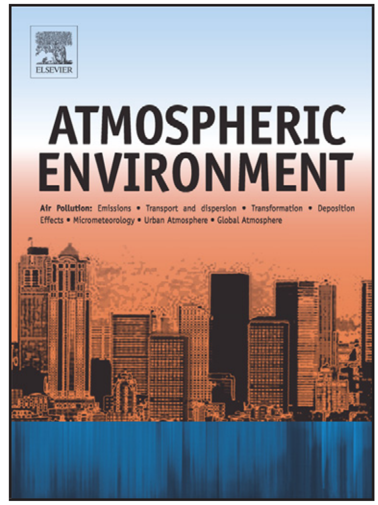

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Pollution events over the East Mediterranean : Synergistic use of GOME, ground based and sonde observations and models

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Abstract.

The behaviour of ozone (O_3) and two important precursors, nitrogen dioxide (NO_2) and formaldehyde (HCHO), over the East Mediterranean in spring from 1996 to 2002 is studied in order to characterise the build-up of tropospheric O_3. The vertical distribution of O_3 observed over Crete during the PAUR II campaign in May 1999 has been used for validation of satellite derived data. Retrievals of O_3 columns from measurements of backscattered radiation by GOME are compared with TOMS, balloon, SAOZ and LIDAR observations. The total O_3 vertical columns vary between 270 and 402 DU and correlate well with changes in air circulation patterns. The total observed variability in tropospheric O_3 is about 25 DU. Chemical box model calculations associate the GOME observed NO_2 and HCHO tropospheric columns with a potential of daily photochemical enhancement in the tropospheric O_3 columns of about 0.8-1 DU over Crete and estimate the daily potential of regional photochemical build-up within upwind polluted air masses at about 2-8 DU. A Langrangian analysis attributes at most 10-20 DU of tropospheric O_3 to stratosphere-troposphere-exchange. The remainder is attributed to long-range transport of O_3 from industrial regions in Central Europe. From 1996 to 2002, in May no significant inter-annual variation in the tropospheric

NO_2 and HCHO columns over Crete has been observed by GOME suggesting no detectable increase in regionally produced tropospheric O_3.

1. Introduction.

The troposphere over the Mediterranean is influenced by air masses transported from surrounding and distant areas (e.g. Central Europe and/or the Balkans) as well as from the stratosphere above. This leads to variations in its composition. Elevated amounts of the ozone (O_3) precursors nitrogen dioxide (NO_2) and formaldehyde (HCHO) are indicators of polluted air masses (Fishman and Crutzen, 1978). In addition, HCHO is formed by the oxidation of biogenic volatile organic compounds (VOCs) (Wayne, 2002) emitted in the areas surrounding the Mediterranean. The mixing with anthropogenic emissions of nitrogen oxides (NO_x) and VOCs under the typically elevated photochemistry conditions in this area strongly favours the regional build-up of pollutants.

The transport of NO_2, HCHO and of O_3 itself over hundreds or even thousands of kilometres is enabled by the sufficiently long lifetimes of these compounds (global mean lifetimes: τ_{NO2}= 1-2 days, τ_{HCHO}= a few hours, τ_{O3}= 1-3 months) (Oltmans et al., 1998; Lawrence et al., 2006). The present study focuses on the changes in tropospheric O_3, NO_2 and HCHO during May from 1996 to 2002 and particularly in the year 1999 when the Photochemical Activity and Solar Ultraviolet Radiation (PAUR II) experiment took place over Crete located in the South East Mediterranean (Zerefos et al., 2002).

The analysis makes synergistic use of remotely sensed and in situ data including satellite based observations by GOME (Global Ozone Monitoring Experiment) (Burrows et al., 1999) and TOMS (Total Ozone Mapping Spectrometer), measurements (Hudson et al., 1998) from balloon and ground based LIDAR and SAOZ instruments (Systeme d'Analyse par Observation Zenithale) (Goutail et al., 1991; 1999), back trajectory analyses, as well as chemistry/transport and chemical box model calculations. After explaining the applied methods (Sec. 2), the usability of GOME data over Crete is shown by comparing total columns of O_3 with SAOZ and TOMS data (Sec. 3.1). Then, different influences (transport and photochemical production) on tropospheric O_3 levels are assessed by use of GOME, TOMS, sonde and LIDAR measurements as well as model results (Sec. 3.2). Finally, starting this detailed analysis for the month of May 1999 (Sec. 3.3), inter-annual and seasonal trends of O_3 precursors including the impact of wind direction are presented (Sec. 3.4).

In particular, the photochemical formation of O_3 was evaluated by chemical box model simulations, whereas the irreversible mixing of ozone rich stratospheric air masses into the troposphere, stratosphere-troposphere-exchanges (STE) and the general long-range transport of air masses were addressed by trajectory analyses.

2. Methods.

2.1 GOME

GOME was launched in April 1995 onboard the second European satellite ERS-2 in a sun-synchronous near-polar orbit at a mean altitude of 795 km crossing the equator at 10:30 am local time. The instrument measures sunlight back-scattered from Earth's atmosphere or reflected by the surface in nadir mode in a wavelength region of 240 to 790 nm with a spectral resolution of 0.2–0.4 nm and a ground pixel size of 40×320 km^2. With 14 orbits per day, global coverage at the equator is reached after three days for a 960 km swath width (Burrows et al., 1999).

