Spatial and temporal variability of tropospheric ozone (O3) in the boundary layer above the Aegean Sea (eastern Mediterranean)

G. Kouvarakis, 1 M. Vrekoussis, 1 N. Mihalopoulos, 1 K. Kourtidis, 2 B. Rappenglueck, 3 E. Gerasopoulos, 2 and C. Zerefos 2

Received 18 October 2000; revised 16 July 2001; accepted 20 July 2001; published 6 September 2002.

[1] To study the spatial and temporal variability of tropospheric ozone in the marine boundary layer over the Aegean Sea (eastern Mediterranean), an O3 analyzer has been installed on board of a passenger vessel traveling on a regular basis in the Aegean Sea (from Heraklion/Crete 35°30'N, 25°13'E to Thessaloniki 40°64'N, 22°97'E) during a period of 14 months (August 1999 to November 2000). In addition, O3 data have been obtained on a daily basis at the regional background station of Finokalia (Crete; 35°30'N, 25°70'E) since September 1997, short-term measurements of O3 were performed over Crete during the PAUR II campaign (May 1999), and the first O3 data from a rural area (40°32'N, 23°50'E) close to Thessaloniki at the north of Greece have been collected from March 2000 to January 2001. This survey extensively points out the existence of a well-defined seasonal cycle in boundary layer O3 with maximum in summer both above the Aegean Sea and at Finokalia. However, the seasonal signal (defined as the summer/winter ratio) is not constant and varies as a function of air mass origin from 1.33 to 1.15 for the N-NE and SW-S sectors, respectively, in line with the geographical location of the O3 precursor sources. Our data show the absence of any significant longitudinal gradient over Crete at least during spring and autumn and the absence of significant latitudinal gradient between the north and south Aegean Sea during all seasons for air masses having similar origin. The above results indicate that long-range transport is the main factor accounting for the elevated O3 levels above the eastern Mediterranean Sea. Thus (1) O3 data from Finokalia, where the longest time series are available for the area, have regional significance and (2) over the entire Aegean basin, ozone values are above the 32 ppbv European Union (EU) phytotoxicity limit throughout the year and above the 53 ppbv EU health protection limit most of the time during the dry season of the year. The very significant correlation between black carbon (BC) and O3 observed during an intensive campaign in May 2000 provides an indication that the high O3 concentrations at Finokalia resulted from ageing of air masses strongly affected by combustion processes.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; KEYWORDS: tropospheric ozone, regional pollution, diurnal variation, background O3, Aegean Sea, eastern Mediterranean


1. Introduction

[2] The greenhouse properties of ozone (O3) [Intergovernmental Panel on Climate Change (IPCC), 1995; Chait et al., 1996; Rooof et al., 1997] and its impact on human health and plants [Seinfeld and Pandis, 1998] have led to the adoption of legislation, which sets upper limits on human exposure to O3 levels (53 ppbv during 8 hours in the EU countries). Elevated O3 levels are often observed over all big European and U.S. cities especially in spring and summer during "photochemical smog episodes," sometimes in restrictions in car circulation and industrial operation. High O3 values have also been reported at South European background stations [European Monitoring and Evaluation Programme (EMEP), 1998]. EMEP pointed out the need for systematic work in the SEANET project.
where data are rather scarce. The specific meteorological and air transport conditions dominating almost year-round over southern Europe (intensive sunlight, high temperatures, etc.) can enhance photochemistry in the atmosphere and result in high ozone levels. In a previous work [Kouvarakis et al., 2000] presented the first long-term O$_3$ measurements at Finokalia (September 1997 to September 1999, Crete island; eastern Mediterranean). They found that the O$_3$ levels observed at Finokalia during the dry period are among the highest reported for rural areas in Europe and are in very good agreement with those observed at the island of Agios Eustratios in the northern part of the Aegean Sea during the Photochemical Activity and Solar Ultraviolet Radiation (FAUR) I modulation factors cam-
Table I. Location of $O_3$ Analyzers Presented in This Article*

