Article
Beitr. Phys. Atmosph., August 1995, p. 191–203
0005-8173/03 0191–13 $ 3.00/0
Vol. 68, No. 3

A Contribution to the Study of Photochemical Smog in the Greater Athens Area

by I. C. ZIOMAS[1], P. SUPPAN[2], B. RAPPENGLÜCK[2], D. BALIS[1], P. TZOUMAKA[1], D. MELAS[1], A. PAPAYANNIS[1], P. FABIAN[2] and C. S. ZEREFOS[1]

[1]Laboratory of Atmospheric Physics, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece
[2]Lehrstuhl für Bioklimatologie und Immissionsforschung der Ludwig-Maximilians-Universität München, 85354 Freising-Weihenstephan, Germany

(Manuscript received October 7, 1994; accepted April 8, 1995)

Abstract

A pilot study was performed in May 1993 concerning photooxidants in the Greater Athens Area, including both experimental and modelling work. The highest ozone and PAN concentrations (about 130 ppb and 6 ppb respectively) were observed at the northern suburbs of Athens. At the eastern part of Attica peninsula the low ozone (maximum observed about 70 ppb) and NO_x levels indicated the absence of precursors in the area. According to the predictions of a three-dimensional mesoscale model, during a pollution episode day (22nd of May, 1993) the wind field over Attica was the combined result of a weak synoptic flow and three see breeze cells, developed over Saronikos Gulf, at Elefsis bay (west part of Attica peninsula) and at Mesogia plain (the east part of Attica peninsula) respectively. For the same day of the campaign the ozone, NO_x and PAN concentrations predicted by the Urban Airshed Model are in rather promising agreement with the observations, although the emission inventory used was based on yearly totals of emissions only.

1 Introduction

Athens, being a city of about 4,000,000 inhabitants, is facing, like most other big cities in the world, serious air pollution problems. The rapid increase of population since 1950, caused by the growth of the industrial and commercial activities in the area, resulted in high air pollution levels during the last two decades. Until mid 80's the main pollutants in Athens were SO_2 and smoke. Photochemical pollution succeeded pollution from inert substances and resulted in the present unpleasant situation of the Athens "nephos" (cloud), a Greek word, that was added in the pollution dictionary, describing the Athens photochemical smog. In recent years, European Union's and World Health Organisation's air quality standards are frequently exceeded in the Greater Athens Area (GAA), especially concerning O_3 and NO_x (Mantis et al., 1992).

Athens is located in an area of complex topography within the Athens basin (~ 450 km^2). The city is surrounded by moderately high mountains (up to 1400 m) forming a channel with only one major opening toward the sea (Saronikos Bay) to the south-west (see Figure 1). The mountains are acting as physical barriers with only small gaps between them. The most important is the channel leading to the north-east part of Attica peninsula, which gives the Athens basin access to the Etesians, the system of semi-persistent northerly winds which reduce the likelihood of prolonged pollution episodes. The GAA gathers about 40 % of the total Greek industrial activities and about 50 % of the total automobile traffic. Most industrial activities consist of textile, cement, chemical, fertiliser, paint, paper and food factories, and are located in the SW part of the city, near the harbour of Piraeus. Moreover, outside the Athens basin and to the west side of the city (about 20 km) lies a large industrial area comprising refineries, steel works, cement and shipyards. The Athens International Airport (Hellinikon) is located at the south-eastern edge of the basin at the shore of Saronikos Bay.

The horizontal and vertical wind pattern is generally the combined result of thermally induced local circulation sysems superposed on the mesoscale and

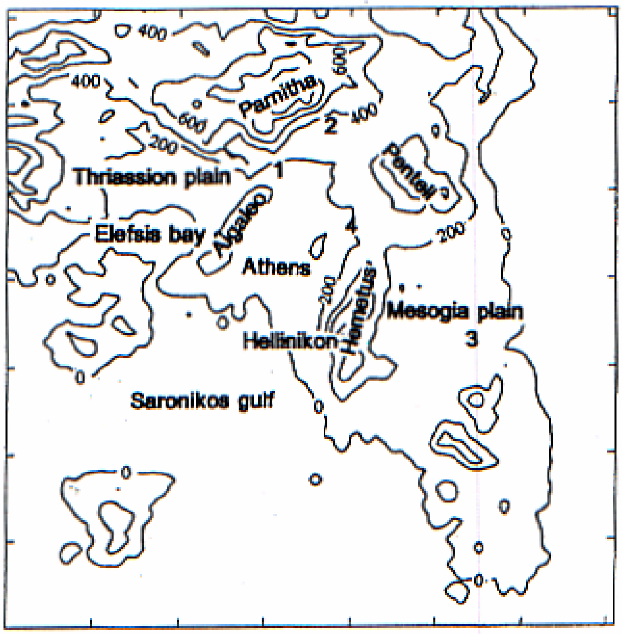

Figure 1 Map of the Greater Athens Area (72 × 72 Km) with contours at 200 m intervals, depicting the measurement sites. 1 Liosia, 2 Thracomacedones, 3 Spata, 4 Marousi.

synoptic wind field. The prevailing winds in the Athens basin are along the axis of the valley (either N–NE or S–SW). A semi-persistent circulation system, consisting of a northern wind flow, is unique to the eastern Mediterranean during the warm part of the year. This system is called Etesians and in the Athens basin it appears as a north-easterly flow. During the appearance of the Etesians, the mean vector wind is strongest and gives maximum ventilation of the basin and thus pollution episodes are not favoured. However, the weakening of the background synoptic wind allows the development of local circulation systems, such as sea/land breezes along the axis of the basin (NE to SW) and anabatic/catabatic flows from the surrounding mountains. In such a case the ventilation of the basin is poor, the Planetary Boundary Layer (PBL) is shallow and the air pollution potential increases.

Numerous scientific papers studying the air pollution in Athens have been published in the international literature (e.g. Lalas et al., 1983; Lalas et al., 1987; Güsten et al., 1988; Mantis et al., 1992; Moussiopoulos et al., 1993) and there is even an international model intercomparison exercise (APSIS) (Moussiopoulos, 1993). However, the exact mechanisms that control the formation of high levels of primary/secondary air pollutants in the Athens basin, as well as their chemical and meteorological evolution, have not been elucidated yet. This is mainly due to the lack of sufficient experimental data, such as hydrocarbons concentrations and speciation, vertical profiles of pollutants and of meteorological parameters. In addition, ozone sampling units are often located close to local NO_x sources and it might be titrated by the NO on a small spatial and temporal scale. It is also clear that relevant mechanisms exist in other densely urbanised Mediterranean coastal areas suffering from intense photochemical air pollution episodes (e.g. Marseilles, Barcelona, Tel Aviv).

