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The role of Anthropogenic and Biogenic Emissions on Tropospheric Ozone Formation over Greece

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Abstract. In the frame of this work, the sensitivity of a grid-based photochemical model on the emission inventory is examined. More precisely, the role of various emission categories on simulated oxidant formation is investigated and especially the biogenic ones. Special emphasis is given on the investigation of the role of the biogenic emissions on tropospheric ozone formation over areas with significant anthropogenic sources. The area of interest is the SE part of the Greek Peninsula where there are various types of anthropogenic pollutant sources and important biogenic sources from forest areas. Ozone air quality simulations were performed using the combined system of the atmospheric model RAMS and the photochemical model UAM. The simulations revealed that there is a significant increase of the calculated ozone concentrations over areas with significant precursor sources when biogenic emissions are taken into account. This increase is more pronounced during the days with a significant regional scale transport.

1 Introduction

The effectiveness of emission control scenarios applied in local or regional scale for the tropospheric ozone reduction is associated with the spatial and temporal characteristics of the emissions. As an important amount of precursor pollutants is emitted by biogenic sources, Chameides et al., (1988) suggested that the effectiveness of such scenarios in urban areas may be limited because of the presence of biogenic volatile organic compounds (VOCs).

The role of the biogenic emissions and their speciation has been investigated by several modelling studies both in N. America and Europe (Simpson, 1995; Roselle et al., 1991). The biogenic VOCs emissions consist of various species but as most important are considered the isoprene and monoterpenes (α-pinene, β-pinene, limonene).

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The isoprene is emitted from various forest types and seems to play a dominant role among the VOCs in boundary layer ozone formation as it is one of the most reactive VOC while the monoterpenes have only a secondary effect on ozone formation (Chameides et al., 1992). Several algorithms have been developed for the calculation of the isoprene emission rates over Europe (Simpson et, al. 1995). Despite this fact, the uncertainties in the estimated isoprene emissions are still high (Simpson, 1995).

An attempt to estimate the biogenic emissions for Greece, was made by Mimilidis et al (1994) who estimated the biogenic non-methane VOCs (NMVOCs) emission rates from Greek forests and Tsiligiridis and Pistikopoulos (1995) who estimated the NMVOCs emission rates from forests in the Attica Peninsula. For their estimates they followed the CORINAIR methodology (C.E.C, 1992). As Mimilidis et al. (1994) suggested, the composition of the emitted NMVOC from all forest categories in Greece on an annual basis is 64% isoprene, 27,6% "unknown" , 5% α-pinene and 2,8% monoterpenes. These results indicates that the isoprene has the highest emission rate from all other biogenic VOCs for the area of Greece.

In the frame of this study, the sensitivity of the calculated ozone concentrations on isoprene emissions was examined by using the combined system of the atmospheric model RAMS and the grid - based photochemical model UAM-IV. The area of interest was the SE part of the Greek Peninsula which is shown in Fig. 1b. The sensitivity study was focused on the calculated ozone concentrations over the Greater Athens Area (GAA). This area includes the Athens Basin and Triassion Plane where important anthropogenic sources of VOCs and NOx are located. The simulation period was from 6 to 8 July, 1994. For this period a large database of meteorological and air quality data is available due to the measuring campaign in the framework of the T-TRAPEM project which was carried out during these days (Kallos et al., 1997). The air quality data were used for the definition of the boundary and background concentrations for UAM-IV simulations. Moreover, the isoprene emission rates have pick values during the summer. For the purposes of this work a detailed isoprene emission inventory has been constructed, using hourly ambient temperature and solar radiation data calculated by RAMS model. The methodology used for the estimation of isoprene emissions over the SE Greece was based on the estimation procedures used for the area of California, US, which shows some similarities with the Mediterranean region. Two simulations were performed with two different emission scenarios A and B. In scenario (A) isoprene and anthropogenic VOCs and NOx emissions were used. In scenario (B) no biogenic emissions but only anthropogenic VOCs and NOx emissions were considered. The predicted ozone concentrations from these simulations were compared by subtracting the resulting concentration fields and by examining the spatial and temporal distribution of the differences as well as the locations of their maxima and their evolution with time. The meteorological and other input parameters used for both simulations were identical.