<table>
<thead>
<tr>
<th>Location</th>
<th>Period</th>
<th>Responsible</th>
<th>Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prasses (35°3’N, 23°13’E)</td>
<td>11–20 May 1999</td>
<td>UMUN, Germany</td>
<td>$O_3$</td>
</tr>
<tr>
<td>El Greco (Aegean Sea)</td>
<td>11–27 May 1999</td>
<td>UMUN, Germany</td>
<td>$O_3$</td>
</tr>
<tr>
<td>Hermión (35°3’N, 25°11’E)</td>
<td>6–31 May 1999</td>
<td>Prefecture of Hermión, Greece</td>
<td>$O_3$/NO$_x$</td>
</tr>
<tr>
<td>Livadi (40°53’N, 23°50’</td>
<td>March to Sept. 2000</td>
<td>LAP, Greece</td>
<td>$O_3$</td>
</tr>
</tbody>
</table>

*The period of their operation, the responsible group, and the existence of additional data discussed in this paper are also reported ECPL, Environmental Chemical Processes Laboratory, UMUN, Technical University of Munich; LAP, Laboratory of Atmospheric Physics.

[5] They also conclude that lack of published long-term measurements in the eastern Mediterranean basin prohibits extrapolation of their data to the whole area covered by the Aegean Sea and the Sea of Crete (area of $1.8 \times 10^5$ km$^2$ representing the SE limits of Europe).

[3] This paper presents for the first time to our knowledge continuous measurements of tropospheric $O_3$ performed onboard of a cruising vessel serving the route Heraklion–Thessaloniki on a routine basis over a period of more than a year. In total, 240 one-way cruises were performed during the periods 10–27 May 1999 and August 1999 to November 2000. These $O_3$ observations are compared with the measurements at the coastal station of Finokalia on northeast Crete since September 1997 and $O_3$ measurements at Livadi station close to Thessaloniki in the north of Greece. All $O_3$ data are analyzed on the basis of the origin of the sampled air masses. The $O_3$ observations at Finokalia are discussed in conjunction with simultaneous NO$_x$ and black carbon measurements at the site. Short-term $O_3$ observations at Prasses on west Crete during the PAUR II experiment are also presented and discussed in conjunction with the simultaneous northeast coast observations at Finokalia. These data will allow us (1) to check the representativity of Finokalia observations on regional scale, (2) to experimentally determine the background surface ozone over the southeast Mediterranean area (Aegean Sea and Sea of Crete, hereinafter called Aegean Sea), and (3) to understand the major factors that control its levels.

2. Experimental Procedures

[4] Table I recapitulates the location of all $O_3$ analyzers discussed in this paper, the period of their operation, the responsible group as well as the existence of ancillary data. Figure 1 presents the location of the sampling ground stations and the track of the vessel. The cruise track was quite constant in space and time: The vessel (El-Greco) used to leave the Heraklion harbor at 0000 LT and reached Thessaloniki after a 21-hour cruise (Figure 1). Then after a stay of 3 hours at Thessaloniki harbor the vessel was returning back to Heraklion. This route was produced 3-times per week. An $O_3$ analyzer (Thermo Electron Model 49C) has been installed at the ship’s bridge. Air was drawn from 2–3 m above the roof of the pilot deck using a Teflon tube. Tests showed that the loss of $O_3$ resulting from the use of the 7-m Teflon sampling line was <1 ppbv and thus lower than the instrument accuracy, in agreement with the conclusions by Gros et al. [1998] and Dickerson et al. [1999]. The zero of the analyzer on board of the vessel as well as of those at the ground stations checked monthly by using

![Ozone Finokalia station](image)

Figure 2. Seasonal variation of $O_3$ (in ppbv) at Finokalia from September 1997 to February 2001.
Figure 3. Weekly mean $O_3$ concentrations at Finokalia (solid diamonds), above the Aegean Sea (El Greco, open circles) and at Livadi (asterisks) from August 1999 to February 2001.

synthetic zero air or by turning off the sampling pump showed a drift less than 2 ppbv. A Teflon filter, changed every 7–10 days, removed the aerosol particles from the inlet lines in all analyzers. $O_3$ data possibly influenced by the vessel exhaust have been identified on the basis of the track of the vessel and the meteorological data registered onboard. These data as well as data obtained 30 min before/after the vessel was entering/leaving the harbors were eliminated.