For this study, GOME data were reprocessed with WFDOAS (Weighting Function Differential Optical Absorption Spectroscopy) Version 1 (Coldewey et al., 2005; Weber et al., 2005) to derive vertical columns of O_3 with an uncertainty of 3%. The retrieval of slant columns of NO_2 in the wavelength region of 425–450 nm (Burrows et al., 1999; Richter and Burrows, 2002) and of HCHO between 337.5 and 359 nm (Ladstätter-Weissenmayer et al., 1998; Chance et al., 2000; Palmer et al., 2002) were accomplished using the IUP Bremen DOAS algorithm. The slant column density (SCD) is the amount of the absorber along the total light path through the atmosphere. The SCD is converted to a total vertical column density (VCD_{tot}), the vertically integrated absorber concentration, by using the so-called air mass factor (AMF) (Rozanov et al., 1997). The AMF is determined via radiative transfer calculations including information about aerosol, surface albedo and vertical absorber profile. In the following, a given column value always refers to the VCD.

GOME observes both, the troposphere and the stratosphere (Burrows et al., 1999). In cloudy conditions, the detection of trace gases below the cloud layer is impossible. For the retrieval of the tropospheric column amounts, only GOME pixels under cloud free conditions with a cloud fraction less than 0.2 as determined by the FRESCO algorithm, (Koelemeijer et al., 2001) were included.

The tropospheric trace gas column densities (VCD_{trop}) were derived by applying the tropospheric excess method (TEM, also called reference sector approach). The TEM is based on the assumption that the stratospheric column of trace gases such as NO_2 and O_3 is approximately constant with longitude (Richter and Burrows, 2002; Chance et al., 2000; Fishman et al., 1990; Leue et al., 2001). This simplification works well for tropical and sub-tropical conditions for O_3 and NO_2 and for NO_2 also for higher latitudes.

Several studies have been published focusing on the retrieval of tropospheric NO_2 (Leue et al., 2001; Richter and Burrows, 2002; Martin et al., 2002) and O_3 (Ladstätter-Weißenmayer et al., 2004) from GOME data. The tropospheric background amount at the reference sector in the Pacific region (180°E/W) and the accuracy of the resulting tropospheric amount for a single measurement are estimated to 25 DU Dobson Units, (1 DU = 2.69×10^{16} molecules cm^{-2}) and 4 DU, respectively, for O_3 (Ladstätter-Weißenmayer et al., 2004) and approximately 1.5×10^{15} molecules cm^{-2} and 2.5×10^{14} molecules cm^{-2} for NO_2, respectively (Boersma et al., 2004; Richter and Burrows, 2002). In contrast to O_3 and NO_2, HCHO is mainly located in the troposphere. Therefore, for a single measurement the tropospheric amount of HCHO can be determined directly with an accuary of 5.0×10^{15} molecules cm^{-2}.

2.2 The chemical box model

The potential of photochemical ozone formation (P_{O3}, in terms of DU day^{-1}) from NO_2 and HCHO tropospheric columns observed over polluted areas upwind the Mediterranean region has been investigated by using a chemical box model. This well established chemical box model has been already applied to simulate the impact of VOCs on O_3, OH and RO_2 radicals in forested areas (Poisson et al., 2001; Tsigaridis and Kanakidou, 2002) as well as the chemistry of NO_x in the marine boundary layer of the East Mediterranean (Vrekoussis et al., 2004; 2006). The model uses the latest knowledge on chemical reactions and reaction rates (Atkinson et al., 2004; 2006). Seasonal and hourly mean values of CO, $J(NO_2)$ and $J(O^1D)$ observed over Crete are used as model input. Isoprene, ethene, propene, ethane, propane and butane mixing ratios are based on measurements performed in the area during an 8-month period (Liakakou et al., 2007). For this study, the model has been initialized by the GOME observations of NO_2 and HCHO over locations, mainly upwind Crete, as listed in table 1. The columns have been translated to equivalent concentrations for a mean boundary layer height of, 1.3 km as observed over Crete in spring, by Zerefos et al. (2002), by assuming that the trace compound mass entirely lies in the boundary layer. This simplified approach fails to simulate changes in the O_3 amount due to the oxidation of VOCs other than HCHO at levels above the regional background. In addition, the results are subject to boundary layer height uncertainties.

2.3 Back-trajectory analyses

Stratosphere-Troposphere-Exchange plays an important role in the ozone budget of unpolluted regimes in the extratropics (Waugh et al., 2000; Randriambelo et al., 1999) and is characterised by the irreversible mixing of stratospheric air masses into the troposphere. To qualitatively and quantitatively assess STE over Crete, a back trajectory analysis using Traj.x, the IUP Bremen trajectory model (Meyer-Arnek et al., 2005), has been carried out. ERA-40 data from the ECMWF (European Centre for Medium Range Weather Forecasts) are used as meteorological input. Clusters of back-trajectories are released over Crete at 0h, 6h, 12h and 18h each day of May 1999 at altitudes between 900 and 100hPa and are followed backwards in time for 5 days. The back trajectories arriving in the troposphere and being influenced by the stratosphere at least once during the recent 5 days are considered to have undergone STE. The tropopause is defined here as the lowermost altitude where either the potential vorticity (PV) exceeds ± 3.5 PV units (PVU) or the potential temperature exceeds 380 K.

Irreversible transport of air masses from the stratosphere to the troposphere and constant ozone content (number of molecules) in each considered air parcel crossing the tropopause are assumed. Maintaining the number of ozone molecules implies that the volume of the considered air parcel is adjusted to the current thermodynamical conditions. This method allows an estimate of the ozone mass being transported from the stratosphere to the troposphere and is subject to the uncertainties associated with the back trajectories calculations discussed by Stohl et al. (2002). Neglecting chemical conversion of O_3, this approach overestimates stratospheric ozone transported to the troposphere.

The altitude dependent stratospheric O_3 number density for each considered air parcel crossing the tropopause is derived from the ROSE/DLR 3D CTM (Rose et al., 1989, Baier et al., 2005) that assimilates O_3 column densities derived from GOME measurements by the means of optimal interpolation.

