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STUDY OF SIZE-SEGREGATED PARTICLE (PM_1, $PM_{2.5}$, PM_{10}) CONCENTRATIONS OVER GREECE

E. KOULOURI[1]
G. GRIVAS[2]
E. GERASOPOULOS[1]
A. CHALOULAKOU[2,*]
N. MIHALOPOULOS[1]
N. SPYRELLIS[2]

[1] *Environmental Chemical Processes Laboratory*
Department of Chemistry, University of Crete
P.O. Box 2208, 71003 Heraklion, Greece
[2] *School of Chemical Engineering*
National Technical University of Athens
9, Heroon Polytechniou str., 15780 Zofgrafos, Athens, Greece

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*to whom all correspondence should be addressed:
e-mail: dchal@central.ntua.gr

ABSTRACT
This study reports particulate matter levels of various size fractions (PM_{10}, $PM_{2.5}$, and PM_1) and identify their controlling factors, in various locations over Greece. It combines long-term data sets involving particle concentrations as measured in the island of Crete in the Eastern Mediterranean and the Greater Area of Athens. Measurements were carried out in various sites at urban (Central Athens and Heraklion, Crete), suburban (Lykovrissi, Athens) and natural background (Finokalia, Crete) locations, for a time period extending from 2004 to 2006.
Size-segregated mass measurements of 3 sizes (PM_{10}, $PM_{2.5}$ and PM_1) are reported. The EU annual limit value of 40 μg m^{-3} for PM_{10} was exceeded on a yearly basis at both of measurement sites in Athens, while frequent exceedances of the 24-h limit value of 50 μg m^{-3} were recorded. Concentration levels of $PM_{2.5}$ and PM_1 were also found elevated, when regarded in perspective to either existing limit values (for $PM_{2.5}$) or levels reported for other large metropolitan areas (for PM_1).
In addition even at the background station of Finokalia in Crete, average PM_{10} concentrations exceeded 30 μg m^{-3}. Moreover, at the same station, average concentrations of $PM_{2.5}$, notably exceed 15 μg m^{-3} (a characteristic value, relative to the USEPA $PM_{2.5}$ air quality standard). At all sites coarse particles have been found to comprise a noteworthy portion of total PM_{10} particles (with $PM_{2.5}/PM_{10}$ ratios ranging between 45-60%), while fine particle mass concentrations heavily relied on those of particles in the submicron range ($PM_1/PM_{2.5}$ ratios spanning between 55-75%).
The short and long-term temporal variability of each fraction were examined and spatial associations were statistically analyzed, in an attempt to identify possible affinities in particle level profiles, effective over a larger regional scale. It has been observed that at several instances, severe particle episodes recorded in the region of Crete have largely affected the Greek mainland and have triggered a response to the monitoring network in Athens. Special focus has been given to events of dust transport from N. Africa, which is found to be more frequent during spring and fall, and during which the PM_{10} limit value of 50 μg m^{-3} is violated and concentrations of even finer particle fractions are affected. Air mass back trajectories were studied, for episode days during dust transport events.
Data of particle chemical composition were utilized, contributing to an initial identification and characterization of major natural and anthropogenic source types, which determine particle concentrations.

KEYWORDS: PM_{10}, $PM_{2.5}$, Submicron particles, Chemical composition, Long Range Transport.

1. INTRODUCTION

Immediately after the announcement of the 1st daughter directive to the EU Framework Directive on Air Quality, which introduced PM_{10} as the regulated particulate matter metric, results from long term monitoring of PM concentrations in the area of Athens, indicated the existence of a serious pollution problem, extending also to fine particle concentrations (Chaloulakou *et al.*, 2003; 2005; Grivas *et al.*, 2004). Apart from problems with regulatory compliance, the magnitude of recorded levels posed a significant threat regarding population exposure. Since then, the problem has been verified by continuous monitoring of PM_{10} concentrations by local authorities, but not only for Athens (Grivas and Chaloulakou, 2006), since results arriving from other large Greek urban agglomerations (like Thessaloniki and Heraklion), indicated violations of PM_{10} limit values as well (Samara and Voutsa, 2005; Gerasopoulos *et al.*, 2006). These facts have given rise to suggestions that the situation regarding PM pollution should probably be considered at a national scale, as has been the case with other European countries (Querol *et al.*, 2004).

