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Variability of ozone in the Eastern Mediterranean during a 7-year study

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Abstract Ozone measurements have been performed in the period 2003–2009 at Akrotiri (suburban) and Finokalia (coastal) monitoring stations on the island of Crete, Greece. The main objectives were to investigate the concentration levels of ozone in the region of Crete, its spatial and temporal variability, the effect of air mass origin and local sources on ozone levels, and the frequency of exceedances of the EU limits for ozone concentrations in the area. The observed mean values for Akrotiri and Finokalia stations were 44.5±8.5 and 49.1±10.6 ppb$_v$, respectively. Ozone concentrations were higher during the 8-month period between March and October (52.3±6.8 and 53.0±7.4 ppb$_v$ for Akrotiri and Finokalia station, respectively) whereas, in the period November–February, the concentrations were lower (37.7±4.7 and 39.1±6.9 ppb$_v$, respectively). The above values indicate that there is not a west-east gradient of ozone concentration in the studied area. At both stations, AOT40 limit values were higher than the limit set by the European Union (Directive 2008/50/EC). Exceedances of the EU target value were encountered during 88 and 67 % of the time in Akrotiri and Finokalia stations, respectively. Differences on the diurnal patterns and daily ozone maxima between the two stations were attributed to the different characteristics of the two stations and to the effect of local pollution sources to Akrotiri station. The average value of the amplitude of the daily cycle (calculated as the difference between maximum and minimum values) in the case of Akrotiri was 8.3 ppb$_v$, and it was about two times the corresponding value in Finokalia (4.7 ppb$_v$), which is an indication of the effect of the anthropogenic emission produced in the city of Chania to the Aktotiri station environment. At Finokalia, the maximum values were observed 2–4 h later than those at Akrotiri. During springtime, the difference in the maximum values appearance was close to 4 h, with the maximum at Akrotiri at 16:00 (LT) and at Finokalia at about 20:00 (LT). This time difference supports the transfer of gaseous precursors and already formed ozone molecules toward Finokalia.

Keywords Atmospheric ozone · Air transport · Back trajectories · Air quality

Introduction

The presence of ozone in the troposphere can trigger a variety of environmental problems including human health problems (Ou Yang et al., 2012; Szyszkowicz et al., 2012; Peng et al., 2013). As an atmospheric gas, ozone participates in many physicochemical atmospheric processes. Especially in the Mediterranean area, ozone levels during summertime are elevated mainly due to intensive sunlight. Long-range transport of ozone or primary pollutants from central Europe is also an important factor which partly determines its seasonal variability and background ozone concentrations (Gerasopoulos et al., 2006; Reid et al. 2008; Sicard et al., 2011). Recent works in Europe and North America demonstrate that there is mainly an increasing trend of tropospheric ozone during the last decades (Oltmans et al., 2006; Derwent et al., 2007; Adame and Sole, 2013). It is also reported that this increasing trend was

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interrupted in the last years and ozone concentration values have reached a steady threshold (Monteiro et al., 2012; Oltmans et al., 2013). Field measurements across the world reveal that the most probable cause for the increase of background tropospheric ozone is the photochemical production of ozone due to the gradual enhancement of anthropogenic primary pollutant concentrations (NO_x, CO, VOCs) (Kalabokas et al., 2008; Zanis et al., 2014). On the other hand, a decrease in NO levels could also lead to reduced ozone destruction and therefore to increased ozone concentrations (Jhun et al., 2014). It is estimated that the amount of ozone arriving from the eastern Pacific to the US coast has increased by approximately 10 ppb_v during springtime, from the mid-1980s to 2002 (Jaffe et al., 2003). In addition, the impact of meteorological conditions and forest fires on ozone ambient levels has been investigated in recent years (Preisler et al., 2010; Jaffe and Wigder, 2012; Adame et al., 2012).

The variability of ozone concentrations in the eastern Mediterranean has been previously studied, and the elevated values were mainly attributed to anticyclonic conditions in conjunction with a persistent northerly flow in the Aegean Sea (e.g., Gerasopoulos et al. 2006; Kalabokas et al., 2008). Overall, ozone concentrations measured in the Mediterranean region are higher (Sicard et al., 2011; Adame and Sole, 2013) than the European Union threshold values (for phytotoxicity and public health) (Directive) 2002; Directive) 2008).

In order to study the fluctuation of long-range transport impacts on surface ozone at the regional scale, long-term ozone measurements were performed at two sites on Crete Island in the eastern Mediterranean, Akrotiri at the western part and Finokalia at the eastern part of the island. The current work aims at determining the spatial gradient variability of surface ozone along the east-west direction and its air mass origins in conjunction with the contribution of local sources (in situ production).

