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Dynamics of fine particles and photo-oxidants in the Eastern Mediterranean (SUB-AERO)

M. Lazaridis[a,*], K. Eleftheriadis[b], J. Smolik[c], I. Colbeck[d], G. Kallos[e], Y. Drossinos[f], V. Zdimal[g], Z. Vecera[h], N. Mihalopoulos[i], P. Mikuska[h], C. Bryant[d], C. Housiadas[b], A. Spyridaki[a], Marina Astitha[e], V. Havranek[i]

[a]*Technical University of Crete, Department of Environmental Engineering, GR-73100 Chania, Greece*
[b]*N.C.S.R. Demokritos, GR-15310 Ag. Paraskevi, Attiki, Greece*
[c]*Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Prague, Czech Republic*
[d]*Department of Biological Sciences, University of Essex, UK*
[e]*University of Athens, Department of Physics, Greece*
[f]*European Commission, Joint Research Centre, I-21020 Ispra (Va), Italy*
[g]*Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Brno, Czech Republic*
[h]*Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete GR-71409 Heraklion, Greece*
[i]*Nuclear Physics Institute, Academy of Sciences of the Czech Republic, Rez at Prague, Czech Republic*

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Abstract

As part of the European project SUB-AERO, comprehensive aerosol and gaseous pollutant measurement campaigns were performed at the Finokalia station (July 2000 and January 2001) on the island of Crete (Greece) in combination with boat measurements in the eastern part of the Mediterranean area. The measurements were performed with the participation of nine European research institutions. The objective of the measurement campaigns was to evaluate and assess the spatial and temporal variability of photochemical pollutants and fine particles. The current overview paper presents the framework and main results of the measurements and modelling studies performed during the project. Extensive measurements of gaseous and atmospheric-aerosol physical, chemical and optical characteristics were performed during the measurement campaigns in conjunction with detailed chemical analyses of the aerosol species. Along with the experimental work mesoscale modelling, using a combination of the UAM-AERO air quality model together with the RAMS prognostic meteorological model, was used to reveal the dynamics of particulate matter and photo-oxidants. Furthermore, regional chemistry transport models were applied to determine the background and initial conditions for the mesoscale modelling.

Keywords: Particulate matter composition; Eastern Mediterranean; Mesoscale modelling

1. Introduction

Long-range transport of photochemical gaseous air pollutants and particulate matter (PM) has been studied extensively in Europe throughout the last decades under

*Corresponding author. Fax: +30 821 37474.
E-mail address: lazaridi@mred.tuc.gr (M. Lazaridis).

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the framework of several national and international efforts (EU, 1996, 1997; Berdowski et al., 1998; EMEP-WMO, 1997; Eliassen and Saltbones, 1983; Zerefos et al., 2002; Kallos et al, 1999). It has been established (e.g. EMEP, 1996; EPA, 1996; Lurmann et al., 1997) that emissions of photochemical pollutants and PM rise up in the air due to buoyancy effects, advect downwind, and disperse horizontally and vertically due to the turbulence field and prevailing meteorological patterns. However, there is scarce information concerning consistent measurement/modelling studies in Southern Europe to reveal the atmospheric composition/variability of ozone and PM.

Research studies show that there is a consistent pattern of geographical variability in Europe with lower concentrations of PM in the far north and higher concentrations in southern countries. This is due to natural emissions of unsaturated hydrocarbons (including isoprene) that are highly reactive, and continuing high emissions of anthropogenic gaseous and aerosol pollutants in Southern Europe (Hoffmann et al., 1997). Aerosol yields obtained from experimental measurements and theoretical estimates also indicate that highly nonlinear aspects are involved in the production of organic aerosols. Furthermore, the Mediterranean region is characterized by a specific natural aerosol load, namely sea spray and North African Desert dust. These natural particulate emissions are involved in heterogeneous reactions with anthropogenic gaseous pollutants and may modify the processes leading to gas-to-particle conversion (Millan et al., 1997; Rodriguez et al., 2002; Bardouki et al., 2003) and to cloud formation (Yang and Levy, 2004). It is also well established that photo-oxidants and PM have to be studied together since the fine fraction of the PM is directly controlled by the airborne concentrations of photo-oxidants and gaseous pollutants (Seinfeld and Pandis, 1998). Therefore, a combined modelling study along with extensive measurements of ozone and fine particles in the Mediterranean area would offer valuable information and insights into their dynamics, interactions and physico-chemical characteristics.

Based on these facts, two extensive measurement campaigns were performed to examine the characteristics and dynamics of photochemical pollutants and fine particles in two sites: the Finokalia station on the island of Crete (Greece) and aboard the research vessel "Aegaeon", which cruised across the Eastern Mediterranean area between the Greek mainland and the island of Crete. Sampling took place at both sites during 4 weeks in July 2000 and at Finokalia for 1 week in January 2001. The Finokalia station (35° 19′N, 25° 40′E) is a remote coastal site eastward of Heraklion (the largest city of the island) atop a hill (elevation 130 m) facing the sea within the sector from 270° to 90° (Mihalopoulos et al., 1997).

During the measurement campaigns, an extensive range of instrumentation was employed to determine the physico-chemical characteristics of aerosol and gaseous pollutants. Measurements focused on size-resolved sampling for the aerosol mass on a daily basis with subsequent analysis for ionic species, crustal and trace elements. In addition, total aerosol mass, equilibrium trace gasses, as well as detailed size-distribution measurements in terms of aerosol number by optical and differential mobility methods for the fine aerosol fraction were undertaken. Other complementary measurements included black carbon (BC) concentration by optical transmission methods, aerosol optical properties, and thermal analysis of selected samples. Relevant photo-oxidants and inorganic trace gases were monitored by prototype and conventional instruments: see Table 1 for a detailed description of the instrumentation available at the Finokalia station and onboard the research vessel.

These measurements together with regional, mesoscale (Lazaridis et al., 2004, 2005a; Spyridaki, 2005), and subgrid (Housiadas et al., 2004) modelling studies were used to investigate the dynamics and characteristics of photochemical and fine particle pollutants in the Mediterranean area. The research work was performed under the auspices of the European Union Fifth Framework Programme (project SUB-AERO).

The specific objectives of the work described herein are to evaluate and assess the physical, chemical and meteorological processes responsible for the spatial and temporal variability of photochemical pollutants and fine particles in the Eastern Mediterranean area with the help of measurements and modelling studies. The current paper is an overview paper of the SUB-AERO project and detailed results are presented in three accompanied papers (Bryant et al., 2005; Eleftheriadis et al., 2005; Spyridaki, 2005). In the following sections, we present a summary of the results from the measurement campaigns together with modelling aspects from the application of the combined UAM-AERO/RAMS system.