Moreover, the explicit geographical location of Greece in the Southeastern part of the Mediterranean, has driven research efforts, also to the study of aerosol phenomena evolving at a wider spatial scale, involving trans-boundary pollution and particle generation and transport due to natural processes. There have been many studies (Kouvarakis and Mihalopoulos, 2002; Bardouki *et al.*, 2003; Vrekoussis *et al.*, 2005) reporting results for the island on Crete, including size-resolved natural background particle levels and particle composition, also providing important material for the examination of additional ecological aspects of particle pollution (radiative forcing, visibility degradation, marine aerosols), apart from health impairments.

A joint effort has been undertaken for the parallel examination of PM levels, characteristics, sources and related environmental processes in Athens and Crete, in order to establish a pathway for understanding and addressing the problem at a nation-wide level. The main objectives of the present work were:

i) to ascertain the role of local sources and to provide a determination of background aerosol concentration levels and
ii) to estimate the relative contribution of natural and anthropogenic sources on the measured particle levels.

To our knowledge these are the first long-term size segregated measurements of aerosol mass in Southern Europe, a region for which a gap in terms of aerosol size distributions has been identified in recent aerosol phenomenology studies.

2. STUDY AREA AND METHODS

The measurement period examined at the present study ranged between August 2005 and August 2006 for the two stations in the Greater Area of Athens. For the island of Crete the reported data cover the period July 2004-July 2006 for the natural marine (Finokalia) site, while a longer time series was available for PM_{10} at the urban site of Heraklion (November 2000- September 2005).

In Athens the first measurement station was set at the area of Lykovrissi, which is characterized as suburban traffic in a residential/industrial zone, and due to a combination of influencing particle source types (traffic, industry, secondary particle formation) has been known to be among the highest PM_{10} sensor points in the Athens basin (Grivas and Chaloulakou, 2006). The other station is characterized as urban traffic (roadside) and is situated at the residential area of Goudi in Central Athens. Specific details regarding site description can be found elsewhere in literature (Grivas *et al.*, 2004; Grivas and Chaloulakou, 2006). Measurements were conducted with a 1-every-3 days sampling frequency at minimum, which is well over the required frequency for indicative monitoring described in the EU directives. Simultaneous 24-h PM_1, $PM_{2.5}$, and PM_{10} measurements were conducted using low volume (16.7 l min^{-1}) samplers (Partisol samplers with cyclonic separators for PM_1 on both sites and $PM_{2.5}$ at Lykovrissi and Harvard impactors for PM_{10} at both sites and $PM_{2.5}$ at Goudi). Particle mass was collected on pre-weighted Teflon-coated glass-fiber filters. Filters were weighed on a Sartorius M2P micro-balance with a resolution of 1μg.

In Crete, measurements were carried out at an urban site at Heraklion, the largest city on the island, and at the natural background site at Finokalia, a remote coastal site in the