3. Results and Discussion

3.1 Total Columns of O_3

To provide deeper understanding and to facilitate the interpretation of the tropospheric O_3 retrieval discussed in the following section, amounts and changes in VCD_{tot} O_3 in the East Mediterranean measured by GOME, TOMS and SAOZ in May 1999 have been investigated.

O_3 VCD_{tot} over Crete retrieved from GOME measurements agree within 2.2% with TOMS data (McPeters et al., 1996) and within 3-4% with the SAOZ observations (Fig. 1). Both differences are smaller than the combined measurement errors of 5%. This comparison of VCD_{tot} O_3 from GOME provides confidence to the satellite results.

The observed VCD_{tot} O_3 exhibits strong fluctuations between 270 and 402 DU. Low values of 270 and 287 DU were observed durnig the periods of May 1st to 5th and May 15th to 23rd, respectively, and maximum values during May 6th to 14th (402 DU) and May 24th to 31st (360 DU). This high variability in VCD_{tot} O_3 is associated with changes in atmospheric circulation as demonstrated by back trajectory analyses (Fig. 2). The atmospheric regime over Crete, located in the sub-tropical region, changes frequently from a tropical to a mid-latitude regime. Therefore, VCD_{tot} O_3 of around 270-290 DU are observed when air masses are transported from the tropics, whereas high O_3 columns of up to 402 DU occur when air is coming from mid-latitudes. Such variations in VCD_{tot} O_3 over regions located at the boundary of tropics and mid-latitudes has been attributed to changes in the location of the subtropical front (Hudson et al., 2003). Since each regime has a unique tropopause height (Hudson et al., 2003), we expect a changing tropopause height over this area. Indeed, the tropopause height, based on the 3.5 PVU criterion, is anti-correlated with the VCD_{tot} O_3 (Fig. 3), which is not expected to be perfect since additional parameters (e.g. ozone chemistry) contribute to the observed total ozone.

3.2 Tropospheric Column of O_3

We further investigate the potential of GOME satellite observations to determine the influence of pollution events on tropospheric O_3, NO_2 and HCHO. During the MINOS (Mediterranean INtensive Oxidant Study) campaign in the East Mediterranean in 2001, GOME measurements yielded accurate tropospheric columns of NO_2 and HCHO with levels close to the detection limit (Ladstätter-Weißenmayer et al., 2003). Hereafter, VCD_{trop} are evaluated for spring, a transition period with expected large variability in VCD_{tot} O_3 as described above. For this purpose, the data from TOMS, LIDAR (Simeonov et al., 1998; Calpini et al., 1997) and ozonesonde (Thompson et al., 2003) measurements over Crete are used and the applicability of the TEM to GOME data is investigated. In the extra-tropical regions, like the Mediterranean, the simplification that stratospheric columns of O_3 are approximately constant at a given latitude, shows limitations because the height of the tropopause can rapidly change within a day as the area oscillates between tropical and mid-latitude regimes. For each regime the daily VCD_{tot} O_3 remains constant with longitude and shows a clearly distinguishable behaviour (Hudson et al. 2003). For a successful calculation of O_3 tropospheric columns with the TEM, the reference profile is required to be located in the same O_3 regime as the profile to be analysed, i.e., with a comparable tropopause height. The tropopause height over Crete as compared to the reference sectors (Pacific and Atlantic) at the same latitude in May for the years 1998-2002, shows usually a difference of 2-3 km, but sometimes also of up to 7 km. Over Crete, the tropopause height is in the range of 11-13 km in most cases, whereas it lies between 14 and 15 km over the reference regions. Caused by these differences, an overestimation of VCD_{trop} O_3 over Crete is expected. As a first approximation, this overestimation is computed from sonde measurements (Thompson et al., 2003) to around 7 DU for May 1999. Consequently, VCD_{trop} O_3 derived from GOME have to be considered with caution. Nevertheless, the synergistic use of GOME, TOMS, LIDAR and ozonesonde measurements is providing robust results (Fig. 4).

To derive the VCD_{trop} O_3 from the ozonesondes, their profile data have been integrated up to 12 km height, equivalent to the tropopause height (derived from the criterion as described above) for the days on which sondes were launched. Ozone profiles from LIDAR measurements have been integrated up to 6 km (maximum height of observations) and extrapolated up to 12 km. The overall uncertainties in the VCD_{trop} O_3 derived from sonde and LIDAR data (up to 6 km) are ±5% and from the total LIDAR profile ±25%. Due to the limited temporal and spatial overlap of GOME and LIDAR observations, the results of these instruments can be directly compared only on the 6th and 8th of May 1999 and differ by 15%. Ozone sonde measurements are available for three days (May 9th–11th, 1999) with no direct coincidence with GOME overpasses over Crete. Direct comparisons of TOMS and GOME measurements show differences of around 30%. Based on the combined results of the four instruments, the VCD_{trop} O_3 increased by 25 DU (from 27 DU to 52 DU) between May 5th and 10th and decreased afterwards, reaching background conditions of 20 DU on May 22nd. These results are in agreement with observations in the Mediterranean by Kourtidis et al., (2002). To determine if the variation in the VCD_{trop} O_3 is mainly localised in the upper or lower troposphere, LIDAR and ozone sonde data were additionally integrated up to a height of 5 km. The results show an increase in of around 7 DU in the lower troposphere, that could be due to dynamical or photochemical build-up of O_3 Fig. (4). This enhancement is correlated to the increase of the total tropospheric amount. The remaining tropospheric O_3 enhancement of 18 DU occurred in the upper troposphere. The ozonesonde profiles measured up to a height of 30-35 km show filaments of this trace gas in an atmospheric layer of 8-10 km height and an increase around 12 km, e.g. on May 10th 1999, indicating strong influence of stratospheric air masses at this altitude associated with the subtropical front during May 1999 (Fig. 5).