Materials and methods

Sites description

Continuous measurements of ozone have been taking place during the period 2003–2009, at two sites on Crete Island, Greece. The first is the Akrotiri station (35° 32′ N, 24° 04′ E, 135 m above sea level (a.s.l.)), situated in a marine/suburban area, 5 km away from the city of Chania in western Crete (population of 90,000), and the second one is the Finokalia station (35° 20′ N, 25° 40′ E, 250 m a.s.l.), a marine/background station in the eastern part of the island, 70 km from Heraklion (population of 175,000) and 150 km from Akrotiri station (Fig. 1). A detailed description of the two stations is given by Lazaridis et al. (2008), Kopanakis et al. (2012), and Kouvarakis et al. (2002).

Instrumentation

At the Akrotiri station, ozone and basic meteorological parameters (wind speed and direction, temperature, and relative humidity) were monitored on a continuous basis. Ozone concentrations were measured using an Ambient O_3 monitor (APOA 360, Horiba, Japan) which is based on the ultra-violet radiation (254 nm) absorption of ozone. Calibration and maintenance of the ozone analyzer were performed according to the manufacturer's recommendations. For the meteorological parameters, standard sensors were used (wind speed sensor 4034BG; wind direction sensor 4122BG; combined temperature/humidity sensor in shelter 3030BG; Theodor Friedrichs & Co, Germany). For data collection, a data logger was used storing data in average of 15-min intervals. Moreover, a solar radiation sensor (Davis, wireless Vantage Pro2™ Plus including UV & Solar Radiation Sensors) was installed and operated, providing radiation measurements in the band from 300 to 1100 nm.

The Finokalia station is a well-established site during the last two decades, part of EUSAAR and ACTRIS networks, reporting to the EMEP (http://finokalia.chemistry.uoc.gr/). In this study, ozone measurements (Thermo electron 49C, Dasibi 1080 AH analyzer) and meteorological parameters that were recorded in a 5-min step were used. The principle of operation of the ozone analyzer is also based on the absorption of ultra-violet radiation.

To test the operation standard of the ozone analyzer at the Akrotiri station and to assure comparability between ozone measurements at the two sites, an intercomparison study was organized at the Finokalia station, for a period of 12 days (17–29 May 2006). Time resolutions for the two instruments were maintained to their original values (5 min for Dasibi 1080 AH analyzer and 15 min for the APOA 360 Horiba analyzer). Hourly average values were computed and the data were used to compare the two instruments. The regression analysis of the hourly data showed a good correlation (R^2=0.96, slope 0.85), and based on this, the measurement data at the Akrotiri station were corrected. To investigate the validity of the above correction forward in time, a second intercomparison campaign was performed in Finokalia for 30 days between 24 January 2014 and 23 February 2014. The results showed that the derived correction from the first intercomparison period could still be applied to the APOA 360 analyzer values.

Back trajectories

Air parcel back trajectory calculations were performed using the HYSPLIT4 model (Hybrid Single Particle Lagrangian Integrated Trajectory), developed by the Air Resources Laboratory of the National Oceanic and Atmospheric Administration (Air Resources Laboratory 2002). The identification of the air mass origin was based on 120-h (5 days) trajectories,

Fig. 1 The site of the two
research stations on the island of
Crete, Greece

calculated at 12 GMT arrival time and an altitude of 500 m, as
representative of inside boundary layer transport. The back
trajectories were computed directly from HYSPLIT web using
GDAS files with 1 degree as spatial resolution. In order to
perform the analysis, the 360° horizon was divided into eight
equal segments (N, NE, E, SE, S, SW, W, and NW).

Results and discussion

Seasonal ozone variation and exceedances of the EU threshold limits

During the 7-year monitoring period (2003–2009), the mean
ozone concentration was 45 ± 9 and 49 ± 11 ppb$_v$ (1 ppb$_v$=
1.98 μg m^{-3}), for Akrotiri and Finokalia stations, respectively.
Those mean values are computed using the whole data set for
each station according to the following procedure. The origi-
nal 15-min (for Akrotiri station) and 5-min (for Finokalia)
station ozone concentration values are used to compute mean
hourly values. The hourly values are then used for the data
statistical evaluation. Table 1 presents a comparison with other
Mediterranean sites of suburban, marine, or rural background,
showing similarly elevated concentrations of ozone. The re-
ported mean ozone concentrations are typical for semi-urban
or rural regions in the Eastern Mediterranean, where elevated
levels of ozone are encountered as it is shown in Table 1. The
mean ozone concentrations during the common periods of
operation of the instruments in the two stations are even closer
to one another (46 ± 9 and 47 ± 10 ppb$_v$, for Akrotiri and
Finokalia, respectively).