northeastern part of the island. The Finokalia station is situated 70 km northeast of Heraklion and a description of the site has been given in previous studies (Mihalopoulos *et al.*, 1997). PM_{10} mass at Heraklion and Finokalia was determined with Eberline FH 62 I-R (Eberline Instruments GmbH) particulate monitors, designed to measure continuously the mass concentration of the suspended particles in ambient air based on β-attenuation. Both PM_{10} instruments have been compared against gravimetric techniques (filters and VI impactors) with very good agreement (slope 1:1) (Gerasopoulos *et al.*, 2006). In Finokalia, size resolved aerosol samples were also collected using a Small-Deposit-area low-volume-Impactor (SDI) (Maenhaut *et al.*, 1996). The inlet preceding the SDI has a cut-off size of 10 µm. The SDI has 12 collecting stages over the particle size range 0.041-10 µm with cut-offs at 0.041, 0.085, 0.138, 0.225, 0.346, 0.585, 0.762, 1.06, 1.66, 2.68, 4.08 and 8.39 µm. The average sampling time was 2 days (from 1 up to 3 days). The PM_{10} values have been obtained by summing the masses from all impactor stages, while the $PM_{2.5}$ and PM_1 values from the SDI have been extracted by summing the corresponding stages (with the actually obtained cut-offs providing $PM_{2.68}$ and $PM_{1.06}$).
Chemical analysis was conducted for 9 major ionic species (NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Na^+, Cl^- SO_4^{2-}, NO_3^-, $C_2O_4^-$) on the particulate mass collected from sites, using ion chromatography. More details on the method of analysis can be found in Bardouki *et al*. (2003).
For the long range particle transport study, 5-day backwards trajectories were calculated using the Hybrid Single particle Lagrangian Integrated Trajectory model (HYSPLIT- 4), developed by NOAA, at isobaric levels corresponding to heights of 1000 m and 3000 m, at the time of arrival of the air mass, at the examined location.

3. RESULTS AND DISCUSSION

Basic descriptive statistics for measured PM fractions across stations are given on Table 1. PM_{10} mean concentrations for PM_{10} for the two sites in Athens well exceeded the limit value of 40 µg m^{-3}. In Crete, the limit value was exceeded at the urban site of Heraklion, while the concentration levels at the remote site of Finokalia appear to comprise a considerable background. Regarding the 24-h limit value of 50 µg m^{-3}, both stations in Athens recorded more than 35 exceedances (59 and 50 for Goudi and Lykovrissi respectively), in spite of infrequent sampling. The percentages of exceedances were 43.4 % and 43.8 %, while compliance with the air quality standard demands a maximum proportion of 9.6 % yearly. Similar is the case in Heraklion where the percentages of the exceedances were 40 % for the yearly period(s) 2001-2004 with sampling coverage of 75 %.

Table 1. Arithmetic mean and standard deviation for size specific particle concentrations measured across sites (µg m^{-3})

	Athens		**Crete**	
	Lykovrissi	**Goudi**	**Finokalia**	**Heraklion**
PM_1	18.5±8.8	20.1±7.4	10.3±4.7	-
$PM_{2.5}$	23.7±10.7	29.3±10.4	17.9±12.4	
PM_{10}	51.3±24.5	52.2±29.1	32.5±27.7	51.0±31,0

Elevated fine particle levels were found in Athens. If viewed within the provisions of the oncoming directive for Cleaner Air in Europe, which sets an annual $PM_{2.5}$ limit of 25 µg m^{-3}, it can be seen that Goudi is a potential non-attainment station, while Lykovrissi is marginal. In any case $PM_{2.5}$ concentrations in both stations exceed the long-existing USEPA limit value of 15 µg m^{-3}. In addition regarding the 24-h limit value, the 98th percentile on both stations is higher than the value of 35 µg m^{-3} (53.2 and 55.2 µg m^{-3} respectively), which has been announced for the new US ambient particulate matter standard. These results in conjunction with previous findings for $PM_{2.5}$ at urban traffic and urban background sites in Athens (Chaloulakou *et al.*, 2003), verify the assumption of a fine particle pollution problem in Athens, on a wide spatial scale. Notably high levels of $PM_{2.5}$ are recorded at the remote station of Finokalia, with the above mentioned limit value of 15 µg m^{-3} exceeded on both years of measurements, with the 98th percentile of concentrations even exceeding 65 μg m^{-3} (current USEPA 24-h $PM_{2.5}$ limit value), for the first year of measurements.

