern flow, the Etesian synoptic regime, N-NE flows are associated with high wind speeds and result to even lower aerosol optical depth. S-SW flow during springtime in some cases brings air loaded with Saharan dust particles over the region that is poor in tropospheric ozone and precursors. Often, these cases are associated with southern stratospheric circulation, resulting in reduced total ozone amounts and hence increased ozone photolysis rates, whereas the dust load reduces nitrogen dioxide photolysis rates. Results are presented from a spectral radiation model, which simulates the spetral UV radiation during some of the above cases. Measurement results from the Athens basin and rural Aegean sites are presented, that compare the ozone levels between normal N flow conditions and Etesian flow.

1 Introduction

It is beyond the scope of this article and its space limitations to give a full and extensive account of Eastern Mediterranean photochemistry. Here, we will discuss some results from the PAUR and PAUR II EU projects that are relevant to the photochemistry of the region. More information on both projects can be found elsewhere (Zerefos et al., 1998; Zerefos and Kourtidis, 2000; Kourtidis et al., 2000).

The main objective of the PAUR project was to investigate how increased penetration of UV-B solar radiation through the atmosphere, resulting from stratospheric ozone depletion, affects photochemical production and chemical transformation of ozone and other photochemically active species in the lower atmospheric layers. As part of the project, an extensive measurement campaign took place in Greece during the period 1.-20. June 1996. During the campaign, data were obtained on atmospheric composition, meteorology and radiation in a small Aegean Sea island (Aghios Efstratios), a suburban site north of Athens basin (Tatoi) and a number of complementary sites, some of them located in urban Athens.

The main objectives of PAUR II (1998-2000) were to measure and model UV-B spectral transmittance through turbid atmospheres and to study the role of stratospheric and tropospheric ozone in the UV-B transfer in the presence of aerosols. The UV modulation by variations in stratospheric ozone and by tropospheric ozone due to enhanced photon pathlengths by scattering from different types of aerosols, namely Saharan, continental and maritime, was studied using experimental data. A 30-day campaign in the south and southeastern Mediterranean took place during May 1999 at various sites. The results presented here are from the two sites (one at 1020 m ASL and one at sea level) on the island of Crete, located between the southern Aegean Sea and the Libyan Sea. May is a month with alternating north winds and southern winds (Saharan) in south Aegean, bringing at the sites in Crete maritime/continental aerosols and Saharan dust, respectively. The measurements during the campaign included total and tropospheric ozone measurements, meteorological observations at local and synoptic scales, optical and physicochemical characterization of aerosols, spectral UV-B, O_3 and NO_2 photodissociation rates and ancillary radiation measurements, as well as atmospheric composition measurements and LIDAR ozone and aerosol profiles.