Figure 2 presents the time series of the daily averaged
ozone concentrations measured at the two stations for the time
period 2003–2009 while Fig. 3 presents basic, mean monthly
statistics (min, max, median, 10 %, and 90 % percentiles). It is
shown that the seasonal pattern of ozone concentrations is
similar in both sites. As it is expected, ozone shows elevated
concentration during spring and summer (with maxima in
summer), whereas the lower values are recorded during the
cold period (October to February). More specifically, maxi-
mum concentrations are observed during June–August with
values higher than 50 ppb$_v$ (on average 58.4 and 57.4 ppb$_v$, at
Akrotiri and Finokalia, respectively). On the other hand, the
lower concentrations are observed during November and De-
cember (averaging 36.2 and 38.2 ppb$_v$, at Akrotiri and
Finokalia, respectively). The above results are in agreement
with other works in the Mediterranean region (Gerasopoulos
et al., 2006; Kalabokas et al., 2008; Velchev et al., 2011;
Fernández-Fernández et al., 2011). It was also reported that
the summer maximum instead of the spring maximum is
found mainly at sites downwind of intense ozone precursors
(Monks 2000). As also depicted in Fig. 2, at Finokalia station,
an increase in the minimum daily values of ozone (by almost
10 ppb$_v$) during 2004 and 2005 was recorded, and it was
followed by a respective decrease in the summertime maxi-
mum daily values in the following years (2008 and 2009).
Detailed analysis of average synoptic meteorological condi-
tions is required to identify possible causes for these changes,
which is not within the scope of the present study.

To track the variability of ozone levels at the two sites, the
annual average concentrations (for the common period) are
shown in Table 2a. Annual ozone values at the two stations
are very close to each other, especially for years 2003, 2004,
and 2009, while in the rest of the years, differences are within
the standard deviation of the means. During the common pe-
riods of operation of the two stations, the average values were
45.7 ± 8.6 and 46.8 ± 10.0 ppb$_v$ for Akrotiri and Finokalia,
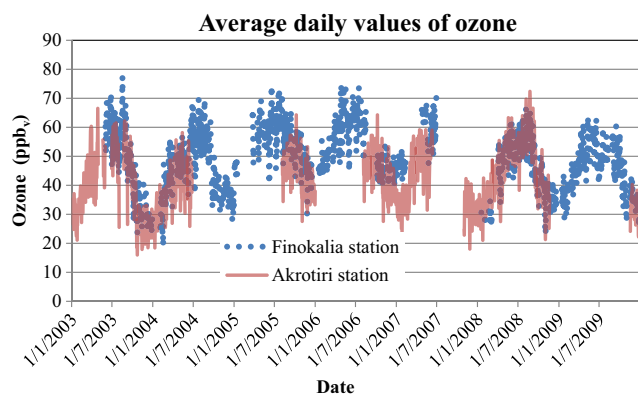respectively.

Table 2b shows the number of daily measurements during
the reported 7-year period and provides statistics on cases
exceeding 60 ppb$_v$ which is the threshold defined in the EU
Directives as the 8-h mean target value for human health pro-
tection. After the analysis of the 7-year data series, average
daily values were computed for 52 and 69 % of the total day

**Table 1** Ozone levels on the island of Crete and other Mediterranean sites

Station, Country	Sampling period	Ozone (ppbᵥ)	Reference
Akrotiri, Crete, Greece	2003–2009	45±9	This study
Finokalia, Crete, Greece	2003–2009	49±11	This study
Finokalia, Crete, Greece	1997–2004	49±11	Gerasopoulos et al. (2005)
Livadi, Greece (a.s.l. 850 m., rural)	2000	48±10	Kouvarakis et al. (2002)
Gozo, Malta (marine)	1997 - 2000	51±4	Nolle et al. (2002)
Mt. Cimone, Italy (a.s.l. 2165 m., alpine)	1996 - 1998	53±8	Bonasoni et al. (2000)
Cabo de Creus, Spain, (a.s.l. 23 m.)	2003 - 2009	40±12	EMEP data base
Navarino Environmental Observatory	2011–2012	53±16	Unpublished data

number, for Akrotiri and Finokalia, respectively. Ozone daily values at Finokalia that are over 60 ppbᵥ represent the 22.5 % of total cases, while the corresponding percentage for Akrotiri station is 7.7 %. The results of Table 2b indicate that for long periods of time, ozone is very close or above the legislated limits, and this is more marked in remote areas like Finokalia, since these areas are not directly affected by primary NO_x emissions that may reduce ozone via titration (as it is probably done at Akrotiri). Exceedances are encountered, as expected, mainly in spring and summer seasons. Regarding the 90 ppbᵥ limit (average 1-h ozone concentration) for warning the public, only 15 exceedances were recorded in Akrotiri (11 during 2006 and 4 during 2008), while there were no exceedances in Finokalia during the measurement's period.