Although PM_1 limit values have not been legislated, a comparison with the USEPA annual limit value for $PM_{2.5}$ (15μg m^{-3}) reveals that the observed submicron particle levels in Athens should be also considered high. In general, PM_1 concentration levels were comparable to those observed at other large Mediterranean urban agglomerations and significantly higher than some reported in Central and Northern Europe (CAFE, 2004). Low PM_1 levels were measured at Finokalia, which when examined in comparison to $PM_{2.5}$ concentrations give an indication about the potential influence of natural sources even on $PM_{2.5}$, at this natural background station. These implications can be explored by examination of particle ratios and statistical associations between the two particle fractions.

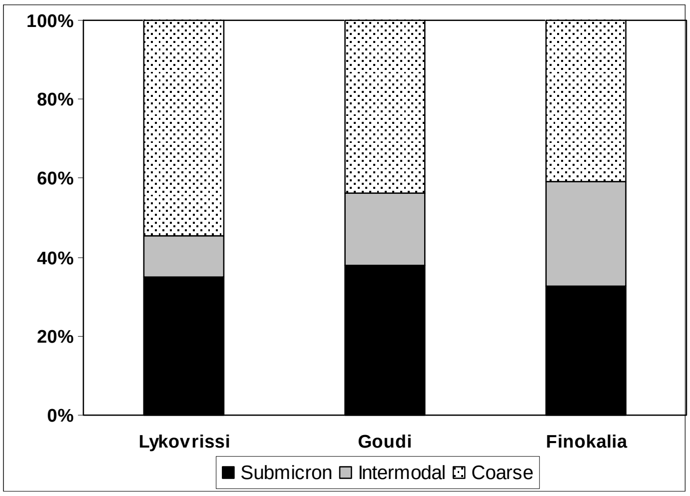

Figure 1. Size resolved contribution to measured PM_{10} mass

Figure 1 presents the relative contribution of particle fractions to total PM_{10} mass. At all sites a considerable proportion of coarse ($PM_{10-2.5}$) was observed. The $PM_{2.5}/PM_{10}$ ratios, for the two stations in Athens were calculated at 0.47 and 0.59 at Lykovrissi and Goudi respectively. These results are comparable with previous observations for Athens and typical for urban agglomerations in the Mediterranean (Chaloulakou *et al.*, 2005). The coarse particle contribution was more prominent in the suburban station of Lykovrissi mainly due to specific site details and reasonably lower at the roadside station of Goudi. At both stations in Athens the intermodal particles comprised only a small fraction of fine particle mass. However, in Finokalia a more uniform distribution of PM mass across these three fractions is observed, with the contribution of $PM_{2.5-1}$ reaching 26%. This fact highlights the possibility of particles deriving from natural sources being measured along with anthropogenic fine particles, in the $PM_{2.5}$ fraction. This is highlighted by regression analysis between PM_1 and $PM_{2.5}$ concentrations, as shown in Figure 2.

A near perfect correlation pattern between PM_1 and $PM_{2.5}$ was observed in Lykovrissi, blemished only by three outlier points, corresponding to extreme natural events of African dust transport. If these were to be omitted from the analysis the coefficient of determination would rise up to 0.96, proving that fine particle mass variability was heavily controlled by submicron particle sources and processes. In Finokalia the diagram reveals the existence of two sets of concentration pairs, corresponding to dust and non-dust events. A separate statistical analysis for each pair results to a slope of 1.1 (r^2 = 0.76) for the non-dust events and 4.1 (r^2 = 0.94) for the dust events. The slope of 1.1 during the non-dust events was rather similar to that observed in Lykovrissi denoting possible similarities in the $PM_{2.5}/PM_1$ ratio, over Greece.

