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Origin and variability of particulate matter (PM_{10}) mass concentrations over the Eastern Mediterranean

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Abstract

Five-year PM_{10} concentrations (2000–05) at Heraklion (urban), Crete, and concurrent measurements of TSP and PM_{10} (2001–02 and 2004–05, respectively) at Finokalia (background) have been used to discriminate between the various sources of PM over the area and investigate the factors that control their levels. PM_{10} concentrations at Heraklion ($51 \pm 33\,\mu g\,m^{-3}$) and Finokalia ($28 \pm 30\,\mu g\,m^{-3}$) lie within the range found for urban and background-rural sites in the Eastern Mediterranean, respectively. Special focus has been given to the influence of transported dust from N. Africa, which is found to be more frequent during spring and fall. The additional effect from local sources has been also calculated at Heraklion (about $20\,\mu g\,m^{-3}$). The EU limit of $50\,\mu g\,m^{-3}$ is exceeded at Heraklion, one in 4 days, during winter and spring (50% due to transported dust) and half of the days during summer and fall (pollution). At Finokalia exceedances are observed in winter and spring during one in 5 days, 80–100% of which are associated with dust events. The mass balance estimation for periods with no influence from dust shows that ions dominate the PM_{10} mass (40–60%) with dust and particulate carbonaceous matter (PCM) comprising the rest. During the identified dust outbreaks, the contribution of dust rises to 60–65%, while the contribution of ions declines to 30% and only 10% is PCM.

Keywords: Particulate matter (PM_{10}); Chemical mass balance; Eastern Mediterranean

1. Introduction

Particulate matter (PM) levels have been monitored during the past decade, mainly because of their effects on health and climate. Aerosols are introduced into the atmosphere from a variety of anthropogenic (transport, industrial activities, biomass burning, etc.) and natural sources (volcanic eruptions, sea salt, soil dust suspension, natural forest fires, etc.). Both sources result in direct emission of PM (primary PM) and emission of gaseous aerosol precursors (leading to secondary PM). In IPCC (2001), it is reported that 3400 million tons of PM are emitted on a global scale per year, with anthropogenic sources responsible for 10% and natural primary particles the other 85%.

A number of epidemiological studies have examined the impact of PM on human health, expressed as increased mortality and morbidity (e.g., Schwartz

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et al., 1996; Dockery and Pope, 1996), varying according to the physical (size, shape, etc.) and chemical (composition) characteristics of the PM (Van Dingenen et al., 2004).

The PM impact on climate is primarily a cooling effect due to increased scattering to space as the atmospheric aerosol burden increases. According to IPCC (2001), the overall cooling by aerosols might be equivalent to a radiative forcing of up to $-2.5\,W\,m^{-2}$, counterbalancing global warming by greenhouse gases (GHGs). Moreover, the indirect effect of atmospheric aerosols on climate, by acting as cloud condensation nuclei (CCN) (e.g., Levin et al., 2003), could be even more important than the direct effect. In addition, particles reduce visibility and play a significant role in the deterioration of monuments and buildings.

The European Union Directive 1999/30/CE has proposed the regulation of the PM_{10} concentrations in two stages: (a) a limit on the annual average concentration of $40\,\mu g\,m^{-3}$ and a 24-h average of $50\,\mu g\,m^{-3}$, not to be exceeded more than 35 times per year by the year 2005; (b) the limit on the annual average is decreased to $20\,\mu g\,m^{-3}$, while the $50\,\mu g\,m^{-3}$ limit should not be exceeded more than 7 times per year, by the year 2010. In all cases, the contribution of natural sources may be excluded, so that exceedances are only related to anthropogenic emissions.

A European aerosol phenomenology reporting on physical and chemical characterizations of the PM in Europe is found in Van Dingenen et al. (2004) and Putaud et al. (2004), respectively. In these studies, data coverage is confined mostly to western European sites while less information is given for sites around large natural PM sources such as the Mediterranean basin, which is influenced by arid and semiarid regions in North Africa (e.g., Sahara and Sahel deserts). Moreover, measurements over the Mediterranean show a distinct inhomogeneity. In particular, a significant number of studies for various site types (background, rural, urban, etc.) have taken place in the Western Mediterranean (e.g., Viana et al., 2003), focusing on the full chemical characterization of the PM (e.g., Querol et al., 2001) and on the influence of dust events (e.g., Rodriguez et al., 2001). In contrast, studies in the Eastern Mediterranean are rather limited most of them being confined to PM or total suspended particle (TSP) levels in big cities (e.g., Ganor and Foner, 2001; Chaloulakou et al., 2003; Karaca et al., 2005; Dayan and Levy, 2005). Besides, the monitoring of PM levels is usually performed during short periods and with a temporal resolution not better than 24 h (Bardouki et al., 2003; Smolik et al., 2003), which does not allow the evolution of certain pollution or dust transport events to be followed. Thus, further knowledge is required regarding background levels, the mechanisms that control atmospheric levels and the chemical characteristics of the PM in the Eastern Mediterranean.

This study aims to identify the factors that control PM levels in the region. It combines data sets from an urban and a natural background station to ascertain the role of local sources and to provide background concentration levels. The high temporal resolution (5 min) of the data provides the opportunity to investigate, in real time, the evolution of pollution episodes and dust events. Further, a first attempt to estimate the mass balance of PM during dust and non-dust periods is made. The study is structured as follows:

- presentation of PM_{10} levels, annual and inter-annual trends;
- analysis of limit exceedances and origin/sources of PM;
- comparison between urban and background station measurements to ascertain the role of local sources over background fluctuations;
- study of the influence of various processes on the diurnal variability of PM_{10};
- mass balance estimation during dust and non-dust periods.

