

Ozone variability in the marine boundary layer of the eastern Mediterranean based on 7-year observations

E. Gerasopoulos, G. Kouvarakis, M. Vrekoussis, M. Kanakidou, and N. Mihalopoulos

Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, Heraklion, Greece

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[1] A 7-year time series (1997–2004) of surface ozone at Finokalia, Crete, in the eastern Mediterranean, was analyzed to investigate the mechanisms that control ozone levels and variability in the area. Transport from the European continent was identified as the main mechanism that controls ozone levels in the eastern Mediterranean, especially during summer when ozone presents a summer maximum (July) of 58 ± 10 ppbv. Radon 222 has been proved a useful tool for the verification of the continental origin of ozone. The role of local photochemistry and pollution becomes important under western flow and stagnant wind conditions. For the whole period, a profound ozone-decreasing trend was also observed with a decline of 1.64 ± 0.15 ppbv yr^{-1} , or 3.1% per year. The sharp decline of ozone during the first 5 years (i.e., 3.4 ± 0.2 ppbv yr^{-1} or 5.6% per year for 1998–2002) has been succeeded by an abrupt increase in 2003 (to the 1999 ozone levels), followed by a return to the “regular” ozone declining levels in 2004. The rates of the decline were higher for the spring and summer concentrations. In parallel with the ozone decline, a shift of the maximum ozone concentrations from summer to spring, attributed to a continuous decrease of the summer ozone concentrations, was also observed, with the year 2002 presenting a clear spring maximum. The decline of ozone and the shift of its maximum to spring could be related to the reduction of ozone precursors that occurred both in western/central and eastern European countries. The severe weather phenomena that influenced mainly central Europe in summer 2002 have also affected ozone measurements at Finokalia, since the induced meteorological disturbance caused the prevalence of NW winds instead of the dominant NE flow.

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1. Introduction

[2] Ozone has been established as an important greenhouse gas (GHG) [e.g., Roelofs *et al.*, 1997] as well as a pollutant [Seinfeld and Pandis, 1997] with definite impact on humans and ecosystems. Thus the knowledge and the control of its levels is a significant task for sustainable development of humanity. The concentration of tropospheric ozone has been changing significantly over the past century. Even though for the most of this period a rise in background levels is consistently reported, during the last decades a more divergent behavior is observed [Vingarzan, 2004]. Until the mid-1980s, the ozone rise is influenced by the enhanced anthropogenic pollution that followed the intense industrialization, mostly in the Northern Hemisphere. After 1980, ozone presented a smaller rate of increase or has remained constant [Logan, 1994], pattern mainly attributed to the decline in NO_x emissions over Europe and North America [Vingarzan, 2004]. In particular, between 1990 and 2000 ozone precursor gases decreased by

29% in a total of 31 European countries (situated in western, central, and eastern Europe) as reported by the *European Environment Agency (EEA)* [2004a] (European Monitoring and Evaluation Programme (EMEP) [see Vestreng, 2003]). There are also a certain number of studies reporting a decline of ozone concentrations either at the proximity of urban areas or downwind of pollution sources [e.g., Cox, 1998; Gardner and Dorling, 2000]. A comprehensive review of ozone trends observed at background stations around the globe is provided by Vingarzan [2004], who demonstrates and discusses the differences among various monitoring stations during the past three decades.

[3] Apart from the trends observed in ozone levels, interesting differentiation has been also observed concerning ozone seasonality. The spring ozone maximum found at many stations seems to be a Northern Hemisphere phenomenon [Janach, 1989; Oltmans and Levy, 1994; Monks, 2000], yet the origins of this phenomenon are still a topic of debate. It is currently believed that it is either associated with the spring maximum of stratospheric concentrations affecting the troposphere via the stratosphere-to-troposphere exchanges [Junge, 1962; Danielsen, 1968], or it is induced by photochemical ozone production involving gases that

Table 1. Data Coverage for the Period 1997–2004^a

Tracer/Data	Period	Relevant Mechanism/Source
O ₃	8/97–12/04	
NO	6/98–8/01, 7/03–7/04	transport, photochemical pollution
NO _z	6/98–12/99, 6/00–1/01, 2/02–7/04	transport, photochemical pollution
BC	1/00–2/02, 9/03–7/04	biomass burning
Rn	7/00–8/00, 7/01–7/04	transport (horizontal/vertical)
T	2/97–3/98, 2/00–5/00, 7/01–7/04	meteo, chemistry
RH	7/01–7/04	meteo
w _s , w _d	2/97–5/00, 7/01–7/04	meteo, transport
W	7/01–7/04	meteo, chemistry

^aThe main source or/and the relevant mechanism linking each tracer to ozone is included in the last column.

built up during winter [Penkett *et al.*, 1993; Dibb *et al.*, 2003; Liu *et al.*, 1987]. Nevertheless, a spring maximum is not observed at all stations in the Northern Hemisphere. Scheel *et al.* [1997] have shown that even though at the northerly European sites a spring ozone maximum is found, this is shifted to late summer in central and south/southeastern Europe. The summer ozone maxima are often related to photochemical production of ozone [e.g., Logan, 1985]. The knowledge and understanding of the spatial distribution of the different seasonal cycles over the globe is critical to the identification of the role of the various mechanisms that control ozone levels and a prerequisite for the definition of control strategies.

[4] There is a remarkable inhomogeneity in the monitoring of ozone over the European continent, with dense coverage over western/northwestern Europe and a lack of available data at the eastern/southeastern parts (for the location of EMEP stations, see <http://www.nilu.no/projects/ccc/emepdata.html>). The need for ozone observations and the analysis of its behavior in eastern and southeastern Europe is imperative. Especially in the eastern Mediterranean the knowledge of ozone variability would be of increased importance. The eastern Mediterranean is the crossroads of air pollution from western and/or eastern Europe [Lelieveld *et al.*, 2002], comprises the boundaries of Europe from the Asian and the African continent, and is affected by intensive photochemistry. Indeed, the specific synoptic conditions prevailing in southern Greece, namely, sparse cloudiness and the prolonged exposure to solar radiation during summer, enhance the role of the local photochemistry that is then limited by ozone precursor availability.

[5] Kouvarakis *et al.* [2000] have presented the first study on two years of continuous ozone measurements over Greece (Crete). An overview of ozone concentration levels over the area can be found in the work of Kourtidis *et al.* [2002] where the exceedance of the 32 ppbv phytotoxicity limit throughout the year is reported. Kalabokas and Repapis [2004] performed a thorough analysis of surface ozone values for the period 1987–1996 at two stations in Athens greater area. They found almost constant summer afternoon values (~60 ppbv), indicating the absence of any significant trends during the reported period. The current study builds upon the earlier one by Kouvarakis *et al.* [2000] and presents a seven-year time series of ozone at Finokalia, in conjunction with a number of related physical and

chemical parameters. First, the annual cycles of a number of parameters are studied in parallel with ozone seasonal variability in order to investigate the relative contribution of transport and local photochemistry and to identify the mechanisms that control ozone's seasonality. A wind climatology pointing out the main sources of air masses arriving over the area provided additional tool for this analysis. The changes in the pattern of ozone's annual cycle and its evolution over the different years are also topics of the present study. Finally, the observed trends in ozone and the examination of periods with abnormal behavior are demonstrated and their causality with pollution from the main European continent and climatological disturbances that occurred over specific periods is examined.