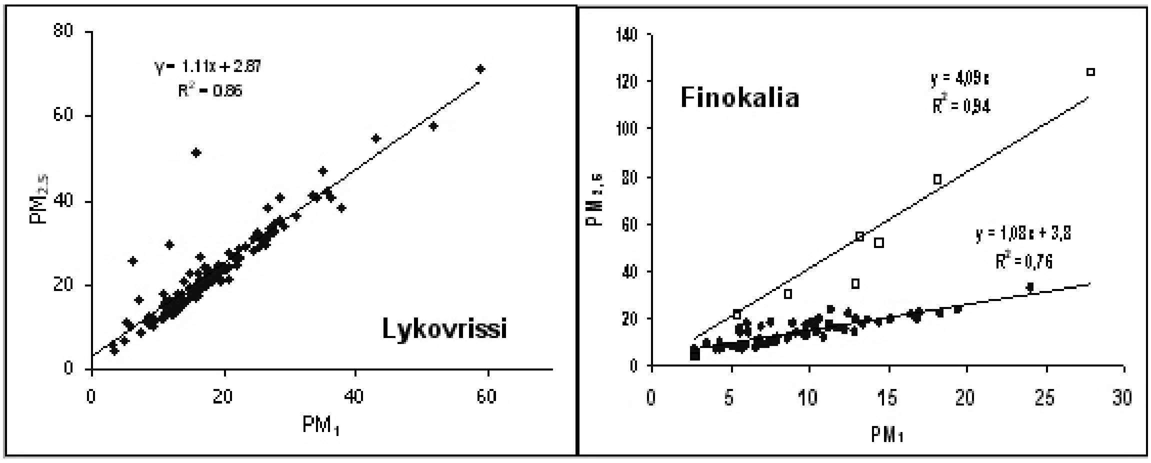

Figure 2. Correlation between PM_1 and $PM_{2.5}$ concentrations (μg m^{-3})

A qualitative assessment of the impact of particle anthropogenic sources can be derived by the examination of the diurnal variability of concentrations and the extent at which it follows human activity patterns. It is apparent that primary and especially traffic-related aerosol sources were mainly responsible for the determination of PM concentrations' short-term variability, as can be seen by diurnal cycles displayed at Figure 3, for the traffic impacted sites. Distinct morning go-to-work and evening peaks are obvious at all three sites. On the contrary, at Finokalia a simple-mode diurnal pattern occurs with enhanced levels during daytime possibly linked to regional photochemical activity.

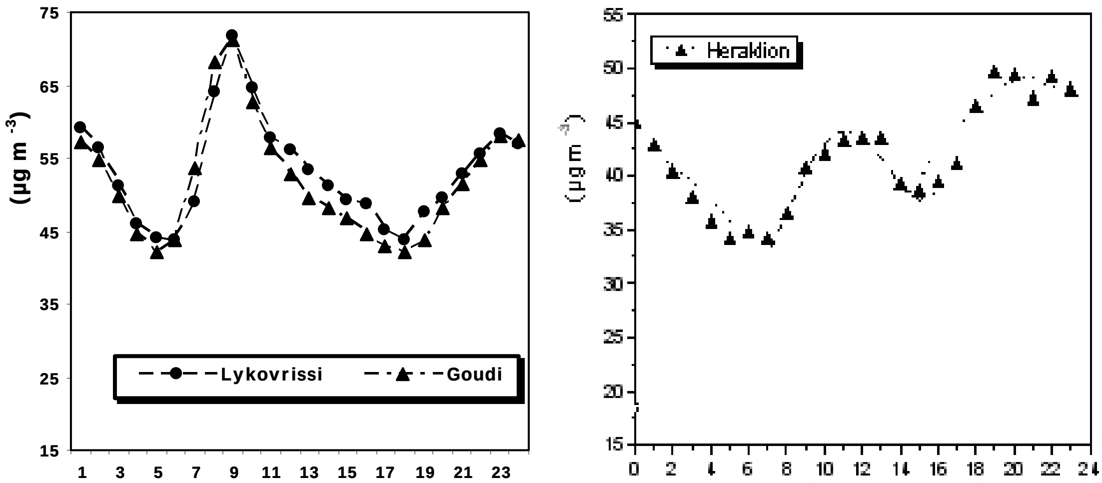

Figure 3. Diurnal variation of PM_{10} concentrations

In addition, a rough estimation about the impact of combustion related sources on various particle fractions can be derived for the stations in Athens by regression analysis with NO_x concentrations, used as an indicator of primary fuel derived emissions (Harrison *et al.*, 1997). Fitted least square lines were well-defined, with R values ranging between 0.63-070, at all cases. The comparison of the average residual of the regression with the average concentration levels revealed the strong influence that primary anthropogenic sources exercise on particle formation processes (contributions of road traffic and combustion related emissions was estimated circa 50 % - 60 % on all size ranges, at both sites).