On the basis of this need, a large-scale experiment was performed during the period 20th of August until the 20th of September, 1994, over the GAA, including, for the first time, all available types of high-tech instrumentation. This campaign is part of a project entitled Mediterranean Campaign of Photochemical Tracers-Transport and Chemical Evolution (MEDCAPHOT-TRACE), which is financed by the European Union (DGXII). The purpose of MEDCAPHOT-TRACE is to study the chemical and meteorological evolution of ozone related trace gases (over land and sea), modulated by the various synoptic and local meteorological conditions (sea/land breeze circulation, local winds, inversion layers etc.) in one of the largest urban agglomerations in the Mediterranean region. Apart from the stations of the existing monitoring network, 18 new stations operated in the city of Athens and in the Athens basin, involving for the first time, advanced remote sensing and in-situ analytical chemistry instrumentation, installed on ground based and airborne platforms. The scientific instrumentation involved in the experiment consists of ground based air pollution measuring systems (Gas analysers and Gas chromatographers), integrated-path air pollution measuring systems (DOAS systems), ground based laser remote sensing systems (LIDAR technique), meteorological instrumentation (slow- and fast-response) and aircraft measurements (air pollution and meteorological).

The data collected from the campaign will form a valuable input to existing dynamic/photochemical models, leading to the design of efficient strategies to abate photochemical air pollution in coastal urban/industrial Mediterranean areas.

In May 1993, preliminary to this complex project, a pilot study "Mediterranean Photochemical Tracers Campaign" (MEDPHOTRAC) has been carried out in order to examine photochemical substances (NO_2, O_3 and PAN) at different locations in Athens. Due to the meteorological situation this period was characterised by moderate photosmog

Table 1 Stations, periods of observation and supplementary parameters.

Measuring sites	Time period	Supplemantary measured parameters
Marousi	May 17th–28th, 1993	PAN
Liosia	May 17th–28th, 1993	PAN
Thracomakedones	May 18th–25th, 1993	NO, NO_2, O_3
Spata	May 18th–27th, 1993	NO, NO_2, O_3

conditions, with only half the ozone levels compared to more severe episodes. Nevertheless, typical photosmog behaviour, diurnal variations etc. could be studied and compared to model computations. For the purposes of the study both experimental and modelling work has been performed. In addition to the monitoring stations operated by the Greek Ministry of Environment (Paliatsos et al., 1994) two more air pollution stations were installed at selected locations, north-west and east of Athens respectively. Also two PAN analysers were installed at existing monitoring stations at the northern suburbs of Athens. Finally, the Urban Airshed Model (UAM) was applied for one day of the campaign and the results were compared with observations. The flow regime used for the application of UAM was calculated using a numerical mesoscale model developed at the Department of Meteorology in Uppsala (MIUU). The results of this pilot study provided valuable information for the design of MEDCAPHOT-TRACE and are presented in this work.

2 Location and Instrumentation

Figure 1 shows the location of the measuring stations. Table 1 summarises the periods of observation and the supplementary parameters measured. The station "Marousi" is located in the north east of Athens, about 7 km off the centre of Athens. Nearby (about 300 m) is one of the big main roads. Around the station there are a few-storied houses with open spaces and some small gardens and greens. The sampling inlet is located 2.5 m above the ground. In addition to the already available data CO, NO, NO_2, SO_2, O_3 and the meteorological parameters wind, temperature and humidity, measurements of PAN were also obtained.

"Liosia" is located in the north west of the agglomeration of Athens, about 10 km from the centre. The station is located between vegetation and fields with trees. There are no high buildings around and only some small industrial complexes. Nearby is a small road which connects Athens with the industrial zone in the west of the Athens basin. At this station CO, NO, NO_2, SO_2, O_3 and the meteorological parameters wind, temperature and humidity are measured routinely while, during the experimental period, a PAN analyser was also installed. The inlet pipe is installed about 10 m above the ground.

For the purposes of the campaign, a third station, called henceforth "Thracomakedones", was installed about 20 km in the northern part of the Athens basin. At this station, continuous measurements of NO, NO_2 and O_3 were obtained during the campaign. The surrounding is a typical suburban area with 1 to 2 storied villas and wide open spaces and streets. The inlet pipe was installed in the second floor.

Finally, the "Spata" station was installed in a small village close to the main road in the first floor of the village hall. The village Spata is located east of a mountain chain, Hemetus (1200 m), which separates the Athens basin from the surrounding area. The measured parameters are NO, NO_2 and O_3.

3 Experimental Results

The following results give an impression of the situation of the photochemical tracers ozone, NO_x and PAN in and around the Athens basin. Also the interactions with the land/sea breeze will be shown in the next few diagrams.

The two stations Marousi and Liosia – located at the same distance from the coastline – show a different

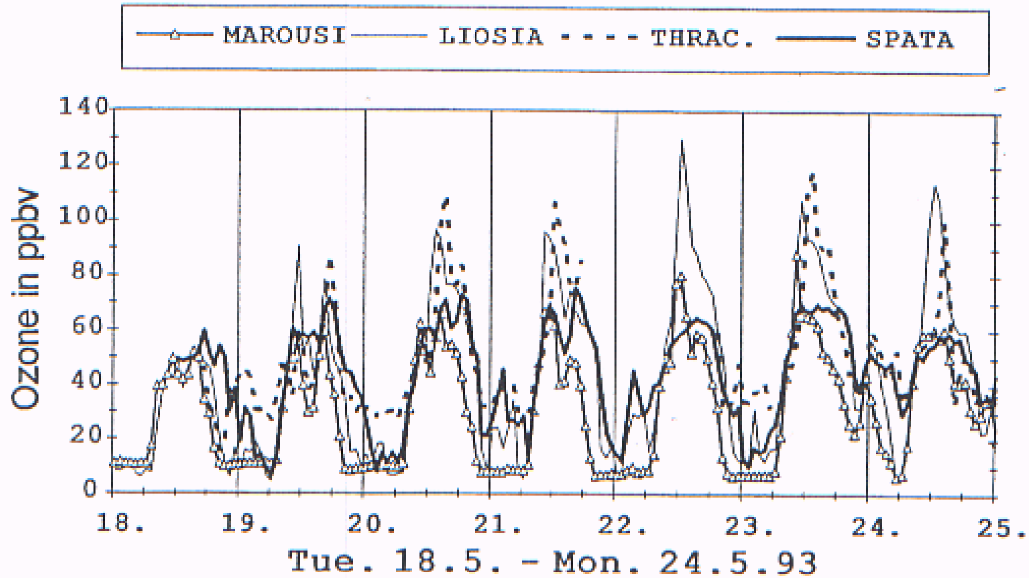

Figure 2 Diurnal variation of ozone as measured between the 18th and the 25th of May 1993 on the measuring sites Marousi, Liosia, Thrakomakodones and Spata.