[5] At Finokalia ($35^\circ50'N$, $25^\circ70'E$) 70 km northeast of Heraklion, at the northern coast of Crete (Figure 1), ozone measurements were performed using a Dasibi 1080 AH analyzer. The instrument is mounted inside a small building, directly exposed to the north sector [Kouvarakis et al., 2000]. Details on the meteorological conditions encountered at this ground station are given by Mideaopoulos et al. [1997] and Kouvarakis et al. [2000].

[6] Livadi ($40^\circ53'N$, $25^\circ50'E$) is a rural village located at an elevation of 850 m above sea level (asl) and a distance of 50 km northwest from Thessaloniki, over a flat, sunken region surrounded by short hills. It has a population of 500 inhabitants, from which only a small fraction lives there on a constant basis. Apart from a limited number of cars, there are no other significant local sources of pollution. A Dasibi 1008-KS ozone analyzer has been used to monitor $O_3$ at Livadi station from March 2000 until January 2001. Calibrations were performed twice a year with an ozone generator from the network for air pollution measurements of the Department for the Environment of the Municipality of Thessaloniki, which is part of the national air pollution monitoring network. Performance checks as specified by the manufacturer were performed every 15 days.

[7] Back-trajectory calculations were made using the HYSPLIT_4 (Hybrid Single-Particle Lagrangian Integrated Trajectory) modeling system. This public domain model (http://www.arl.noaa.gov/ready/hysplit4.html) is documented in the international literature [Draxler and Hess, 1998]. The meteorological data used in the calculations were

Figure 4. Normalized diurnal variation of $O_3$, NO, and NO$_2^*$ at Finokalia during four distinct seasons in 1999 (October, January, April, and July).
Figure 5. Normalized diurnal variation of O$_3$ above the Aegean Sea (solid circles) during four distinct seasons (October, January, April, and July). For comparison, the normalized diurnal variations simultaneously observed at Finokalia (open diamonds) are also depicted.

Figure 6. Seasonal variation of O$_3$ at Finokalia for 4 years (from 1997 to 2000) and for the following four wind sectors: N-NE, NW, SW-S, and west.
obtained from the National Weather Service's of the U.S. National Center for Environmental Prediction (NCEP).

3. Results and Discussion

3.1. Data Presentation

3.1.1. Finokalia station data

[8] Kouvarakis et al. [2000] have presented the O₃ data obtained at Finokalia from September 1997 to September 1999. One and a half years of additional data are included in the present study where the whole data set covering 3.5 years (September 1997 to February 2001) is considered. As shown in Figure 2, O₃ observations from September 1999 to February 2001 follow the same seasonal trend as in the earlier years with higher values during summer and lower during winter. Despite the existence of a clear interannual variability in O₃ concentrations, especially during the dry period (April to September), the reported period is not long enough to allow accurate conclusion on the existence of possible trends.

3.1.2. Vessel data

[9] Figure 3 presents the weekly variation of O₃ during the 120 round-trip cruises in the Aegean Sea. Each point (open circles) corresponds to the mean O₃ concentration measured over the whole vessel track during the 3 round-trips of the same week. For comparison the 24-hour mean data collected simultaneously at Finokalia (solid diamonds) as well as the Livadi (asterisks) are reported. The weekly mean O₃ observations on board of the El Greco vessel range from 32 to 65 ppbv with a seasonal trend in line with that of simultaneous measurements at Finokalia. The observed differences between the two data sets are not significant (O₃ Finokalia = 0.99 O₃ vessel; r² = 0.71) with the exception of one period (July 2000) that will discussed further (section 3.5). Thus (1) generally the O₃ levels measured at Finokalia can be considered as representative of the Aegean Sea and (2) over the entire Aegean basin values are above the 32 ppbv EU phytotoxicity limit throughout the year and above the 53 ppbv EU health protection limit most of the time during the dry season of the year.