2. Experimental

2.1. Sampling and analysis

The mass concentration of PM with aerodynamic diameter lower than $10\,\mu m$ (PM_{10}) is routinely monitored at two sites on the island of Crete, Greece in the Eastern Mediterranean. One is an urban site at Heraklion (35°19′N, 25°8′E), the largest city on the island, the other is a natural background site at Finokalia (35°20′N, 25°40′E), a remote coastal site in the northeast part of the island. The Finokalia station is situated 70 km northeast of Heraklion and a description of the site is given by Mihalopoulos et al. (1997). According to the criteria proposed by the Europen Environment Agency (Larssen et al., 1999), Heraklion and Finokalia are characterized as ‘‘urban’’ and ‘‘natural background’’ stations, respectively.

The PM_{10} mass at both the sites was monitored with an Eberline FH 62 I-R (Eberline Instruments GmbH) particulate monitor, designed to measure continuously the mass concentration of the suspended particles in ambient air based on β-attenuation. The FH 62 I-R performs direct mass collection and simultaneous measurement during sampling on a glass fibre filter (type GF 10) by a two-beam compensation method and single filter-spot position. The air flow rate is $1\,m^3\,h^{-1}$ and measurement of PM_{10} mass is conducted in the range 0–$5000\,g\,m^{-3}$ with a resolution of $1\,\mu g\,m^{-3}$. The short time resolution of 5 min permits the determination of variations in particulate concentration in real time. Both instruments have been compared against gravimetric techniques (filters and VI impactors) with very good agreement (slope 1:1; Koulouri et al., 2005). At Heraklion, the PM_{10} mass monitor is located outside the city centre, on top of the roof of one of the highest buildings, 2 km from the sea shore. At Finokalia, the sampling is performed 3 m above ground.

To understand the origin and the processes that control PM at Heraklion, two aerosol-sampling campaigns have been performed (8–27 September 2001 and 12–30 April 2002). During these campaigns, filter samples have been collected and analyzed for main ions, organic and elementary carbon using Teflon and Quartz filters, respectively. The duration of the sampling was 24 h during the first campaign (15 samples) and 6–12 h during the second campaign (52 samples).

During the period February 2001–April 2002, major ions were also quantified in a series of samples exceeding the $50\,\mu g\,m^{-3}$ level, using the glass fibre filters of the FH 62 I-R particulate monitor.

A comprehensive description of the IC measurements and the methodology for the filter analysis can be found in Kouvarakis and Mihalopoulos (2002). Analysis for both elemental (EC) and organic carbon (OC) was performed at JRC-Ispra using a multi-step flash heating technique, where evolved carbon was oxidized in CO_2 and measured with an NDIR detector, as described in Putaud et al. (2000).

3. Results

3.1. Data presentation

PM_{10} measurements at Heraklion cover the period November 2000–September 2005, while at Finokalia they cover the period September 2004–September 2005. The time resolution of the measurements was 5 min and both hourly and daily averages were computed for the needs of the current analyses. At Finokalia, TSP concentrations are also available for the period May 2001–June 2002 with a resolution of 2 days on average. All measurements are presented in Fig. 1.

The average of the PM_{10} daily means at Heraklion for the whole period was $51 \pm 33\,\mu g\,m^{-3}$. During 2004–05 at Finokalia, the average was $28 \pm 30\,\mu g\,m^{-3}$ (average $\pm$ standard deviation) while the TSP average for the period 2001–02 was $36 \pm 37\,\mu g\,m^{-3}$. The mean annual cycle of PM_{10} at Heraklion (medians) shows modest variability with distinct peaks in July and October, while at Finokalia relatively enhanced levels are found during the period March–October (not shown). At both sites, the use of averages instead of medians depicts the influence of dust during the transition seasons (spring–fall). In Table 1, a brief overview of PM measurements with emphasis on areas around the Mediterranean is given to allow comparison with the PM levels reported in this study. Taking into account that different time periods are covered by each study, the PM_{10} levels at Heraklion lie within the range found for urban areas in the Eastern Mediterranean while Finokalia has levels typical for background rural sites.

As shown in Fig. 1, increased PM_{10} levels are observed at Heraklion after 2003. A mean of $44 \pm 21\,\mu g\,m^{-3}$ is calculated during 2000–02 and $58 \pm 40\,\mu g\,m^{-3}$ during 2003–05, a difference significant at the 99% confidence level (t-test, $p = 4 \times 10^{-14}$). In particular, 2003–04 concentrations are higher by 46% compared with 2001–02 levels, while in 2005 values declined. Desert dust transported from Africa (see below) or changes in the precipitation rate cannot explain the enhanced levels of PM_{10} observed during the 2003–04 period. Thus, enhanced PM levels in 2003–04 are most likely due to pollution. It is difficult to assess whether or not this pollution is locally produced or arises from long-range transport. Unfortunately, no concurrent PM_{10} data exist for Finokalia; however Gerasopoulos et al. (2005) examined long-term measurements of ozone at Finokalia and showed that the heat wave over central Europe in 2003, combined with intensified wind transport during summer, had raised pollution levels in the area.