The assessment of the impact of elevated ozone is more appropriately investigated via the accumulated exposure above a threshold concentration rather than through the mean growing season concentration. For this reason, an index of accumulated exposure above the threshold concentration of 40 ppbᵥ (AOT40) has been used as the principal measure of ozone pollution for assessing effects on vegetation (Adame and Sole, 2013). AOT40 is calculated as the total product of the concentration above the threshold concentration and time. More specifically, AOT40 is "accumulated ozone exposure over a threshold of 40 ppb" and is calculated as the sum of

the difference between hourly concentrations greater than 40 ppb over a given period using only the 1-h values measured between 8:00 and 20:00 Central European Time (CET) each day from 1 May to 31 July for each year, for vegetation protection and from 1 April to 30 September each year for forest protection (EU Directives 2002/3/EC and 2008/50/EC). The average AOT40 of 3 years with adequate data (2003, 2004, and 2008) has been indicatively calculated. The value of AOT40 for Akrotiri was equal to 16,912 ppbᵥ h, whereas for the Finokalia station, the AOT40 value was equal to 15,040 ppbᵥ h, both values being higher than the limit set by

Akrotiri station
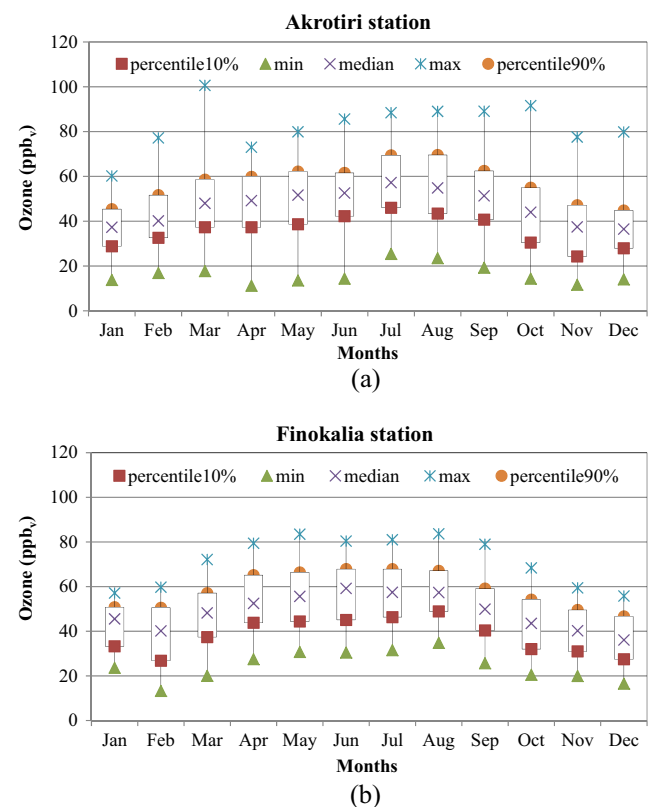
Finokalia station

Fig. 3 Minimum, median, maximum, 10 %, and 90 % percentiles of ozone hourly concentrations (2003–2009) at Akrotiri and Finokalia stations, by month

Fig. 2 Time series of mean daily values of ozone at Akrotiri and Finokalia stations during the period 2003–2009

Table 2 (a) Averages of yearly ozone levels (from common daily means values) during the 2003–2009 period; (b) number of days of hourly ozone concentration above 60 ppb$_v$ limit

a

Station	O$_3$ > 60 ppb$_v$	Total number of daily measurements
Akrotiri, Western Crete	103 (7.7 %)	1334
Finokalia, Eastern Crete	375 (22.5 %)	1670

(b)

Station/yearly ozone concentration	Akrotiri, Western Crete	Finokalia, Eastern Crete
2003	42±11	43±13
2004	43±6	43±9
2005	47±5	52±6
2006	45±5	48±6
2007	44±9	53±8
2008	50±9	47±10
2009	36±4	36±3

the European Union (Directive 2008/50/EC) (9000 ppb$_v$ h, calculated over the period May–July). Therefore, exceedances of the EU target value for Akrotiri and Finokalia station are 88 and 67 %, respectively. Similar results were reported by Sicard et al. (2011) for another Mediterranean site in France.

Diurnal ozone variation

Figure 4 shows the normalized diurnal course of ozone concentration per season at the two stations under study. The amplitude of the daily cycle (calculated as the difference between maximum and minimum values) in the case of Akrotiri ranges from 6.4 in winter to 9.8 and 11.4 ppb$_v$ in summer and autumn, respectively. The average value is 8.3 ppb$_v$, and it is about two times the corresponding value in Finokalia (4.7 ppb$_v$). The same applies for the amplitude of the daily cycle in Finokalia, which is calculated at 4.1 ppb$_v$ in winter and 6.1 ppb$_v$ in summer. This finding is an indication of the effect of the anthropogenic emission produced in the city of Chania to the Aktotiri station environment.