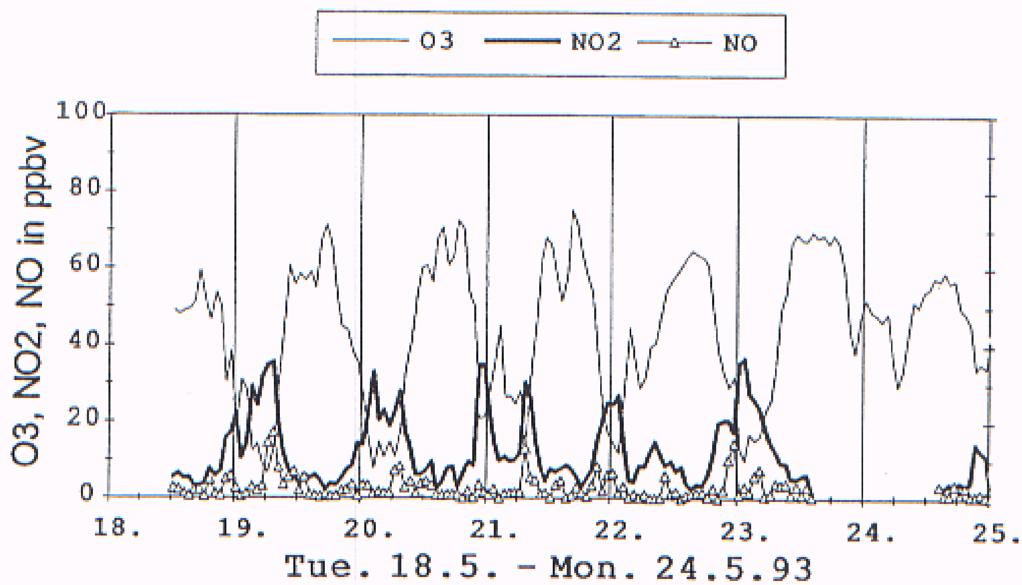

Figure 3 Diurnal variation of ozone, NO_2 and NO as measured between the 18th and the 25th of May 1993 at the measuring site Spata.

photochemical behaviour. Between the 18th and the 23rd of May there was a typical ozone episode with an increasing difference between these stations up to 50 ppb (Figure 2). During the first days of the campaign, due to the synoptic conditions, the sea breeze circulation over Saronikos Gulf was not well established. The ascending photochemical production during the morning hours was disturbed in most of the measuring stations by the strengthening of the southern wind from about 1.5 m/s to about 4 m/s. At this time there was a depressing ozone mixing ratio. On the other hand, the continuing photochemical reactions lead, after about two hours, to a second maximum in the same range as the first maximum. During the episode days this double peak disappeared because of the well established sea breeze, which resulted in a more steady wind flow during midday hours. During the maximum of difference there was an ozone mixing ratio of about 80 ppb in Marousi and 130 ppb in Liosia.

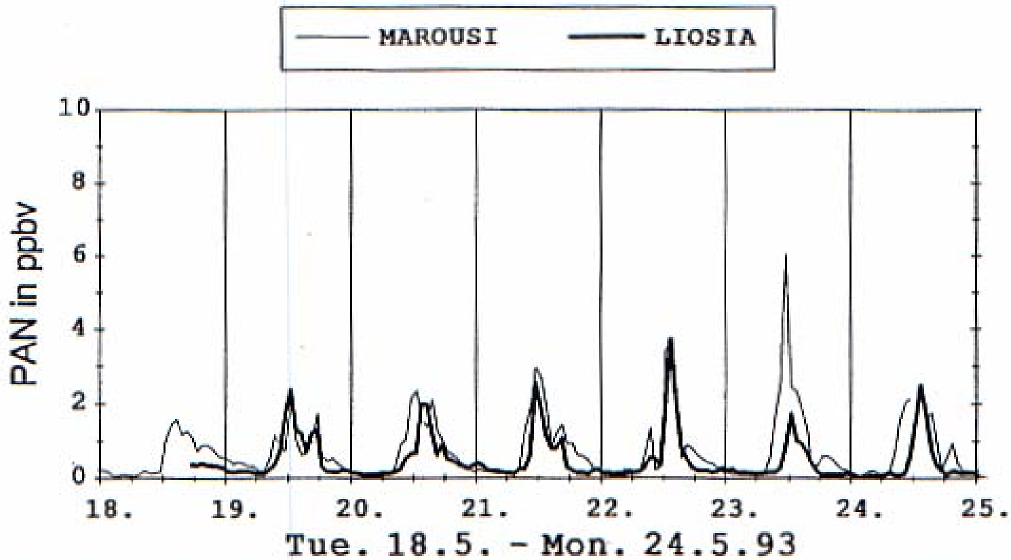

Figure 4 Diurnal variation of PAN as measured between the 18th and the 25th of May 1993 at the measuring sites Marousi and Spata.

In comparison to the other stations the following assumption can be established. In the background situated station Thracomakedones higher concentrations of ozone were observed. At this station, the higher values of ozone were reached after midday. During the morning hours ozone levels were low at this site due to the smaller amount of precursors. After turning the wind system the whole palette of gaseous components flows over Athens to Thrakomakedones and increases the ozone production in the afternoon. The maximum values are about 10 to 20 ppb higher than at Liosia.

The data obtained at the station Spata (Figure 3) show the typical diurnal variation of ozone and the nitrogen oxides of a less precursor influenced location. The photochemical production in the morning leads to a steady state maximum which will be held over some hours. The maximum values of ozone at this station are approximately 70 ppb.

The effect of the sea breze circulation reflected in the ozone data (Figure 2) can also be seen in the PAN values of Liosia and Marousi (Figure 4). But there are quite smaller differences between the stations. Only on the 23rd of May there is a difference of 4 ppb when the maximum of PAN in Marousi reaches 6 ppb. This can be attributed to a volume increase of motor vehicles traffic during the weekend. These observed PAN concentrations are considered to be rather high compared with PAN concentrations measured in other metropolitan areas in Europe such as Paris, Cologne, Munich, Copenhagen or London (Penkett et al., 1975; Grennfelt et al., 1992; Becker et al., 1985; Tsalkani et al., 1987; Fabian et al., 1994).

4 Overview of Models Applied

4.1 The Dynamical Model

In this section only a brief summary of the MIUU model is given. A more detailed description can be found in other literature references (Enger, 1986; Tjernström, 1987).

The MIUU model is a three-dimensional mesoscale model with a terrain influenced coordinate system (Pielke and Martin, 1981). The basic equations of the model are transformed in the terrain influenced coordinate system and include:

- the primitive equations of atmospheric motion as simplified by the incompressible and hydrostatic approximations,
- prognostic equation for potential temperature,
- continuity equation for calculation of the vertical velocity,
- diagnostic equation of hydrostatic pressure, represented by Exner function.

In the above equations, the pressure terms have been decomposed into two parts. The large scale pressure force is expressed with the geostrophic wind, and the other two pressure terms in the equations represent the mesoscale forcing. Given the condition that the terrain slope is much less than

45°, the pressure field is determined according to Pielke and Martin (1981).

The turbulence closure in this model is based on the approach developed by Yamada and Mellor's (1975) 'Level 2.5' model, that is only one prognostic equation besides the equations for the mean quantities is introduced, namely the turbulent kinetic energy equation. The remaining turbulent moments are determined by diagnostic expressions.

The prognostic equations are solved by using a forward-in-time, upstream-in-space finite difference scheme for the advection terms. For diffusion terms, a semi-implicit centered scheme is used. Coriolis terms in the momentum equations are fully implicit in order to dampen inertial oscillations. The differential equations are solved by using a Gaussian elimination method.

The vertical grid levels are log linearly spaced, with mean and turbulent quantities vertically staggered. The vertical coordinate contains 20 levels and the model top is at 8,000 m AMSL.