2. Field campaigns

2.1. Sampling site

Two measurement campaigns were conducted at the Finokalia station, Crete, and one campaign aboard the research vessel "Aegeon" while cruising in the Mediterranean Sea. The location of the site is shown in Fig. 1a as well as a typical back trajectory: back-trajectory calculations were performed on a daily basis during the measurement campaign to elucidate the origin of air masses arriving at the land-based station. Back trajectories were computed with the computational system

Table 1
Measurements at Finokalia and on the research vessel "Aegaeon" during the SUB-AERO project measurements (July 2000 and January 2001)

Determinant	Instrument/technique	Methodology	Boat campaign	Summer campaign	Winter campaign
Aerosol scattering coefficients	NEPHELOMETER	Measuring particle scattering at three wavelengths 450:550:700 nm	*	*	*
Size resolved aerosol number concentrations	LASER AEROSOL SPECTROMETER (LAS-X)	Optical counter with resolution of 46 nominal size bins of sub and supermicron range from 0.1 to 3 μm diameter.	*	*	*
Size resolved aerosol number concentration	SCANNING MOBILITY PARTICLE SIZER (SMPS)	Condensation particle counter fed with aerosol classified by an Electrostatic Classifier (TSI, Inc.) (size range varied at different sites)	*	*	*
Black carbon	AETHALOMETER	Measures light attenuation through deposited aerosol to provide BC concentrations	*	*	*
Black carbon	PARTICLE SOOT ABSORPTION PHOTOMETER	Measures light absorption to determine BC concentrations	*	*	*
Gaseous concentration of atmospheric O_3	OZONE ANALYSER	Photometric assay of O_3 concentrations at 245 nm in a dynamic flow system	*	*	*
Chemical and gaseous species concentration	DENUDER/FILTER PACKS	Chemical adsorption of gaseous species (HCl, HNO_3, HONO, NO_2, SO_2) in equilibrium with related aerosol. Ion chromotographic analysis of, NO_3^-, SO_4^{2-}, Cl^- and NH_4^+	*	*	*
Mass size distribution of PM_{10}	BERNER IMPACTOR	Inertial classifier (10 stages from 8–0.016 μm)	*	*	*
Mass size distribution of TSP	HIGH VOLUME IMPACTOR	Inertial classifier mainly for the coarse aerosol	*	*	*
Temperature, wind direction, RH, P	METEOROLOGICAL MEASUREMENTS	Meteorological parameters by standard sensors on a mast	*	*	*
Gaseous concentration of atmospheric NO_x	NO_x ANALYSER	Chemiluminescence	*	*	*
Gaseous concentration of atmospheric nitrous and nitric acid	WET EFFLUENT DIFFUSION DENUDER/ CHEMILUMINECSENCE	Chemiluminescence	*	*	*

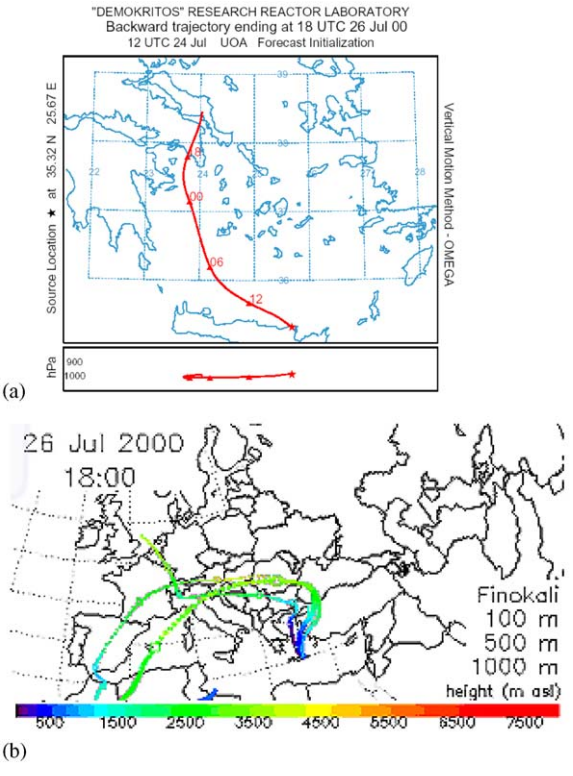


Fig. 1. Back trajectory for the Finokalia station, Crete, Greece on 26 July 2000 using the (a) Cm-Hysplit and (b) ECMWF gridded data.

Cm-Hysplit (Customized Meteorology-Hybrid Single Langrangian Particle Integrated Trajectory). As clearly attested by its name, Cm-Hysplit is an extended version of the well-known atmospheric model Hysplit (Draxler and Hess, 1998; NOAA Air Resources Laboratory, 2001). The in-house developed version has the ability to employ a customized input meteorological source. This is done with the help of appropriate routines that enable the conversion of ASCII gridded meteorological data to a model compatible format (Housiadas, 1999). During the experimental campaign the meteorological data were provided by the Regional Weather Forecasting System "SKIRON" (Nickovic et al., 2001). The 72-h back trajectories were computed starting from 10 July 2000 at 10:00 (local time). In addition, back trajectories using directly gridded data from ECMWF were also calculated (see Fig. 1b). The two trajectory calculations compare very well; a more detailed comparison is beyond the scope of the current overview paper.

Mihalopoulos et al. (1997) describe the Finokalia site in detail and report concentrations of the major soluble ions collected over a 1-year period. They found significant correlations between nss-SO_4^{2-} (non-sea salt sulphate) and NH_4^+ and Cl^- and NO_3^-. The variations in the ion concentrations were discussed in conjunction with meteorological data and 5-day back trajectories of air masses. Ozone concentrations at Finokalia exhibit a well-defined seasonal cycle with a maximum during summer months and elevated levels (up to 80 ppbv) during daytime (summer) and over time periods of several days (summer) (Kouvarakis et al., 2000).

The field campaigns covered both the summer (10 July–3 August 2000) and winter periods (7 January–14 January 2001). The 5-day cruise took place between 25 and 30 July 2000 to coincide with the summer campaign. The boat cruised in the Aegean Sea along selected routes determined by forward and back-trajectory modelling, considering the sampling site in Crete to be the end point (Smolik et al., 2003; Eleftheriadis et al., 2005).

The aim of the experiment was to measure key aerosol and gaseous species over the sea and within an air mass that would later reach the Finokalia sampling site where the same parameters were measured simultaneously. It was essential that both sampling platforms were sampling from the same air mass and that the time lag between the two measurements was known. The course of the vessel was continuously adjusted to follow the forecasted movement of the relevant air masses; forecasts were received regularly onboard. On the first day, a trip of around 6 h was required in order to reach the forecasted area of interest. During the following 3 days the previously described course tracking was successfully performed. Subsequent analysis confirmed that for the 6-h-interval trajectories received onboard there was satisfactory agreement on position and time between the forecasted trajectory and the vessel course. From the early hours of 29th July it was not possible to continue the air-mass tracking exercise because southerly winds were established in the area bringing the sampled air at Finokalia from the Lybian Sea. However, measurements were made at a northern location in the Aegean independently of the Finokalia measurements. Detailed results from the shipboard measurements are given in a separate paper (Eleftheriadis et al., 2005).

2.2. Atmospheric conditions and meteorology

The synoptic conditions over the Central and Eastern Mediterranean in July 2000 were characterized by a high-pressure system over the Central and Eastern Mediterranean and the Northern Africa. The passage of relatively shallow disturbances over Southern Europe towards the Balkans and the Black Sea resulted in the strengthening of the pressure gradient over NW Turkey and the Dardanelles Gap. As a result, a westerly flow was evident on the 15th and 16th while on the following 7 days the Etesians were established. Between 18th and 28th July 2000 the air masses reached Finokalia from the north. They originated mainly from the western coast of the Black Sea and during the last 3 days of this period, where peak mass concentrations were observed, from

the Aegean Sea. On the last 2 days, trajectories originated from north of Crete, moved first to Africa and then changed direction, finally arriving at the Finokalia site from the southeast.