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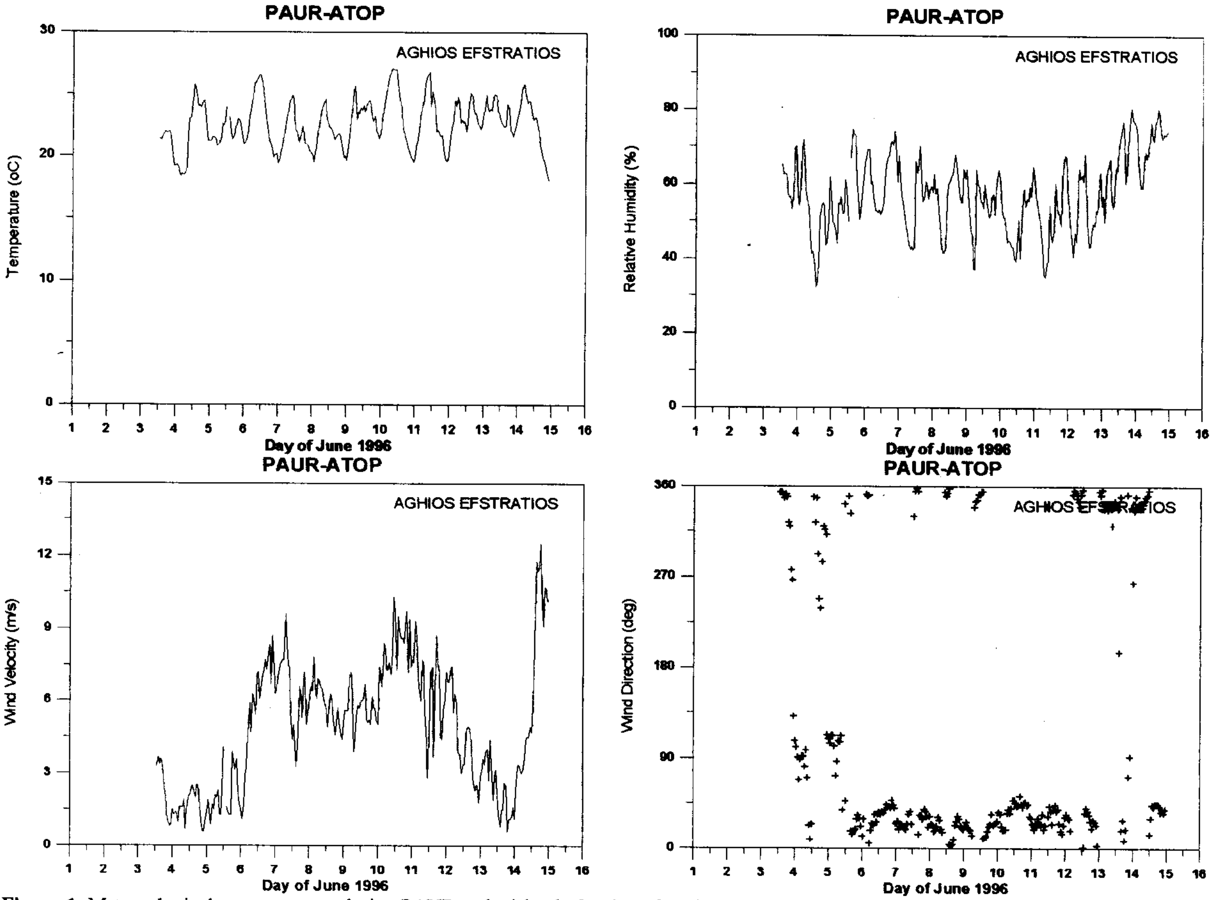

Figure 1: Meteorological measurements during PAUR at the island of Agios Efstratios, located in the Central Aegean Sea, Greece.