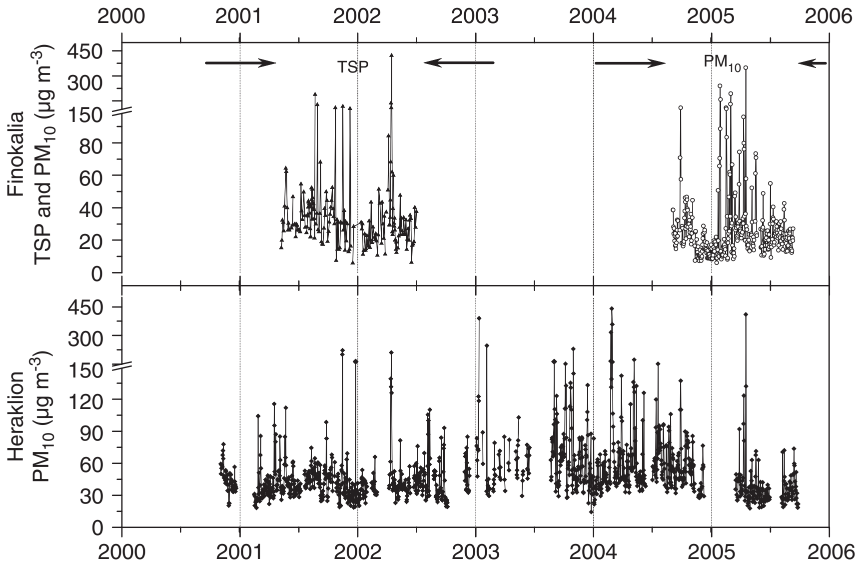

Fig. 1. PM_{10} and TSP measurements at Finokalia (upper panel) and PM_{10} at Heraklion (lower panel) during the period November 2001–September 2005.

Table 1
Annual means of PM_{10} levels reported for different type of sites (background, rural, urban, etc.) grouped by geographical location

Area	Location	Type of location	Period	Reported values ($\mu g\,m^{-3}$)	Source
Eastern Mediterranean	Crete	Background	2004–05	28 ± 30	This study
	Crete	Urban	2000–05	51 ± 31	This study
	Athens	Urban	1999–2000	75	Chaloulakou et al. (2003)
	Instanbul	Urban	2002–03	47	Karaca et al. (2005)
	Tel Aviv	Urban	2000–02	57	Dayan and Levy (2005)
SW Europe	S & E Spain	Rural	1996–99	18–30	Rodriguez et al. (2001)
	C. Spain	Urban	1999–2000	41	Querol et al. (2001)
	NW Spain (Basque)	Background	1996–2000	16	Viana et al. (2003)
	NW Spain (Basque)	Urban	1996–2000	25–30	Viana et al. (2003)
	NW Spain (Basque)	Industrial-traffic	1996–2000	35–50	Viana et al. (2003)
Europe	Continental Europe	Background	1994–2001	7 ± 4	Van Dingenen et al. (2004)
	Continental Europe	Rural	1996–2000	10–25	Van Dingenen et al. (2004)
	Continental Europe	Near city/urban	1996–2000	20–45	Van Dingenen et al. (2004)
	Continental Europe	Kerbside	1996–2000	35–55	Van Dingenen et al. (2004)

3.2. *Factors controlling PM_{10} levels over Crete*

3.2.1. *Origin of PM*

The daily averages of PM_{10} at Heraklion were sorted by wind direction and are shown in Fig. 2. The choice of the sectors is described in detail by Mihalopoulos et al. (1997) and Kouvarakis et al. (2000). The identification of the wind direction was based on 5-day back-trajectories calculated by the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Hess, 1998). Both averages and medians of PM_{10} given in Fig. 2 show a distinct enhancement when air masses arrive from the SE–S–SW direction. This fact suggests that dust arriving often from deserted areas in N. Africa (e.g., Sahara) should contribute significantly to PM levels over the area. The PM_{10} concentrations related to the south sector are about 70 $\mu g\,m^{-3}$ and it is very important to notice that the 24-h limit of 50 $\mu g\,m^{-3}$ is exceeded more than half of the time during southerlies. Moreover, the increased standard deviation indicates the potential for different dust loadings over the area depending on the intensity of the dust events that may result in mean daily values over 140 $\mu g\,m^{-3}$. The situation is more consistent for air masses from the NW–N–NE sectors giving values in the range of 40–50 $\mu g\,m^{-3}$. Overall, it is shown that increased PM levels over the area are observed when southerlies prevail, demonstrating the role of dust particles carried from N. Africa under these conditions.

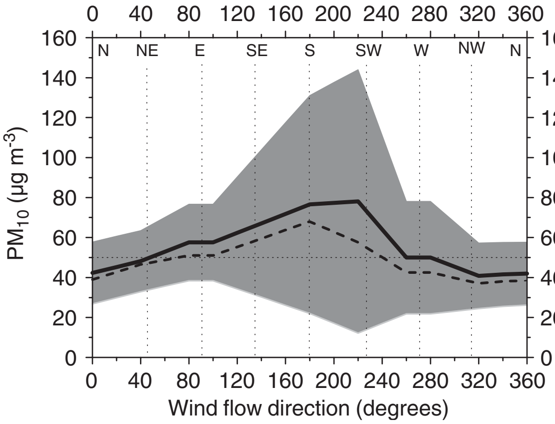

Fig. 2. Average (continuous line), median (dash line) and standard deviation (grey area) of PM_{10} concentrations at Heraklion for the period November 2000–September 2005 sorted by wind flow direction.