During the winter period the meteorological conditions were characterized by a low-pressure system which on 6th January lay over the eastern part of the Mediterranean. A relatively strong northerly flow was evident over the NE Mediterranean, which dissipated throughout the following 24-h as the depression drew away towards the Middle East. To the west, a deep and extended Atlantic depression covered Central and Southern Europe. This system reached the Central Mediterranean on 8th January and then moved northeastward through the Balkans towards the Black Sea. From the 8th to the 9th of January a southerly synoptic flow was established over the area of interest. As the depression moved away towards the Black Sea, a high-pressure system progressively developed over the Central Mediterranean. On 10th January a relatively strong north-westerly synoptic flow was apparent over the Central and NE part of the Mediterranean. This flow dissipated throughout the following 24-h. On 11–12 January, the synoptic flow over the area under consideration was relatively weak. The wind field over the land was modified by the landscape. Over the Aegean maritime area a weak northerly current was established, while over the Central Mediterranean and the Ionian Sea the synoptic flow was westerly. On 13th January a new depression from the west reached the Central Mediterranean while a strong anticyclonic circulation dominated over Central and Eastern Europe. These synoptic conditions favoured the development of a strong pressure gradient over the NE Mediterranean region. A strong southerly flow was evident over the Ionian Sea and the southern part of the Aegean while a strong easterly north-easterly flow prevailed to the north.

2.3. Instrumentation and methods

The instruments deployed during the measurement campaigns are listed in Table 1. Measurements were conducted during the periods 10–31/7/2000 and 7–14/1/2001 at Finokalia and from 25–29/7/2000 onboard the research vessel "Aegaeon" the instruments were deployed in a similar manner at all locations and times. Instruments collecting integrated aerosol and gaseous samples (Denuders, BLPI impactors and filters) were placed on the roof or the top deck of the Finokalia station and Research vessel, respectively. Quasi real-time aerosol instruments and gas analysers were placed indoors. Aerosol instruments (SMPS, Las-x, Nephelometer and Aethalometer (AE-31) sampled isoaxially from a common inlet tube extending about 2 m over the roof (Bryant et al., 2005). During the "Aegaeon" cruise measurements the inlet for the equivalent instruments and the denuder/filter pack assembly was fitted with a PM_2 impaction head, which removed coarse aerosol from the air stream.

Samples collected by the denuder/filterpack systems were analysed by ion chromatography (IC) to determine concentrations of HCl, HNO_3, HONO, NO_2, SO_2, NO_3^-, SO_4^{2-}, Cl^- and NH_4^+ The low-pressure cascade impactor samples were first analysed gravimetrically and then a portion of the substrates by IC for common anions and cations, and proton-induced X-ray emission (PIXE) for an extensive range of trace and crustal elements (Al, Si, K, Ca, Ti, Fe, S, Cl Pb, Zn, Cu, Ni, Mn, Cr and V). IC analysis details are given in Bardouki et al. (2002). All samples from the impactor measurements were analysed by PIXE (Smolik et al., 2003).

The raw mass size data were inverted into smooth mass size distributions by the MICRON code (Wolfenbarger and Seinfeld, 1990). The inverted distributions were integrated to obtain PM_1 and PM_{10} mass concentration fractions (Smolik et al., 2003). In addition, analysis of both elemental (EC) and organic carbon (OC) collected on eight filters (total PM mass holder) during summer and eight filters during winter was performed using a thermo-optical technique.

Particle size distributions in the submicron range (8–316 nm) were measured with a Scanning Mobility Particle Sizer (SMPS). Another SMPS measured submicrometer aerosols in the range 15–723 nm in diameter onboard the research vessel. Size distributions in the range of 0.1–3 μm for the aerosol number concentration were also obtained in 46 nominal size bins by means of an optical counter (PMS Las-x). Measurements with this instrument were made at 3-min time intervals throughout the campaigns at Finokalia.

During both the summer and winter campaigns, aerosol optical and physical properties were also measured. Aerosol scattering coefficients were measured with a three-wavelength integrating nephelometer (TSI model 3563). The TSI 3563 measures both the total particle scattering coefficient (σ_{sp}) and the hemispherical backscattering coefficient (σ_{bsp}) at three wavelengths: 450, 550 and 700 nm. The TSI 3563 also possesses sensors that measure other relevant parameters such as the temperature, pressure, and relative humidity of the sampled air. These additional data were measured concurrently with the scattering coefficients. The nephelometer was set to record data at 5-min time intervals (Bryant et al., 2005).

A commercial instrument (PSAP; particle soot absorption photometer; Radiance Research; Seattle, USA) was used to measure in quasi-real time the light absorption coefficient of ambient aerosols. Furthermore, an Andersen Instruments aethalometer was used on board of "Aegaeon" and during the winter at Finokalia to determine BC concentrations. Its operating

principle involves measuring the optical attenuation of aerosol samples deposited on a filter and converting it to the equivalent BC concentration through the application of a calibration factor. Sampling was conducted at 5-min time intervals.

2.4. Results and discussion

The time series of PM_1 and PM_{10} for the summer (Finokalia station) campaign are shown in Fig. 2a and three different periods can be identified. During the first period (10–17 July 2000) the PM_{10} mass concentration varied between 20 and 40 $\mu g\,m^{-3}$. During the next period (18–25 July 2000) the PM_{10} mass concentration was practically constant, being about 30 $\mu g\,m^{-3}$, and after that it increased for 2 days up to almost 70 $\mu g\,m^{-3}$ (27th July 2000) followed by decrease to about 35 $\mu g\,m^{-3}$ (30th July 2000). The PM_1 concentrations increased gradually during the whole period from about 5 to about 15 $\mu g\,m^{-3}$. The distributions were predominantly bimodal with mode mean diameters around 0.4 and 5 μm and with minimum between both modes at around 1 μm (Smolik et al., 2003). Such distributions seem to be typical for atmospheric aerosols collected by different impactors at other locations (see e.g. Horvath et al., 1996).

In Fig. 2b, mass concentrations of PM_1 and PM_{10} from the boat measurements are shown. The direct comparison of the two sets of mass concentration data using backward wind trajectories and position of the boat with respect to the Finokalia station is difficult for this small number of 24 h integrated values. Nevertheless, a similar increase in PM_{10} concentration occurred on the boat, as well as at Finokalia. It can also be seen that both PM_1 and PM_{10} concentrations were higher on the boat than at the Finokalia station. Similarly as at the Finokalia, the distributions were mostly bimodal with mode mean diameters in the range 0.3–0.4 μm and 4–5 μm, minimum between both modes was about 1 μm. Fig. 2c shows PM_1 and PM_{10} mass concentrations measured at the Finokalia station during the winter campaign. In comparison to the summer measurements both PM_1 and PM_{10} were lower. PM_1 decreased during the whole period from 9 to 4 $\mu g\,m^{-3}$ with a minimum of almost 2 $\mu g\,m^{-3}$ during the middle of the campaign, whereas PM_{10} varied between 10 and 20 $\mu g\,m^{-3}$. All but one distribution was bimodal with mode mean diameters in the range 0.3–0.4 and 4–5 μm with minimum between both modes close to 1 μm. Fig. 2d presents an example of a "Finokalia" and "Aegaeon" parallel measurement where the similarity of the two