The wind at the lower boundary (defined as the sum of the terrain height, the zero plain displacement and the surface roughness length) is equal to zero. The derivatives of the horizontal wind components and temperature at the upper boundary are set to zero. The temperature at the lowr boundary is given as a function of time.

In the horizontal a telescoping grid is employed, the grid distance being 1 km in the central parts of the model. The total amount of grid points on each vertical level is 35×35, covering a horizontal domain with dimensions 100×82 km^2. The time step was chosen at 20s which allows the model to be stable yet reducing the execution time.

The model was verified against measured data in a number of investigations (e.g. Tjernstrom, 1987; Enger, 1990; Enger et al., 1993) and was even applied successfully for Athens area in previous studies (Melas and Enger, 1993; Melas et al., 1995).

4.2 The Photochemical Model

The UAM is a three dimensional photochemical grid model which calculates the concentrations of inert and chemical reactive pollutants by simulating the physical and chemical processes in the atmosphere that affect pollutant concentrations (Scheffe and Morris, 1993). The basis for the UAM is the atmospheric diffusion equation that represents a mass balance in which emissions, transport, diffusion, chemical reactions and removal processes are expressed in mathematical terms. The UAM accounts for spatial and temporal variations as well as differences in the reactivity of emissions.

The first complete application of the early version of UAM was performed in the early 70's (Reynolds et al., 1974; Roth et al., 1974). Since then UAM was continuously improved. In the present work the version of UAM used is the most recent one, which uses the Carbon Bond IV chemical mechanism (Gery et al., 1989), and the Smolarkiewitcz numerical integration scheme to solve the advection equation (Smolarkiewitcz, 1983).

The UAM simulates the emission, advection and dispersion of precursors and the formation of ozone within every grid cell of the modelling domain. For this purpose the following steps have taken place for the preparation of the input data:

a) The modelling domain, GAA, has been divided to a 40×36 grid (grid cell: 2×2 km^2) and the topographical and land use data have been prepared for this area.
b) An emission inventory has been also prepared for the main primary pollutants (NO_x CO and VOC). The main categories of sources considered for the preparation of the inventory are traffic and industrial installations.
c) The initial concentrations were estimated using measurements from the monitoring network of PERPA. In order to minimise the effects of initial concentrations, the UAM was initiated 24 hours before the day of interest.

4.3 The Emission Inventory

The success of the model predictions is strongly depended on the accuracy of the emission inventory (spatial distribution of the sources and temporal variation of the emissions). Unfortunately for Athens an accurate and well documented inventory of emissions does not exist. The only available data are yearly totals of emissions of the main pollutants (NO_x, CO and VOC) for the whole GAA, separately for traffic and industrial sources, for the reference year 1990. From these data the total emissions for 1993 were calculated, assuming that industrial emissions remained constant and taking into account that about 30 % of the private cars were replaced by new ones equipped with three way catalyst. Then using available traffic volume data as well as data concerning the spatial distribution of the industrial sources within the GAA (PERPA, 1989) an inventory was constructed and used as input for the application of UAM. It is acknowledged that the accuracy of this inventory is rather rough but, in our

Table 2 Annual emissions in Kt for the GAA for the years 1990 and 1993.

	VOC (Kt)		NO_x (Kt)		CO (Kt)	
	1990	1993	1990	1993	1990	1993
Traffic	81.1	78.6	27.8	24.5	538.0	463.0
Industry	21.8	21.8	7.0	7.0	0.5	0.5

Table 3 Time interval of the four traffic zones and the corresponding daily total emissions.

	Time interval	Percentage of daily total emissions
Time Zone A:	02 : 00 to 06 : 00 LST	10.25 %
Time Zone B	07 : 00 to 08 : 00 LST	10 %
Time Zone C	09 : 00 to 22 : 00 LST	70 %
Time Zone D	23 : 00 to 01 : 00 LST	9.75 %

Table 4 Source speciation profile splits using Carbon Bond IV speciation classes (weight %).

Olefin	0.067929
Paraffin	0.562909
Toluene	0.124112
Xylene	0.119906
Formaldehyde	0.010896
Aldehyde	0.020786
Ethane	0.095621

opinion, sufficient for the purposes of the present study. It must be noted, however, that the construction of a more accurate inventory is necessary if photochemical models are to be used for development of pollution abatement strategies (Pilinis et al., 1993; Alexopoulos et al., 1993). The total emissions for 1990 and 1993 are shown in Table 2. For each kind of sources daily emissions were then calculated assuming constant emission rates throughout the year.

The daily values give, however, insufficient information about the temporal and spatial distribution of traffic emissions over the GAA. In order to acquire emissions with reasonable diurnal variation, the 24 hour period of the day was divided into 4 time zones, each one corresponding to different traffic volume in the GAA. The traffic conditions are considered to be constant within each time zone and a specific percentage of the total daily emissions was attributed to each one of them (Table 3). The daily emission rate of each pollutant was then multiplied by the above percentages to produce the total mass of each pollutant emitted during each time zone.

The spatial distribution of the emissions for each one of the time zones was calculated as following:

The grid cells were divided into four categories:

a) Cells with **high** emissions (total number of cells = N)

b) Cells with **medium** emissions, that are assumed to have 50 % of the emissions of the high emissions cells (total number of cells = K)

c) Cells with **low** emissions, that are assumed to have 20 % of the emissions of the high emissions cells (total number of cells = L)

d) Cells with **no** emissions (total number of cells = M)

The number of grid cells N, K, L and M varies from one time zone to another, since the traffic conditions are different, e.g. N = 44 for time zone A and N = 32 for time zone B. If the total emission of one pollutant during the time zone A (5 hours total) is W kg then for a cell with high emissions the corresponding hourly emission rate is given by Eq. (1)

$$\text{Hourly emission rate (kg/hour)} = W / [(N + 0.5K + 0.2L) * 5] \quad (1)$$

After this final calculation the emission rates of NO_x, CO and HC in kg/hour are derived for every single cell of the grid for every hour of the day.

The available data for the industrial emissions in the GAA were the fuel consumption percentage for every municipality of GAA. Based on these percentages, the yearly industrial emissions (Table 2) were spatially distributed over the GAA. No annual cycle of industrial operation is considered to exist. As far as the diurnal variation of the industrial emissions is concerned, four major industries in GAA are considered to operate on a 24 hour basis, while all the rest are assumed to operate 16 hours, from 07 : 00 to 22 : 00 LST.

No other emissions e.g. from the Hellenikon airport and the harbour of Piraeus, were included in this inventory. Since the simulation of the model concerns a day of the warm period of the year, emissions from central heating were not taken into consideration.