2 Meteorological conditions

During the simulation period (6-8 July 1994) stationary conditions were established over the greatest part of the Mediterranean region. A high pressure system with weak pressure gradient was installed over the area resulting in a weak synoptic flow at surface and aloft. During the night, a NW flow was evident over the area of interest while during the day thermal local circulations were favoured. These conditions leaded to the formation of stable lower tropospheric layers due to the large scale subsidence in association with the transport of relatively warm air masses and the relatively low winds. Stagnant atmospheric conditions were likely to occur over the GAA especially during 7 of July. A detailed analysis of the meteorological conditions prevailing during the period 6 - 8 July 1994 is given in Peleg et al. (1996) and Kotroni et al. (1998).

3 Models and Data used

3.1 The RAMS model

The Regional Atmospheric Modeling System (RAMS) has been developed at Colorado State University and ASTER Division of Mission Research Corporation (Pielke et al., 1992). RAMS uses the full set of primitive dynamical equations with optional parameterization schemes for turbulent diffusion, solar and terrestrial radiation, sensible and latent heat exchange between the atmosphere, multiple soil layers, the kinematic effects of terrain and a vegetation canopy.

An important feature of RAMS is its capacity of performing two-way interactive grid nesting which allows local fine-mesh grids to resolve small atmospheric systems, while simultaneously modeling the large-scale environment of the systems on a coarser grid.

3.2 The UAM-IV model

The UAM is a three-dimensional photochemical grid model designed to calculate the concentrations of both inert and chemically reactive pollutants by simulating the physical and chemical processes in the atmosphere that affect pollutant concentrations (Morris et, al., 1990). The UAM is based on the atmospheric diffusion or species continuity equation which represents a mass balance including all of the relevant emissions, transport, diffusion, chemical reactions and removal processes. In detail, the spatial distribution and composition of biogenic and anthropogenic NOx and VOC emissions, the spatial and temporal variations in the wind field, the dynamics of the boundary layer, the chemical reactions involving VOC, NOx and other important species, the diurnal variation of solar isolation and temperature, the loss of ozone and ozone precursors by dry deposition and the ambient background of VOC, NOx and other species are considered in the simulation of the photochemical processes. The UAM-IV implements the version IV of the Carbon Bond Mechanism (CB-IV) for solving chemical kinetics. As the spatial and temporal variation and differences in the reactivity (speciation) of the emissions are considered in UAM-IV, the model is suitable for evaluating the effects of emission control scenarios on urban air quality.

3.3 Model Setup

3.3.1 RAMS model setup

In order to accurately represent the interaction of various scale circulations due to the complexity of the physiographic characteristics of southern Greece, three-nested grids have been defined (Fig.1a). The outer model domain (1) had a horizontal grid increment of 32 km , the intermediate (2) , had a horizontal grid increment of 8 km and the finer one (3) had a horizontal grid increment of 2 km Twenty-three vertical levels following the topography were used in all grids, having 180 m vertical spacing near the ground, stretching to 1 km at an altitude of 6 km and remaining constant up to about 16 km. The inner grid has been defined on a way to include in addition to the GAA, the island of Evoia on the East, the Corinthian Gulf on the West, and the eastern coast of Peloponnese. This extended finer grid was considered as necessary in order to be able to accurately simulate the atmospheric flow over such a complex terrain and avoid any possible lateral boundary influence.

The simulation started at 0000 UTC, 6 July, 1994 and ended after 72 hours. The ECMWF 1° gridded analysis fields were used in order to initialize the model and to nudge the lateral boundary region of the coarser grid. The ECMWF field of the climatological sea-surface temperature (1° resolution) was used. Topography was derived from a 30 sec terrain data while vegetation type data with 10 min horizontal resolution have been used for all grids.