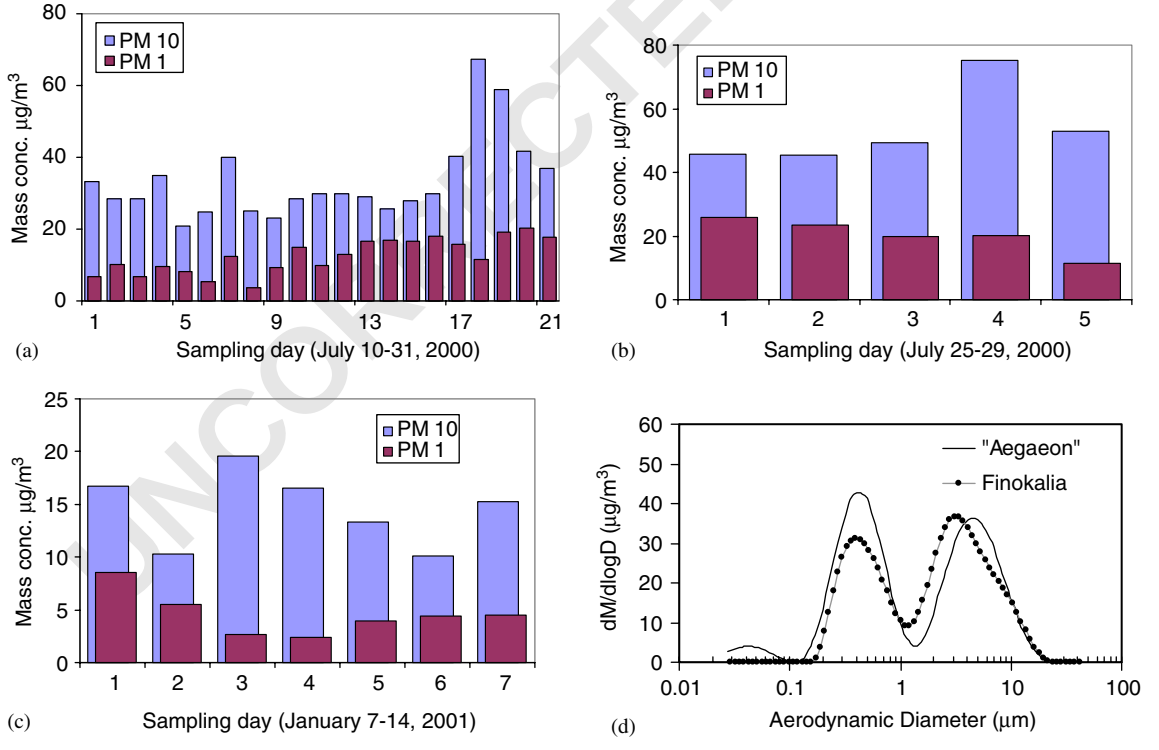


Fig. 2. (a) Daily PM1 and PM10 mass concentrations at Finokalia 10–31/7/2000. (b) Daily PM_1 and PM_{10} mass concentrations aboard of the research vessel Aegaeon 25–29/7/2000. (c) Daily PM_1 and PM_{10} mass concentrations at Finokalia 7–14/1/2001. (d) Parallel measurements of size distribution of aerosols at Finokalia station and onboard the research vessels Aegaeon.

distributions in the coarse and fine fraction is observed (Eleftheriadis et al., 2005; Smolik et al., 2003).

It is found that the MBL size distribution for the summer period of the measurements was influenced by outbreaks of continental pollution advected over the sea, giving a pronounced peak of aerosol mass in the accumulation mode, unlike the well-known distribution of marine aerosol found in the remote ocean (Quinn et al., 2000).

Detailed chemical analysis of the PM samples was performed (Smolik et al., 2003; Bardouki et al., 2003). The measurements showed elevated concentrations of Si and potassium (K) at specific dates which together with Meteostat pictures and back trajectories showed the important contribution of Saharan dust events in the area. Elevated levels of K were also found at PM_1 samples at the beginning of the summer campaign. These elevated K levels have attributed to forest fire events in Greece during this period (Smolik et al., 2003; Sciare et al., 2003).

In addition, from the aerosol scattering coefficients, the aerosol backscattered fraction or back/total scattering ratios ($R = \sigma_{bsp}/\sigma_{sp}$) were derived for the three nephelometer wavelengths (450, 550 and 700 nm) (see example in Fig. 3).

Fig. 3 shows the variation of the volume distribution for 0.25 and 0.45 μm particles with time. Size-distribution data was obtained by the Las-x and the 0.25 refers to the midpoint of the relevant size bin. These ratios give information about the angular dependence of scattering and are necessary for the estimation of aerosol scattered diffuse radiation reaching the ground. R is therefore very useful for describing the cooling effect of aerosol on climate, as it is a measure of the fraction of the scattered radiation that is returned to space. Mean back/total scattering ratios were the same for both campaigns (0.15), ranging from 0.11 to 0.18 during the summer and 0.13 to 0.18 in the winter. The summer values compared well with other remote coastal sites such as NOAA Sable Island where R ranged from 0.14 to 0.16 (CMDL, 1993). A detailed description of measurements of aerosol optical properties has been given in an accompanied paper by Bryant et al. (2005).

In addition, from the BC concentrations measured by the Aethalometers and PSAP, the absorption coefficient (σ_{ap}) was calculated. Fig. 4 displays the BC mass concentration measured at Finokalia. BC concentrations are a measure of anthropogenic aerosol arriving at the site. The highest levels observed are in the range of values attributed to Western Mediterranean air masses in other studies (Quinn et al., 2000). A number of aerosol filter samples were analysed for EC and OC content by a thermo-optical technique (Bardouki et al., 2002). Although concentrations varied between 0.09–0.68 and 0.28–2.23 $\mu g\,m^{-3}$ for EC and OC, respectively, their ratio (EC/OC) was quite constant at the Finokalia site, with an average value of 0.3 both during summer and during winter. The concentration of particulate organic matter (POM) was determined by multiplying the OC concentration by 1.7, which is the

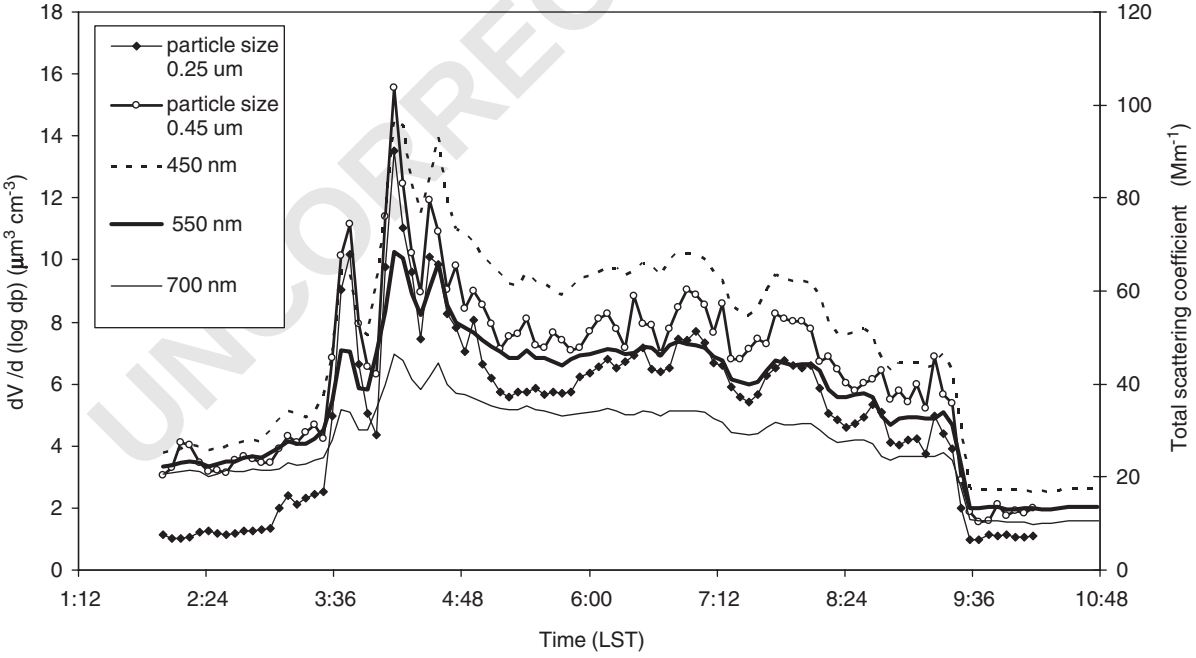


Fig. 3. Size fractionated volume distribution and total scattering coefficient, 14 July 2000.