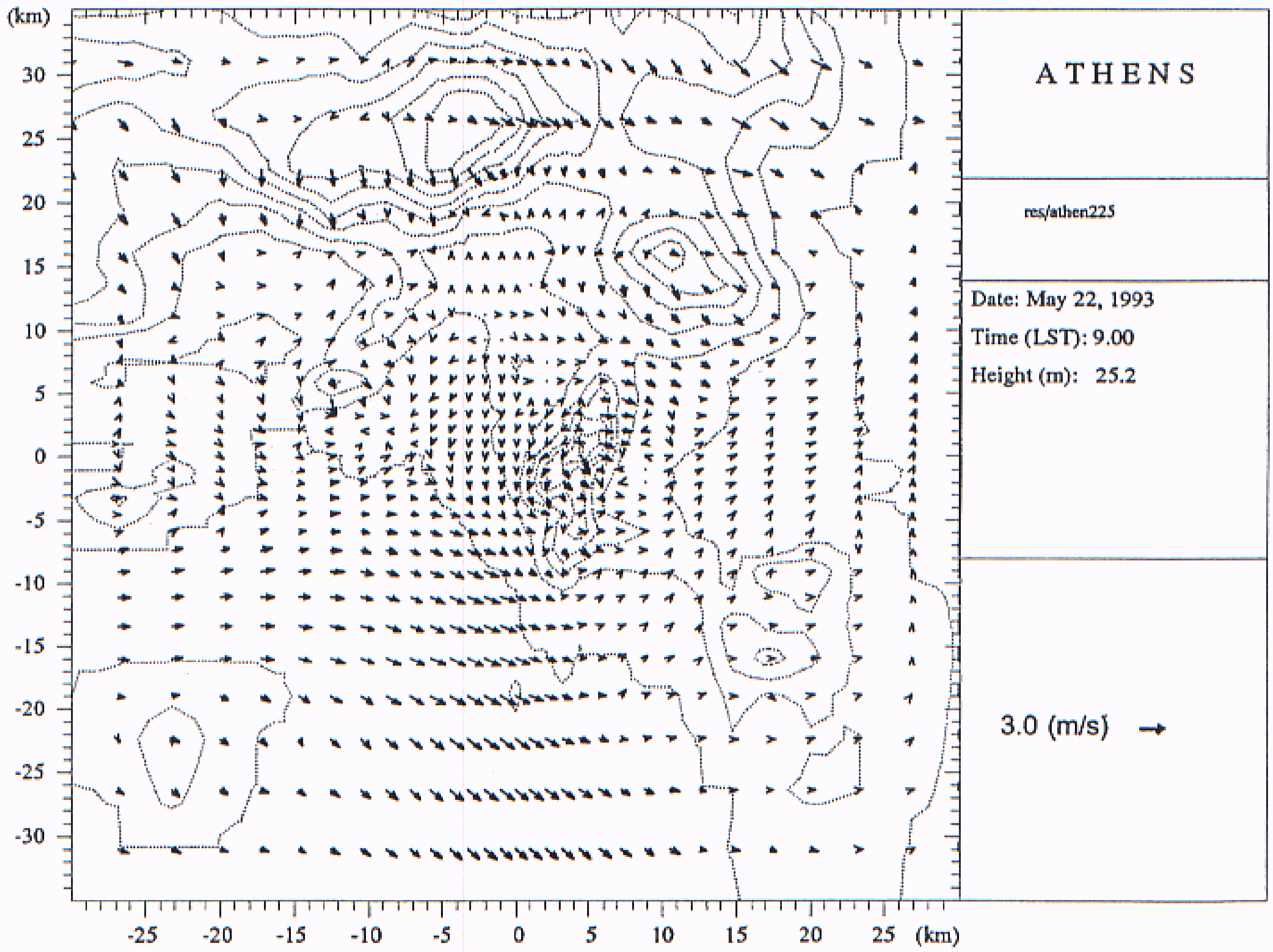

Figure 5 Simulated wind fields at 9.00 LST.

The speciation of hydrocarbons used is presented in Table 4 and is based on the work of Smylie et al. (1991). Finally, NO emissions were considered to be 90 % of the NO_x emissions, while NO_2 is the remaining 10 %.

5 Model Results

The day of the experimental campaign selected for applying the numerical models was the 22nd of May, 1993, when the highest ozone concentrations of this photosmog episode were observed. During this day, Greece was under the influence of anticyclonic conditions associated with weak pressure gradients and clear skies. The geostrophic wind, estimated from surface synoptic maps, was from the NNE with speeds of ~ 2.8 ms^{-1}. Figures 5–6 show the simulated horizontal wind fields at 9.00 and 14.00 LST. The corresponding height is approximately 25 m above the surface. For clarity of presentation, a small fraction of the computational domain near the lateral boundaries is omitted. The simulated wind fields are quite variable both in time as well as in space and several significant features can be identified.

In the morning hours (Figure 5) a westerly flow is established over Saronikos gulf while the winds over most of the Attica peninsula are low with variable directions. The surface wind pattern over Athens basin is dominated by very weak (> 1 ms^{-1}) northerly flow. The air mass practically stagnates over Athens basin. During daytime, the situation changes drastically due to the development of thermally induced local circulations. In Figure 6 the simulated horizontal wind field for 14.00 LST is shown. The