3.2.2. Limit exceedances

A statistical analysis on the frequency of days with PM_{10} concentration exceeding the 24-h limit of 50 $\mu g\,m^{-3}$ has been performed (Fig. 3). At Heraklion and for the period December–June about one in four of the days show a mean daily PM_{10} concentration above the limit. Between January and May, the limit is also exceeded at Finokalia during ~20% of the days. The situation is entirely the opposite between July and November. At Heraklion a limit exceedance is observed during 40–55% of the days (1 out of 2 days), while at the same time at Finokalia PM_{10} values stay constantly below the limit. The analysis has been repeated for Heraklion (denoted as Heraklion CP—Common Period) during the period that measurements were available also at Finokalia (September 2004–September 2005). Even though common data do not cover the whole year, the results show a resemblance with Finokalia limit exceedances and only in September a difference is observed (possible reasons are discussed in Section 3.4). The origin of the high PM loading is shown at the upper panel of Fig. 3 as the percentage of the days exceeding 50 $\mu g\,m^{-3}$ for which back-trajectories suggest the occurrence of transported dust from the south (North Africa). At Heraklion an average of 40% of the limit exceedances might be due to transported dust throughout the year, excluding summer when the percentage is only 6%. Especially during

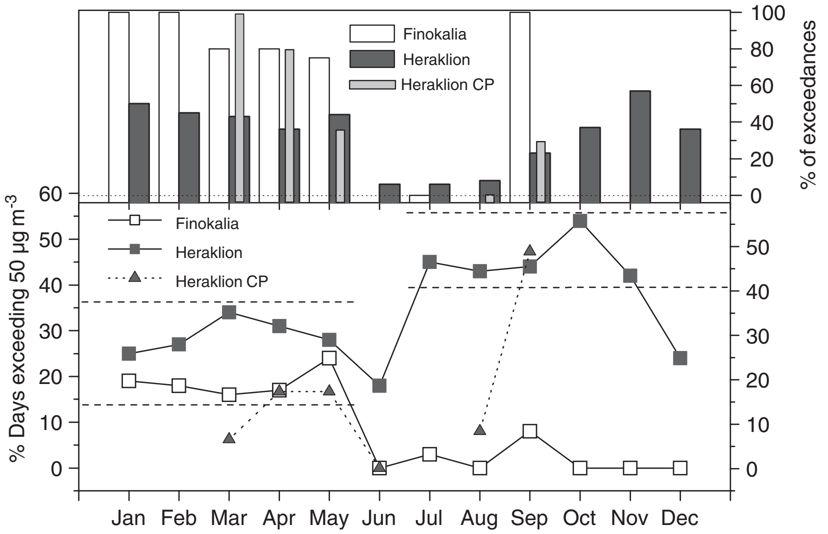

Fig. 3. Lower panel: percentage of the days with PM_{10} concentrations higher than the 50 $\mu g\,m^{-3}$ limit (per month). Upper panel: percentage of the exceedances that is attributed to dust events. Statistics are based on November 2000–September 2005 measurements at Heraklion and September 2004–September 2005 at Finokalia. The same analysis is repeated for Heraklion during the common period September 2004–September 2005 denoted as CP (Common Period).

July–September, when almost half of the time PM_{10} concentrations are above 50 μg m^{-3}, pollution is responsible for most of the PM_{10} exceedances observed at Heraklion. In March and April 2005 (CP) the contribution of southerlies, and thus of possibly dust-enriched air masses, is as frequent in Heraklion as in Finokalia. Finally, the vast majority of the less-frequent exceedances at Finokalia are related to air masses coming from the south.

3.3. Relation between the urban (Heraklion) and the background (Finokalia) sites

3.3.1. Comparison between PM at Heraklion and Finokalia

Frequency distributions of the PM_{10} daily averages at the two stations were calculated and log-normal distributions were fitted on the resulting points (not shown). A broader distribution is found for Heraklion shifted to higher values as expected. The central value of the log-normal distribution at Heraklion is 41.7±0.4 μg m^{-3}, while at Finokalia it is 20.7±0.4 μg m^{-3}. When the fitting is applied on the CP of measurements at the two sites (September 2004–September 2005), no change to the patterns is revealed and the same difference (21 μg m^{-3}) is calculated, indicative of the additional influence of the urban environment.

The regression line between the PM_{10} concentrations at the two sites is presented in Fig. 4 and a high correlation ($R^2 = 0.84$) is revealed. The significant correlation, in combination with the slope of 1.12, shows that the PM_{10} variability at Heraklion is controlled by the background levels, while the intercept of 15 μg m^{-3} demonstrates the influence of the city effects. Linear regressions were also applied for each month separately. In spring, a slope of 0.96±0.18 and an intercept of 11±4 demonstrate the common fluctuation of the PM levels at both Heraklion and Finokalia due to long-range transported aerosols that affect the regional background (spring data enclosed in the dotted curve in Fig. 4 lie near the 1:1 line). Similar conclusion is deduced with data from the south sector, which have a slope of 1.08 ($R^2 = 0.98$). In summer and fall, the slope rises to 1.41±0.14 with an intercept of 19±3 that may result from the influence of local pollution as also revealed by the frequency distributions. The above results clearly indicate the dominant role of: (i) regional background in controlling PM loads at both the locations and (ii) long-range transported dust.

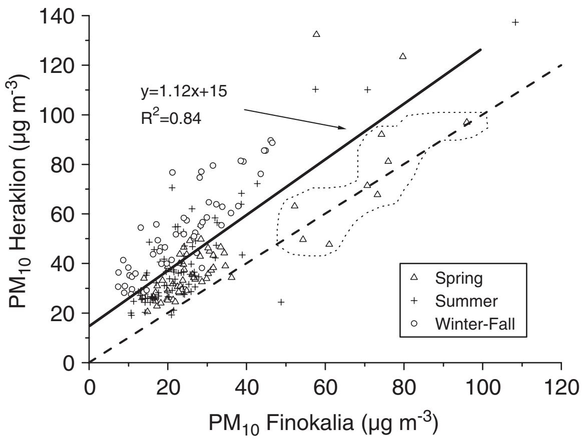

Fig. 4. Scatterplot between PM_{10} at Finokalia and Heraklion. Different symbols are used for each season (see internal label) and a linear regression line is fitted to the data (continuous line). The dotted curve includes spring data that lie near the 1:1 line.