2. Data and Methods

[6] Continuous surface ozone observations since August 1997, are used in conjunction with meteorological data (temperature (T), relative humidity (RH), wind speed (w_s) and direction (w_d), nitrogen oxides (NO, NO_z) and tracers of continental origin (radon 222) and of burning activities (black carbon)) (Table 1). All measurements are conducted at Finokalia (35°20'N, 25°40'E), the monitoring station of the University of Crete situated 70 km northeast of Heraklion, at the northern coast of Crete. A recent description of the site is given by Vrekoussis *et al.* [2004], and information on the instrumentation used for all the measurements has been presented elsewhere [Kouvarakis *et al.*, 2002; Sciare *et al.*, 2003a]. To certify the long-term stability of ozone measurements, several qualification assurance (QA) processes are followed: (1) inlet filter change on a monthly basis (and immediately after dust events), (2) zero and span checks every 3 months, and (3) calibration with transfer standard every 6 months. Similar QA processes are followed by all stations reporting data to EMEP as Finokalia (<http://www.nilu.no>). Moreover, intensive experimental campaigns take place at Finokalia almost every year (mostly during summer) enabling inter-comparison of our instruments with instruments brought by other participants.

[7] In order to discriminate the role of transport in the variability of ozone a number of parameters were measured to mark the origin of air masses. Thus pollution, either transported or local, was identified via NO and NO_z. NO_z which is the sum of the reactive nitrogen species, here expresses mainly the sum of NO₂, NO, PAN, and HNO₃. Black carbon (BC) has been used as a tracer of burning activities [Sciare *et al.*, 2003b]. For the identification of either long-range transport of air masses of continental origin or vertical transport in the free troposphere, measurements of the radionuclide (radon 222) have been used. Rn-222 has a half-life of 3.8 days, a time suitable for the distinction between freshly arrived continental and maritime or higher tropospheric air masses.

[8] Finally, the monitored meteorological parameters, namely, temperature (T), relative humidity (RH), wind speed (w_s), and wind direction (w_d), were applied to provide insight into the role of meteorology to ozone variability. As an indicator of the intensity of the atmospheric photochemical activity, the solar irradiance (W in watt m⁻²) is used.

[9] All data except Rn have been recorded with a 5-min time resolution. Hourly and daily averages were extracted

Table 2. Basic Statistics for the Data Presented in Table 1^a

Tracer/Data	Unit	Range (Min–Max)	Average ± std	Median
O ₃	ppbv	19–83	49 ± 11	48
NO	pptv	10–300	57 ± 41	43
NO _z	ppbv	0.2–4.3	1.2 ± 0.5	1.1
BC	ng m ⁻³	80–2650	498 ± 325	423
Rn	Bq m ⁻³	70–4800	1625 ± 681	1521
Temp	°C	3–38	17.6 ± 6.1	17.6
RH	%	17–92	64 ± 13	66
w _s	m s ⁻¹	1.2–32.2	6.9 ± 3.7	6.5
W	watt m ⁻²	7–621	360 ± 160	388

^aFor the extraction of the information the daily means are used.

for the needs of the analyses. Air sampling for Rn activity measurements was conducted on a 2-hour basis. For the construction of the hourly time series, Rn activity is assumed to be constant within each 2-hour sampling. Some basic statistics on the daily means of the main parameters are presented in Table 2.

3. Surface Ozone Levels and Observed Variability

[10] The ozone daily mean observations over the past seven years are shown in Figure 1. Two main features are clearly observed: the prominent seasonal variation and the general decline of ozone levels throughout the period.

[11] The maximum ozone concentrations decrease from about 75 ppbv in 1998 to 60 ppbv in 2002 corresponding to a drop of 20%. The gradual decrease of ozone maxima is interrupted in 2003 when maximum values rise to 75 ppbv but then in 2004 a decline is again observed. More consistent is the behavior of ozone minimum concentrations since they continue their descent for the whole period with values from about 35 ppbv in 1998 down to 25 ppbv in 2004. A comprehensive analysis of the observed interannual decreasing trend and the seasonal fluctuation follows.

4. Annual Cycles and Their Governing Mechanisms

[12] A significant part of the variability of ozone is linked to its seasonality. The annual cycles of ozone and relevant parameters studied here (derived from the monthly means over the 7 years of observations) are presented in Figure 2.

[13] Ozone presents a clear summer maximum (July) of 58 ± 10 ppbv whereas minimum concentrations are found in December (36 ± 7 ppbv) (Figure 2a). In Figure 2a the annual variation of the solar irradiance (summer maximum June–July) is also shown. This seasonal pattern is in full accordance with that of ozone, with the 24-hour summertime values well above 500 watts m⁻² and four times higher than those during winter. The observed abundance of solar radiation indicates that the prevailing summer conditions in southern Greece favor intense photochemical activity, yet ozone balance in the troposphere by means of chemical production and destruction is also dependent on the availability of its precursors.

[14] In Figure 2b the observed annual cycles of NO and NO_z are presented together with those of black carbon (BC) and radon 222 (Rn). Both NO and NO_z monthly means

reveal a late summer/early fall maximum, and this feature remains relatively consistent over the years. For those years with maximum NO monthly means ranging between 30 and 45 pptv, the maximum is observed in October (mean value 38 ± 6 pptv). The September maximum shown in Figure 2b is due to the September peak value of 80 ± 27 pptv in 1999. During this particular month the hourly averages have repeatedly exceeded 150 pptv (up to 500 pptv) and especially from 1 to 11 September 1999 the daily averages were mostly well above 100 pptv. Considering the short residence time of NO in the atmosphere and taking into account that during this period attenuated winds (down to 3 m s⁻¹ compared with the mean value of 7 m s⁻¹ for the 7-year period), mostly from the west, prevailed, then NO high concentrations are attributed to local sources. NO_z maximum is found in September (1.6 ppbv), but when the monthly means (1998 and 2002) do not exceed 1.4 ppbv then a shift to a summer maximum is observed. Apart from the main late summer/early fall maxima, secondary peaks are also revealed for both NO and NO_z. Thus NO shows a secondary peak in May which, however, is again due to a few days with NO daily averages above 60 pptv in May 1999. Once more, this period is related to low wind speeds (about 4–5 m s⁻¹) coming mainly from the west or from mixed directions, indicative of stagnant conditions. An NO_z secondary peak is found during February–March, and it is observed in two of the three years (1999 and 2004) for which late winter/early spring measurements of NO_z are available. The local NO and NO_z emissions would be expected to peak during summer taking into account that the sources are mainly the various means of transportation and that the rush tourist period is in summer. Moreover, enhanced emissions during winter from fuel combustion should not be disregarded. Nevertheless, the measured levels of NO_z are high enough (exceeding the ppbv level) to be attributed only to local pollution and thus their seasonality is most probably driven by transport from continental Europe.

[15] BC shows two maxima of about 700–720 ng m⁻³ in August and January–February (Figure 2b). Since BC is mainly used as a tracer of transported products from burning

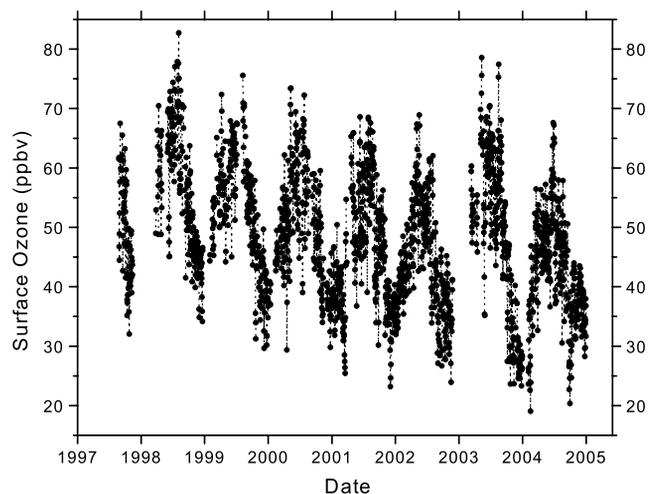


Figure 1. Time series of ozone (daily means) for the period 1997–2004.