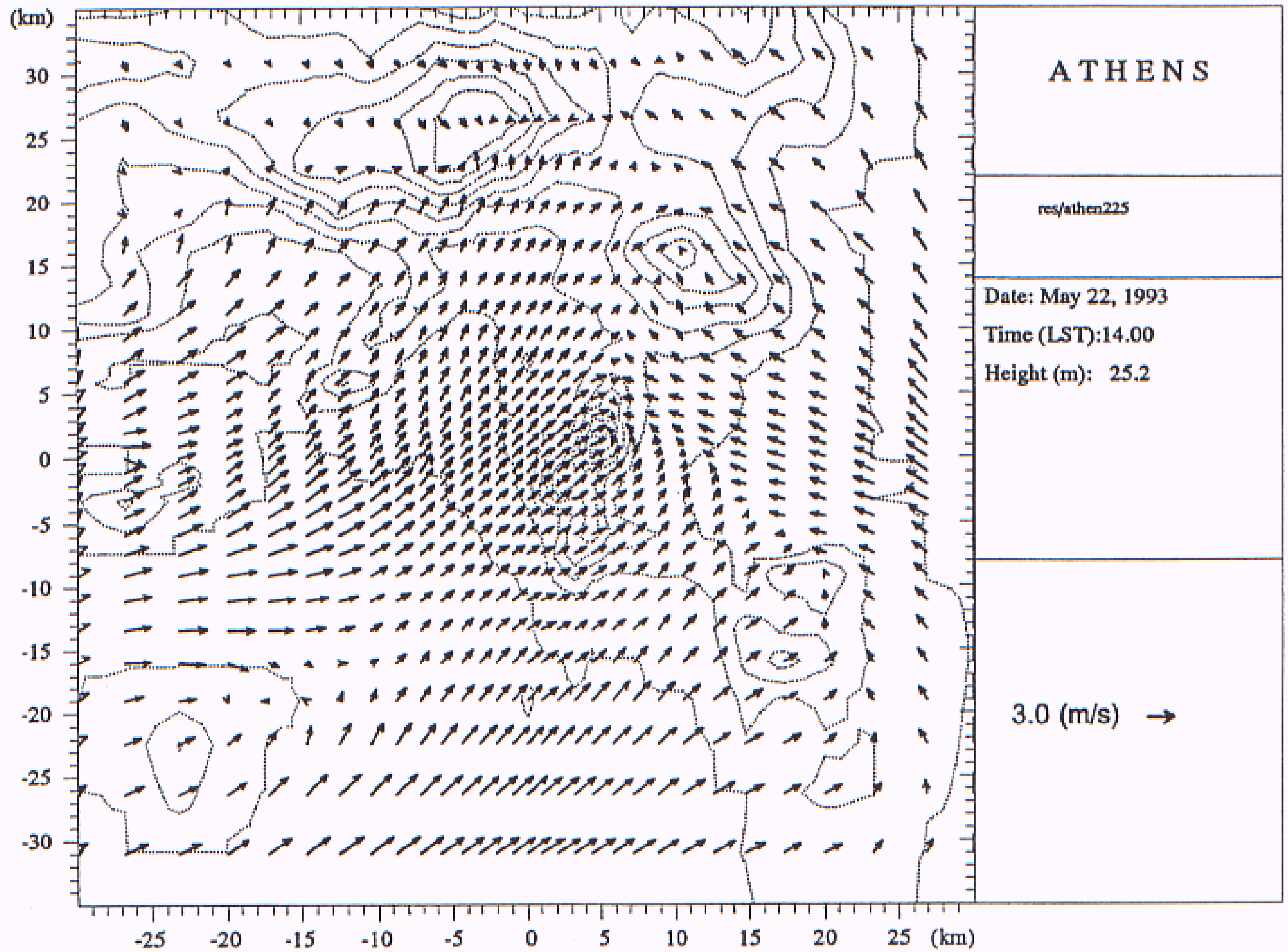

Figure 6 Simulated wind fields at 14.00 LST.

temperature difference between land and water reaches the maximum at this time, resulting in a strengthening and deepening of the sea breeze circulation. The flow over the sea is generally from the W with wind speeds ~ 5 ms^{-1} but there is a splitting in the vicinity of the coast of the Athens basin and part of the air moves in over the Athens basin. This is due to the sea breeze circulation which diverts a part of the flow towards the Athens basin. The winds over Athens area are from SW with wind speeds of the order of 3–4 ms^{-1}. The notable wind deceleration downwind of the shoreline is resulting from the high roughness of the city. Another sea breeze system is generated in the west side of mountain Aigaleo, at Thriassion plain, where the flow is from the SW with speeds of the order of ~ 3–4 ms^{-1}. In the east part of Attica peninsula, at Mesogia plain, model results show that the flow is generally from ESE, corresponding to a third sea breeze system. The wind speeds at 25 m AGL are of the order of 4 ms^{-1}. Finally, it should be mentioned that the simulated thermal structure of the atmosphere (not shown here) reveals that the convective boundary layer over the land surface is very shallow in the vicinity of the shoreline and is increasing gradually to a height of 400 m AGL at about 10 km downwind the shoreline.

Another interesting feature in the flow field is the blocking of low level winds by the mountains. A large portion of the air is forced to move around the mountains, i.e. through the gaps between them, while another portion flows over the mountains. Air masses from the industrialised Thriassion plain are entering the Athens area mainly through the gap between Aigaleo and Parnitha while air from Athens basin is exiting through the gap between

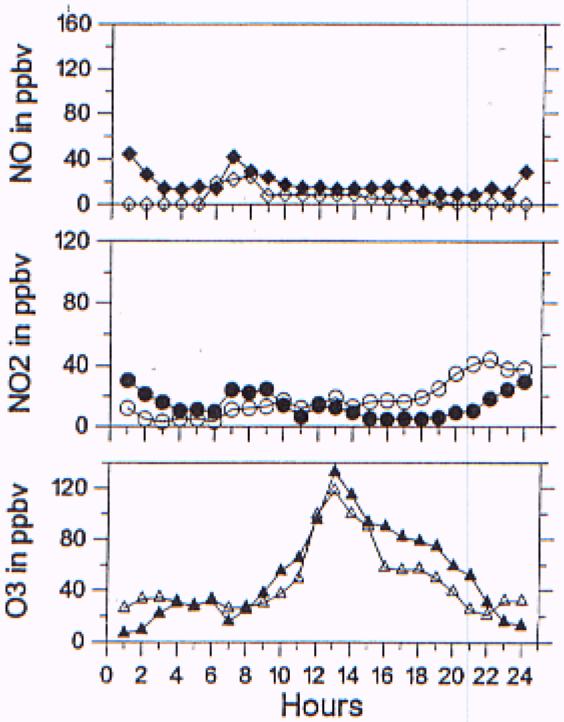

Figure 7 Comparison of the diurnal variation of NO, NO_2 and ozone at Liosia predicted by UAM (empty symbols) with observations (filled symbols).

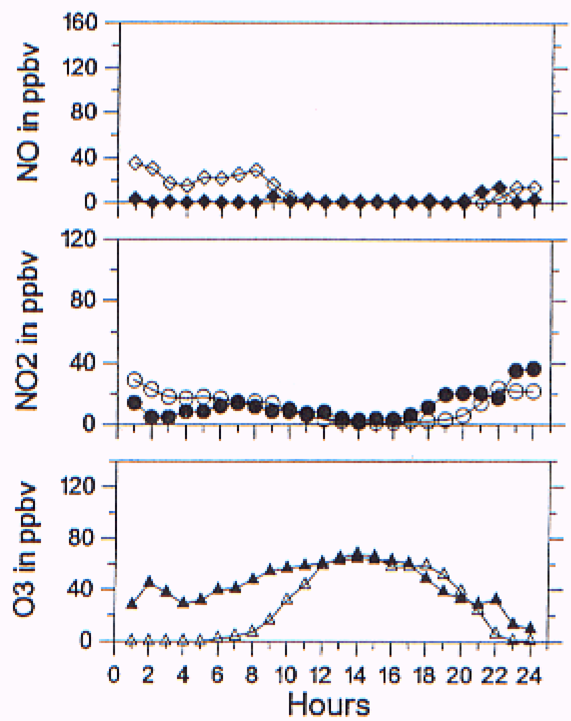

Figure 9 Same as Figure 7 but for the station of Spata.

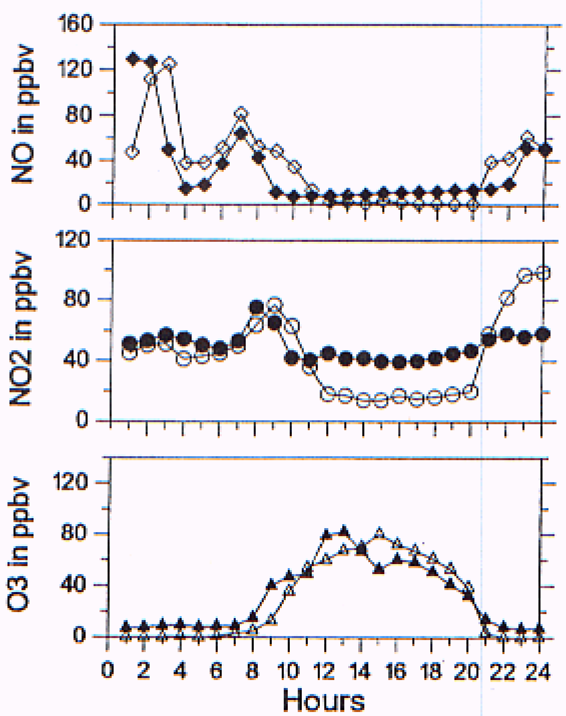

Figure 8 Same as Figure 7 but for the station of Marousi.