3.3.2. Example of the simultaneous influence of dust on both the sites

During dust events that influence simultaneously the two sites, characteristic common fluctuations of PM_{10} are observed. The evolution of such an event can be observed during April 2005 (Fig. 5). At the beginning of the period (10–12 April), a moderate event is observed with maximum values up to 250 μg m^{-3} (hourly values) as a result of S–SE winds. The wind direction changed gradually to the west inducing lower loads (below the 50 μg m^{-3} limit), while on 16 and 17 April, one of the most intense events over the last years took place with trajectories indicating air masses from the south. Maximum values at Finokalia reached 2500 μg m^{-3}, while at Heraklion the upper limit of the instrument (1000 μg m^{-3}) was reached.

3.4. Diurnal variability of PM

The diurnal variability of PM_{10} concentrations at the two sites is extracted from the hourly values (Fig. 6a, note the different scale for the two sites). At Heraklion two peaks are found, one at mid-day (9:00–13:00 LT) and the other in the evening (18:00–23:00 LT). In Fig. 6b the seasonality of the amplitudes of these two peaks denoted as A_{day} and A_{night}, respectively, are presented. A_{day} presents a summer maximum while A_{night} maximizes in winter.

The A_{night} peak of PM_{10} coincides with the respective peaks of CO and SO_2 (unpublished). Since both CO and SO_2 are indicators of combustion processes, the nighttime peak in winter is

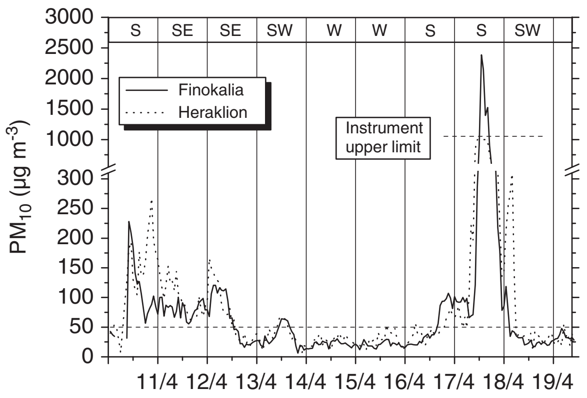

Fig. 5. Simultaneous evolution of PM_{10} concentrations (hourly values) at Heraklion and Finokalia for the period 10–20 April 2004, for which a moderate (10–12 April) and the most intense event (17 April) of the whole period are shown.

associated with local pollution (central heating, secondary traffic peak). The low-speed wind conditions and the temperature gradient in winter result in a low MBL that traps pollution. In summer, more intense winds and higher MBL result in low A_{night}, while local pollution or pollution transported from the north seems to be the origin of the summer mid-day peak A_{day}.

At Finokalia, a simple-mode diurnal pattern occurs with enhanced levels during daytime (amplitude ~4 $\mu g\,m^{-3}$; Fig. 6a). No particular seasonality concerning the amplitude of the diurnal cycle is found and the early morning (6:00–8:00 LT) enhancement of the PM_{10} levels in spring and summer is the only remarkable feature. The fact that this early morning peak coincides with the increase of NO_x at Finokalia (Fig. 2b in Gerasopoulos et al., 2006) probably demonstrates the effect of regional sources of pollution. The second peak (10:00–12:00 LT) coincides with the increase in ozone (Fig. 2a in Gerasopoulos et al., 2006) and is thus linked to regional photochemical activity.

4. Chemical characterization of PM with focus on dust

A number of PM_{10} limit exceedances are isolated at Heraklion and special focus is given to their chemical characterization. During the period February 2001–April 2002, nine major exceedances were studied in detail (Fig. 7a) and for each case a number of 2–13 samples have been analyzed for ionic composition including nss-Ca^{2+} for the identification of the influence from dust. Previous studies in the area have demonstrated the use of nss-Ca^{2+} as a tracer of crustal aerosols (Sciare et al., 2005). In addition, two intensive campaigns took place in fall 2001 (1 September–15 October) and spring 2002 (12–30 April) during which apart from ionic composition, OC and EC were measured. Thus, three main components of PM were derived: (i) main anions and cations; (ii) particulate carbonaceous matter (PCM) as the sum of EC and particulate organic matter (POM) = 1.4OC (Putaud et al., 2000); and (iii) dust estimated from Ca^{2+} using a dust/Ca^{2+} ratio of 10.9 based on experimental data (Sciare et al., 2005). The contribution of the different components was investigated (mass balance estimation) during dust and non-dust periods. In the fall, the dust event of the 25–27 September was chosen for the mass balance estimation, while as a case of non-dust period, samples during 8–11 September 2001 were taken (Fig. 7b). For spring, we investigated the event of 12–17 April 2002, and the period 24–28 April 2002 was used as the non-dust case (Fig. 7c).