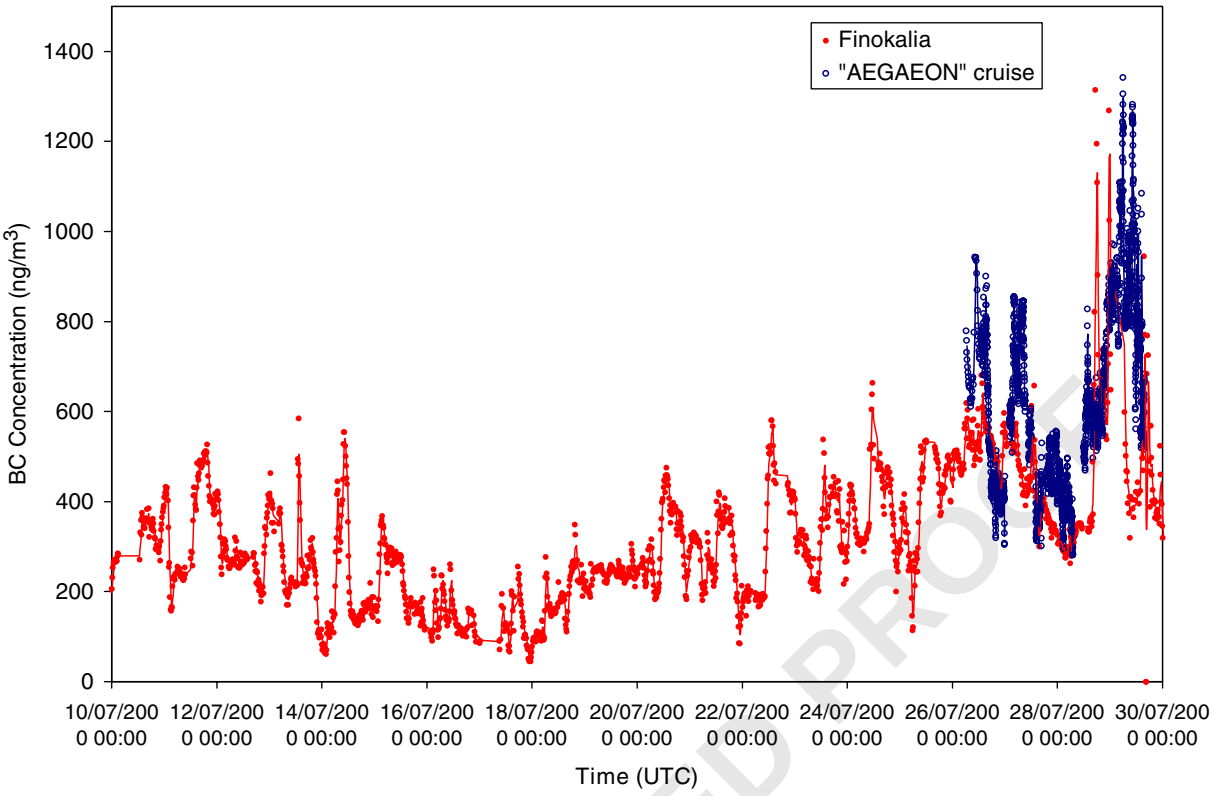


Fig. 4. BC mass concentration measured on the vessel Aegaeon and Finokalia.

average ratio of the mass of carbon-containing species to carbon mass assumed to be distributed between the fine and coarse modes with a ratio of $\frac{7}{3}$ (Quinn et al., 2000).

Particle size distribution and concentration measurements were also carried out in the aerosol submicrometer range 8–50 nm with a SMPS. An example of such measurements is shown in Fig. 5a and b. Fig. 5 shows the particle number concentration ($\#\,cm^{-3}$) and the D_p refers to the geometric mean particle diameter. The colour scale refers to $\#\,cm^{-3}$. During the summer period the SMPS measured monomodal distributions with the accumulation mode mostly between 90 and 200 nm and total concentrations starting from about $10^3\,\#\,cm^{-3}$. Moreover, several new particle formation events caused usually by local pollution were recorded at Finokalia. Two short events of this type were observed, e.g. in the morning hours of 15th July (see Fig. 5a). A second SMPS measured submicrometer aerosols in the range 15–800 nm in diameter onboard the research vessel. Slightly higher total concentrations (usually above $2\times10^3\,\#\,cm^{-3}$) were recorded there with typically monomodal size distributions and with accumulation mode position between 100 and 220 nm. No clear new particle formation event was observed during the boat campaign. Winter measurements at Finokalia gave broader range of measured number concentrations with lower background values (around $500\,\#\,cm^{-3}$) and higher peaks (above $10^4\,\#\,cm^{-3}$) in comparison with summer. Number distributions were usually bimodal, the accumulation mode laid between 120 and 200 nm, the additional Aitken mode was between 40 and 100 nm. Several new particle formation events were observed with the nucleation mode growing quickly and merging with the Aitken mode. Example of such an event is shown in Fig. 5b.

Furthermore, chemical analyses of gaseous pollutants (ozone, nitrogen dioxide, and nitrous and nitric acids) from both the summer and winter campaigns as well as the boat measurements were performed using novel analytical techniques (Mikuška, and Večeřa, 2000). In general, only small changes in the concentrations of the measured pollutants were observed. During the winter period concentrations of NO_2 were typically in the range 0.2–1.5 ppb, while concentrations of O_3 ranged from 30 to 50 ppb. These NO_2 and O_3 concentrations were on average lower during the winter campaign than during the summer campaign [0.5–3 ppb (v/v), NO_2]. Ozone concentrations were typically 40–80 ppb (v/v) in the summer. The boat data exhibited a number of episodes with rapid changes in both O_3 and NO_2. The observed