Pendeli-Parnitha. The direction of the wind at the opening between the mountains Hemetus and Pendeli is either ESE or WSW, depending on the relative intensity of the two sea breeze cells, over Saronikos Gulf and the sea east of Attica peninsula respectively.

In Figures 7, 8 and 9 predicted ozone, NO and NO_2 concentrations from the application of UAM and the respective observations at the stations Liosia, Marousi and Spata, for the 22nd of May, 1993 are presented. As it appears from these figures the results of UAM are rather promising for all stations, especially concerning the time and the amplitude of the daily maximum. The observed differences between the stations Liosia and Marousi are also predicted by the UAM, as well as the differences between the stations within the Athens area and the station Spata.

For the first hours of the day the results of UAM are in good agreement with the observations with the exception of the Spata station where UAM underestimates the ozone concentrations, probably due to overestimation of the NO_x emissions which lead to the overestimation of the observed NO_x concentrations (Figure 9). During the midday hours a sharp

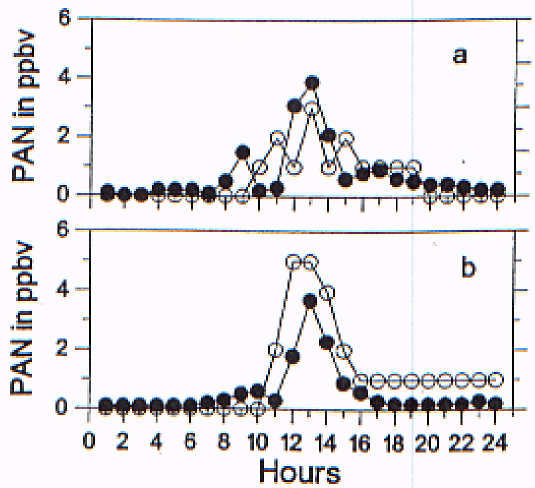

Figure 10 Comparison of the diurnal variation of PAN predicted by UAM (empty symbols) with observations (filled symbols).
a: Station of Marousi; b: Station of Liosia

increase of ozone is predicted and observed at Liosia and the daily maximum occurs (13 : 00 LST). According to the MIUU predictions the station Liosia starts receiving air from southern directions from about 10 : 00 to 11 : 00 LST, due to the see breeze cell developed over Saronikos Gulf. This air is obviously rich in ozone precursors, emitted from the city activities and thus high levels of ozone are produced. The daily ozone maximum at Marousi is predicted about 60 ppb lower than at Liosia, probably due to higher NO_x emissions at the vicinity of Marousi which result in higher NO_x concentrations (Figures 7–8). For the same reason the predicted and observed nighttime ozone at Marousi is close to zero. According to the air flow predicted by MIUU, the Spata station is receiving air from unpolluted (sea) or less polluted area (southern part of Attica peninsula). Since there are only limited emission sources in the area, the ozone maximum is not very pronounced while NO_x concentrations are very low. According to UAM predictions, which are in good agreement with the observations, ozone concentrations at this station remain almost constant (about 75 ppb) from 10 : 00 until 18 : 00 LST.

In Figures 10a and 10b the model predicted and the observed PAN concentrations for Marousi and Liosia are presented respectively. The predictions of UAM for Liosia are in rather good agreement with the observations. The amplitude of the predicted daily maximum at Liosia is about 1 ppb higher than the observed. At Marousi, however, UAM predicted that the maximum PAN concentration is about 1 ppb lower than the observed. At both stations high PAN concentrations are predicted to last for more hours than the observed ones. The time of appearance of the predicted maximum PAN concentrations coincides with the respective ozone daily maxima both at Liosia and at Marousi.

6 Concluding Remarks

In the present study, results are presented from a pilot study that was performed in May 1993 concerning photooxidants in the Greater Athens Area, including both experimental and modelling work.

The highest ozone and PAN concentrations (about 130 ppb and 6 ppb respectively) were observed at the northern suburbs of Athens. Results presented in this study show that the highest ozone concentrations are observed at the north west part of the GAA. During episode days, when a sea breeze circulation was well established over Saronikos Gulf, the highest ozone concentrations reached 130 ppb at station Liosia. At station Thracomakedones, which is located about 10 km NE of Liosia, the maximum ozone concentrations were usually about 10 ppb higher than Liosia. At the non urbanised east part of Attica peninsula, the measurements at station Spata showed typical diurnal variations of ozone and nitrogen oxides of a less precursor influenced location. The diurnal variation of PAN concentrations measured at Liosia and Marousi appeared to be closely correlated with the respective diurnal variation of ozone, at the same locations. The maximum levels of PAN observed, during the pollution episode days of the campaign, were about 4 ppb at Liosia and about 6 ppb at Marousi.

In addition to the experimental campaign, numerical model simulations were performed in order to study the diurnal and the spatial variation of photooxidants in the Greater Athens Area. For this purpose, a dynamic (MIUU) and a photochemical dispersion model (UAM) were utilised. The day selected for applying the numerical models is the 22nd of May, 1993 when relatively high ozone concentrations were observed. The application of UAM requires knowledge of the spatial and temporal distribution of the pollutant emissions in the area under study. By using available traffic volume data and yearly totals of emissions of the main pollutants (NO_x, CO and VOC) an emissions inventory for the GAA was constructed and used as input data to the UAM.

Three sea breeze cells were predicted by the MIUU model to appear in the area under study, during the simulation day. The first sea breeze cell was established over Saronikos Gulf and resulted to a SW flow of air masses over the Athens basin, which started at about 10 : 00–11 : 00 LST. The second see breeze cell was developed west of Athens, where the flow was again SW. Finally the third sea breeze cell appeared at the eastern part of Attica peninsula, where the wind direction over land was ESE. During the midday hours the simulated thermal structure of the atmosphere reveals that the convective boundary layer over the land surface is very shallow in the vicinity of the shoreline and is increasing gradually to a height of 400 m AGL at about 10 km downwind the shoreline.

The predicted diurnal variation of the O_3 concentrations is characteristic for the respective site. The results at a grid point corresponding to the less precursor influenced location of the Spata station, show a small diurnal amplitude while there is a broad ozone maximum during daytime. The diurnal variation of the predicted ozone concentrations for Marousi site shows a large diurnal amplitude with the peak appearing at the early afternoon hours while, for the same day, the observations exhibit a double peak, a pronounced one (~ 80 ppb) at midday and a secondary (~ 60 ppb) during early afternoon hours. Ozone levels are moderate during daytime hours and almost negligible during nighttime. This is attributed to the rather high NO_x emissions at the vicinity of the station. Even higher concentrations are predicted at a grid point corresponding to the station of Liosia. The local NO_x emissions at the vicinity of the Liosia station are low and the predicted ozone maximum at a grid point corresponding to the location of this station is about 60 ppb higher than the respective at the Marousi station. The sharp increase of ozone concentrations during morning-to-midday hours coincides with the onset of the sea breeze at this station. During sea breeze conditions the station is receiving air from the city which is rich in ozone precursors.