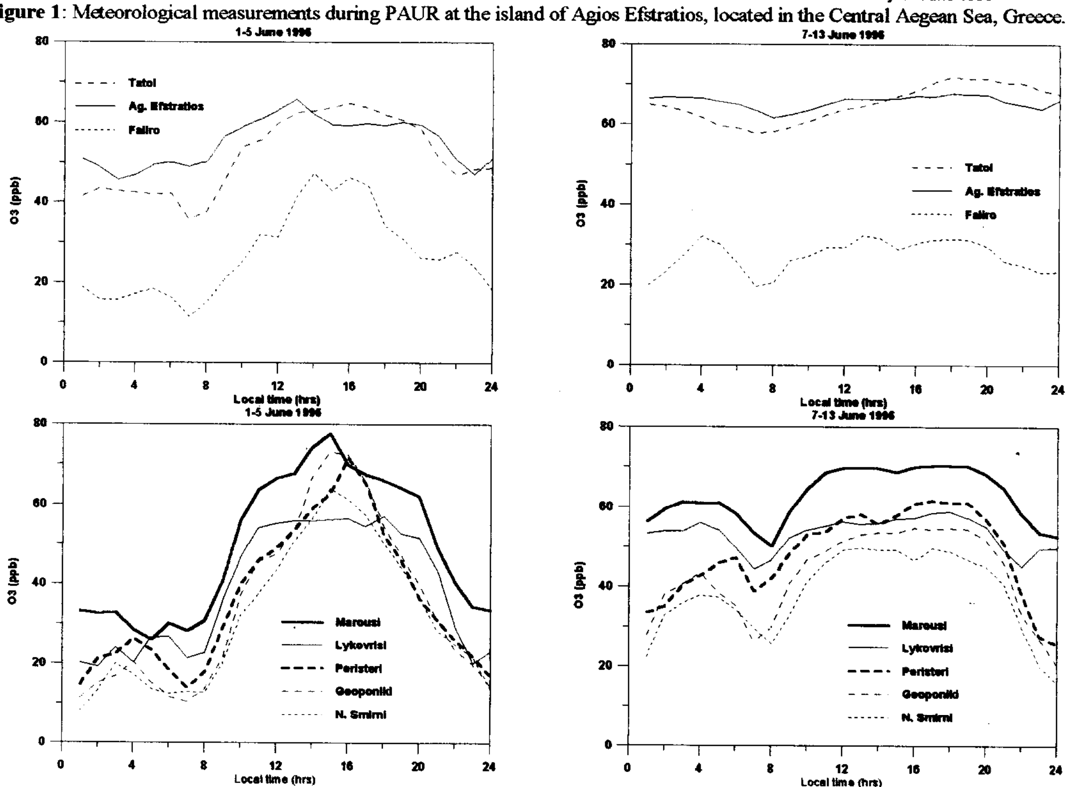

Figure 2: Mean diurnal variation for surface ozone (ppb) for two different time periods during PAUR, at various measuring stations. At the upper panel, the measuring stations depicted are in the Central Aegean (Ag. Efstratios), the entrance of the Athens basin to the North (Tatoi) and the exit of the basin to the South (Faliro). At the lower panel, measuring stations of the Air Pollution Monitoring Network of the Ministry of the Environment within the urban area of Athens are depicted. The stations as shown in the legend start from the northernmost to the southernmost.

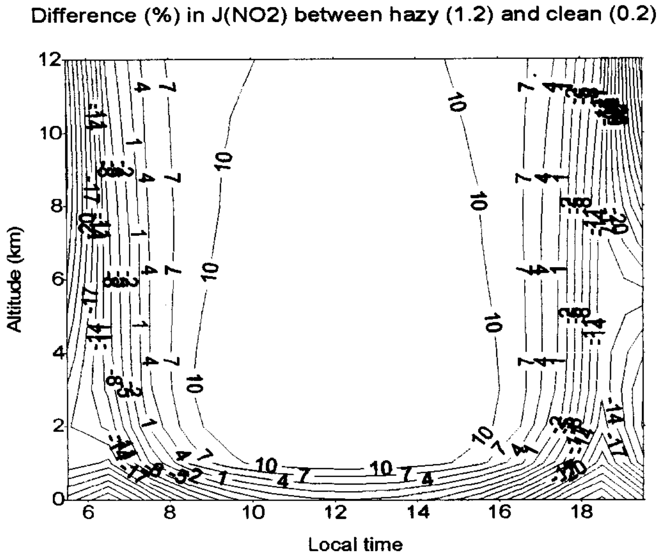

Figure 3. Percent difference on J(NO2) for an increase in aerosol optical depth from 0.2 to 1.2, corresponding to Etesian flow and normal northern flow conditions, respectively.

A side objective of both projects arised from the evidence of high regional background tropospheric ozone levels over Eastern Mediterannean (Kourtidis et al., 1997; Kouvarakis et al., 2000). The study of the mechanisms maintaining the enhanced tropospheric ozone over the Aegean Sea and interrelationships with the UV radiation field were hence also part of the project. The measured physicochemical and oprical atmospheric parameters during the two campaigns described above allowed for a better understanding of the photochemistry of the Eastern Mediterranean region and the influence excerted by the alteration of different synoptic regimes. The results presented here thus focus on some of the general differences of the measured physicochemical and oprical atmospheric parameters during different synoptic conditions at the abovementioned rural and urban locations in Eastern Mediterranean.

2 Results and discussion

The semi-stationary Azores anticyclone, the Anatolian/Iraqi Plateau low-pressure system and the differential heating between the land of North Africa and South Europe define synoptic circulation over the Eastern Mediterranean during the warm part of the year. The above factors establish a flow pattern that is mainly from the North. A characteristic example is the N-NE strong winds across the Aegean Sea, which are known as Etesians (e.g. Kallos et al., 1993). Northern flows transport over the region air from Eastern and Central Europe. When the flow pattern is from S-SW, air from Africa is transported over the region, sometimes loaded with Saharan dust particles. Often, these cases are associated with southern stratospheric circulation, resulting in reduced total ozone amounts. During the PAUR project campaign (June 1996), Etesian flows prevailed during 6-13.6, resulting in N-NE winds, with speeds 4-10 m/s (Fig.1). These were alternated with N-NW, less intense winds. During the PAUR II project campaign (May 1999), N flows wer alternated with S-SW flows that transported air from the Sahara. The cases encountered during the two experiments resulted in quite distinct regional photochemical regimes, in terms of ozone and precursor levels, spectral UV radiation, photolysis rates and aerosol load/composiiton (Saharan, maritime, aged continental and mixed). Measurements at rural sites during the two experiments allowed the determination of impact of the different synoptic regimes on the regional photochemistry of Eastern Mediterranean. Additionally, during PAUR, measurements in the Athens basin allowed the determination of the impact of the Etesian flow on the ozone levels in the city of Athens and the surrounding areas.