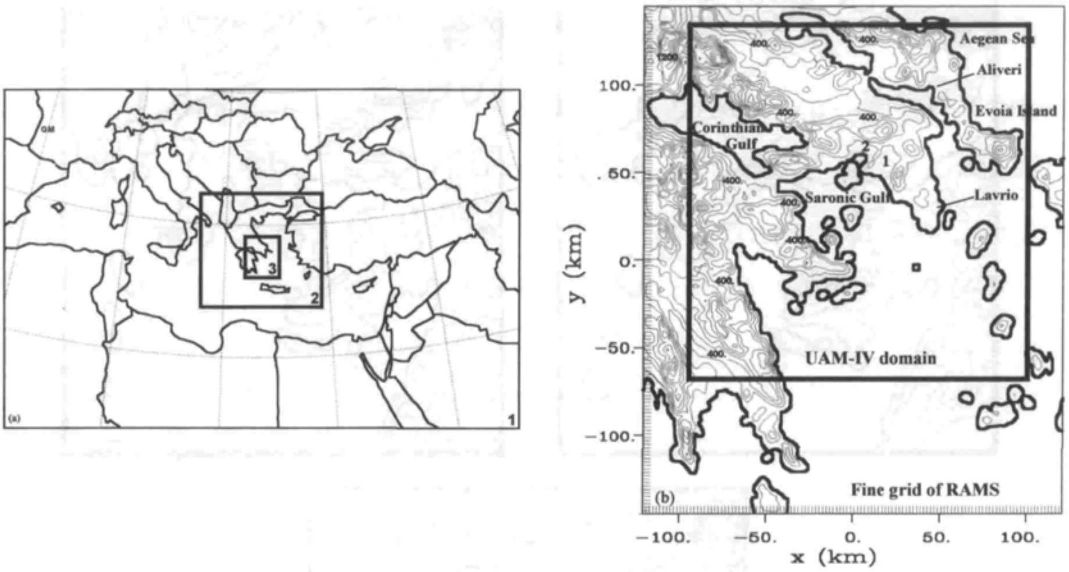

Fig. 1. (a) Domain of the three nested grids used for RAMS simulations, (b) domain of the grid used for UAM-IV simulations (topography contours are plotted every 200 m). 1. Athens Basin, 2. Triassion Plane.

3.3.2 UAM-IV model setup

For the UAM-IV simulations the domain presented in Figure (1b) has been used. The required gridded meteorological data were provided by the calculated meteorological fields of RAMS. UAM-IV grid has the same resolution as the fine grid of RAMS (2x2 km) with 90x140 grid points. The analysis of the model results concerns the first layer of the model which extends from surface up to approximately half the height of the mixing layer at each grid point. The boundary and initial conditions used in the simulations represent average ambient concentrations over the modeling area derived from the measurements performed by a research aircraft in the frame of the T-TRAPEM campaign during the simulation period (Kallos et al., 1997; Peleg et, al., 1996). The simulations started at 0000 UTC, 6 July, 1994 and ended after 72 hours.

The anthropogenic emission inventory (Fig. 2a,b) concerns the gridded hourly emission rates of anthropogenic NMVOCs and NOx emitted from the GAA (Moussiopoulos et al., 1995) appropriately adjusted to recent changes and in order to be used as input in the specific model. Emissions from the power plants located at Aliveri and Lavrio were also included in the data (Kallos et al., 1995). Concerning the biogenic emission inventory, the isoprene emissions for the SE part of Greek Peninsula (Fig. 2c) were estimated in a hourly basis for the period 6 - 8 July, 1994 with a resolution of 2 km, by using the forest coverage and speciation data provided by the 1st National Forest Inventory and according to the methodology suggested by CORINAIR (C.E.C, 1992). The ambient temperature and solar radiation data for the calculation of the emission factors were provided in a hourly basis by RAMS model.

4 Discussion

4.1 Meteorological fields

The calculated surface wind fields on 7 and 8 July 1994 are shown in Figure 4. On 7 July 1994 a NW flow prevails over the SE Greece, during the night (Figs 3a, c) with wind speed intensities ranging from 6 to 8 m/s. This flow becomes westerly and weakens (4m/s) over the Athens Basin. During the day, the development of sea-breeze cells is evident at the coastal areas on 7th of July (Fig. 3b, 1200 UTC). A southerly flow prevails over the Saronic Gulf and the GAA at noon until late afternoon, as a result of the interaction between the mesoscale flow which develops around the Peloponnese and the sea-breeze over the Saronic Gulf. This flow is very weak over the maritime area east of Peloponnese and is strengthened close to the Athens Basin coastal areas as it is combined with the sea breeze. Under these conditions regional scale transport is not favored. During the night between 7 and 8 of July, the NW flow is weaker than the previous night. During the day hours of 8 July, a strengthening of the pressure gradient over the Dardannelles gap results in regional-scale flow from northerly directions over the Aegean (Fig. 3d, 1200 UTC). Despite the fact that this flow is relatively weak, it opposes the mesoscale flow around Peloponnese. The sea-breeze from the Saronic Gulf towards the Athens Basin develops during noon and afternoon hours and the near surface wind