3.3 Build-up and transport of tropospheric trace gases over the Mediterranean region in May 1999

During May 1999, GOME measurements indicate that the VCD_{tot} and VCD_{trop} O_3 loading is mainly influenced by the origin of the air masses arriving over Crete (Fig. 2). When air masses are not affected by Western European pollution (e.g. May 1st-5th) or originate in Northern Africa (e.g. May 15th-23rd), like those prevailing in South wind regimes, anthropogenic influence on these air masses is negligible and tropospheric ozone levels over Crete remain low. In contrast, air masses being transported from industrial regions in Central Europe (e.g. May 6th-14th) or from Western Europe, the Balkans and the Black Sea (May 24th-31st) towards Crete, are strongly influenced by anthropogenic emissions. The VCD_{trop} of NO_2 and HCHO observed by the GOME instrument over Crete in an air mass that has passed over pollution sources are higher than the VCD_{trop} over the starting area of the trajectory a few days earlier when located over the relatively clean Atlantic ocean. This difference in the VCD_{trop} over two different areas is mainly attributed to emissions and processing during transport. For instance, when an air mass originating from the West Atlantic ocean (May 6th) passed over West Europe before reaching Crete on May 9th, the observed VCD_{trop}, over the starting point of the trajectory and over Crete respectively, were for NO_2 0.8 $x10^{15}$ and $1.1x10^{15}$ molecules cm^{-2} and for HCHO $1.1x10^{16}$ and $1.4x10^{16}$ molecules cm^{-2}. Similarly, air masses originating from the East Atlantic (May 26th) transported over Northern Europe and Balkans arrived over Crete on May 31st. The observed VCD_{trop}, over East Atlantic and over Crete, respectively, were for NO_2 $1.4x10^{15}$ and $1.8x10^{15}$ molecules cm^{-2}, and for HCHO $1.6x10^{16}$ and $1.8x10^{16}$ molecules cm^{-2}. However, when air masses are mainly influenced by South wind regimes the tropospheric NO_2 amounts over Crete are around $5.0x10^{14}$ molecules cm^{-2} and HCHO around $2.5x10^{15}$ molecules cm^{-2}.

The tropospheric O_3 increase rates vary between 0.4-0.9 DU h^{-1}, as deduced from radiosonde measurements from Heraklion and LIDAR measurements carried out on Crete in May 1999.

Similar results (0.4 to 2 DU h^{-1} and 0.3±0.1 DU h^{-1}) assuming a constant mixing ratio profile (from surface to the tropopause at 12 km), are derived from surface hourly observations at Finokalia (Kouvarakis et al., 2002; Gerasopoulos et al., 2006). During the PAUR experiment, Zanis et al. (2002) evaluated a morning net O_3 production rate of 0.8-1.3 ppbv h^{-1} corresponding to a column increase of 0.5-0.9 DU h^{-1}. Taking into account a 12-hour photochemical activity per day over the area during May, the LIDAR observations suggest a dynamical and/or photochemical build-up of 6.3-10.5 DU day^{-1} (based on the mean value of 0.7 DU h^{-1}) of tropospheric O_3, including the associated uncertainties.

The involvement of STE in the observed ozone increase has been also investigated. Figure 6a shows the monthly mean fraction of backtrajectories influenced by the stratosphere and arriving over Crete in May 1999. Up to about 30% (of the considered air parcels in the altitude range between 10 and 12 km) are influenced by the stratosphere. These results are subject to back trajectory calculation uncertainties and applicability to satellite observations (Stohl et al., 2002). When considering the transport of O_3 into the troposphere (according to the methodology described in section 2.3), a tropospheric O_3 amount of about 10 DU originates from the stratosphere. Peak values of up to 20 DU (26th May 1999) can be seen in the time series of STE-ozone in the vicinity of Crete for May 1999 (Fig. 6b).

3.4. Seasonality and inter-annual variation in spring

The representativeness of the May 1999 study presented here is investigated by studying the inter-annual trends and seasonal variations of tropospheric O_3 precursors over Crete. For the years 1996 to 2002 the monthly mean VCD_{trop} are in the range of $1.5x10^{14}$-$1.6x10^{15}$ molecules cm^{-2} for NO_2 (lowest in March and highest in July) and $4.1x10^{14}$-$8.3x10^{15}$ molecules cm^{-2} for HCHO (lowest in December and highest in July) (Figs. 7a/b). Comparing the winter (DJF) and summer (JJA) seasons, an increase of $4.1x10^{14}$ molecules cm^{-2} is deduced for NO_2 tropospheric columns and of $4.2x10^{15}$ molecules cm^{-2} for HCHO VCD_{trop}. Similar seasonality (agreement within 10%, r^2=0.53) deduced from ground-based NO_2 observations in 2002 (Vrekoussis et al., 2007) (Fig. 7a). The magnitudes of the seasonal variations of both NO_2 and HCHO VCD_{trop} are twice the uncertainties of the retrievals. This significant increase in HCHO VCD_{trop} can be attributed to VOCs from biogenic, anthropogenic, and biomass burning sources.

Focusing on May, no clear inter-annual trend is observed from 1996 to 2002. The monthly mean of NO_2 and HCHO VCD_{trop} from GOME equal $1.1x10^{15}$ molecules cm^{-2} and $4.7x10^{15}$ molecules cm^{-2}, respectively. These columns correspond to boundary layer mixing ratios of

0.4 ppb NO_2 and 1.5 ppb HCHO (assuming a boundary layer height of 1.3 km) in reasonable agreement with observations of NO_2 (0.42±0.49 ppb) (Vrekoussis et al., 2006, 2007) and of HCHO under 'unpolluted' conditions at Heraklion, Crete, in 2002 (~1 ppb) (Mihalopoulos N., personal communication).