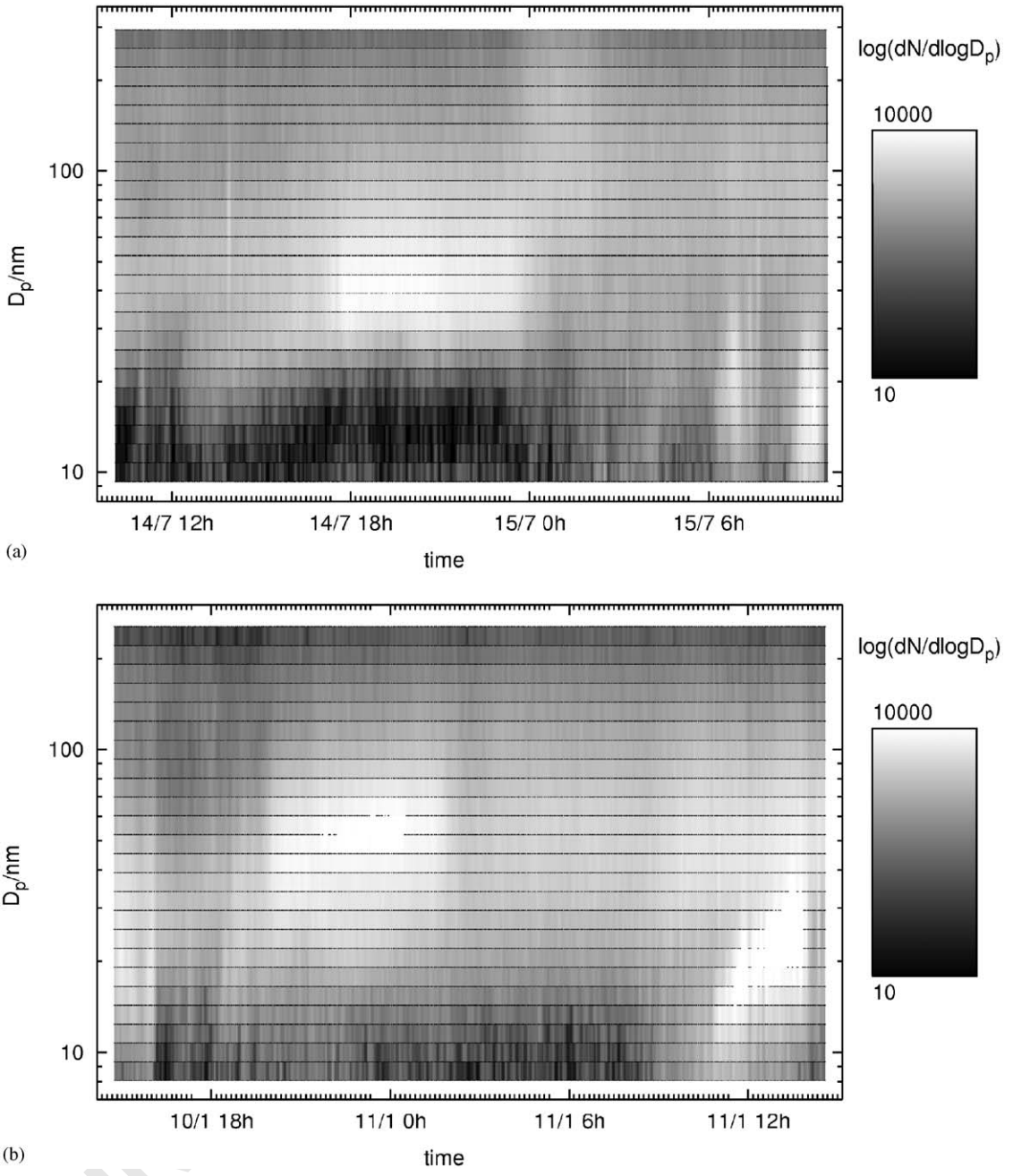


Fig. 5. (a) Summer particle number size distributions (Finokalia, from 10:00 h 14 July 2000 to 10:00 h 15 July 2000). (b) Winter particle number size distributions (Finokalia).

changes are attributable to gas-phase chemical reactions: O_3 decreased due to the presence of nitric oxide (NO) in air, which results from emissions of nitrogen oxides from fossil-fuel combustion. In the presence of O_3, NO is rapidly converted into NO_2, followed by further oxidation of NO_2 that leads to the formation of a range of compounds, the most important of which are nitric and nitrous acids. These episodes can be simply correlated to incidents when the sampling point of the analysers passed through a smoke plume. Concentrations of HONO and HNO_3 at Finokalia were lower in the winter than during the summer, typically of the order of 0.13–0.07 ppb, respectively, for HONO and 0.45–0.04 ppb for HNO_3. Concentrations of nitric and

Table 2
Particulate matter physical characteristics in the Eastern Mediterranean during the SUB-AERO project

Parameter	Finokalia (Summer)	Finokalia (Winter)	Aegean sea (Summer)
PM1 ($\mu g\,m^{-3}$)	12.5 ± 4.9	4.6 ± 2.1	20.2 ± 5.5
PM coarse ($\mu g\,m^{-3}$) (PM10–PM1)	21.0 ± 10.6	10.0 ± 4.4	$33.5 + 14.7$
Aitken (10–100 nm) (cm^{-3})	0.85e3	1.55e3	1.05e3
Number concentration (cm^{-3})	1.68e3	1.99e3	3.47e3
	(8.7–316 nm)	(7.23–294 nm)	(14.9–723 nm)
Scattering coefficient 550 nm	$4.42 \times 10^{-5}\,m^{-1}$	$1.83 \times 10^{-5}\,m^{-1}$	—
Absorption coefficient	$6.34 \times 10^{-6}\,m^{-1}$	$1.40 \times 10^{-6}\,m^{-1}$	—

Table 3
Aerosol chemical characterisation during the SUB-AERO project

Parameter	Finokalia (Summer)	Finokalia (Winter)	Aegean sea (Summer)
SO_4 ($\mu g\,m^{-3}$)	6.88 ± 0.96	2.36 ± 0.38	8.51
NO_3 ($\mu g\,m^{-3}$)	2.75 ± 0.41	1.53 ± 0.23	2.86
Cl	2.28 ± 0.36	2.06 ± 0.30	1.98
NH_4	2.38 ± 0.38	0.77 ± 0.086	1.53
Fine (PM1) crustal elements ($ng\,m^{-3}$)	485 ± 458	220 ± 96	490 ± 329
Coarse (PM10–PM1) crustal elements ($ng\,m^{-3}$)	3215 ± 3373	553 ± 373	7016 ± 5015
Fine (PM1) trace elements ($ng\,m^{-3}$)	23 ± 9	11 ± 4	45 ± 8
Coarse (PM10–PM1) trace elements ($ng\,m^{-3}$)	14 ± 6	5 ± 2	28 ± 8
BC ($\mu g\,m^{-3}$)	0.44 ± 0.16	0.15 ± 0.04	0.63 ± 0.22
OC ($\mu g\,m^{-3}$)	1.32 ± 0.61	0.45 ± 0.19	3.64 ± 0.62

Table 4
Gaseous species measurements during the SUB-AERO project

Parameter	Finokalia (summer) (ppbv)	Finokalia (winter) (ppbv)	Aegean sea (summer) (ppbv)
O_3	60	41.7	59.4[a]
NO_2	2.25[a] (10–20/7)	0.52[a]	7.1[a]
NO	<0.05	<0.05	
SO_2	0.84[b]		1.56[b]
HNO_3	0.45[b](20–30/7)	0.04[c]	0.33[b]
	0.15[c](10–20/7		
HONO	0.13[c] (10–20/7)	0.07[c]	0.12[c]
HCl			5.37[b]
NH_3			0.87[b]

[a]Prototype chemiluminescence ozone and nitrogen dioxide detectors.
[b]From annular denuder measurements.
[c]Prototype wet effluent diffusion denuder technique/chemiluniscent detection.

nitrous acids in the ambient air of the Aegean Sea were typically below 50 ppt (v/v).