3.2. Temporal Variability of O₃ Above the Aegean Sea

3.2.1. Diurnal variation of O₃

3.2.1.1. Finokalia station data

[10] Kouvarakis et al. [2000] showed the existence of a weak diurnal variation at Finokalia (of the order of 10%) in
October 1997. However, absence of NOx measurements by Kouvarakis et al. [2000] prohibited identification of the factors controlling O₃ diurnal variations. From fall 1998 to summer 2000 a Thermo Environmental Model 42C high-sensitivity chemiluminescence NOx analyzer with detection limit of 50 pptv operated at Finokalia in parallel with the O₃ analyzer to monitor NO and NOx. As the NOx instrument was used “off the shelf,” it is known that its Molybdenum converter converts in addition to NO₂, peroxyacetyl nitrate (PAN), gaseous and particulate HNO₃, and organic nitrates [Anton et al., 1996, and references therein]. In our case the measured NOx concentrations include in addition to NO₂, PAN, and organic nitrates. Gaseous HNO₃ is mainly deposited on the Teflon sampling line [Fehsenfeld et al., 1987] and particulate nitrate was removed by the Teflon filter inserted in the inlet of the sampling line. Thus NOx = (NO + NO₂ + PAN) instead of NOx will be used in the following discussion [see also Clavas, 1999]. Figure 4 presents the normalized diurnal variation of O₃, NO and NOx at Finokalia during four distinct seasons (October, January, April, and July). With the exception of January, during all the other months O₃ presents a weak diurnal variation (of the order of ±8%) with minimum early in the morning (i.e., between 0700 and 0900 LT). The early morning O₃ minimum is associated with a clear maximum in NO and the afternoon O₃ maximum with low NO, which indicates that the weak diurnal variation of O₃ could have photochemical origin. During January the same pattern exists; however, the amplitude is only 3%, which can be explained by the weaker solar intensity. During the whole examined period, NO concentrations ranged between the detection limit of 50 pptv (most of the time) and 100 pptv and NOx between 0.1 and 4 ppbv. The very low NO/NOx ratio indicates (1) influence of our station by aged air masses and (2) that the high concentrations of O₃ are likely due to region-wide pollution and long-range transport. Note that the amplitude (in percentage) of the diurnal variation of ozone observed at Finokalia is in agreement with that observed in remote marine locations [see e.g., Johnson et al., 1998; Ottmans and Levy, 1994; Ayers et al., 1997; Bremaud et al., 1998]. However, the pattern of the diurnal O₃ cycle at Finokalia, although in agreement with model calculations (maximum amplitude between 0900 and 1400 LT calculated by De Laat and Lelieveld [2000]), is quite different from that reported for the remote marine locations. Indeed, all campaigns conducted in these areas reported that maximum ozone concentrations over the oceans occur late at night and minimum in the late afternoon [De Laat and Lelieveld, 2000, and references therein]. Several authors tried to simulate and understand the factors controlling the
Figure 8. Latitudinal variation of O$_3$ (in ppbv) above the Aegean Sea during four selected cruises, from Heraklion to Thessaloniki, conducted in October, January, April, and August. Solid circles, EL Greco data; open diamonds, observations at Finokalia simultaneously with the EL Greco data.

Figure 9. O$_3$ mean concentrations (in ppbv) from 1100 to 1700 LT as a function of latitude and longitude in October, January, April, and July (four seasons).
of the marine BL do not exist for our area. However, because the water of the Aegean Sea is quite deep (ranging from 200 to 2000 m) and the winds are often very strong (especially during summer), the surface layer will show little heating during the day, and thus the depth of the atmospheric boundary layer is expected to show little diurnal variation [Dickerson et al., 1999]. However, since a diurnal trend is observed at air temperature recorded at Finokalia (higher values during midday), then vertical mixing cannot be ruled out. Then both photochemistry and boundary layer dynamics can influence the observed O3 diurnal variation.