The long term temporal variability of size segregated concentrations is displayed in Figure 4. Particle concentrations inside the Athens basin are known to be highly correlated across stations and especially among stations of similar characterization (Grivas *et al.*, 2006). Thus, only the monthly variation in Lykovrissi is displayed. Characteristically high concentrations of PM_{10} on February and April at both sites were relevant to the intensity of African dust intrusion

events on these months, which resulted at the measurement of some severely high concentrations. The seasonal pattern was different for fine particle concentrations due to the different nature of monitoring locations, with higher concentrations being recorded during the winter at Lykovrissi and the reverse pattern existing in Finokalia.
Especially, PM_1 data at both locations has been examined after separation in warm (April to September) and cold seasons (October to March). PM_1 levels at Lykovrissi during summer are found to be only 15 % higher to those observed at Finokalia, whereas during winter this difference becomes 115 %. Chemical composition measurements showed similar trend for ammonium sulphate, a compound accounting for about 50% of the fine aerosol mass. The above results denote the importance of regionally evolving secondary processes during summer, compared to emissions related to local sources during winter.

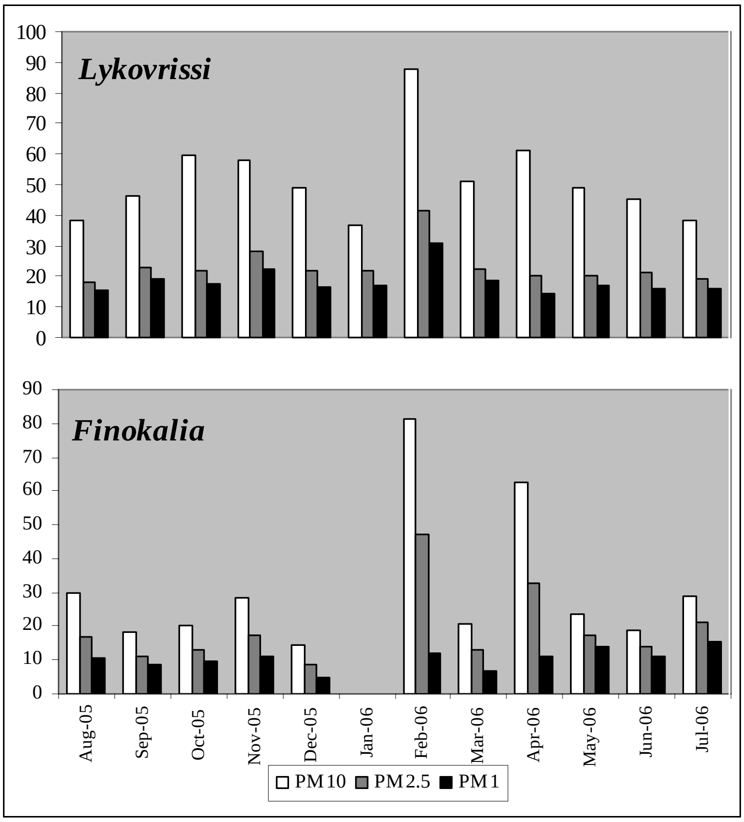

Figure 4. Monthly variation of concentrations (μg m^{-3})