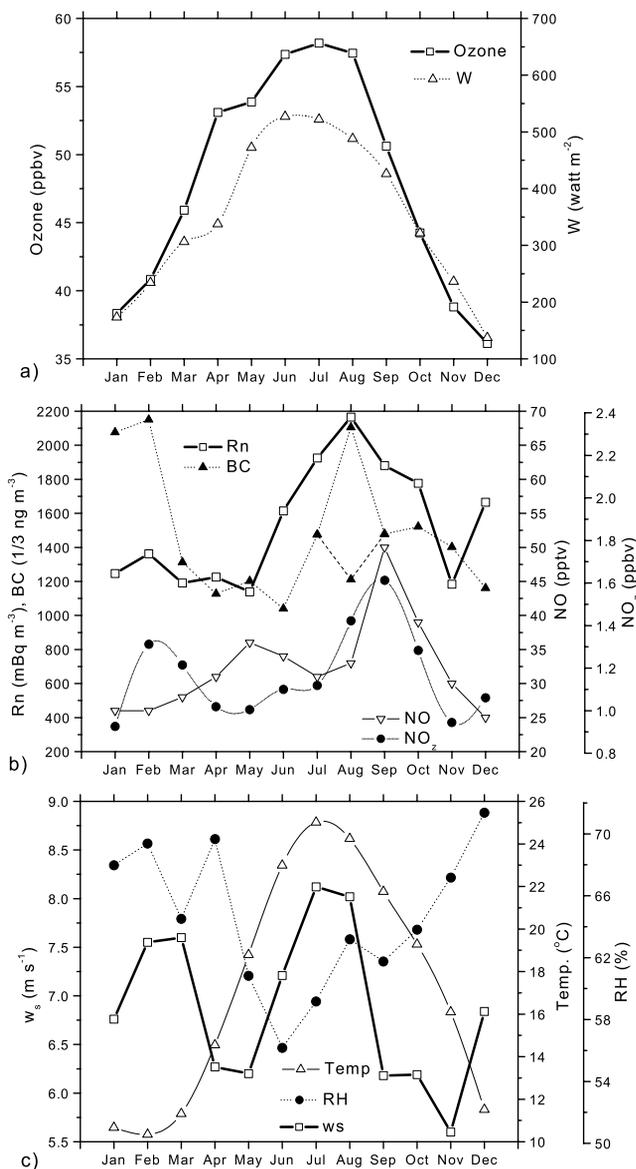


Figure 2. (a) Annual cycles of ozone and solar irradiance. (b) Annual cycles of physical (BC, Rn) and chemical (NO, NO_z) parameters. Two values are provided for BC in August, with the lowest not including August 2001. (c) Annual cycles of the meteorological parameters (w_s, T, RH).

activities, for the interpretation of its seasonality the episodic nature of its emission in the atmosphere should not be disregarded. However, the dry summer conditions favoring e.g. fires, low scavenging, do control the seasonality of burning emissions. Thus the August maximum is exclusively due to a prominent peak in August 2001 (average 1200 ng m⁻³), and is linked to biomass burning events covering an extended area in Bulgaria and the northern coast of the Black Sea [Salisbury et al., 2003; Balis et al., 2003]. In none of the two other years with summer BC data available (2000 and 2004) was an August peak observed. Excluding August 2001 data, then the mean value for August drops from 700 to 400 ng m⁻³ and the summer peak is smoothed still appearing slightly higher than in

spring. The winter maximum as found in 2001 and 2002 seems to have a more periodic than episodic nature since it is probably associated with local transport of fuel combustion products (central heating). This can be further supported by the very low wind speed (1.5–4 m s⁻¹), with trajectories denoting local influence.

[16] For radon (Rn-222) a clear annual cycle is revealed with a summer maximum in August (2.2 Bq m⁻³), whereas a constant background of 1.2 Bq m⁻³ is found during winter/spring (Figure 2b). Rn reflects directly the change in wind direction, as Rn emission from the ground over the continents is continuous. Of course, when analyzing the seasonal pattern of Rn, the difference in the emanation rates from the ground has to be taken into account. The broad summer peak of Rn agrees well with the ozone maximum confirming the critical role of transported continental influence as an ozone controlling mechanism in the area. A detailed analysis of Rn data will be presented elsewhere.

[17] Finally, the mean annual cycles of the meteorological parameters are presented in Figure 2c. Temperature reaches its maximum values during summer, anticorrelated with RH that presents its minimum in June. An interesting point is revealed from the seasonal cycle of the wind speed (Figure 2c). The increase of the 1.5–2 m s⁻¹ may not appear significant in absolute values. Nevertheless, the fact that the two peaks are found in early spring and summer may be strongly related to the annual cycles of the measured chemical and physical parameters.

[18] Wind climatology and trajectory analysis: To investigate the importance of these two w_s peaks, it is necessary to explore the seasonal distribution of the wind direction. For this, 6 sectors of air mass origin have been defined as shown in Figure 3 [Mihalopoulos et al., 1997; Kouvarakis et al., 2000]. The identification of the wind direction was based on the 5-day back-trajectories calculated by the

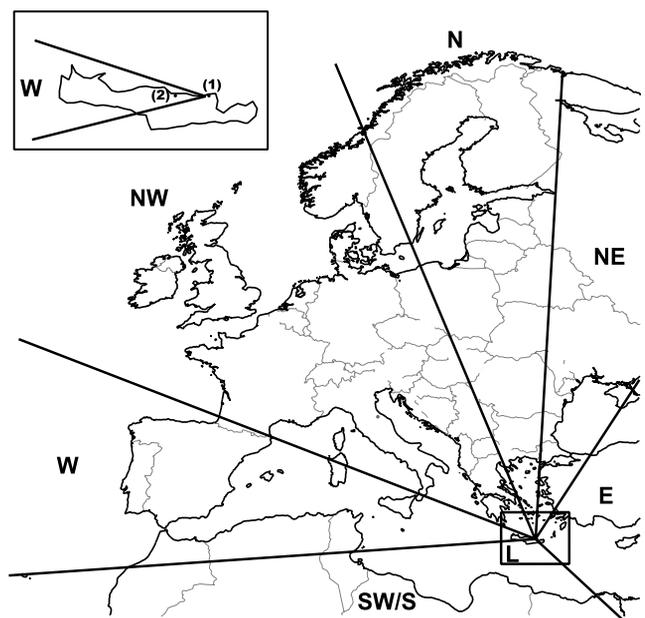


Figure 3. Classification of wind sectors for air masses arriving at Finokalia station. Crete Island is shown at the top left with the position of Finokalia (1) and Heraklion (2) denoted on the map.

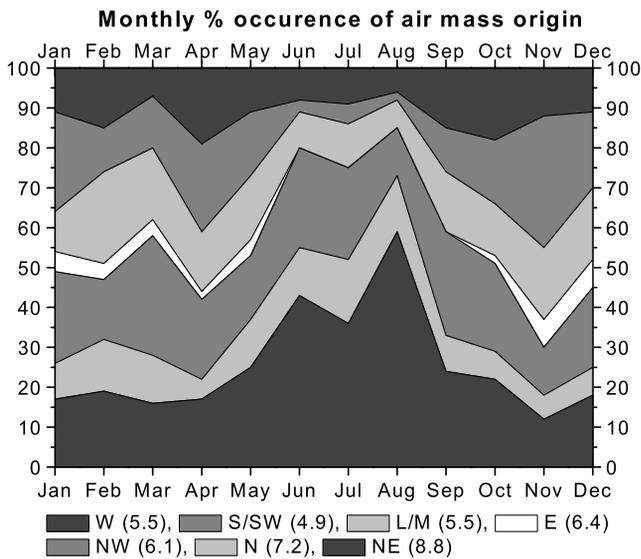


Figure 4. Seasonal variability of the percentage occurrence of different air mass origins. The S and SW sectors as well as the L (local) and M (mixed) sectors are summarized to one category. Numbers in parentheses are the average wind speed at Finokalia for each wind sector in m s^{-1} .

HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory Model) [Draxler and Hess, 1998]. The climatology of air mass origin produced is illustrated in Figure 4. The major findings are the general prevalence of northerlies over the year and the characteristic excess of NE during summer. Higher wind speeds are also observed from the NE/N sector. The bimodality of the w_s seasonal variation is also in good agreement with the change in air mass

origin. Thus the summer peak of w_s coincides with the remarkable persistence of the NE direction (40–60%), the spring and fall drops correspond to the increase of the NW occurrence which becomes either comparable or higher than that of NE, whereas the November minimum is linked to the S/SW sector.

[19] With the establishment of the major characteristic of the wind climatology in the area it is interesting to calculate the levels of all quantities when sorted according to the different origins of the air masses. The mean values of all parameters for each wind sector were calculated at two heights for the end point of the trajectories (1 and 3 km above Finokalia station were chosen as representative of inside and outside the boundary layer). The resulting rose diagrams for the height of 1 km are shown in Figure 5.

[20] Ozone concentrations are higher when air masses originate from the NE sector (Figure 5a). The difference of ozone concentration from the value the day before was also calculated to include the persistency in ozone time series. Ozone departure from the previous day maximizes for the N direction (or the broader NW/NE direction when medians are considered instead of averages) (Figure 5b). NO higher values are observed when trajectories indicate the prevalence of W winds (Figure 5c). This result can partly explain the relative low ozone concentrations for the same sector due to the titration of the latter by NO. It has to be noted that the W sector actually expresses influence from local sources as the air masses sweep inhabited areas of the island situated at the west of the station, including Heraklion that is the major city of Crete (Figure 3). Enhanced NO_z is obtained for the wide NW/NE sector whereas for the W sector concentrations, although lower, remain above the ppbv level. The pattern revealed for Rn is consistent with its choice as tracer of continental origin (Figure 5f). Thus Rn presents its maximum concentrations under the NW/NE

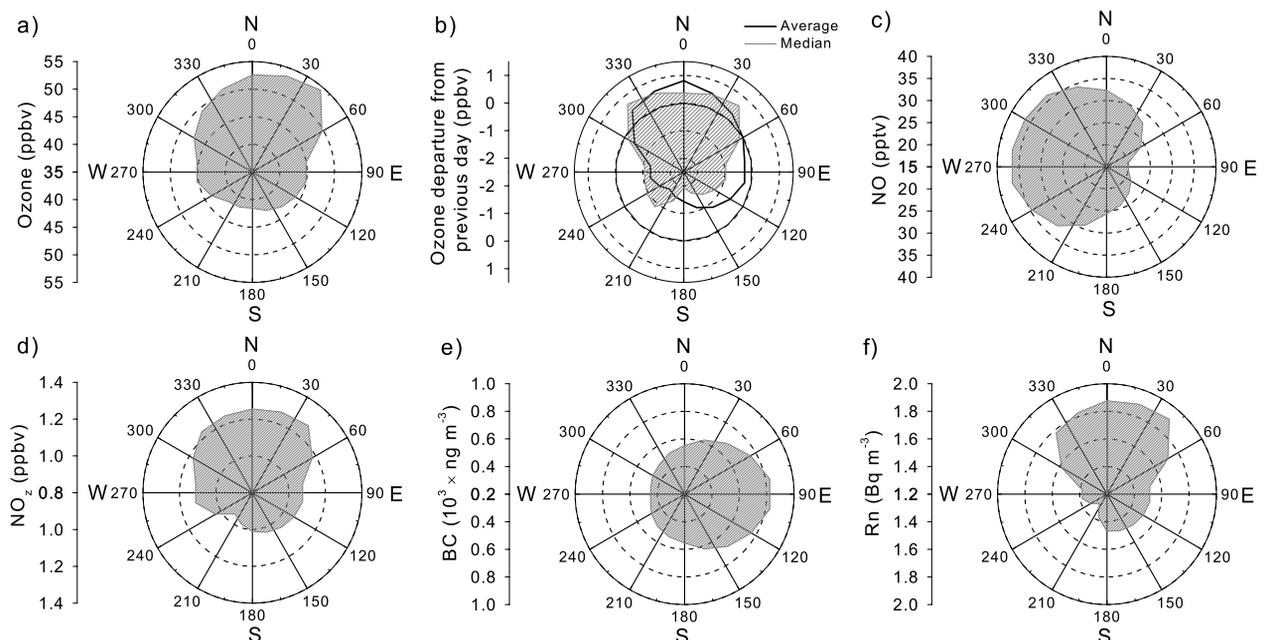


Figure 5. Rose diagrams of the source contributions to the levels of the parameters: (a) ozone, (c) NO, (d) NO_z, (e) BC, and (f) Rn. (b) Departure of ozone from its concentration the day before is also presented.

Table 3. Single Regression Analysis of Ozone With Physical, Chemical, and Meteorological Parameters^a

	Total	Winter	Spring	Summer	Fall
O ₃ vs		<i>Chemical and Physical Parameters</i>			
NO	(+) 1%	(+) 3%	(+) 2%	(−) 0%	(+) 4%
NO _z	(+) 5%	(+) 4%	(+) 0%	(+) 2%	(+) 31%
BC	(+) 3%	(+) 0%	(+) 21%	(+) 19%	(+) 17%
Rn	(+) 5%	(+) 1%	(+) 0%	(+) 4%	(+) 23%
		<i>Meteorological Parameters</i>			
Temp	(+) 13%	(+) 2%	(+) 1%	(+) 10%	(+) 0%
RH	(−) 8%	(−) 6%	(−) 6%	(−) 22%	(−) 1%
1/w _s	(−) 8%	(+) 2%	(−) 3%	(+) 13% ^b	(−) 12%
W	(+) 35%	(+) 29%	(+) 26%	(+) 5%	(+) 21%

^aThe squared correlation coefficient (r^2) of each regression is given together with the sign of the correlation (in parentheses). In italics are shown coefficients that correspond to correlations significant at the 99% confidence level and in bold those which explain an essential part of ozone's variability. For the regressions the daily means of the parameters were used, and the analysis was performed once for the whole data set and for each season separately.

^bCorrelation with w_s instead of $1/w_s$.

wind influence, whereas the contribution from local emissions is much smaller as indicated by the lower values for the W and S sectors. The fact that both Rn and ozone reveal similar patterns with maxima associated with the extended NW/NE sector indicates that ozone enhancement is mainly due to transported pollution. More specifically, w_s average (8.8 m s^{-1}) and maximum (23.2 m s^{-1}) values for the NE sector indicate that the air masses can cover on average a distance of between 800 and 2000 km maximum, in one day. Finally, the maximum values of BC are displaced to the E (Figure 5e). It should be noted that the BC average for the E sector is derived from a considerably smaller number of values compared to the NE average, thus masking the high BC transported via the NE sector as well. The E/NE origin of high BC shows the influence of fires taking place near Crete (e.g. Greek islands in the Aegean Sea, Turkish coast facing the Aegean) or even further (e.g. main continental Turkey, former Soviet Republics, Russia), all situated inside the E/NE sector [Salisbury et al., 2003; Sciare et al., 2003a, 2003b].