Measurements of meteorological parameters at a rural station in Central Aegean (Ag. Efstratios) during June 1996 are presented in Fig.1 and were typical for theAegean basin during the PAUR campaign. The period 6-13.6.1996 corresponds to pronounced Etesian flow, with strong N-NE winds of 4-10 m/s. The mean diurnal variation of surface ozone during this period, as compared to normal northern flow conditions, is presented in Fig. 2 for rural and urban (Athens basin) stations. Ozone values at rural sites were around 65 ppb with little diurnal amplitude during the period of the pronounced Etesian flow. At the urban stations in the Athens basin, Etesian flow impacts the ventilation of the basin and results in flat diurnal variations of ozone. Athens lies at the Saronikos gulf, and is surrounded by mountains at three sides. Thermal flows and orographic circulation define the ventilation of the city. Sea breeze from south to north develops when the synoptic flow is weak, and air is trapped below an inversion resulting in serious air quality problems. Weak northern winds during the first days of June resulted in ozone values in Athens during noon around 10 ppb higher than during Etesian flow (Fig. 4). When the synoptic flow from the north is strong, as is the case for the Etesians, the sea breeze circulation is overwhelmed by the synoptic flow and the city is ventilated better. This resulted in ozone values during noon that were higher, although the good vertical mixing caused by the strong Etesians did not allow dry deposition and titration from NOx emissions during nightime to deplete ozone in the PBL substantially, thus the daily mean ozone concentrations were higher (Fig. 2).

Another feature of this period of the Etesian flow is that the aerosol optical depth values fell from 0.9-1.2 to 0.2. This impacted the photolysis frequencies of NO_2 considerably. Figure 3 presents a modelling study for the island of Agios Efstratios, that compares the diurnal variation of the vertical distribution of $J(NO_2)$, for two discrete aerosol scenarios. The TUV (Tropospheric Ultraviolet) model, well documented in the literatutre (Madronich, 1993), was used for the study. The "hazy" scenario corresponds to a total aerosol optical depth of 1.2, which was the maximum