[11] The pattern of the diurnal variation observed at Finokalia (minimum at the end of the night and maximum in the afternoon) agrees, for example, with observations at Cape Grim (Tasmania) by Ayers et al. [1997], who performed measurements partially in relatively polluted air that was transported from the Australian continent. The depletion of ozone observed at Finokalia during night can be due to removal of O3 and NO2 through NO3 formation. Indeed, measurements of NO3 radicals at Finokalia in July 2000 revealed the presence of important NO3 levels (up to about 300 pptv (U. Platt personal communication, 2000)).

Table 3. O3 Concentrations During the Short-Duration Cruises of El Greco in the Aegean Sea

<table>
<thead>
<tr>
<th>Ozone, ppbv</th>
<th>Finokalia</th>
<th>El Greco</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>SD</td>
<td>Average</td>
</tr>
<tr>
<td>55.8</td>
<td>3.9</td>
<td>54.8</td>
</tr>
<tr>
<td>53.5</td>
<td>6.2</td>
<td>51.0</td>
</tr>
<tr>
<td>48.0</td>
<td>6.3</td>
<td>45.0</td>
</tr>
<tr>
<td>52.4</td>
<td>3.8</td>
<td>54.6</td>
</tr>
<tr>
<td>47.9</td>
<td>3.9</td>
<td>48.4</td>
</tr>
<tr>
<td>b</td>
<td>b</td>
<td>b</td>
</tr>
</tbody>
</table>

*Observations are in ppbv.
Figure 12. (a) Observations of black carbon (ng/m$^3$, right $y$ axis, open circles) and O$_3$ (ppbv, left $y$ axis, solid line) from 5 to 14 May 2000. (b) Regression between BC (ng/m$^3$, $y$ axis) and O$_3$ (ppbv, $x$ axis) during the same period.

Figure 14. The 5-day back trajectories arriving (top) at Finokalia and (bottom) on board El Greco before and after the “low O$_3$ period” observed in July 2000. The date of the trajectory is given in day/month/hour in local time.

During sunrise photolysis of such levels of NO$_2$ could significantly contribute to the NO$_x$ budget in the area, in agreement with our observations that indicate an early morning source of NO$_x$ (Figure 4). During the FAUR I experiment (June 1996 [Zerefos et al., 1998]) diurnal variation of ozone similar to that observed at Finokalia has been also reported for Agios Efstratios (a small island in the northern Aegean), indicating that such diurnal pattern could be typical for the whole Aegean Sea. It is worthwhile noting that the afternoon maximum in the O$_3$ diurnal variation observed both at Finokalia and Agios Efstratios suggests that local ozone production is still occurring, i.e., that NO$_x$.

Figure 13. O$_3$ concentrations (in ppbv) at Finokalia (solid diamonds) and on board El Greco (open circles) during July 2000.
has not fallen off enough for photochemical destruction to occur. Thus there may also be implications for air quality downwind of this reservoir of photochemical smog.

3.2.1.2. Vessel data

[12] Figure 5 presents the normalized diurnal variation of O$_3$ above the Aegean Sea during four distinct seasons (October, January, April, and July). For comparison, the Finokalia data are also depicted. A very good agreement in the observed diurnal pattern of O$_3$ is observed for all seasons between the two data sets. The similar diurnal amplitude of O$_3$ above the Aegean Sea and at Finokalia, indicates that the regime of NO$_x$ above the Aegean is similar to that observed at Finokalia.

3.2.2. Seasonal variation and air mass origin dependence

[13] To investigate a potential link between the seasonal pattern of O$_3$ observed at Finokalia and the changes in wind origin and/or in sources (photochemical reactions of O$_3$ precursors), 5-day back trajectories were calculated for the whole sampling period of 3.5 years, and O$_3$ data have been classified according to the wind sectors defined by Mihalopoulos et al. [1997]. As discussed by Mihalopoulos et al. [1997] and Kouvourakis et al. [2000], during summer (June-August) N-NW sectors account for more than 90% of the total air masses origin. This contribution drops to 50% for the remaining of the year when S-SW and west winds are of almost equal frequency of occurrence and account for about 20 and 30% of the wind origin, respectively.