[21] Single and multiple regression analysis between parameters: The link between ozone and the parameters proxy for the different mechanisms that control ozone levels in the area has been further investigated by regression analysis (Table 3). During fall, NO_z, BC, and Rn explain a significant part of ozone's variability ($r^2 = 31, 17,$ and 23% , respectively). Note that BC is positively correlated with ozone during all seasons except winter. Significant correlations are revealed with the meteorological parameters when all data are used, whereas when analyzing the data per season, RH appears significantly anticorrelated with ozone during summer. The anticorrelation between ozone and RH can be attributed to ozone enhancement linked to transport in the free troposphere of drier upper tropospheric air masses rich in ozone. During summer/fall the correlation of ozone with w_s (in most cases $1/w_s$ provided better correlations) is in accordance with the results of the trajectory analysis showing that high speed winds from the NE sector transport significant quantities of ozone while lower speed winds from the W indicate increased NO levels from local sources and thus lower ozone concentrations via titration. Finally, the high correlation with solar irradiance

(35%) for the whole period is worth noticing, especially since this correlation is retained during all seasons with the exception of summer, when the maximum of photochemical activity would be expected.

[22] Since some of the parameters express the same or complementary ozone controlling mechanisms/sources, their high covariance with ozone as revealed from the single regression analyses may be attributed to the same part of ozone's variability. Thus multiple regression analysis has been also performed to discriminate on the relative importance of the parameters and to attempt to provide an ozone-predicting tool. The analysis was performed independently on the chemical/physical and the meteorological parameters, using in both cases solar irradiance W as one of the independent variables. The analysis was repeated for different seasons as well. To avoid erroneous conclusions from bias due to extreme outliers, the predicted and residual scores of the dependent variable (O₃) were examined (residual analysis), and values that fell outside of the ± 2 sigma (standard deviation of the residuals) were omitted before the multiple regression analysis was repeated.

[23] The first set of independent variables applied as predictors of ozone was NO, NO_z, Rn, BC, and W. Rn and BC were rejected by the model due to the 95% confidence level ($\alpha 0.05$). The resulting linear regression model that can better describe ozone's variability by means of physical/chemical parameters on an annual basis is the following:

$$O_3 = (-174 \pm 26) \cdot NO + (4.8 \pm 0.9) \cdot NO_z + (0.043 \pm 0.003) \cdot W + (33.4 \pm 1.5). \quad (1)$$

When analysis was performed per season, in spring the contribution of NO to ozone variability did not prove significant, while in summer the consideration of Rn increased the explained ozone variability by 5%. The latter is obviously related to the fact that during summer, when the NE winds prevail (w_s is also higher), the increased covariance between ozone and Rn is due to their transport from the continental Europe (in accordance to the rose diagrams). The maximum explained ozone variability of 58% was in fall, whereas in summer the solar irradiance W was found to be a poor predictor, though still significant. This is probably due to the smaller variability of W due to the extended period of clear, sunny days during summers inducing less variability to W. The use of the 10:00–16:00 (LT) averages instead of the daily means of the parameters (i.e. focusing on the photochemically active period of the day) did not produce any statistically significant improvement to the model.

[24] The second set of independent variables used was T, RH, $1/w_s$ and W. Temperature (T) was rejected by the model due to the 95% confidence level ($\alpha 0.05$). The resulting linear regression model based on the meteorological parameters on an annual basis is the following:

$$O_3 = (-0.11 \pm 0.02) \cdot RH + (-15.5 \pm 2) \cdot 1/w_s + (0.041 \pm 0.0019) \cdot W + (42.4 \pm 1.8). \quad (2)$$

In winter the contribution of RH was negligible (RH proved a better predictor in summer when higher variability of RH

Table 4. Basic Statistical Information on the Application of the Multiple Linear Regression Analysis for the Prediction of O₃ Concentrations for the Whole Period^a

Dependent Variable: O ₃					
	Stand. Beta	Partial Correl.			
	Regr. Coef.	Coef.	Adjusted R ²	F	p-Level
<i>First Set of Independent Variables</i>					
W	0.74	0.70	0.49	81.4	1.5E-36
NO	-0.37	-0.40			N _{obs} : 249
NO _z	0.29	0.32			
<i>Second Set of Independent Variables</i>					
W	0.61	-0.18	0.47	224.6	0.0E+00
1/w _s	-0.21	0.63			N _{obs} : 743
RH	-0.14	-0.28			

^aThe first subtable applies to equation (1), and the second subtable applies to equation (2) (see text).

is evidenced). In spring the temperature (T) became a reliable predictor with negative sign, in contrast to the positive correlations revealed from the single regression analysis. This anti-correlation can be attributed to the fact that while in single regression analysis temperature acts as a proxy for meteorology, in multiple regression analysis the corresponding part of ozone variability is covered by RH, W, or w_s. In this case, temperature possibly expresses mainly the increase in the rate of ozone chemical destruction. Once more the solar irradiance W was degraded during summer. Finally, the inclusion of “the previous day” ozone concentration enabled explanation of 83% of ozone variability, indicating the high persistence in ozone time series due to its long lifetime. Additional information concerning the overall goodness of the fits and the explained variability of ozone by each predictor for both data sets is summarized in Table 4.

[25] Concluding, the relative contribution of the predictors from the first set to ozone prediction is W:NO:NO_z/10:5:4 as revealed from the standardized regression coefficients (*Beta*), and a 49% of ozone’s variability has been explained. In the second set, the relative contribution of each predictor is W:(1/w_s):RH/9:3:2 and the explained variability is 47%, of particular significance, compared to the first set, considering the higher number of observations.

5. Changes in the Pattern of Ozone Annual Cycle

[26] The annual cycle of surface ozone at Finokalia is comprised of two modes leading to summer and spring maximum, respectively. The observed annual cycle is the convolution of the two modes and its shape depends on their relative contribution. These two modes, henceforth referred to as the spring and the summer mode, respectively, are investigated in this section in order to track any changes to ozone seasonal variation during the studied period.

[27] The annual cycle of ozone for the whole period (1997–2004) has been presented in Figure 2a. When focusing on the individual cycles, it is seen that the minima take place always in December; nevertheless, a more complicated behavior is derived for maximum values. Thus, during the first 2 full years (1998–1999), a distinct July maximum is observed with the monthly mean values exceeding 65 ppbv. A secondary minor peak is observed in April during both years forming a “hump” over the main

summer mode, possibly indicating the interaction of the two modes considered previously. In 2000 the maximum seems more flat forming a plateau of about 58 ppbv between May and August. In 2001, apart from an August maximum (59 ppbv), there is also a prominent peak of equal amplitude in April. The year 2002 seems exceptional since it serves as a temporal end of the decline in ozone maximum (Figure 1) and it has a clear spring maximum (May). Summer ozone concentrations in 2002 are the lowest of the whole period. In 2003 an abrupt rise of summertime ozone is observed with the ozone maximum found in June. A summer maximum (August) is also observed in 2004. Therefore a progressive shift of ozone maxima from summer (in 1998) to spring (in 2002) has been observed to accompany the general decline of the values, whereas in 2003 and 2004 a return to summer maximum is encountered.