(a) *Ca^{2+} vs PM_{10}*: A very good correlation between PM_{10} and Ca^{2+} during all nine cases depicted in Fig. 7a is revealed, with Ca^{2+} possessing 2–5% of the PM_{10} mass on average (Fig. 8). For the intense event that took place between 15 and 16 April 2002, Ca^{2+} contributed 8–12% of the PM_{10} mass, probably indicating a different dust source. Indeed, several studies (e.g., Chiapello et al., 1997) report that the content of Ca^{2+} in airborne dust depends on the source area (northern Sahara or sub-Sahara and Sahel).

(b) *Mass balance estimation between dust and non-dust periods*: The mass balance estimation and the comparison of the components summation with the PM_{10} mass is presented in Fig. 9. The error bars correspond to the day-by-day variability of the estimated percentages. Similarities are found among the component contributions for the two seasons. For the non-dust periods, a 40–60% of the PM_{10} mass is ions, 20–25% is PCM and 25–35% is dust (Fig. 9a). During the dust periods dust becomes dominant (60–65%) over both ions and PCM, since their contributions are almost decreased by half (30% and 10%, respectively, Fig. 9b). The sum of the components agrees with PM_{10} mass in all cases except for the fall dust event (70%). In the latter case, a significant part of the discrepancy can be attributed to the estimation of the dust.

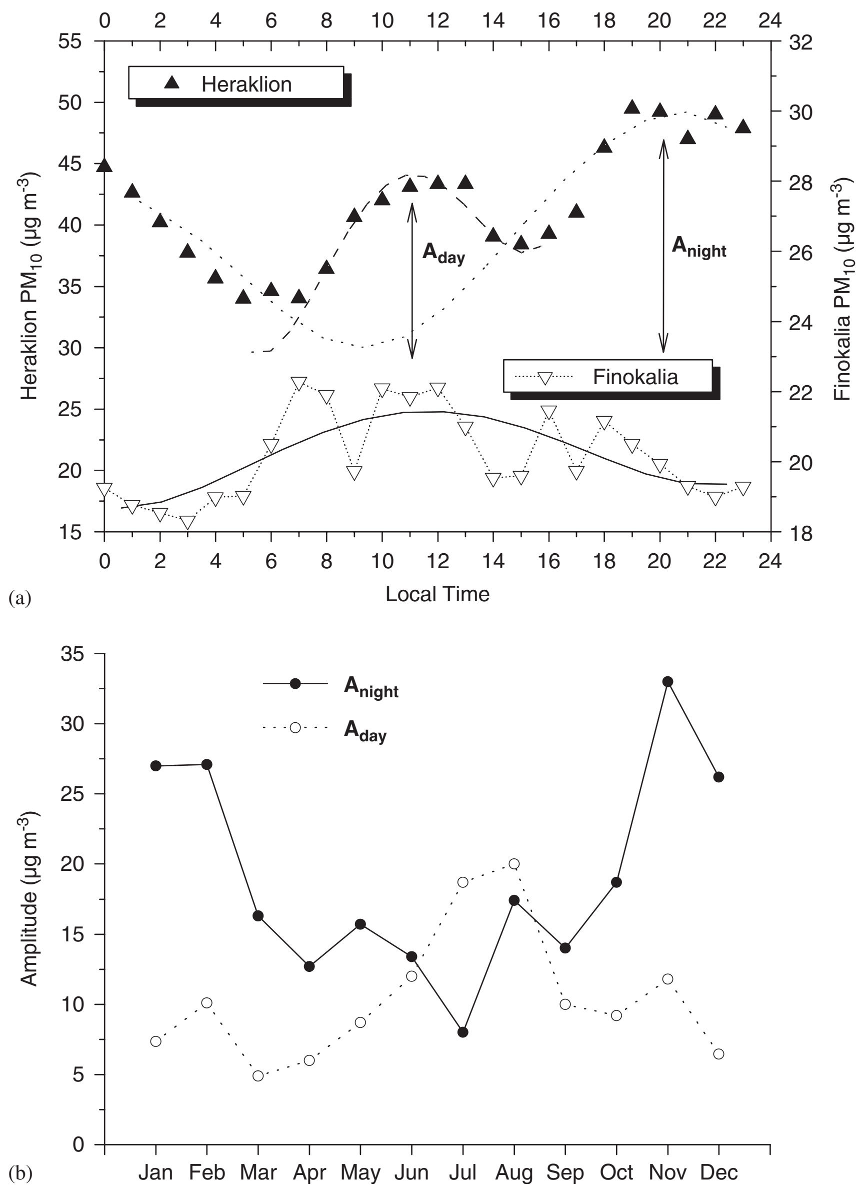

Fig. 6. (a) Average diurnal cycles of PM_{10} concentrations at Heraklion and Finokalia. Polynomial fitted lines are used for the easier visualization of the daily (dash line) and the late evening (dot line) peaks at Heraklion and the general tendency at Finokalia (continuous line). (b) Seasonal variability of the amplitude of the daily (A_{day}) and the late evening (A_{night}) peaks at Heraklion.

Indeed, the indirect dust estimation using the ratio dust/Ca^{2+} may include a considerable uncertainty (up to 40%, Vrekoussis et al., 2005). Based on our calculations, the ratio dust/Ca^{2+} uncertainty may explain deviations between the sum of the three components and the measured PM_{10} from 6% up to 20%, without taking into account the uncertainty of the PM_{10} concentrations. Moreover, the spring dust event presented a different Ca^{2+}/PM_{10} ratio than the general tendency as already shown in Fig. 8.

The results of the two campaigns conducted at Heraklion (urban) may be considered not to be representative of the extended area. However, we note that the PM_{10} monitor at Heraklion is located out of the city centre and that the two campaigns were conducted during periods when differences in PM_{10} levels between Finokalia and Heraklion were small.