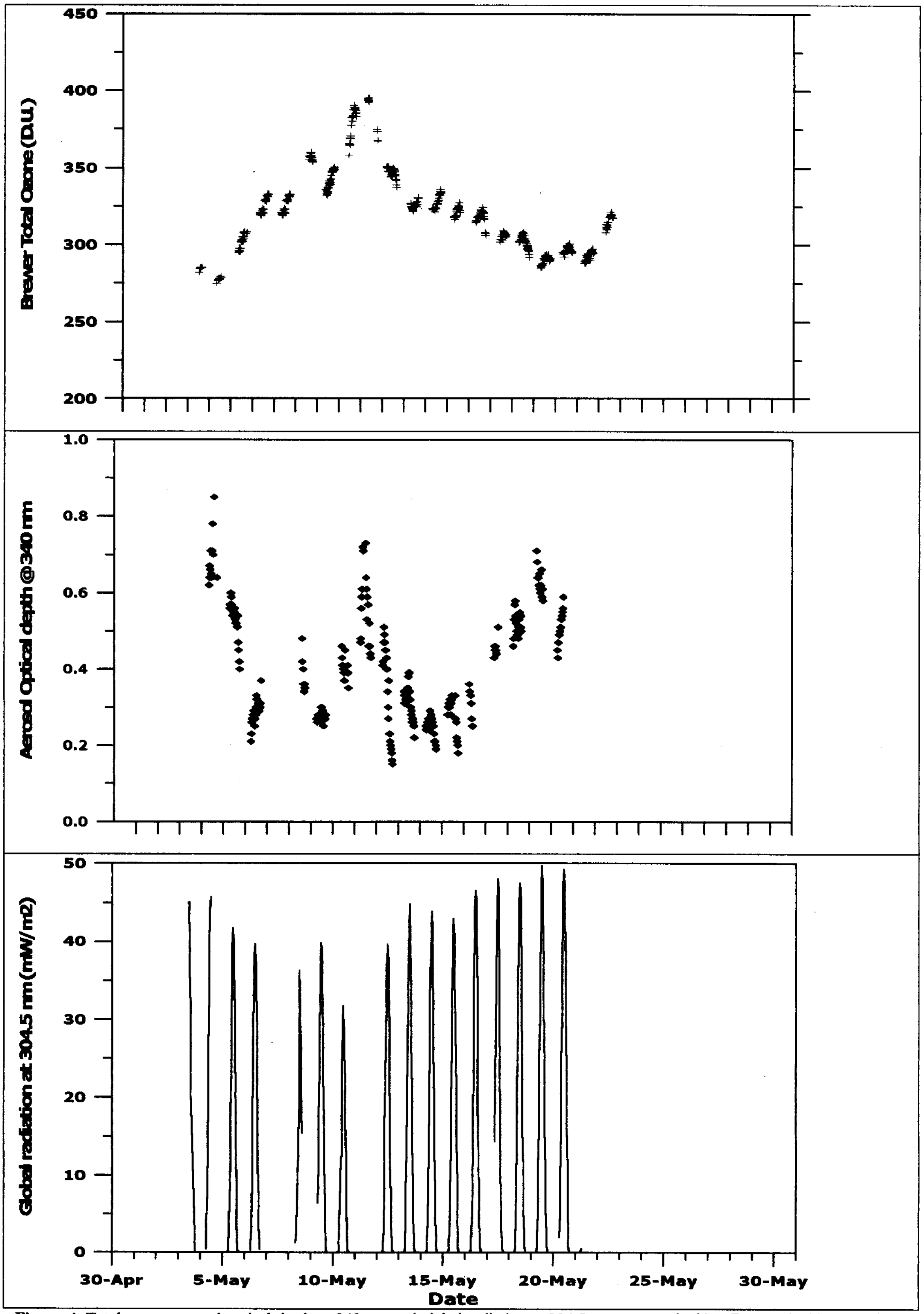

Figure 4. Total ozone, aerosol optical depth at 340 nm and global radiation at 304.5 nm measured with a Brewer double monochromator in Crete during the MAY 1999 PAUR II campaign.

measured during the June 1996 PAUR campaign, and the "clean" one corresponds to the minimum one. Most of the aerosols were assumed to lie in the PBL. As it is indicated in Fig. 3 the enhanced presence of aerosols in the lower troposphere during normal northern flow conditions as compared with Etesian conditions leads to smaller $J(NO_2)$ values at the surface. However, the $J(NO_2)$ field at higher altitudes is variable and also depends on the solar zenith angle (SZA). So, high aerosol results to reduced $J(NO_2)$ values when the sun was low, but with decreasing SZA the $J(NO_2)$ values above the polluted PBL were enhanced by 4-10% compared to the clean, Etesian conditions.

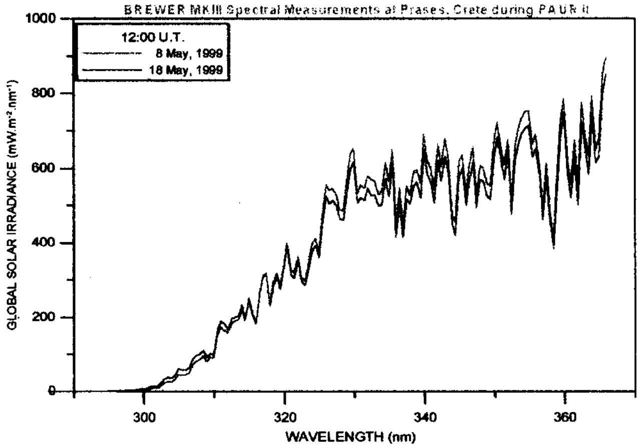

Figure 5. Comparison of the spectral UV radiation during northern flow (8 May, 1999) and southwestern Saharan flow (18 May, 1999) from Brewer double monochromator measurements during PAUR II.