When examining the diurnal variations as a whole, it is apparent that the difference in amplitudes is due to lower nighttime levels rather than higher maxima, reflecting partly the more efficient ozone removal mechanisms at the Akrotiri station. It is well known that ozone can be removed by dry deposition and chemical reactions (Lin et al., 2010). NO$_x$ concentration data were not available for the two sites, but higher values are expected for Akrotiri due to the proximity of the station to the nearby city of Chania (90,000 inhabitants). It is reported that in urban sites, NO can quickly remove surface ozone (Wang et al., 2013). This ozone titration during increased NO levels could result in the appearance of lower daily amplitudes in Akrotiri. Furthermore, low wind speeds lead to low pollutant

dispersion, and thus, part of them can be due to ozone titration. Especially, at low surface wind speeds, lower than 4 m/s measured at 10 m above the ground, the effect of deposition seems to be important (Chang et al., 2004). The mean wind speed between 08:00 to 16:00 in the region of Akrotiri, Crete, is about 3.9± 1.7 m/s, and therefore, a significant impact on the ozone concentration levels is expected due to the deposition processes, whereas in total, the wind speed at Finokalia shows three times higher values than those at Akrotiri station.

Moreover, at Finokalia, the ozone maxima are observed 2–4 h later than those at Akrotiri. During springtime, the difference is about 4 h (16:00 (LT) at Akrotiri and about 20:00 (LT) at Finokalia). The prolongation and slower ozone production at Finokalia, in contrast to a more abrupt morning ascend at Akrotiri, indicate a long path transfer of precursors or ozone toward Finokalia and an apparent urban influence at Akrotiri, from primary pollutants produced in the city of Chania, only 5 km away that contribute to the ozone evolution. More specifically, NO emissions resulting mainly from vehicular traffic could under stable atmospheric conditions contribute to the ozone decrease during 8:00–9:00 LT and to the consecutive rapid increase between 9:00 and 12:00 LT. Similar diurnal variation between 08:00 and 12:00 LT was reported for the Aljarafe suburban station (Notario et al., 2012), near the city of Seville (Spain). Daily minima, as expected, are found early in the morning, while during the warm/dry periods, ozone increase begins 1–2 h earlier in comparison to the cold/humid seasons, reflecting the solar radiation cycle, in conjunction with other factors like the concentration of primary pollutants, and wind direction and speed. An additional analysis was focused on the amplitude of ozone diurnal cycle. In particular, the afternoon (12:00–18:00 LT) ozone values of a summer (May to July 2008) and a winter (December 2009) period were calculated (Table 3). Those two periods of special

Fig. 4 Average (2003–2009) of 24-h pattern of surface ozone at Akrotiri and Finokalia station plotted as a deviation of the corresponding hourly mean values for four seasons

(a) **Akrotiri station**

(b) **Finokalia station**
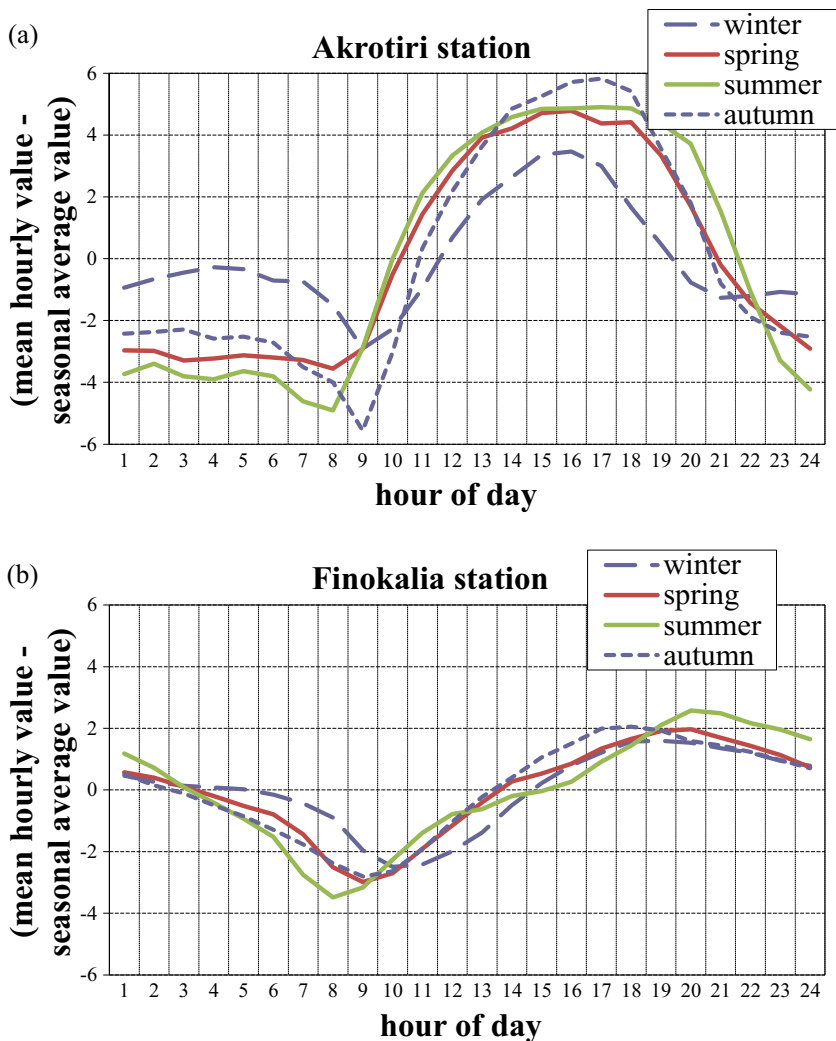
climatic significance were chosen since continuous, parallel data for both stations were available. It is revealed that even though the daily averages at both stations are quite close, when looking at the afternoon values, Akrotiri shows higher values by 5.1 and 2.4 ppb$_v$ in the summer and winter periods, respectively, demonstrating the effect of the urban environment to the ozone diurnal cycle.