Attempting to calculate correlation coefficients for pair wise comparisons in such a large geographical scale is a process not expected to produce solid results. However, in this case, where data from a natural background station were available, associations for particles having long residence times in the atmosphere could be examined. In the case of submicron particles moderate (although statistically significant) correlations were obtained between the Athens stations and Finokalia (within 0.3-0.4, when dust transport events were excluded). This investigation should be supplemented with time-delayed associations and correlation analysis for species like sulphate, known to evolve in a regional level.
The importance of aerosol transport has been demonstrated so far in this document. Backwards trajectory calculations were made to track the origin of air masses carrying particles from long distances and contributing to the appearance of severe episodes. A typical African dust transport event is displayed through the back trajectory of Figure 5. On 7/4/2006, the highest PM_{10} concentrations for the study period were recorded in Athens, reaching up to 197 μg m^{-3} at Lykovrissi and 299 μg m^{-3} at Goudi. An additional fact aiding to the identification of particle origin during these events were the levels of Ca^{2+} ions, which are characteristic for geological particles and were measured at their highest level, specifically over three times

their period average. A very high PM_{10} concentration was also recorded at Finokalia (113 μg m^{-3}), while $PM_{2.5}$ reached 56 μg m^{-3}.

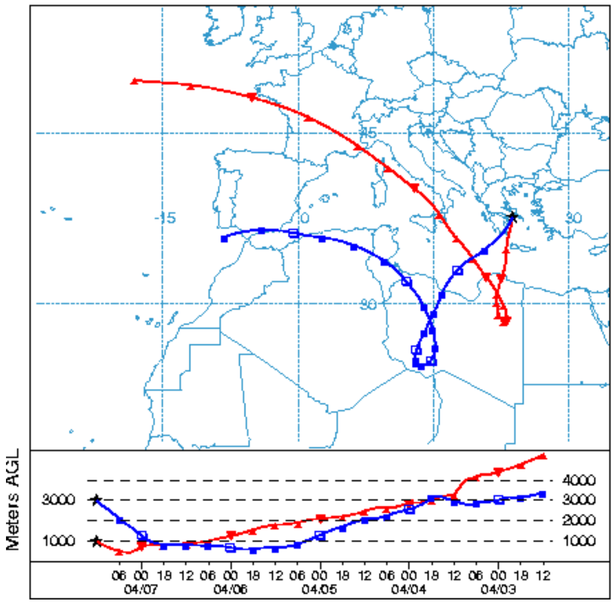

Figure 5. 5-day kinematic back-trajectories arriving at Athens on 7 April 2006

5. CONCLUSIONS

- Size-segregated mass measurements of 3 sizes (PM_{10}, $PM_{2.5}$ and PM_1) have been conducted in 3 locations all over Greece for a time period extending from 2004 to 2006: A natural background (Finokalia, Crete), a suburban (Lykovrissi, Athens) and an urban location (Central Athens) respectively. In addition PM_{10} data were available for Heraklion (Crete), covering the period 2000-2005.
- The EU annual limit value of 40 μg m^{-3} for PM_{10} was exceeded on yearly basis at all urban and suburban sites and frequent exceedances of the 24-h limit value of 50 μg m^{-3} were recorded at all locations. Concentration levels of $PM_{2.5}$ and PM_1 were also found elevated, when regarded in perspective to either existing limit values for $PM_{2..5}$ (even in the natural background site of Finokalia) or levels reported for other large metropolitan areas, for PM_1.
- Examination of the diurnal variability of PM_{10} showed the existence of distinct traffic related peaks at all urban and suburban sites, whereas at the natural background site a simple-mode diurnal pattern occurs with enhanced levels during daytime, possibly linked to regional photochemical activity.
- The PM_1 size category seemed to better represent the anthropogenic particle fraction, since during dust events, it is possible that particles deriving from natural sources are measured along with anthropogenic fine particles, in the $PM_{2.5}$ fraction (as has been demonstrated for the natural background site).
- Finally during the warm season the difference in PM_1 and sulfur between urban and natural locations is only subtle, highlighting the role of regionally evolving processes. On the other hand local anthropogenic sources dominate during the cold-season.