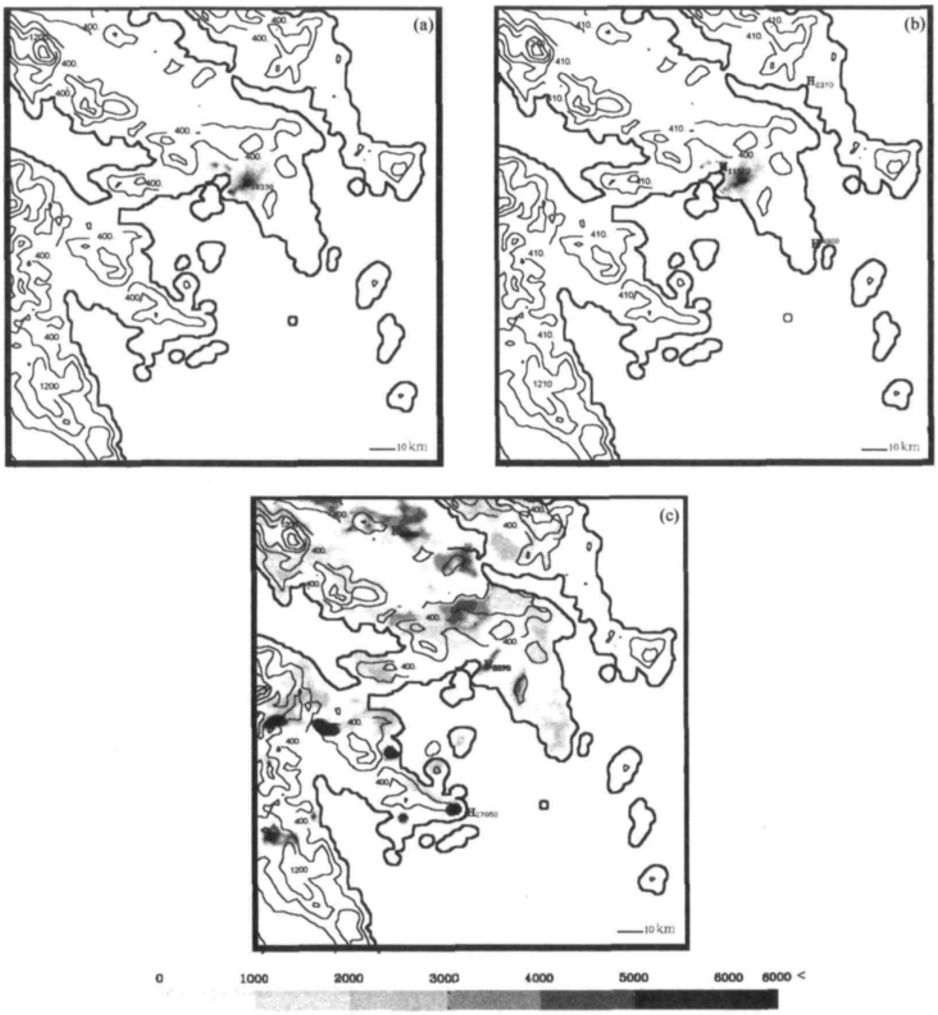

Fig 2. Hourly emission rates in 500 gr_moles/h intervals (a) antrhopogenic VOC, (b) antrhopogenic NOx and (c) isoprene, at 12.00 UTC of 7 July 1994.

speed reaches 6 m/s over the waters offshore of Athens. The strengthening of the northerly flow favors the transport of air masses from Evoia Island which are enriched with isoprene (Fig 3c), towards the GAA.

4.2 UAM-IV simulations

The model results from both scenarios have been compared by examining the spatial distribution of the differences between the calculated ozone concentrations. The maximum difference in calculated ozone concentrations occurs over the GAA during the day. The calculated ozone concentrations when the isoprene emissions are involved are much higher than the predicted concentrations with no isoprene emissions taken into the account. More specifically, on 7 July 1994 the predicted ozone, when isoprene is used, is much higher and the differences reach 39 ppb at 1200 UTC over the area of Hymettus mountain in the SE part of the Athens Basin (Fig. 4a). Note that Hymettus is covered with forests to a large extent. Later on, at 1400 UTC, the maximum difference is evident over the urban area of the Athens Basin and reaches 55 ppb (Fig. 4b). During the evening, the maxima of the differences between calculated ozone concentrations are evident in the NW part of the Athens Basin over Parnitha Mountain. The calculated ozone is higher when the isoprene is involved and the differences reach 35 ppb (2000 UTC, Fig.4c). On 8 July the differences on concentrations between the two scenarios are much higher. The presence of isoprene emissions results in about 80 ppb higher concentrations during the day. The maximum differences appear over the western part of the Athens Basin and the Thriassion Plane. In detail, differences which reach 80 ppb appear at 1100