Another interesting point, as shown in Fig. 4, is that during night (00:00–06:00 LT), there is stabilization of ozone levels at Akrotiri, whereas at the same time, the concentration of ozone decreases at Finokalia. This difference may be due to the relative distance of each station from the seashore and the surrounding mountains, as well as the different altitude and boundary layer (Sicard et al., 2011; Gerasopoulos et al., 2006; Millán et al., 2000, and references therein). Between 06:00 and 08:00 LT, a further decline is observed in both sites. In addition, at Finokalia, during winter night hours, ozone exhibited higher values (the average difference between 21:00 and 04:00 is 1.5 ppb$_v$), forming a secondary daily peak. Given that there is no photochemical production during this period of the

Table 3 Average ozone concentration (in ppb$_v$) and standard deviation in ozone measurements (in ppb$_v$) during two time periods using (a) the daily average observational data and (b) the average data in the time frame between 12:00 and 18:00 LT at the Akrotiri and Finokalia stations

Station	May–July 2008		December 2009	
	Daily average O$_3$ (ppb$_v$)	12:00–18:00 LT average O$_3$ (ppb$_v$)	Daily average O$_3$ (ppb$_v$)	12:00–18:00 LT average O$_3$ (ppb$_v$)
Akrotiri, Western Crete	54.3 (±4.1)	59.0 (±5.8)	35.6 (±3.4)	37.5 (±3.8)
Finokalia, Eastern Crete	53.5 (±4.9)	53.9 (±6.1)	34.6 (±2.5)	35.1 (±3.1)

day, this change may be due to the above reasons (distance from the seashore, high of boundary layer, etc.) or to anticyclonic conditions which support the development of a very stable nocturnal boundary layer (NBL) (Salmond and McKendry, 2002).

Relation between ozone and air masses origin

In order to examine the importance of the air masses origin, to ozone levels and to the variability of ozone concentrations, an analysis of the traveled paths of the air masses reaching the two stations was carried out using the HYSPLIT4 model. Different air mass trajectories are likely to transport variable ozone or ozone precursors over the area, whereas local recirculation of air masses combined with local ozone production should also be taken into account. In climatological terms, N, W, and NE winds prevail over the Aegean Sea and Crete Island. NW and S wind directions are less common, while wind trajectories from SW, SE, and E are rare in the extended region (e.g., Gerasopoulos et al., 2005; Kopanakis et al., 2012). The analysis is covering 5 days prior to the arrival of the air masses to Akrotiri and Finokalia, and the time periods that the air masses remained over certain areas are taken into account. As depicted in Table 4, during the days that air masses arrive from south directions, ozone levels are lower by 20–25 % in comparison to days with northerlies, and this is observed in both stations. This finding supports the fact that ozone is mainly produced along the path from the European continent toward Crete and is superimposed on local background (e.g., Gerasopoulos et al., 2005). On the 24-h basis, values are similar except for the N and E sectors when Finokalia ozone levels are higher. An analysis concentrated on the 12:00–18:00 LT periods was performed to obtain more representative results in terms of boundary layer variability since the afternoon measurements are representative of a well-mixed boundary layer air, (Fernández-Fernández et al., 2011; Kalabokas et al., 2008). The results showed that ozone concentrations at Akrotiri are higher independently of the air mass origin, except for the N and E-SE sectors, (t test, at 99 % confidence level, $p=4\times10^{-52}$) which is expected, since Akrotiri is more influenced by local pollution sources. Kalabokas et al. (2008) performed a detailed analysis of the correlation between the 7 % of the highest and lowest average daily afternoon ozone concentrations (12:00–18:00 LT) recorded at Finokalia during the summer periods of the years 1998–2000 with the synoptic weather characteristics of the Eastern Mediterranean area and the air masses origin. They reported that that surface ozone levels are significantly affected by the prevailing