Additionally, the composite distributions of NO_2 and HCHO over Greece were determined from GOME for May in 1996 to 2002 (Figs. 8a/b). Background conditions for NO_2 and HCHO over Crete (1.1×10^{15} and 4.7×10^{15} molecules cm^{-2}, respectively) and enhancements of NO_2 due to pollution over the urban areas of Athens and Thessaloniki as well as Istanbul can be observed. Tropospheric amounts of NO_2 and HCHO from GOME for background conditions for Crete, clean-air Atlantic ocean and polluted air regions upwind Crete for May, averaged over 1996-2002 are listed in table 1. The NO_2 and HCHO VCD_{trop} are a factor of about 2 and 1.5, respectively, higher over Crete than over the Atlantic. To distinguish between natural and anthropogenic influences, the ratio of HCHO/NO_2 is calculated from GOME data. The lowest values (1.5-2.6) of this ratio are determined over the most polluted upwind regions (the Po-Valley, Istanbul, Thessaloniki, and Athens) due to fresh emissions of NO_x and not sufficient breakdown of emitted VOCs to form HCHO. The ratio increases towards Crete to a value of 4.3. This could indicate that during the transport, the short lived NO_2 is converted to HNO_3 (Vrekoussis et al., 2006) and the air masses are potentially enriched in HCHO from regional sources affecting this marine location (Liakakou et al., 2007). Additionally, based on the chemical box model (Sec. 2.2), the photochemical production of O_3 associated with the observed NO_2 and HCHO VCD_{trop} under the conditions prevailing over Crete, for a day of 12-hours was calculated (Tab.1). The results underline that P_{O3} over urban polluted regions is higher (1.1-2.1 DU day^{-1}) compared to clean-air regions Atlantic and Crete, (≤1.0 DU day^{-1}). Similar results are also obtained when including other VOCs besides HCHO in this calculation (P_{O3_VOC}). This is done as a sensitivity test by assuming 10 times higher HCHO or, only for Crete, by using real observed VOC background concentrations. The deduced P_{O3_VOC} has to be considered as the order of magnitude of the VOC impact on tropospheric chemistry since global models (Myriokefalitakis, 2006; Wittrock et al., 2006) estimate a VOC to HCHO concentration ratio over the continents surrounding the Mediterranean between 4 and 10. As can be seen from table 1, Crete is mainly influenced by clean-air conditions and therefore the local production of tropospheric O_3 is expected to be negligible in May. Nevertheless, polluted air masses are occasionally transported to this region. The dependency of the tropospheric amounts of NO_2 and HCHO on wind direction from 1996 to 2002 deduced from GOME is shown in figures 9a/b. These figures reinforce the results for 1999, showing higher NO_2 and HCHO VCD_{trop} (by 1.1 and 1.2 times, respectively) when Crete is influenced by air masses from Europe and the Balkan (NW-N-NE) compared to those observed when air masses are coming from the west. Similar results are observed when comparing the NW-N-NE and SW-S sectors (factor of 1.6 for NO_2 and of 1.4 for HCHO). Therefore, except for these described sporadic meteorological conditions, Crete can be considered as an unpolluted area.

Conclusions

The synergistic use of GOME data with back trajectory analysis and box model calculations enabled the detection of significant changes in pollutant tropospheric columns related to general air circulation patterns. When the Mediterranean is influenced by air masses from Central Europe, the Balkans and the Black Sea, pollution leads to an increase in NO_2 and HCHO VCD_{trop} and, consequently, VCD_{trop} O_3. From the observed VCD_{trop} O_3 increase of about 25 DU, only about 1 DU day^{-1} can be attributed to local and 2-8 DU day^{-1} to regional O_3 photochemical build-up within upwind polluted air masses and about 10 DU (peaking up to 20 DU) in maximum to STE, depending on the meteorological situation. The remaining part (up to 13 DU) is to be attributed to long-range transport of O_3 from polluted regions. Urban areas upwind Crete like Athens, Thessaloniki, Istanbul and the Po Valley can be seen from GOME as pollution sources. Thus, when air masses are reaching Crete from the NW-N-NE wind sector, passing over these areas, an increase in the tropospheric amounts of NO_2 and HCHO is observed by GOME compared to situations with air masses originating from the SW-S sector.

The analysis of GOME data for the 7-year period (1996-2002) shows no significant year-to-year change in the tropospheric amounts of NO_2 and HCHO and consequently in the production of tropospheric O_3 in May. The observed seasonal variation of the NO_2 and HCHO $VCDs_{trop}$ indicates higher values during the warm period of intensive photochemistry attributed to long range transport of NO_x from upwind pollution sources and also increased biogenic emissions of VOC. The monthly mean VCD_{trop} of both NO_2 and HCHO are 1.6-3.5 and 1.1-1.4 times less than over upwind pollution regions and can be considered as background conditions for the East Mediterranean.

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Trace Gas	Atlantic (6°N-22°N; 27°W-40°W)	Crete (34°N-36°N 24°E-26°E)	Athens (36°N-38°N 21°E-24°E)	Thessaloniki (37°N-39°N; 22°E-27°E)	Istanbul (39°N-42°N; 27°E-32°E)	Po Valley (42-45°N; 7°E -14°E)
NO_2	≤6.0x10^{14}	1.1x10^{15}	2.0x10^{15}	2.3x10^{15}	2.4x10^{15}	4.4x10^{15}
HCHO	3.1x10^{15}	4.7x10^{15}	4.9x10^{15}	4.6x10^{15}	4.5x10^{15}	6.6x10^{15}
$HCHO/NO_2$	>5.2	4.3	2.6	2.0	1.9	1.5
P_{O3}	<0.3	0.8-1.0 (*)	1.1-1.3	1.4-1.8	1.4-1.8	1.4-2.1
P_{O3}_VOC	0.0-1.2	(*)	2.1-3.9	2.6-5.2	2.6-5.2	3.6-7.9

Table 1: Mean NO_2 and HCHO tropospheric column densities (molecules cm^{-2}) and the corresponding $HCHO/NO_2$ ratio based on GOME data as well as the photochemical O_3 production (DU day^{-1}) with and without VOCs impact for different regions (used grid boxes given in parenthesis) for May (1996-2002). The given ranges reflect uncertainties in the boundary layer height. (*) For Crete VOC observations have been used to intialise the model.