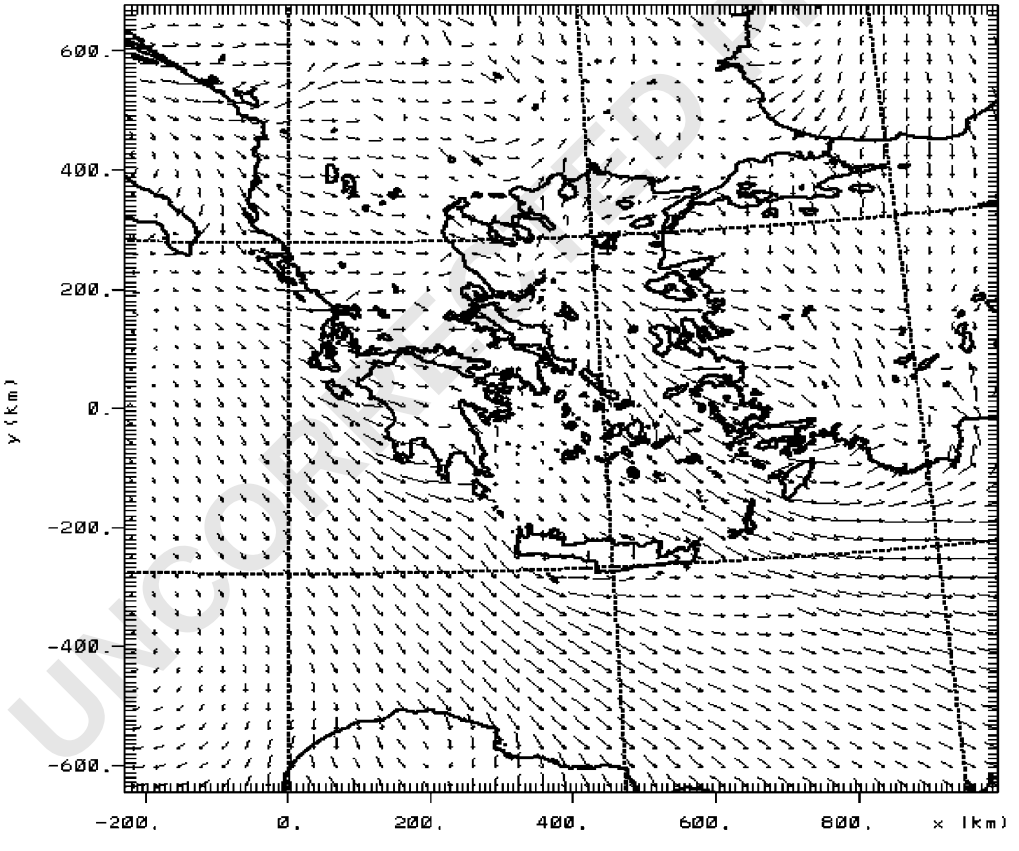
A summary of the results obtained from the measurement campaigns is presented in terms of the arithmetic mean of measured values in Tables 2–4. Table 2 summarizes physical characteristics of the PM, and Table 3 presents aerosol chemical characterization. Table 4 contains the concentration of trace gases, including those in equilibrium with aerosol species.

The data presented give a measure of the variability observed on the aerosol parameters discussed in this study. Higher aerosol mass concentrations during the summer results from soil dust produced locally or transported from regional sources. This is supported by the large increase in the concentration of crustal elements measured in the coarse aerosol fraction during that period (Smolik et al., 2003; Eleftheriadis et al., 2005). The study of back trajectories calculated for the

last 2 days of the campaign indicate that the air mass reaching the measurement area both in Finokalia and the shipboard platform also indicates the Sahara as the source area. The mean value for the mineral aerosol mass during the measurements onboard the Aegaeon platform is strongly influenced by this event, while the Finokalia mean value derived from 21 measurements appear closer to its normal value. In addition, aerosol mass concentrations might be lower in winter due to precipitation scavenging during the winter rainy period. On the other hand, aerosol number concentrations are higher during the winter mainly due to the contribution of the Aitken mode. In the absence of direct emission sources in the area and the sporadic nature of the concentration peaks (Smolik et al., 2001), it is reasonable to assume that nucleation events occurring upwind were responsible for these observations during the winter period. The measurements in the Aegean sea were performed during a period dominated by stagnation in the area and show relatively high concentrations of aerosol mass and number probably originating from local land sources and other ships in the vicinity. The same behaviour was observed at Finokalia during the respective period.

3. Modelling

Along with the experimental work, a detailed modelling study was performed using the UAM-AERO mesoscale air quality model (Lurmann et al., 1997) including state-of-the-art modules for photochemical oxidants and fine aerosols to study the transport/chemistry interactions in the Eastern Mediterranean area. Meteorological input data were provided by the RAMS (Pielke et al., 1992) prognostic meteorological model, whereas regional data on background concentrations were obtained from either the EMEP trajectory oxidant model (Simpson et al., 1995) or the NILU-CTM



JULY 12 2000		grid 2			
z = 43.7 m	2000-07-17-1200.00 UTC	min	max	inc	lab*
vectors *	3 m/s horiz	0.8433E-01	15.97		

Fig. 6. Wind field at $z = 45$ m at grid (1), 1200 UTC, 17 July 2000. Wind arrows are plotted every second grid point.

(NILU-Chemistry Transport Model) model (Flatøy et al., 2000).

In the modelling efforts, the combined UAM-AERO/RAMS modelling system was applied to study the dynamics of photochemical gaseous species and PM processes in the Eastern Mediterranean area between the Greek mainland and the island of Crete. In particular, the modelling system is applied to simulate atmospheric conditions for two periods, July 2000 and January 2001.

Fig. 6 shows the simulated surface wind fields near the surface on 17 July 2000 at 1200 UTC. After the passage of the low-pressure system, the northerly current of the Etesians is gradually established. The combined UAM-AERO/RAMS modelling system was used to simulate both the summer and winter measurement periods. The emission inventories are based on EMEP data (EMEP-WMO, 1997), whereas more detailed inputs for biogenic emission, resuspended dust, sodium and chlorine were calculated using newly developed methodologies combined with the UAM-AERO model.

Predicted aerosol and gaseous species concentrations patterns in the Eastern Mediterranean area show the importance of the long-range transport component and the significance of biogenic and natural emissions sources. Two different background air-quality data sets were used: EMEP and NILU-CTM data. The initial concentrations specified from these air-quality data sets, representing 3-D hourly values (in ppm), were also used as background concentrations in the domain. In the results presented herein the NILU-CTM model predictions were used.

Spatial surface patterns of predicted 1-h average PM_{10} concentrations on 30th July 2000 are shown in Fig. 7. For PM_{10} we observe high concentrations over the Aegean Sea. These concentrations are well correlated with high wind speeds and elevated sea salt emissions. In general terms, the modelling results obtained for all simulation periods and scenarios are satisfactory (Lazaridis et al., 2005a). As an example, in Fig. 8 a comparison between modelled and measured results for O_3 is shown for a specific summer period.

Detailed presentation of the modelling studies applied to the SUB-AERO measurement periods can be found in the literature (Lazaridis et al., 2004, 2005a; Spyridaki, 2005). The comparison between modelling results with measured data was performed for a number of gaseous species and aerosols. The UAM-AERO model underestimates the PM10 measured concentrations during