[28] To visualize the shift of the maximum, the percentage departure of each month from the annual mean of the specific year is plotted for three critical years: 1999, as the first full studied year of ozone decline (chosen instead of 1998 since they show identical cycles, but in 1998 January and February data are missing); 2002, expressing the end of the decline of ozone maximum and 2003, as the year of the return to “regular”, considering summer maximum as typical for our area (Figure 6). The shift from the summer maximum in 1999, typical for central European sites, to the clear spring maximum in 2002, typical for European sites across the coastline facing the Atlantic, is clearly evidenced. A change in 2003 back to summer maximum is also seen and this maximum is shifted to August in 2004, as already mentioned.

[29] Supposing that the shift of the maximum is the result of the relative contribution of the spring and summer modes and that the 2002 annual cycle is a pattern for which the minimization of the summer mode has taken place, it is interesting to follow the behavior of the summer mode within the whole period. For this reason, the seasonal cycle of 2002, simulating the spring mode, has been subtracted from the annual cycles of all years and the remaining summer modes are shown in Figure 7. The gradual “weakening” of the summer mode is well defined and it is expressed both via a decrease in the maximum and a change of the kurtosis of the distributions (decrease to the width of

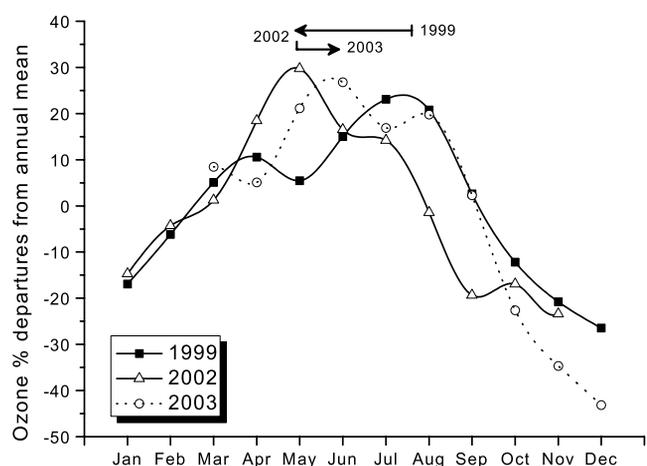


Figure 6. Percentage departures of each month from the annual mean of the specific year.

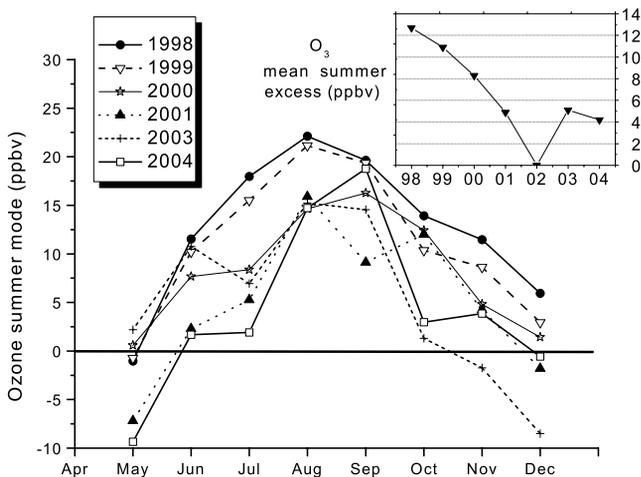


Figure 7. Deconvolution of ozone annual cycles based on the 2002 spring maximum seasonality. The small panel presents the mean excess of ozone concentrations between May and December to the ones in 2002.

the distributions). To quantify this weakening, the mean excess of ozone concentrations during May–December from the corresponding period in 2002, was calculated for all studied years and presented in the internal panel of Figure 7. Monthly ozone concentration between May and December was on average 12 ppbv higher in 1998 than in 2002, while an enhancement by 4–5 ppbv is observed in 2003 and 2004. However, the summer 1998 ozone levels were not reached.

[30] The year-to-year weakening of the summer mode relatively to the spring mode has been highlighted and it is in full agreement with both the decreasing trend in ozone concentrations and the shift of the maximum from summer to spring. As a result, the shape of ozone annual cycles has changed. To investigate this change, a Gaussian distribution has been fitted to the daily means of ozone concentrations for each year. It has to be noted that the data was first detrended so that no bias would be superimposed on their seasonal pattern. The fitting procedure provided us with an estimate of both the amplitude and the width (FWHM: full width at half maximum) of each annual cycle. Excluding 1998 for which there is no data available for January–February, a rather consistent trend for both the amplitude and the width of the annual cycles is obtained. More specifically, from 1999 to 2002 both the amplitude and the width of the annual cycles decrease (Figure 8). This decrease has been numerically evaluated by fitting a number of curves and the result was that an exponential decrease best describes the found relation. Thus the amplitude of the annual cycles drops from 35.3 ± 7.5 ppbv in 1999 to 20.5 ± 1 ppbv in 2002 (values after \pm correspond to the standard error of the fit), a decrease of 42%. The rate $d(\text{amplitude})/dt$ is reduced from 9.7 ppbv yr^{-1} in 1999 to 1.2 ppbv yr^{-1} in 2002. Moreover, the width ranges between 8.3 ± 1.4 to 4 ± 0.3 months (52% decrease), with the rate $d(\text{width})/dt$ dropping from 2.2 in 1999 to 0.8 mo yr^{-1} in 2002. In 2003, the amplitude climbs to 53.6 ppbv and the width to 8.7 months constituting the most prominent cycle of the seven-year period under study, whereas in 2004 both the amplitude and the width reach the corresponding levels in

2000. However, 2000 and 2004 have different skewness with peaks shifted more to spring in 2000 and to summer in 2004. The fitting process reveals a plateau after 2002 indicating that 20 ppbv and 3–4 months can be considered a typical amplitude and width for an annual cycle where the spring mode is dominant.

6. Ozone Trends

[31] Having thoroughly investigated the seasonal variability of ozone surface concentrations and the change of the annual cycle patterns, focus was placed on the observed decreasing interannual trend of ozone during the seven years 1997–2004 ($1.64 \pm 0.15 \text{ ppbv yr}^{-1}$; the slope is calculated via a simple regression analysis, \pm refers to the standard error of the slope estimation). This trend is more clear and constant for the years 1998–2002 (Figure 1) ($3.4 \pm 0.2 \text{ ppbv yr}^{-1}$). Over this subperiod the annual mean value of ozone dropped from 56 ± 11 ppbv (mean \pm standard deviation of daily averages) down to 44 ± 9 ppbv. It should be noted that the studied period of seven years is relatively short, thus limiting the climatological character of the observed fluctuations. Therefore “trend” is used here to emphasize the statistical significance of the observed change in ozone concentrations during the reported period.

[32] With the use of the Mann Kendall test [Kendall, 1948] the statistical significance of the above mentioned trend (1998–2002) was further investigated. The value obtained from the test ($\tau = 0.288$) was by far higher than the corresponding one for the 99% confidence level ($\tau_{(99\%)} = 0.049$) indicating that there is a significant trend at the 99% c.l. It remains to clarify the factors that have led to this decrease and why this trend was partly interrupted in 2003.