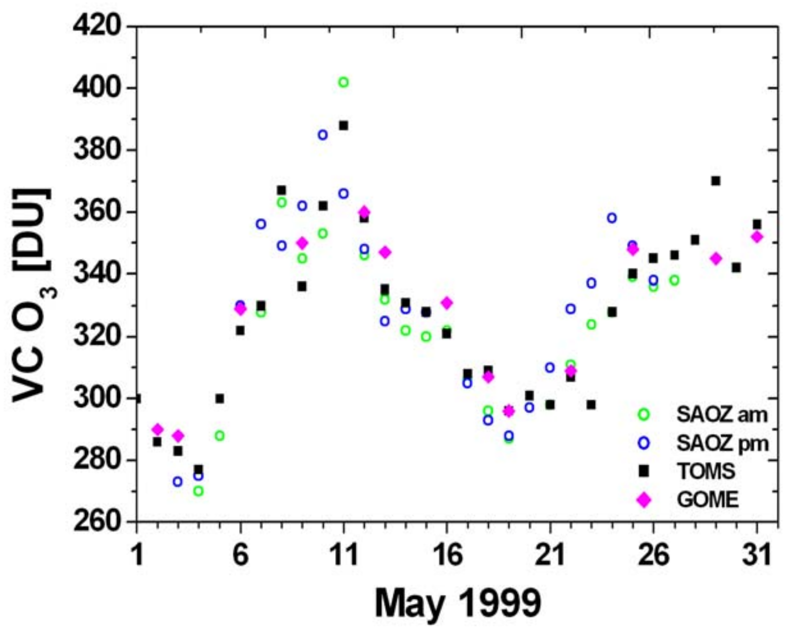
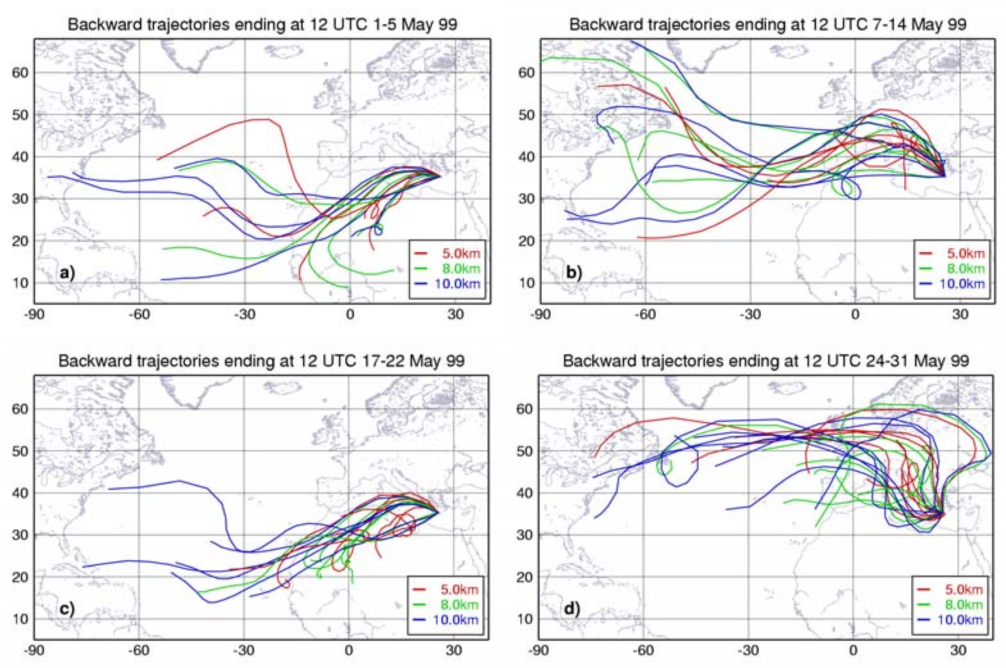


Fig. 1. VCD_{tot} O_3 (DU) over Crete measured by GOME, compared to measurements by TOMS and SAOZ for May 1999.



Figs. 2a-d. a) 5-day back-trajectories of air masses arriving at Finokalia in 1999 showing strong influence from the tropical upper troposphere (1st-5th May), b) the upper troposphere over industrialised regions in Europe (6th-14th May), c) Northern Africa free troposphere (15th-23td May), and d) NW Europe, the Balkans and the Black Sea free troposphere (24th-31st May), calculated using Traj.x.

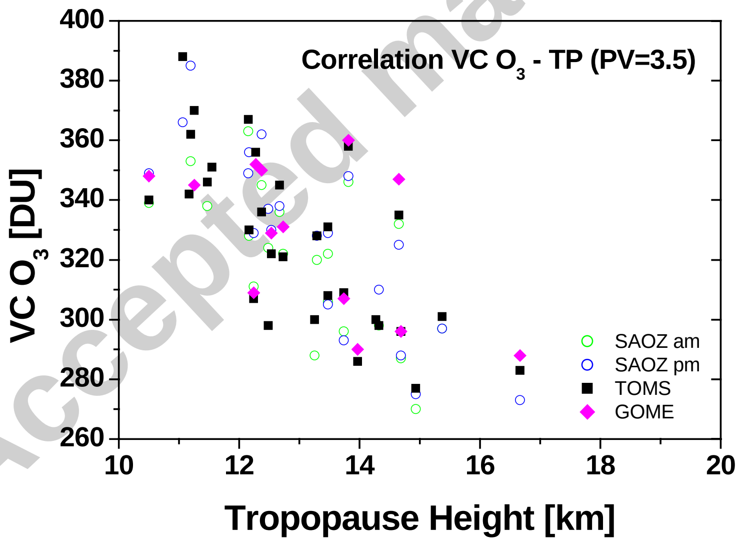


Fig. 3. Variability of VCD_{tot} O_3 (DU) over Crete as a function of the tropopause height.