[14] As shown in Figure 6, a clear seasonal trend in O$_3$ is observed for all sectors for which enough data are available. However, the seasonal signal (defined as the summer/winter ratio) is not constant and varies as a function of air mass origin. It ranges from 1.33 to 1.15 for the N-NE and SW-S sectors, respectively, in line with the geographical location of the O$_3$ precursor sources (most of them located over continental Europe, i.e., in the N-NE and NW sectors).

3.3. Latitudinal variability of O$_3$ above the Aegean Sea

[15] A very good illustration of the role of air masses origin on O$_3$ distribution above the Aegean sea is presented in Figures 7a and 7b comparing the O$_3$ concentrations observed on board the vessel and at Finokalia under two different situations. During the first case (Figure 7a), Finokalia experienced air masses originating from the south sector during the whole cruise. This was also the case of the El Greco data, at the beginning of the cruise and until the vessel reached the middle of its cruise. Then a clear change in the air mass origin was observed with air masses arriving at the vessel from the NE sector, whereas Finokalia was remaining under south wind influence. This event can explain the roughly 10 ppbv higher O$_3$ concentrations observed at the end of the cruise than at Finokalia.

[16] During the second case (Figure 7b) the 5-day back trajectories indicate a constant NE airflow during the whole cruise as well as at Finokalia. This common origin for both air masses sampled onboard El Greco and at Finokalia can explain the absence of differences in O$_3$ between the two data sets.

[17] Given the dependence of O$_3$ levels on air mass origin discussed in section 3.2 and by Kouvourakis et al. [2000], the observations, presented in Figure 8, were performed during four cruises carefully chosen to be under the influence of air masses of the same origin from the beginning to the end of the cruise and with those arriving at Finokalia. Figure 8 depicts the latitudinal variation of O$_3$ observed above the Aegean Sea during the selected cruises, from Heraklion to Thessaloniki, conducted in October, January, April, and August, months covering the four seasons. Using this criterion, i.e., eliminating differences in O$_3$ induced by the air mass origin, no significant latitudinal gradient is detected during the four seasons (Figure 8). In addition, correlation coefficients between the two O$_3$ data sets (at Finokalia and on the vessel) were always statistically significant ($r^2$ ranging from 0.83 to 0.87). To better illustrate the absence of significant latitudinal variation of O$_3$ in the Aegean Sea, the O$_3$ data collected on board El Greco during its cruises in the Aegean Sea have been assimilated in five boxes of $1^\circ \times 1^\circ$ (Figure 1, boxes 2–6). Boxes 1 and 7 correspond to Finokalia and Livadi stations, respectively. Figure 9 presents the O$_3$ mean observations from 1100 to 1700 LT as a function of latitude and longitude during the four seasons (October, January, April, and July). Absence of clear latitudinal trend of O$_3$ arising above the Aegean Sea in Figure 9 is in agreement with the previous findings.

[18] O$_3$ measurements have been also performed on board El Greco over the Aegean Sea during the PAUR II campaign (11–27 May 1999). These observations (depicted in Figure 10a) revealed also the absence of any significant latitudinal variation between the Finokalia data and those collected on board El Greco (Table 2) in agreement with the conclusions drawn earlier.

3.4. Longitudinal variability of O$_3$ above the Aegean Sea

[19] The longitudinal variability of O$_3$ above the Aegean Sea is studied during two campaigns: (1) an 1-month experiment performed on the western Crete (Prasses, Figure 1) in the frame of the PAUR II program and (2) several short-duration cruises performed in the Aegean Sea during the period August 1999 to November 2000 on board El Greco.