[33] Interannual ozone trends have also been extracted for different seasons. The calculations were performed in two different ways: (1) for the whole period 1997–2004 with abnormal behavior around 2003 interrupting the decline and thus excluded from the calculations, and (2) for the period 1998–2002 (Table 5). In both cases the maximum decline is observed in the spring and the summer concentrations. In

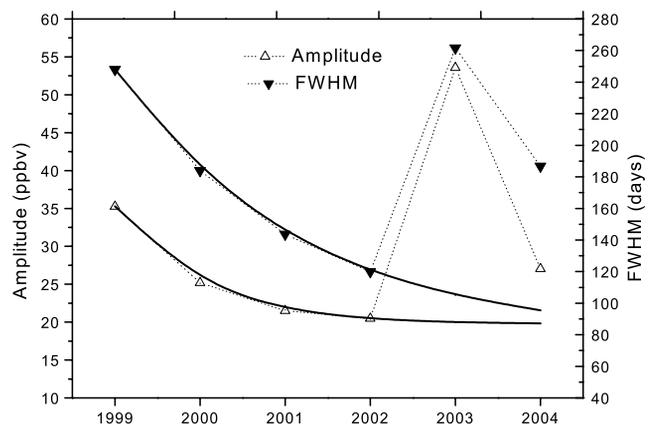


Figure 8. The amplitude and the full width at half maximum (FWHM) of the individual annual cycles as derived from the fitting of a Gaussian distribution on the daily values for each year. Their decline is simulated by an exponential relation presented by the solid lines.

Table 5. Results of Linear Regressions for the Study of the Ozone Trend During Different Seasons

		Ozone Trend, ppbv yr ⁻¹	std	R-Square
1997–2004 ^a	winter	-1.46	0.41	0.81
	spring	-1.87	0.37	0.89
	summer	-1.82	0.44	0.85
	fall	-1.38	0.16	0.94
1998–2002 ^b	winter	-2.77	0.30	0.97
	spring	-4.90	0.91	0.94
	summer	-4.03	0.53	0.95
	fall	-2.54	0.71	0.76

^aOverall trend exists for 1997–2004; 2003 was considered a temporary interruption.

^bOzone trend for 1998–2002.

the subperiod the slopes are much higher than for the whole period, with ozone concentrations declining by 4 to 5 ppbv per year in spring and summer. Moreover, the observed ozone trend is not affected by any interannual changes of circulation patterns (mostly between NE and NW) and this is supported by the similar rates of ozone decrease when discriminating the data based on the origin of the air masses (1.8 and 1.4 ppbv yr⁻¹ for NE and NW, respectively).

[34] The negative ozone trend observed at Finokalia station is in line with the reduction in emissions of ozone precursors and mainly NO_x [TOR-2, 2003; TROTREP, 2004]. A decrease in NO_x of the order of 30% is reported for a number of sites over central Europe in the 1990s [EEA, 2004a]. Indeed, during 1990–2000 a reduction of similar magnitude occurred in 15 western/central European countries (28%) and in 10 accession countries (30%) located in eastern Europe [EEA, 2004a]. Although the emissions reduction in western/central European countries is rather homogenous, the picture is not that clear for the extended eastern European area since apart from the reduction in the 10 accession countries, an increase is observed for Turkey emissions [Solberg *et al.*, 2005], while exact inventories for Russia are not available. Concerning the NO_x emissions in Greece, Kalabokas *et al.* [1999] comparing the periods 1988–1990 and 1995–1997, have calculated changes at three stations in Athens (from +3.2% to -26.1%), while in Greece an overall increase of 9.7% (1990–2002) has been reported [EEA, 2004b].

[35] The relation between ozone decline and emissions reduction is also investigated in a few modeling studies. Solberg *et al.* [2005] using a regional scale CTM modeled the change in ozone levels resulting from the reduction in the total European anthropogenic emissions of NO_x and VOC (24% and 33%, respectively) from 1990 to 2000, and found a 15 ppb decline in ozone peak values in Nordic countries, in line with observations. Similarly, Derwent *et al.* [2003] using a photochemical trajectory model analyzed the observed changes in ozone levels in UK and estimated that a downward trend of ozone up to -3.4 ppb yr⁻¹ can be attributed to changes in the emission of VOC, SO₂, CO, and NO_x during the 1990s.

[36] The present study has shown that a certain number of parameters, namely, NO, NO_z, w_{ss}, RH, and W explain a significant part of ozone variability. However, no explanation for the observed interannual trend could be provided by the multiple regressions, since no significant trend was revealed for the measured parameters. Therefore we investigated the

influence on ozone interannual variability of the changes in the direction of the air masses arriving at the station.

[37] The monthly ozone anomaly calculated as the deviation of ozone monthly means per year from the 1997–2004 mean of each month was compared to the corresponding anomalies of air mass origin (wind direction anomaly). Interesting results were revealed for the NE and NW sectors as seen in Figure 9. Therefore it seems there is some link between the interannual trend of ozone levels and the changes in the air mass origin. The more characteristic case is during the period May 2002 to March 2003 when the abrupt decrease of the NE winds occurrence was reflected in a decrease in ozone (Figure 9a). At the same time an increase in the NW winds was observed (Figure 9c). The change of the air mass origin followed the extreme weather phenomena taking place over Europe in 2002. Extended natural damage in considerable parts of central and southern Europe took place during the first half of August 2002. Devastating floods that occurred in the Russian Black Sea coast, in Saxony, and in the Czech Republic, as well as incessant precipitation in many other countries (e.g., 312 mm rain in 24 hours at Zinnwald-Georgenfeld station in Germany) have undoubtedly induced a climatological disturbance in central Europe [James *et al.*, 2004]. Thus the summer of 2002 was rather wet and cold with low photochemical activity. On the contrary, a very dry summer occurred in 2003, which may have partly caused the increase in ozone level (intense photochemical activity).

[38] The ozone response to the changes of wind direction is also evidenced at other periods, for example, around March 1999 when an increase in NW wind occurrences was reflected as a drop in ozone and April 2001 when an analogous decrease of NE wind occurrences was also reflected in ozone concentrations. To investigate this covariance, the correlation coefficients between ozone and wind direction anomalies at a shifted 13-month window were calculated. Each coefficient was attributed at the central month of the 13-month period and the covariance is shown in Figures 9b and 9d. From these diagrams an increased correlation with the NE winds (significant at the 99% confidence level) is observed after November 2001, while the anticorrelation with the NW winds persists over a longer period and becomes significant after August 2000. Periods of significant covariance are also revealed in the beginning of the seven years.

[39] The negative correlation between ozone anomaly and the NW wind occurrence and the positive correlation with the NE winds are more obvious during 2002–2003. These correlations indicate that the change of the prevailing wind patterns from NE to NW in 2002 and 2003 has allowed measurable impact of the extreme events occurred in central Europe on the ozone concentrations at Finokalia station. The absence of detailed information concerning the emissions in eastern Europe prohibits further interpretation of the significant correlation during the rest of the period, and clearly additional investigation is needed.

7. Summary and Conclusions

[40] In this study, a 7-year time series of surface ozone concentrations at Finokalia, Crete, east Mediterranean, has been analyzed in order to investigate the mechanisms that