Now we will discuss northern versus S-SW synoptic conditions, as encountered during PAUR II. The meteorological conditions during PAUR II (May 1999) were favourable for the study of the background atmospheric composition in the presence of aerosols. W/NW/N/NE flow was alternated with SW flow that transported air from the Sahara. Total ozone exhibited very large (120 D.U.) fluctuations during the campaign (Fig. 4). The aerosol optical depth varied from around 0.15 to around 0.8 during the campaign, being highest during Saharan dust events (Fig. 4). Three Saharan dust episodes were encountered, centred around the 3[rd], 19[th] and 26[th] of May, of which the one on the 19[th] of May was sampled by the full set of the deployed instrumentation. Global irradiance at low wavelengths was influenced mainly by the variations of the overhead ozone column (Figs. 4, 5), while at higher wavelengths the dependance was more on the aerosol load (Fig. 5). The measured spectral radiation during the 8[th] of May, as compared with the 18[th] of May (Fig. 5), demonstrates how the compination of varying total ozone and aerosol amount (Fig. 4) alters the fingeprint of spectral radiation. During the time of the recording of the spectra of Fig. 5, total ozone was around 350 D.U. and 290 D.U. and aerosol optical depth at 340 nm was around 0.35 and 0.5 during the 8[th] and the 18[th] of May, respectively.

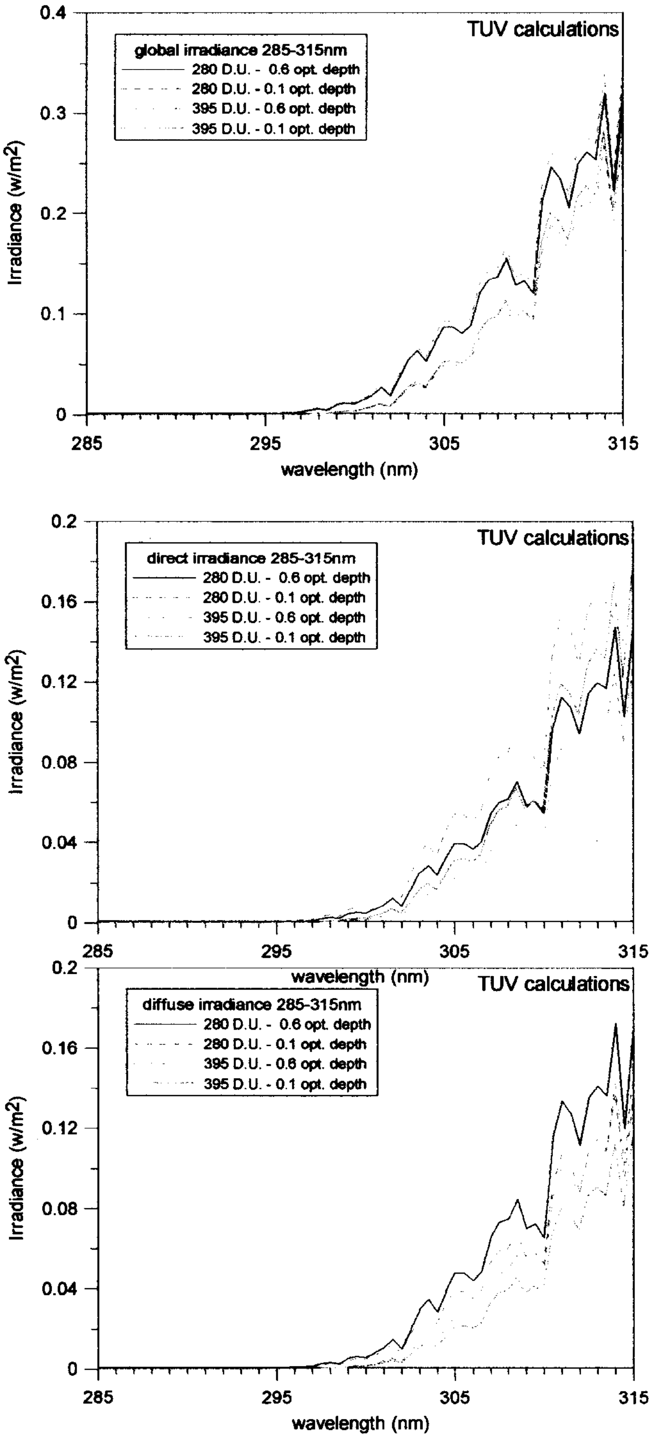

Figure 6. Model calculations for the global (a), diffuse (b) and direct irradiance (c) for the scenarios indicated