REFERENCES

Bardouki H., Liakakou H., Economou C., Sciare J., Smolik J., Zdımal V., Eleftheriadis K., Lazaridis M., Dye C., Mihalopoulos N. (2003) 'Chemical composition of size-resolved atmospheric aerosols the eastern Mediterranean during summer and winter', *Atmos. Environ.*, **37**, 195-208.

CAFE (2004). Clean Air for Europe, Working group on Particulate matter. Second position paper on particulate mater.

Chaloulakou A., Kassomenos P., Grivas G., Spyrellis N. (2005) 'Particulate Matter and Black Smoke concentration levels in Central Athens, Greece', *Environ. Int.,* **31**, 651-659.

Chaloulakou A., Kassomenos P., Spyrellis N., Demokritou P., Koutrakis P. (2003) 'Measurements of PM_{10} and $PM_{2.5}$ particle concentrations in Athens, Greece', *Atmos. Environ.,* **37**, 649-660

Gerasopoulos E., Kouvarakis G., Babasakalis P., Vrekoussis M., Putaud J.P. and Mihalopoulos N. (2006) 'Origin and variability of particulate matter (PM_{10}) mass concentrations over the Eastern Mediterranean', *Atmos. Environ.,* **40**, 4679-4690.

Grivas G., Asteriou C., Chaloulakou A., Spyrellis N. (2004) 'Particle number size distribution at a roadside location in Athens, Greece', *J. Aerosol Sci.,* **35**, S553-S554.

Grivas G., Chaloulakou A. (2006) 'Artificial neural network models for prediction of PM_{10} hourly concentrations, in the Greater Area of Athens, Greece', *Atmos. Environ.*, **40**, 1216-1229.

Grivas G., Chaloulakou A., Samara C., Spyrellis N. (2004) 'Spatial and Temporal Variation of PM_{10} mass concentrations within the Greater Area of Athens, Greece', *Water Air. Soil Pollut.,* **158**, 357-371.

Grivas G., Diapouli E., Kanouta V., Biscos G., Chaloulakou A., Spyrellis N., Koutrakis P. (2006) 'First results from an integrated fine particulate matter (PM_1 and $PM_{2.5}$) study in the Greater Area of Athens, Greece'. *7th International Aerosol Conference*, September 2006, St. Paul, MN, USA.

Harrison R.M., Deacon A.R., Jones M.R. (1997) 'Sources and processes affecting concentrations of PM_{10} and $PM_{2.5}$ particulate matter in Birmingham (U.K.)' *Atmos. Environ.,* **31**, 4103-4117.

Kouvarakis G., Mihalopoulos N. (2002) 'Seasonal variation of dimethylsulfide in the gas methanesulfonate and non-sea-salt sulfate in the Eastern Mediterranean atmosphere', *Atmos. Environ.*, **36**, 7083-7094.

Maenhaut W., Hillamo R., Mäkelä T., Jafferzo J.-L., Bergin M.H., Davidson, C.I. (1996) 'A new cascade impactor for aerosol sampling with subsequent PIXE analysis', *Nucl. Instr. and Meth.Phys. Res. B,* **109/110**, 482-487.

Mihalopoulos N., Stephanou E., Pilitsidis S., Kanakidou M., Bousquet P. (1997) 'Atmospheric aerosol composition above the Eastern Mediterranean region', *Tellus*, **49B**, 314-326.

Querol X., Alastuey A., Rodrıguez S., et al. (2004) 'Levels of particulate matter in rural, urban and industrial sites in Spain', *Sci. Total Environ.*, **334-345**, 359-376.

Samara C., Voutsa D. (2005) 'Size distribution of airborne particulate matter and associated heavy metals in the roadside environment', *Chemosphere*, **59**, 1197-1206.

Vrekoussis M., Liakakou E., Kocak M., Kubilay N., Oikonomou K., Sciare J., Mihalopoulos N. (2005) 'Seasonal variability of optical properties of aerosols in the Eastern Mediterranean', *Atmos. Environ.*, **39**, 7083-7094.