Table 4 Ozone concentrations (in ppb$_v$) sorted by wind origin at two research stations for 809 cases for daily and afternoon (12:00–18:00) values

	24-h	Finokalia station	Akrotiri station 12:00–18:00 LT	Finokalia station
N	45.9±8.3	48.2±10.0	50.3±10.6	49.1±10.5
NE	49.8±8.4	50.1±9.7	55.2±11.2	51.9±10.0
E	41.9±6.2	45.7±7.9	45.9±8.4	46.0±8.5
SE	41.3±9.5	38.1±11.5	40.0±10.1	38.9±12.4
S	36.2±6.8	37.2±8.5	39.4±8.0	37.0±9.0
SW	40.8±6.9	40.3±8.9	44.6±6.6	40.6±10.2
W	45.3±7.2	46.2±8.7	48.1±8.5	46.4±9.0
NW	49.1±8.0	49.0±9.4	53.6±9.2	50.5±9.5
All data	45.7±8.6	46.8±10.0	49.8±10.7	47.6±10.6

anticyclonic conditions in the area. Furthermore, highest ozone levels are associated with air masses arriving from the northern sector, while lowest ozone concentrations are correlated to air masses from the western-south-western sector. These findings are in agreement with the current study.

Overall, the mean midday values were 49.8±10.7 and 47.6±10.6 ppb$_v$ for Akrotiri and Finokalia, respectively. Given the variability of the values, as expressed via the standard deviation, it can be deduced that there is no significant spatial variation of ozone and therefore no indications of a west-east gradient on ozone levels, in the region under study (Kouvarakis et al. 2000; Zanis et al., 2014)

As also revealed by the analysis, the air mass trajectories arriving at both sites were almost identical. To incorporate the regional perspective in the analysis, data were also divided into two groups depending on whether the concentration at Akrotiri station was higher or lower compared to that at Finokalia (Table 5). The following analysis was also concentrated on the 12:00–18:00 LT period. Values overlapping, within±3 ppb$_v$, were considered as equal. In total, 24.4 % of the daily values during the common period had higher values at Akrotiri station, 34.5 % showed higher values at Finokalia, and for the rest, 41.2 %, the two concentrations were equal.

Under N air mass dominance, ozone at Finokalia is more frequently higher than at Akrotiri demonstrating the transport of ozone-rich air masses or precursors from over the Aegean Sea and regional urban agglomerations (e.g., Istanbul, Athens, and Izmir), influencing less Akrotiri which is situated to the west part of the island. When air masses come from NE, this picture is reversed with Akrotiri values being equal or higher than those at Finokalia. This may be due additionally to local

Table 5 Wind origin at the Finokalia and Akrotiri stations during the measurement period

Wind direction	O₃ (Akr.) = O₃ (Fin.)	O₃ (Akr.) > O₃ (Fin.)	O₃ (Akr.) < O₃ (Fin.)
N	24.6	20.3	32.3
NE	27.0	26.9	19.0
E	3.0	2.0	6.5
SE	0.6	1.0	0.0
S	8.7	6.6	8.2
SW	5.7	6.1	4.7
W	21.3	24.9	23.3
NW	9.0	12.2	6.1

sources located in Crete eastern of the Akrotiri station which enrich the airborne air masses with urban and agricultural emissions.

Case studies

Characteristic time periods were examined to demonstrate changes in ozone levels incurring due to different air masses origin. The specific periods were selected in order to cover different ozone patterns (associated with different meteorological parameters), and there was also available parallel data for both stations.

Period I: 11–31 August 2005

A characteristic example of rapidly flactuating ozone concentrations is the period 11–31 August 2005. Figure 5 shows the daily variations of ozone at the two stations for the above summer period. In this period, over the Aegean Sea, NE winds known as etesians (or *meltemia*) are dominant for long periods. In particular, during the periods 11–13, 19–22, and 26–31 of August, 2005, strong NE winds were blowing in the area. Those winds transfer primary and secondary pollutants from urban agglomerations like Athens, Istanbul, and Izmir over the Aegean, so that the ozone concentration is increased by 5–10 % (average Akr., 50.1, and Fin., 60.5 ppb$_v$ O₃) in both sites compared to intermediate intervals (14–17 and 23–25 of August, 2005) when west winds arrive in Crete and lower concentrations of ozone are recorded (average Akr., 47.2, and Fin., 54.1 ppb$_v$ O₃).