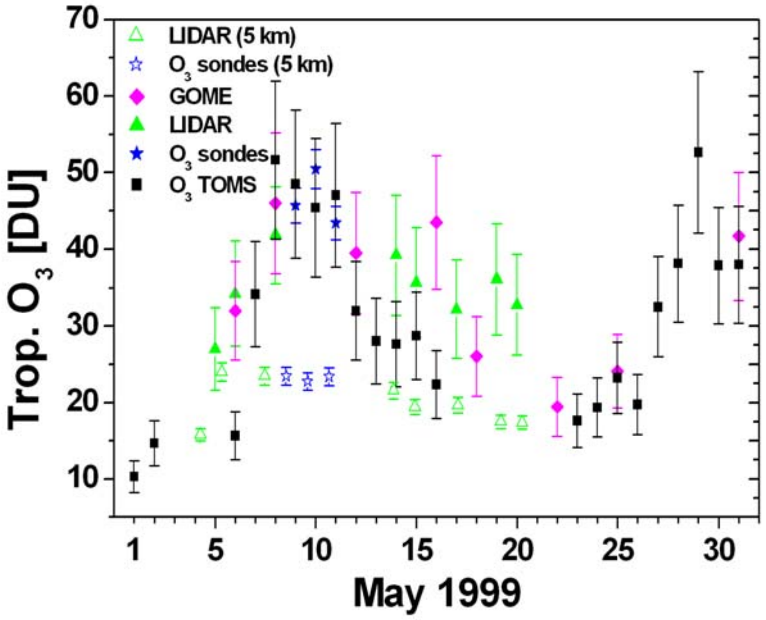


Fig. 4. Variation of VCD_{trop} O_3 (DU) derived from GOME, ozonesondes, LIDAR and TOMS observations over Crete, in May 1999; tropospheric O_3 column up to a height of 5 km.

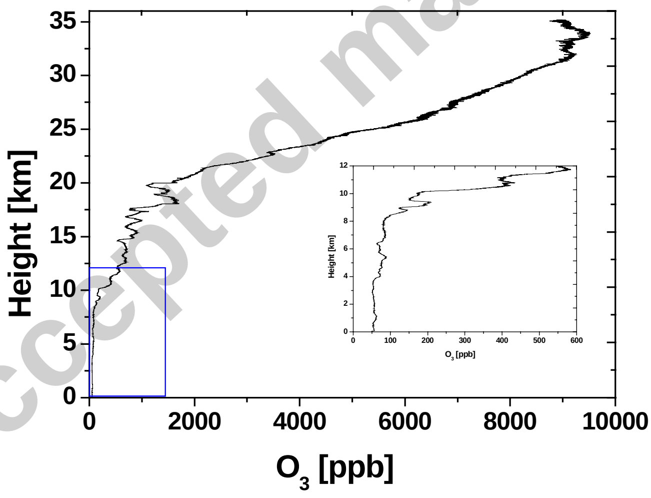
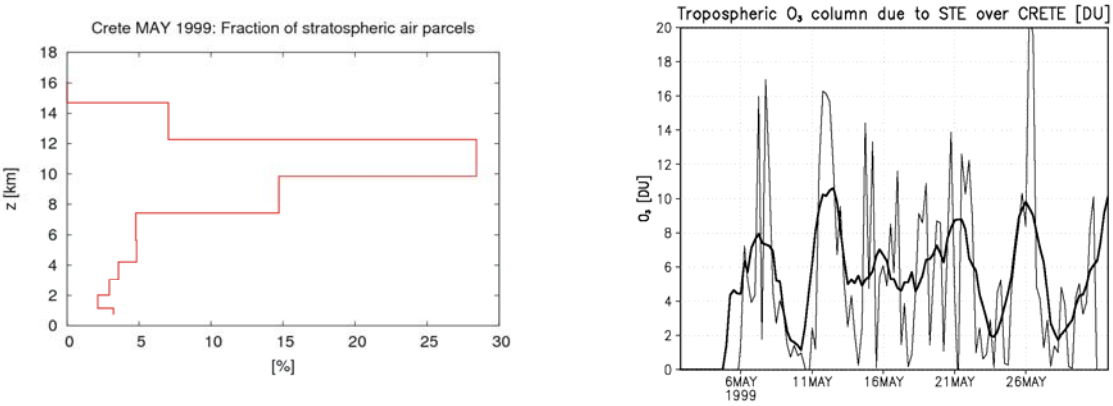
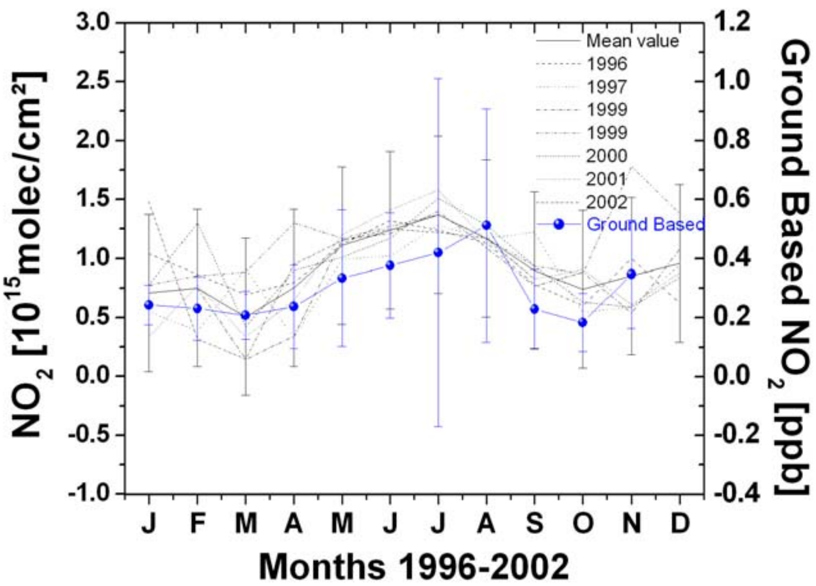
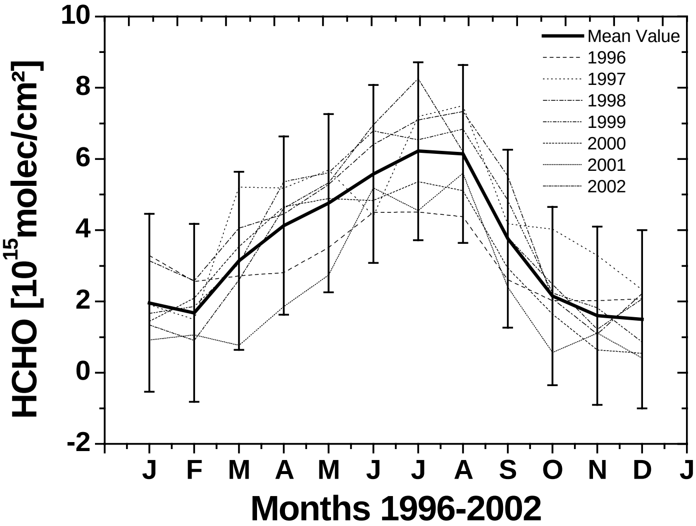