The forecast ozone and PAN concentrations for the 22nd of May, 1993 were in rather promising agreement with the respective observations, in terms of the diurnal amplitude as well as the time and the magnitude of the maximum concentrations. The agreement is slightly worse for the NO_x concentrations but it can still be considered as satisfactorily.

It should be pointed out that NO_x concentrations are more directly influenced by local emissions and the accuracy of the predictions heavily relies on the accuracy of the constructed emission inventory.

It is thus suggested that the present results are only promising and the use of photochemical dispersion models for the development of pollution abatement strategies, shouldn't be encouraged unless a more accurate inventory is constructed for the GAA.

Finally, the results of this pilot campaign indicated the urgent need for further research concerning the Athens "nephos" and gave valuable information for the design of a large-scale experiment (MEDCAPHOT-TRACE), which was performed during the period 20th of August until the 20th of September, 1994, over the GAA. The main objective of MEDCAPHOT-TRACE is to study the meteorological and chemical evolution of ozone related trace gases, modulated by the various synoptic and local meteorological conditions (sea/land breeze circulations, local winds, inversion layers etc.).

Acknowledgements

The authors wish to thank the staff of the Directory of Air and Noise Pollution Control, Ministry of Environment, Physical Planning and Public Works, Athens, Greece and especially the Director Mr. N. Spyropoulos, Mr N. Manalis, Dr. L. Vyras and Mr. P. Zikos for their help during the measuring campaign and for providing the data from the pollution monitoring network in GAA.

References

Alexopoulos, A., D. Asimakopoulos and *E. Mitsoulis*, 1993: Model for traffic emissions. Atmos. Environ. **27B**, 435–446.

Becker, K. H., W. Fricke, J. Lobel and *U. Schurath*, 1985: Formation, transport and control of photochemical oxidants. In Air pollution by photochemical oxidants (R. Guderian, Ed.) 1–125, Springer, Berlin.

Enger L., 1986: A higher order closure model applied to dispersion in a convective PBL. Atmos. Environ. **20**, 879–894.

Enger L., 1990: Simulation of dispersion in moderately complex terrain-Part A. The fluid dynamic model. Atmos. Environ. **24**, 2431–2446.

Enger L., D. Koracin and *X. Yang*, 1993: A numerical study of the boundary layer in complex terrain. Part 1. Sensitivity tests of boundary conditions and external forcing. Boundary-Layer Meteorology **66**, 357–394.

Fabian, P., C. Haustein, G. Jacobi, B. Rappenglück, P. Suppan and *P. Steil*, 1994: Photochemical smog in the Munich metropolitan area. Beitr. Phys. Atmosph. **67**, 39–56.

Gery, M. W., G. Z. Whitten, J. P. Killus and *M. C. Dodge*, 1989: A photochemical kinetics mechanism for urban and regional scale computer modelling. J. Geoph. Res. **94**, 12925–12956.

Grennfelt, P., U. Samuelson, T. Nielsen and *E. L. Thomsen*, 1992: The presence of PAN in long-range transported polluted air masses. In: 2nd Eur. Symp. on Phys. Chem. Behav. Atmos. Pollut. (B. Versino, H. Ott, Eds.) 619–624, Reidel, Dordrecht.

Güsten, H., G. Heinrich, T. Cvistas, L. Klasinc, B. Rus, D. P. Lalas and *M. Petrakis*, 1988: Photochemical formation and transport of Ozone in Athens, Greece. Atmos. Environ. **22**, 1855–1861.

Lalas, D. P., D. N. Asimakopoulos, D. G. Deligiorgi and *C. G. Helmis*, 1983: Sea breeze circulation and photochemical Pollution in Athens, Greece. Atmos. Environ. **17**, 1621–1632.

Lalas, D. P., M. P. Tombrou, M. P. Petrakis, D. N. Asimakopoulos and *C. G. Helmis*, 1987: An experimental study of the horizontal and vertical distribution of ozone over Athens. Atmos. Environ. **21**, 2681–2693.

Mantis, H. T., C. C. Repapis, C. S. Zerefos and *I. C. Ziomas*, 1992: Assessment of the potential for photochemical air pollution in Athens: A comparison of emissions and air pollutant levels in Athens with those in Los Angeles. J. Appl. Meteor. **31**, 1467–1476.

Melas, D. and *L. Enger*, 1993: A numerical study of flow in Athens area using the MIUU model. Environ. Software **8**, 55–64.

Melas, D., I. Ziomas and *C. Zerefos*, 1995: Boundary layer dynamics in an urban coastal area under sea breeze conditions. Accepted for publication in Atmospheric Environment B.

Moussiopoulos, N., 1993: Athenian photochemical smog: intercomparison of simulations APSIS), background and objectives. Environmental Software **8**, 3–8.

Moussiopoulos, N., Th. Flassak, P. Sahm and *D. Berlowitz*, 1993: Simulations of the wind field in Athens with the nonhydrostatic mesoscale model MEMO. Environmental Software **8**, 29–42.

Paliatsos, A., L. G. Vyras, I. C. Ziomas and *G. Amanatides*, 1994: Routine air pollution measurements in Athens: rationalization of the monitoring network using spatial correlation analysis. Fresenius Environmental Bulletin, accepted for publication.

Penkett, S. A., F. J. Sandalls and *E. J. Lovelock*, 1975: Observations of peroxyacetyl nitrate (PAN) in the air of southern England. Atmos. Environ. **7**, 139–141.

PERPA, Directorate for Air Pollution Controll, Ministry of Environment, Physical Planning and Public Works, Greece, 1989: The Atmospheric Pollution in the Area of Athens. Tech. Rep. (in Greek).

Pielke, R. A. and *C. L. Martin*, 1981: The derivation of a terrain following coordinate system for use in a hydrostatic model. J. Atmos. Sci. **38**, 1707–1713.

Pilinis, C., P. Kassomenos and *G. Kallos*, 1993: Modeling of photochemical pollution in Athens, Greece. Application of the RAMS-CALGRID modeling system. Atmos. Environ. **27B**, 353–370.

Scheffe, R. D. and *R. E. Morris*, 1993: A review of the development and application of the Urban Airshed Model. Atmos. Environ. **27B**, 23–39.

Smylie, M., J. L. Fieber, T. C. Myers and *S. Burton*, 1991: A preliminary examination of the impact on emissions and ozone air quality in Athens, Greece from various hypothetical motor vehicle control strategies. European Conference on new fuels and clean air, 19 June 1991, Antwerp, Belgium.

Smolarkievicz, P. K., 1983: A simple positive definite advection scheme with small implicit diffusion. Mon. Weath. Rev. **111**, 479–486.

Tjernström, M., 1987: A study of flow over complex terrain using a three dimensional model. A preliminary model evaluation focusing on stratus and fog. Annales Geophysicae **5B**, 469–486.

Tsalkani, N., P. Perros and *G. Toupance*, 1987: High PAN concentrations during nonsummer periods: A study of two episodes in Creteil (Paris), France. J. Atmos. Chem. **5**, 291.

Yamada, T. and *G. L. Mellor*, 1975: A simulation of the Wangara atmospheric boundary layer data. J. Atmos. Sci. **32**, 2309–2329.