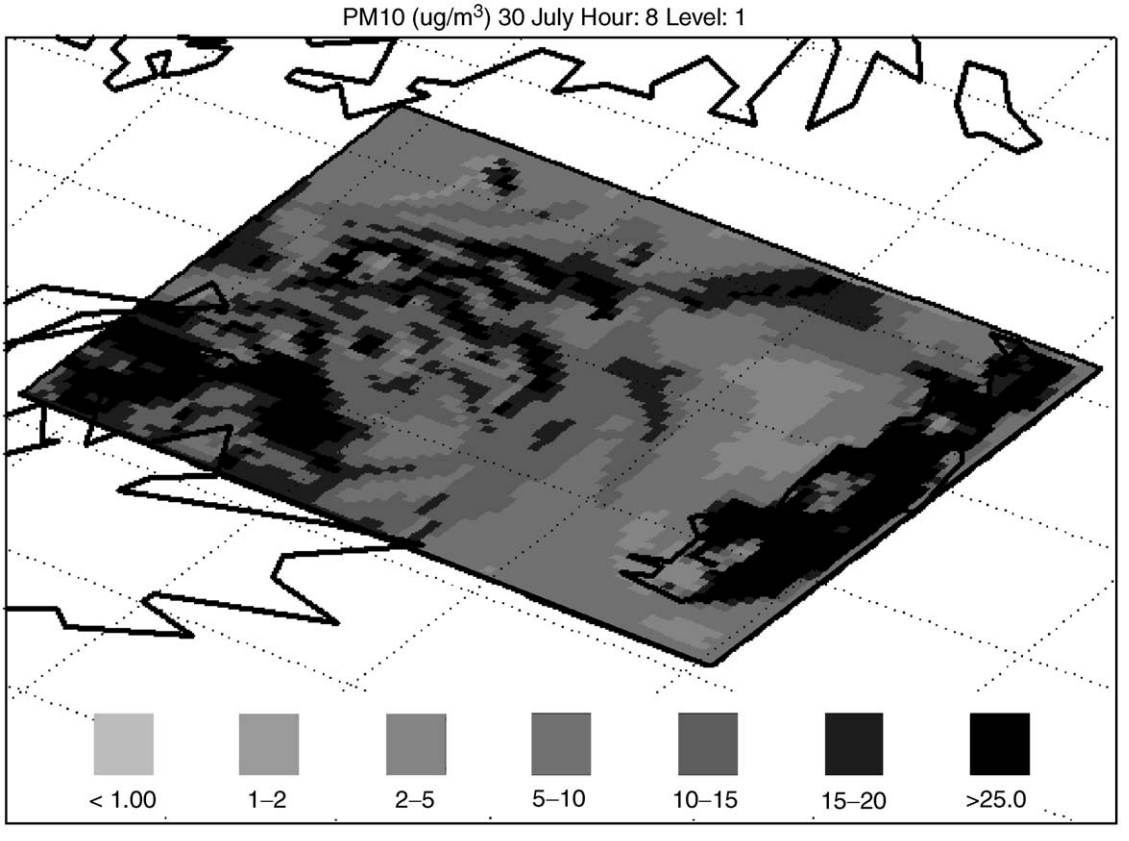


Fig. 7. Surface spatial distribution of PM_{10} at 30th July 21:00 h.

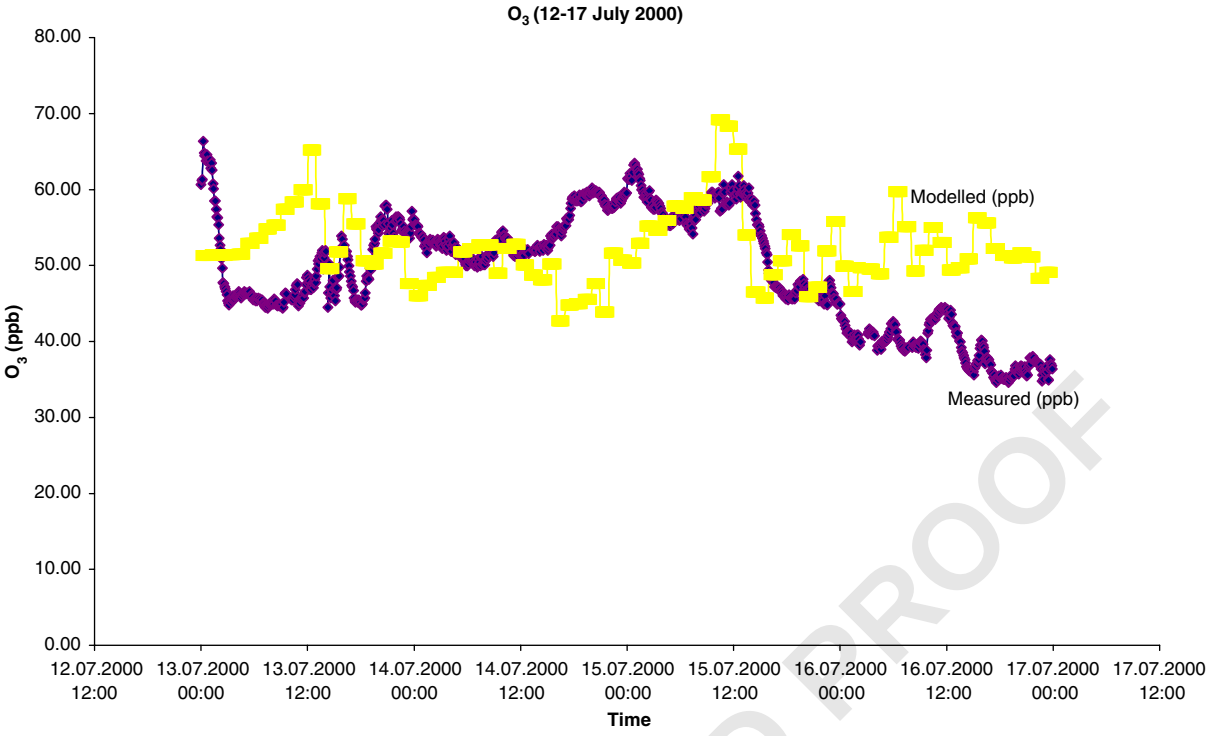


Fig. 8. Comparison between modelled and measured ozone concentrations at the Finokalia station for the period 12–17 July 2000.

summer and winter campaigns. In agreement with the measured data it was found that aerosols in the area are mainly composed of sulphate, sea salt and crustal materials, and with significant amounts of nitrate, ammonium and organics. During winter the PM and oxidant concentrations were lower than the summer values. A large uncertainty remains in the size-resolved emission inventories for PM as well as detailed data on the regional transport component of aerosols. The modelling study reveals the importance of the long-range transport for the observed levels of aerosols and photo-oxidants and the significant contribution of natural sources (e.g. sea salt, Saharan dust, forest fires) to the aerosol load in the area (Lazaridis et al., 2005a; Spyridaki, 2005).

4. Conclusions

The extensive measurement and modelling activities performed during the European project SUB-AERO resulted in a comprehensive database on the distribution of photo-oxidants and fine particle concentrations over the Eastern Mediterranean area and simulation results have provided insights into their interactions and dynamics (Smolik et al., 2003; Eleftheriadis et al., 2005; Bryant et al., 2005; Bardouki et al., 2003). In particular, detailed PM measurements reveal that emissions from vessels in the Mediterranean as well as Saharan dust and forest fires contribute significantly to the aerosol mass. Resuspension from the soil appears to be important in the aerosol size distribution especially during the summer period.

The results from the current campaigns show that the Eastern Mediterranean basin is moderately to highly polluted during the summer and relatively unpolluted during the winter. Elevated pollutant loadings in summer result from stable meteorological conditions and the absence of wet removal mechanisms. The aerosol measurement campaigns at Finokalia also suggest that the site is significantly influenced by aged pollution plumes, arriving from upwind source regions across Europe. Optical and physical properties of the aerosol size distribution suggest that mineral dust (e.g. Saharan dust) and marine components (e.g. sea spray) also contribute to aerosol mass in the Eastern Mediterranean, which is in agreement with previous work of Kallos et al. (1996).

The modelling studies (Lazaridis et al., 2004, 2005a; Spyridaki, 2005) show that the combined UAM-AERO/RAMS modelling system is an efficient platform for the simulation of the transport and dynamics of PM and photo-oxidant precursors. The UAM-AERO/RAMS modelling system was successfully applied to simulate the dynamics of PM and photo-oxidants in the Eastern Mediterranean area. The modelling studies reveal the

importance of photo-oxidant and fine aerosols dynamics in the Mediterranean area. Comparison of the modelling results with measured data is satisfactory. The simulation results show that the plume from Athens and other urban areas, as well as long-range transport, contribute to the aerosol mass in the greater area of Eastern Mediterranean.

The data obtained from the measurement and modelling studies under the current work together with recent results from previous and on-going research studies in the area aim to provide a critical data set that will allow the understanding and the prediction of the dynamics of air pollutants in the Eastern Mediterranean area.

Uncited references

Andreae, 2002; Bond et al., 1999.

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