Fig. 5. O_3 profile (ppb) from sonde measurements on May 10th 1999.

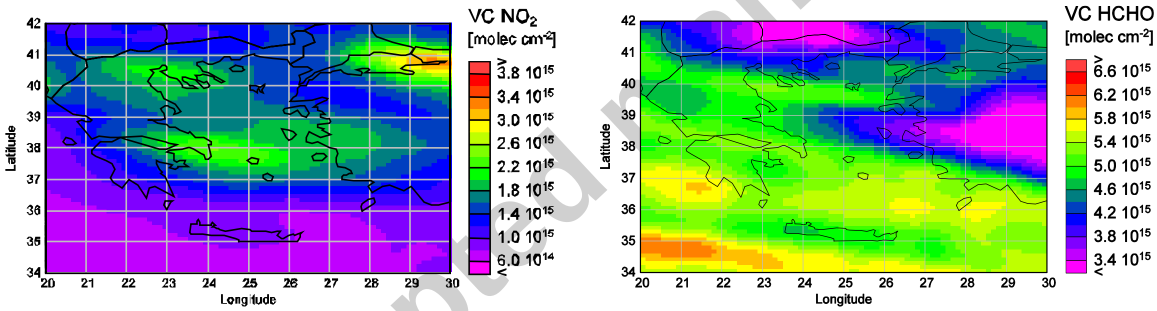


Figs 6a/b. ROSE model results: a) Altitude dependent monthly mean fraction of stratospheric influenced trajectories (%) arriving in the troposphere over Crete. b) Timeseries of VCD_{trop} O_3 (DU) due to STE over Crete in May 1999 (thin line indicates the 6-hourly mean and the thick line a two-day-running-mean of the STE-ozone column density).

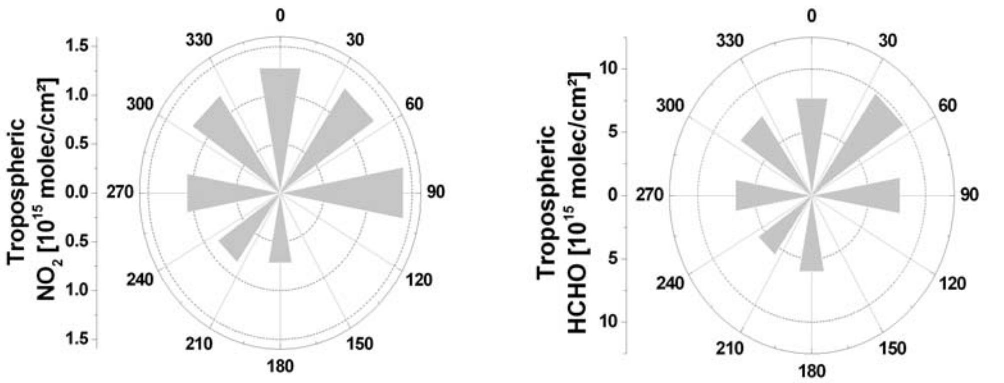




Figs. 7a/b. a) Monthly averages over Crete for VCD_{trop} NO_2 for 1996-2002 molecules cm^{-2}; including retrieval errors for the mean value of $6x10^{14}$ molecules cm^{-2} (left axis) and boundary layer NO_2 observations for 2002 ppb including retrieval errors; (right axis, blue coloured), b) Monthly averages of VCD_{trop} HCHO columns from GOME for 1996-2002 (molecules cm^{-2}) including retrieval errors for the mean value of $2.5x10^{15}$ molecules cm^{-2}.



Figs. 8a/b. Monthly composites of tropospheric NO_2 a) and HCHO columns b) (molecules cm^{-2}) for May 1996-2002 from GOME.



Figs 9a/b. VCD_{trop} NO_2 a) and HCHO b) (molecules cm^{-2}) for 1996-2002 from GOME as function of wind sector as determined from the back trajectories.