While below 318 nm UV levels are higher during the 18[th] of May, above 318 nm UV levels are higher during the 8[th] of May. Figure 6 presents some modelling calculations for solar UV radiation at ground level (also with the TUV model). These model calculations also examine the impact of concurrently changing total ozone and aerosol amounts on the spectral UV radiation. These impacts, during alternating northern and Saharan flow will determine how ozone production will be affected, since the ozone photolysis frequencies are weighted towards lower wavelengths that nitrogen dioxide photolysis frequencies and the former are thus influenced more by changes in total ozone column while the latter are influenced more by changes in the aerosol amount.

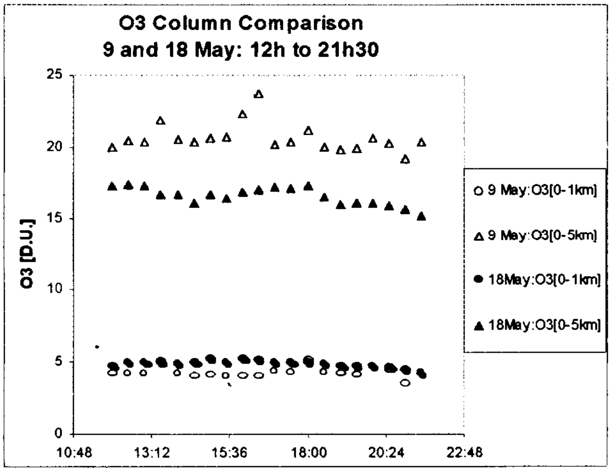

Figure 7. Comparison of the integrated tropospheric ozone column (0-1 km and 0-5 km ASL) during northern flow (9 May, 1999) and southwestern Saharan flow (18 May, 1999) from LIDAR determinations.

Tropospheric ozone also exhibited large variations (around 45 to around 65 ppb), depending on the synoptic flow and origin of the air mass (Fig. 7). High summertime background ozone values previously reported for three rural sites in Eastern Mediterranean (Kourtidis et al., 1997; Glavas, 1999; Kouvarakis et al., 2000), were confirmed to persist throughout the troposphere of the whole region during northern flow (Fig. 7). During southern flow, ozone levels from the top of the boundary layer to 5 km ASL are around 10 ppb lower than during NW-N-NE flows. This demonstrates also the influence of the continental European outflow on the ozone levels over Eastern Mediterranean.

3 Conclusions

At the regional level, Eastern Mediterranean summertime photochemistry is characterised by two main regimes: The "Northern flow regime" and the "Saharan dust episode regime". The former is associated with variable total ozone amounts, moderate ozone precursor levels, high tropospheric ozone levels from medium and long-range transport, and variable aerosol load, which in cases of strong Etesians gets very low (AOD 0.1-0.2). The latter regime is associated often with low total ozone levels, low tropospheric ozone and ozone precursor levels and high Saharan dust amounts. In the boundary layer, ozone photolysis frequencies are inversely proportional to the overhead total ozone column, while nitrogen dioxide photolysis frequencies are inversely proportional to the aerosol load and are influenced by various aerosol properties. Above the PBL, nitrogen dioxide photolysis frequencies increase with increasing aerosol load.

Hence the balance of ozone formation and destruction will be determined by the synoptic regime, since it influences critical terms such as precursor levels and photolysis frequencies. Until very recently, models tended to seriously underestimate summertime ozone levels over the area (Kouvarakis et al., 2000). It has been suggested that missing regional emission sources in the models might be the reason for the discrepancy, these sources being biogenic emissions, biomass burning and shipping (Kouvarakis et al., 2000; Jonson et al., 2000). However, there might be additional factors contributing to the discrepancy, such as vertical mixing parameterisation and photolysis rates parametarisation, which can now be tested with the PAUR and PAUR II observational dataset.

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