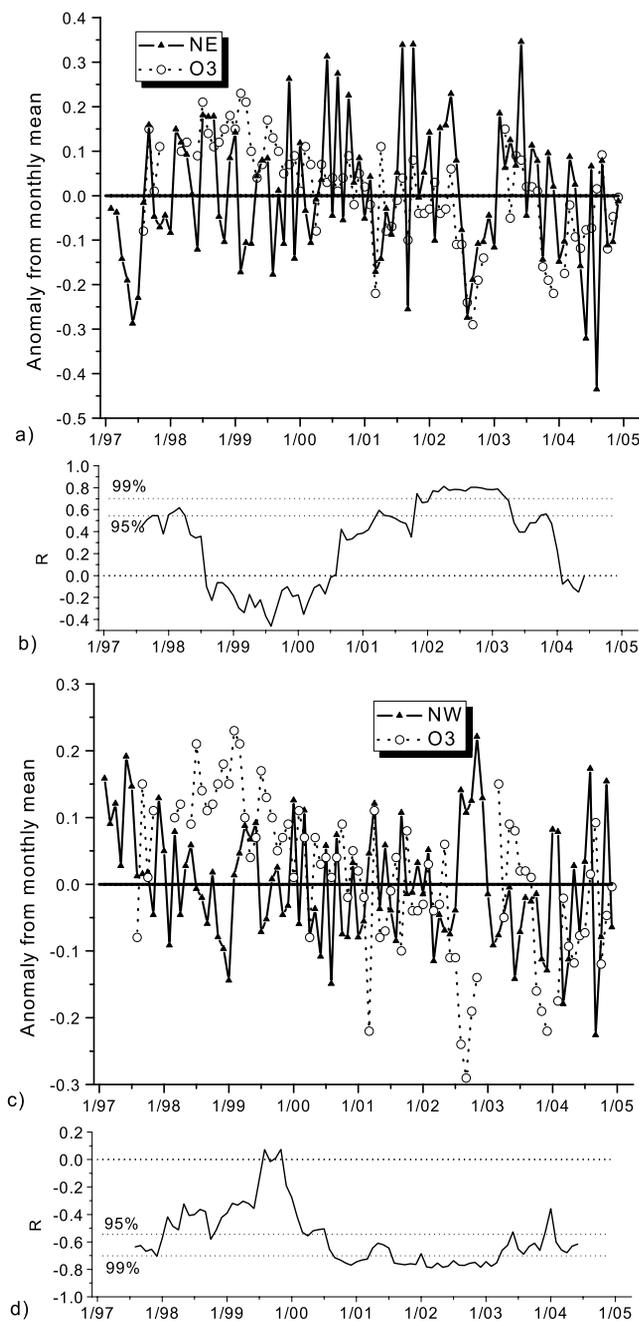


Figure 9. (a) Ozone anomalies: deviations of ozone monthly values from the 1997–2004 mean of each month, $\{O_3(m, y) - \text{mean}O_3(m)\} / \text{mean}O_3(m)$, against the anomalies of occurrence of air masses, $\text{AirMass}\% \text{Occur}(m, y) - \text{mean}\text{AirMass}\% \text{Occur}(m)$, originating from the NE sector (m , month; y , year). (b) Correlation coefficients between ozone and air mass origin anomalies (see text). The 95% and the 99% confidence levels are also plotted. (c) Ozone anomalies against the anomalies of occurrence of air masses (as in Figures 9a and 9b) originating from the NW sector (m , month; y , year). (d) Correlation coefficients between ozone and air mass origin anomalies for the NW sector. The 95% and the 99% confidence levels are also plotted.

control ozone levels and variability in the area. The abundance of solar radiation in summer indicates that the prevailing conditions in the area favor intense chemical activity; nevertheless, it is shown that for the most of the period transport from the continental Europe is more important. Thus, during summer, the profound prevalence of NE winds and also the peak in wind speed (w_s) (Figure 2c) indicate that summertime high ozone concentrations are transported from northeastern Europe. This is also supported by the rose diagram for Rn which presents a NE maximum pattern similar to that of ozone, demonstrating their common continental origin and the poor covariance between ozone and solar irradiance in summer.

[41] The contribution of the W/SW and local winds becomes relatively important in November, April, and partly in January (Figure 4), in coincidence with the lower wind speed. Thus pollution from regional sources under stagnant conditions affects considerably Finokalia station. The secondary peaks of NO and NO_z in May and February, respectively, are linked to local emissions by fuel combustion and the same sources are also responsible for the January–February peaks of BC (Figure 2b).

[42] The mechanisms controlling the seasonality of ozone have been presented in the previous paragraphs. The higher frequency variability of ozone (in the order of few days - meteorological condition changes) has been also described by means of the two equations provided in section 4, derived from multiple regression analysis, denoting W, NO, NO_z, RH and w_s as the most important predictors. However, the interannual variability of ozone cannot be reproduced mainly because no trends are observed in the relevant parameters. The observed interannual variability of ozone is characterized by mainly three features: a decreasing trend throughout the period under study (1997–2004), a shift of the maximum from summer to spring from 1997 to 2002 and a gradual change in the amplitude and width of the annual cycles.

[43] Observed ozone decline for the whole period (1997–2004) was $1.64 \pm 0.15 \text{ ppbv yr}^{-1}$, or 3.1% per year, while when trends were derived for the subperiod 1998–2002 a decrease of $3.4 \pm 0.2 \text{ ppbv yr}^{-1}$, or 5.6% per year was revealed. Compared to the decline ozone trends reported for a number of background stations by Vingarzan [2004], the observed trend at Finokalia is much more intense (the different time periods should be noted). Taking into account that the main mechanism of ozone control, especially during summer when maximum concentrations are typically observed, is found to be transport from the European continent, then the observed trend reflects the emissions reduction that has occurred over Europe during the last decade. The reduction in NO_x of 28% and 30% for 15 western/central and 10 eastern European countries, respectively [EEA, 2004a], could have caused the decline in ozone annual mean levels at Finokalia by 20% between 1998 and 2002. However, this relationship should be considered with caution since: (1) the response of ozone to ozone precursors changes is not linear, (2) the effect is not spatially simultaneous but transport processes are involved, and (3) similar emissions reduction are not observed in Greece. Ozone trends were also calculated for all seasons separately and for the whole period (1997–2004) ozone declined more rapidly in spring ($-1.87 \text{ ppbv yr}^{-1}$) and summer ($-1.82 \text{ ppbv yr}^{-1}$). When

only the 1998–2002 period is considered, then the maximum drop is again observed for spring and summer, but with much higher rates (-4.9 and 4.03 ppbv yr⁻¹, respectively). The weakening of spring ozone concentrations has been observed at other European surface ozone stations as well [Schuepbach et al., 2001; TROTREP, 2004], while the summertime ozone decline follows the discussion of emissions reduction and is in agreement with our conclusions on the role of transport from continental Europe during summer.

[44] In parallel with the ozone decline, a shift of the maximum concentrations from summer (1998) to spring (2002) has been also observed. This shift is actually induced by the continuous weakening of the summer mode in ozone concentrations until 2002. Actually, during all August months the average ozone concentration is 15–20 ppbv higher than that in August 2002. The weakening of the summer mode is attributed to emissions reduction in the main European continent. This indicates that summer ozone concentrations at Finokalia station could provide a useful tool to the identification of changes in European emissions. Apart from the shift of the maximum ozone concentrations from summer to spring as a consequence of the summer mode weakening, a change to the pattern of ozone annual cycle was revealed which is illustrated via the decrease in both the amplitude and the width of each cycle.

[45] The exceptionality of year 2002 has been demonstrated, and the main feature is that it presents a clear spring maximum. During the period May 2002 to March 2003 a rapid decrease of the NE winds occurrence was observed in parallel with an increase in the NW winds, inducing an analogous reduction in ozone. The change in the wind flow enabled the climatic disturbance in central Europe to affect the surface ozone levels at Finokalia.

[46] Therefore the current analysis demonstrated the following: (1) Transport from the continental Europe is the main mechanism that controls ozone levels in the eastern Mediterranean. (2) The role of local photochemistry and pollution becomes important at Finokalia station under western flow and stagnant wind conditions. (3) Observed ozone decline trends in the eastern Mediterranean reflect the emissions reduction of precursors in the main European continent. (4) Climatological disturbances and precursor trends seem to be adequately captured by surface ozone concentrations at Finokalia station, providing useful evidence on European emission changes.

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- E. Gerasopoulos, M. Kanakidou, G. Kouvarakis, N. Mihalopoulos, and M. Vrekoussis, Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, 71409 Heraklion, Greece. (mihalo@chemistry.uoc.gr)