During the two intensive campaigns at Heraklion, the mean levels for the main ionic species were

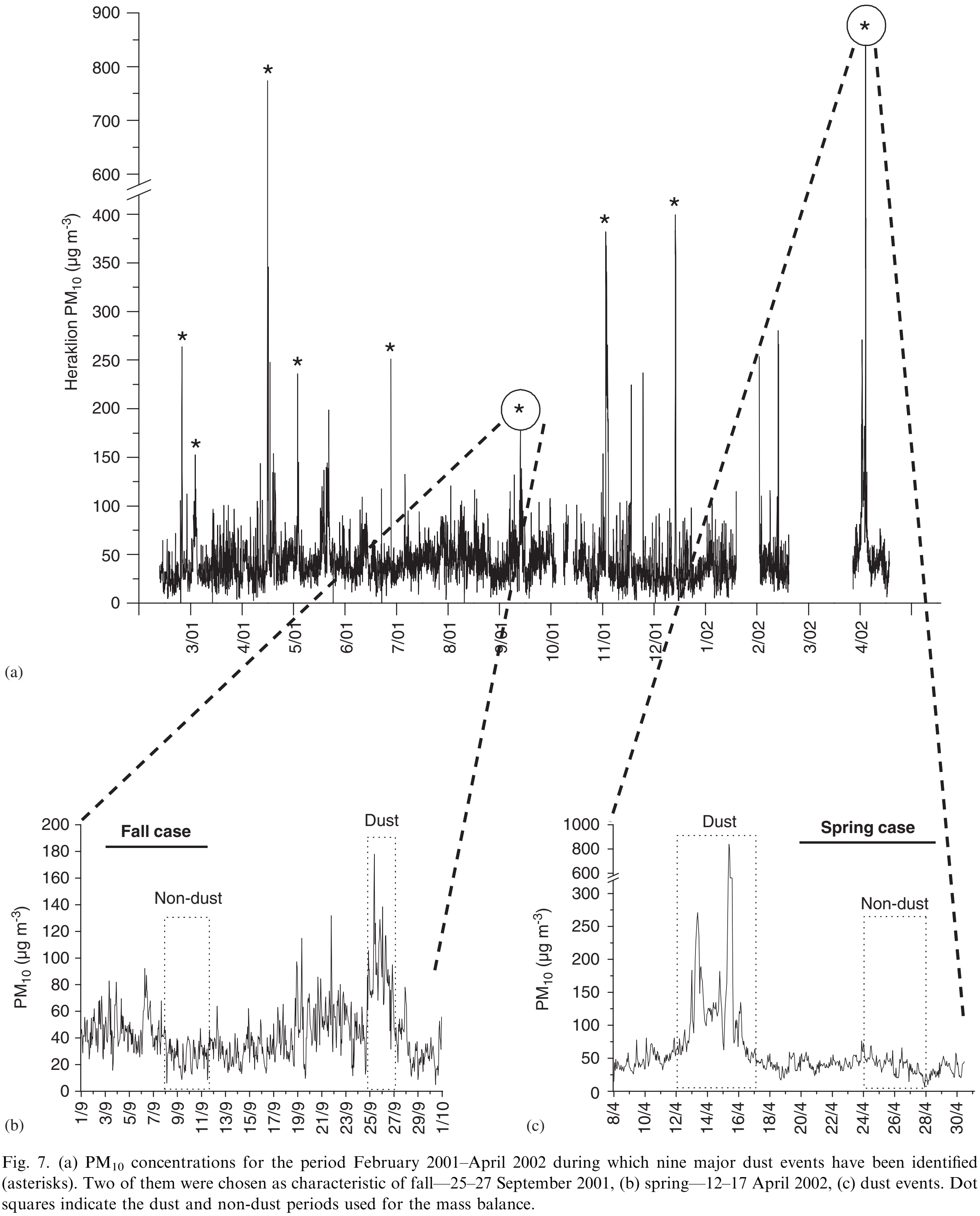

Fig. 7. (a) PM_{10} concentrations for the period February 2001–April 2002 during which nine major dust events have been identified (asterisks). Two of them were chosen as characteristic of fall—25–27 September 2001, (b) spring—12–17 April 2002, (c) dust events. Dot squares indicate the dust and non-dust periods used for the mass balance.

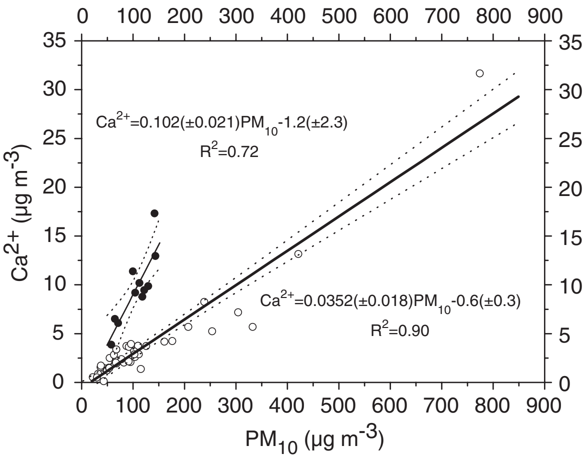

Fig. 8. Scatterplot between PM_{10} and Ca^{2+} during the dust events denoted in Fig. 7a (empty circles). The most intense case during 15–16 April 2002 is presented separately (full circles). Linear regression lines (continuous line) with the standard error of the estimation (dot lines) are also shown.

compared with those observed at Finokalia. No significant differences were found for the main ions, including Ca^{2+}, between the two locations. For EC and OC, no concurrent measurements exist for Finokalia; however PCM cannot account for more than 25% of the total mass. Note that during both campaigns OC significantly correlated to EC, with slope ranging from 3.7 to 4.2 during the spring and fall campaigns, respectively (Fig. 10). Both ratios are above those observed for urban areas (2–3.5; Castro et al., 1999) and in good agreement with the values reported for Finokalia (Bardouki et al., 2003; Sciare et al., 2003) and thus indicative of long-range transport.