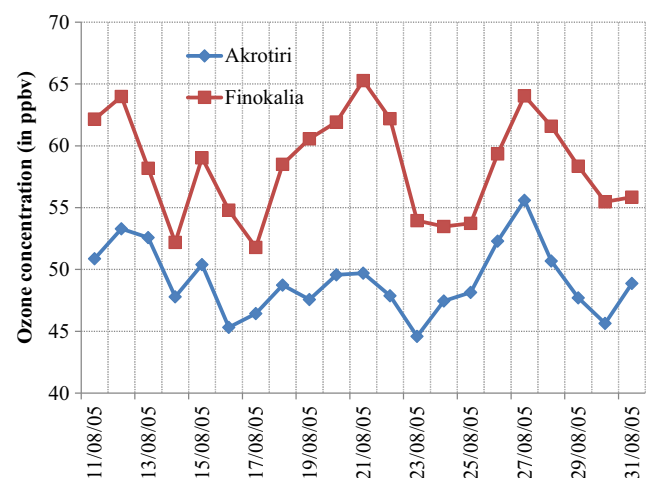### Period II: 20 February–5 March 2005

Figure 6 shows the daily variation of ozone at the two stations for the winter-spring period, 20 February 2008 to 5 March 2008. In this case, ozone concentrations at Akrotiri were markedly higher than those at Finokalia. The smallest difference between daily ozone concentrations at the two stations was encountered during a 3-day period (27–29 February 2008), when air masses arrived to Crete from north-west Europe. In the 1st of March, 2008, during which the highest

difference was observed, the air masses were more local and reached Akrotiri from western direction after they passed over the city of Chania. Those air masses were enriched with ozone and other anthropogenic urban pollutants while following this air trajectory.

Conclusions

Ozone measurements were performed during the period 2003–2009 at the Akrotiri and Finokalia monitoring stations on the island of Crete, Greece. Both stations showed high values of tropospheric ozone with daily average ozone concentrations for the whole period equal to 44.5±8.5 and 49.1±10.6 ppb$_v$ for Akrotiri and Finokalia stations, respectively. The values are closer when the 809 common days of measurements are considered (45.7±8.6 and 46.8±10.0 ppb$_v$ at Akrotiri and Finokalia station, respectively), whereas for the time frame between 12:00 and 18:00 LT, ozone is somewhat higher at Akrotiri station than at Finokalia (49.8±10.7 and 47.6±10.6 ppb$_v$).

In the island of Crete, no significant spatial variation or a west-east gradient on ozone levels exists, whereas similar

Fig. 5 Daily mean ozone concentrations at Akrotiri and Finokalia station for the summer period of 11–31 August 2005

Fig. 6 Daily mean ozone concentrations at Akrotiri and Finokalia station for the summer period of 20 February 2008 to 5 March 2008
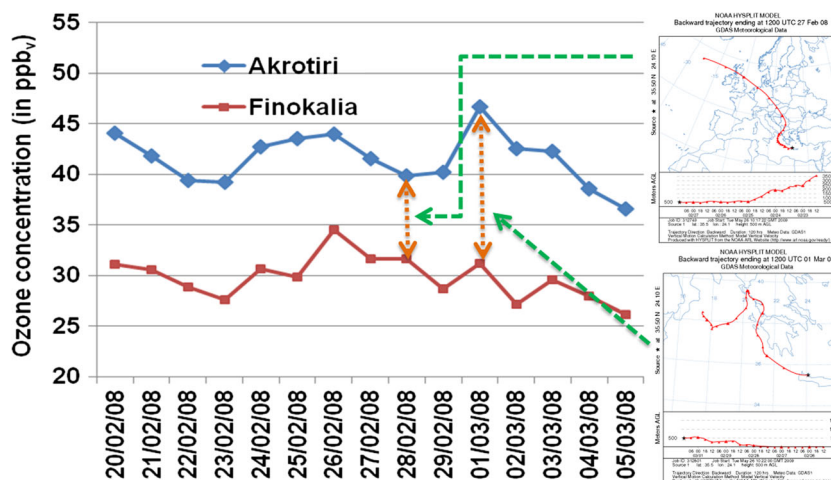
ozone concentration values at other Mediterranean sites indicate common origin of ozone in the eastern Mediterranean basin (Kalabokas et al., 2008; Kleanthous et al., 2014). Data analysis revealed that ozone in the area is mainly produced in other regions, and it is transported over Crete via long-range transport year-round. Additionally, it is appeared that the role of local photochemistry and in situ ozone production or removal is more evident in Akrotiri due to the proximity of the station to the nearby city of Chania. The effect of the urban environment is more profound when comparing the diurnal variation of the ozone concentration in the two stations. Furthermore, the current study demonstrated and confirmed that air masses originating from continental Europe play an essential role to the elevated ozone concentrations in the region.

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