3.4.1. The PAUR II program

[20] Details on the PAUR II experiment and its objectives are given by Zerefos et al. [2002]. During this period, O$_3$ concentrations have been simultaneously monitored at three locations on Crete covering the island from the west to the east (Prasses, Heraklion, and Finokalia, Figure 1). The meteorological situation during the campaign is described by Zerefos et al. [2002]. Figure 10 presents the spatial variation of O$_3$ at the three locations on Crete (Figures 10b and 10c). In Figures 10b and 10c, O$_3$ observations at Finokalia are plotted for comparison purposes. The O$_3$ data from the city of Heraklion have been selected as described by Kouvourakis et al. [2000], and only those associated with low NO$_x$ concentrations are presented here. It is clear that no significant longitudinal variation is observed for the O$_3$ data collected over Crete during May (Table 2). The mean O$_3$ concentration measured at Finokalia (eastern Crete) and Prasses (western Crete), for common sampling period, was 56.8 and 57.5 ppbv, respectively. Therefore, owing to the absence of both longitudinal and latitudinal gradient in O$_3$, the longest time series of O$_3$ observations available for the
area and collected at Finokalia have regional significance. Differences in the O₃ concentrations observed, for instance, on 16 and 23 May (marked with stars) can be easily explained by trajectory analysis. Indeed, on 15 May the higher O₃ observed at Finokalia than at Prasses is attributed to the air mass origin from the NW sector at Finokalia and from the west sector at Prasses. In addition, on 23 May the air masses originated from the west at Prasses and from the south at Finokalia.

3.4.2. Short-duration cruises

[21] Figure 11 presents the track of the vessel during these cruises, which contribute in increasing our data set regarding the O₃ distribution above the Aegean Sea and confirm our conclusions. Table 3 summarizes the O₃ observations at Finokalia and during the cruises, also indicating the period of measurements and the number of cruises. The agreement between the O₃ concentrations measured at Finokalia and on board during all the short-duration cruises is very good.

3.5. Impact of Human Activities on O₃ Levels Above the Aegean Sea

[22] Recently, Letieveld and Dentener [2000] investigated the factors controlling tropospheric O₃ by using a global three-dimensional model, which is able to simulate the observed high O₃ levels above the Mediterranean Sea. They estimated that in the extratropical Northern Hemisphere, tropospheric O₃ is strongly affected by industrial and fossil fuel related emissions. In addition to these emissions, the Mediterranean Sea is affected by intense biomass burning activities during summer. Below, we present two cases to illustrate the influence of these anthropogenic sources (fossil fuel related emissions and biomass burning) on O₃ levels above the Aegean Sea.

3.5.1. Fossil fuel/industrial emissions

[23] In May 2000 and especially from 3 to 15 May, Finokalia station has been affected by air masses of various origins. A slow shift from south (3 May) to north (6–10 May) and then again to southwest sectors (12 May) has been observed. During that period, measurements of black carbon (BC) have been performed at Finokalia by the University of Crete using a particle scattering absorption photometer (PSAP) analyzer with a frequency of one sample every 5 min. BC is an excellent tracer of combustion [Seinfeld and Pandis, 1998, and references therein]. Since during the studied period, no biomass burning activities have been reported for the area, BC presence was exclusively due to industrial/fossil fuel related emissions. The observations of BC are depicted in Figure 12a together with the simultaneous measurements of O₃. During that period, BC and O₃ present similar variations. The significant correlation between BC and O₃ ($r^2 = 0.72, p <$
0.001; Figure 12b) indicates that the high \(O_3\) concentrations at Finokalia result from ageing of air masses strongly affected by anthropogenic combustion activities. From the regression depicted in Figure 12b a background \(O_3\) concentration of 46.8 ppbv is estimated for the area during the month of May. This is in excellent agreement with the mean value of 47.1 ppbv \(O_3\) calculated for the south sector for this period (see Figure 6).

3.5.2. Biomass burning activities

[24] Figure 13 presents the \(O_3\) concentrations measured both at Finokalia and on board \textit{El Greco} during July 2000. The decrease in \(O_3\) concentrations observed during the period 13–18 July in both data sets, with \(O_3\) near or below 30 ppbv is due to (1) the existence of exceptional, for the season, meteorological conditions and (2) the extensive biomass burning events all over Greece (relevant satellite imagery was presented at the NOAA Operational Significant Events Imagery site http://www.avci.noaa.gov). Figure 14 presents a trajectory analysis during the “low \(O_3\) period” for Finokalia. Almost similar conditions affected the \textit{El Greco} data during that period. For both locations a clear change in air mass origin is observed: Before the “\(O_3\) decline event,” air masses had recent influence from the north sector (12 July). On 13 July they turned to the south sector (13 July), then to the NW for a day (15 July) and finally to the north sector (18 July) after spending 2 days (16 and 17 July) in the west sector.