5. Conclusions

Five-year PM_{10} concentrations (November 2000–September 2005) at Heraklion, Crete (urban) and 1 year (September 2004–September 2005) at Finokalia (background) have been analyzed in conjunction with complementary chemical composition analyses. The present analysis shows that:

- PM_{10} levels at Heraklion ($51 \pm 33\,\mu g\,m^{-3}$, 2000–05) are within the range found for urban areas in the Eastern Mediterranean, while at Finokalia ($28 \pm 30\,\mu g\,m^{-3}$, 2004–05) typical background levels for rural sites were measured.
- The measurements at both the stations capture in full detail the evolution of dust outbreaks from

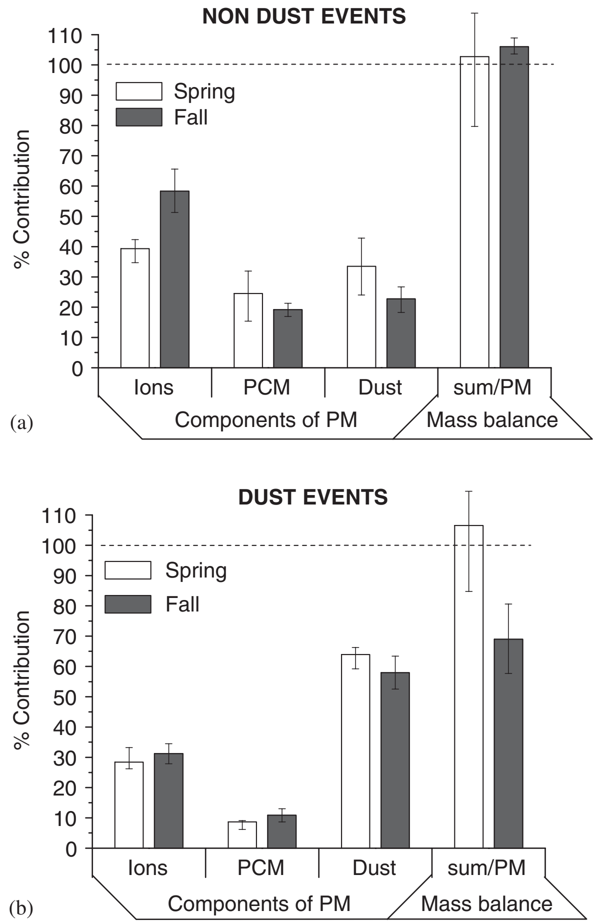

Fig. 9. (a) Mass balance of the particulate matter, during periods in the fall and spring not influenced by dust, comprising the three components namely ions, PCM and dust. Values are given as medians and error bars correspond to 1st and 3rd quartile. (b) The same during the dust cases are denoted in Fig. 7b and c.

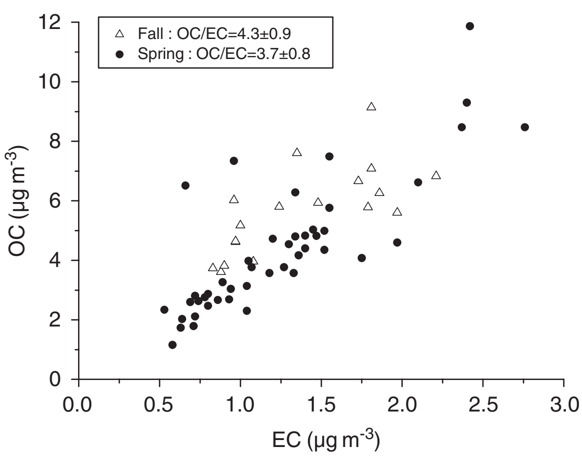

Fig. 10. Scatterplot between EC and OC during 1 September–15 October 2001 and 12–30 April 2002 at Heraklion.

the south that are more frequent in the transition periods (spring–fall). The dust levels at the urban site follow background fluctuations with the effect of local sources (about $20\,\mu g\,m^{-3}$) superimposed.

- The EU limit of $50\,\mu g\,m^{-3}$ (24-h average) is exceeded at Heraklion 1 in 4 days in winter and spring, and half of the days in summer and fall. In summer, the vast majority of the exceedances are attributed to photochemistry of pollutants locally emitted or pollution transported from the north, while almost half of the exceedances are due to dust transport during the rest of the season. During winter and spring at Finokalia, concentrations higher than the limit are observed 1 in 5 days, while in summer and fall the exceedances are not frequent. However, in 80–100% of the cases, the exceedances are linked to dust events.
- An increase of PM_{10} levels in 2003–04 by 46% compared with levels during the period 2000–02 was observed, in agreement with enhanced ozone levels in the area for the same period, as reported by Gerasopoulos et al. (2005). This increase is attributed to the heat wave that influenced central Europe in summer 2003.
- Ions dominate the PM_{10} mass (40–60%) while the rest is shared between dust (25–35%) and particulate carbonaceous matter (PCM) (20–25%), based on mass balance results for periods with no effects from dust. During the identified dust outbreaks, the contribution of dust rises to 60–65%, the contribution of ions declines to 30%, and only 10% is PCM.

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