[25] Figures 15a and 15b present a trajectory analysis in conjunction with a presentation of \(O_3\) concentrations during two events: One during the \(O_3\) decrease on 16 July (Figure 15a) and the other after it on 22 July (Figure 15b). During the “low \(O_3\) period” (16 July) the trajectory analysis revealed that Finokalia was under the influence of air masses originating from the west sector. Air masses of almost similar origin were sampled on board \textit{El Greco}. However, the air masses before reaching the vessel passed over the mainland Greece and have been enriched in \(NO_2\) (high \(NO_2\) levels due to fresh burning) resulting in \(\sim 30\) ppbv lower \(O_3\) observed on board the vessel than at Finokalia. On the other hand, on 22 July (Figure 15b) the air masses arriving at both locations from the north sector resulted in similar \(O_3\) concentrations at Finokalia and on the vessel.

4. Conclusion

[26] During a 14-month period, \(O_3\) concentrations have been monitored on board the passenger vessel \textit{El Greco} traveling in the Aegean Sea in the S-N direction. A total of 120 round-trips have been performed, and the observed \(O_3\) concentrations ranged from 10 to 93 ppbv (average 50 ± 8 ppbv). The \(O_2\) levels observed above the Aegean Sea are comparable to those measured at Finokalia at the NE coast of Crete during the same period (51 ± 8.5 ppbv) and confirm the existence of elevated \(O_3\) values in the area, exceeding in several occasions the 53 ppbv EU limit for human exposure.

[27] No statistically significant latitudinal gradient has been observed over the Aegean Sea, indicating that most of
O₃ above this area originates from long-range transport. This conclusion is also supported by the fact that the observed O₃ diurnal variation at Finokalia that could be due to photochemistry is very weak. Similarly, no longitudinal gradient has been observed between the west and the east parts of Crete. These observations support that the O₃ observations at the monitoring station of Finokalia are representative of the regional background in the eastern Mediterranean.

[38] The very significant correlation between black carbon and O₃ observed during an intensive campaign in May 2000 in the absence of biomass burning events indicates that the high O₃ concentrations at Finokalia result from ageing of air masses strongly affected by industrial activities, in agreement with the results of Lieveleid and Dentener [2000]. The continuation of O₃ monitoring at Finokalia is expected to provide valuable information on potential changes in the oxidation power of the atmosphere in an area where important climatic changes are expected to occur [Charison et al., 1991; Roelofs et al., 1997].

[29] Acknowledgments. We thank Miaoan Lines for providing us facilities to measure O₃ on board of their vessel El Greco, Hans-Peter Dorn for collaboration and valuable help in measuring O₃ at Finokalia station, F. J. Demener for communicating the output of his model calculations for the area, Maria Kanakidou and the three anonymous reviewers for their helpful and constructive comments, M. Tserbakakis and M. Vourakakis from the Prefecture of Heraklion for providing the O₃ and NOₓ data of the Heraklion city, and the European Commission, Environment and Climate Programme (ENV4-CT97-0623) and University of Crete (ELKE) for financial support. We also acknowledge the availability of the staff of the vessel El Greco and the hospitality of Michalis Lariatis at Finokalia during the experiments.

References


E. Gerasopoulos, K. Kourtidis, and C. S. Zerefos, Laboratory of Atmospheric Physics, Physics Department, Aristotle University of Thessaloniki. Campus Box 149, Thessaloniki 54006, Greece.

G. Kouvarakis, N. Mihalopoulos (corresponding author), and M. Vrekoussi, Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, P.O. Box 1470, 71409 Heraklion, Greece (Mihal@chemistry.ucc.gr)

B. Rippeljueck, Chair of Bioclimatology and Air Pollution Research, Technical University of Munich, Freising-Weihenstephan, Germany