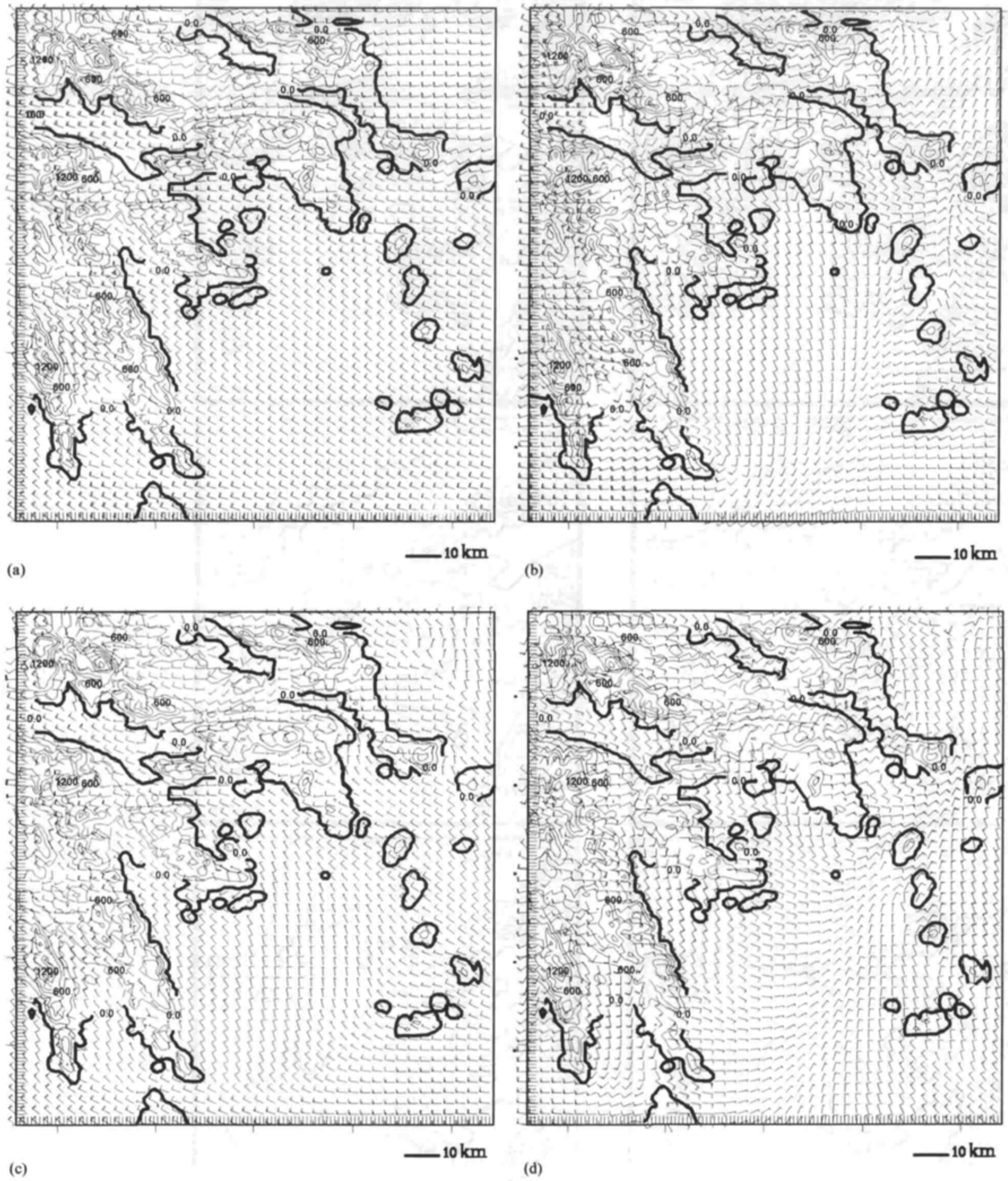

Fig. 3. Winds at z=86 m above ground level from the fine grid of RAMS at a) 0000 UTC of 7 July 1994, b) 1200 UTC of 7 July 1994, c) 0000 UTC of 8 July 1994, d) 1200 UTC of 8 July 1994. Barbs are plotted every third grid point. One barb equals $4 ms^{-1}$, one half barb equals $2 ms^{-1}$. Topography contours are plotted every 300 m.

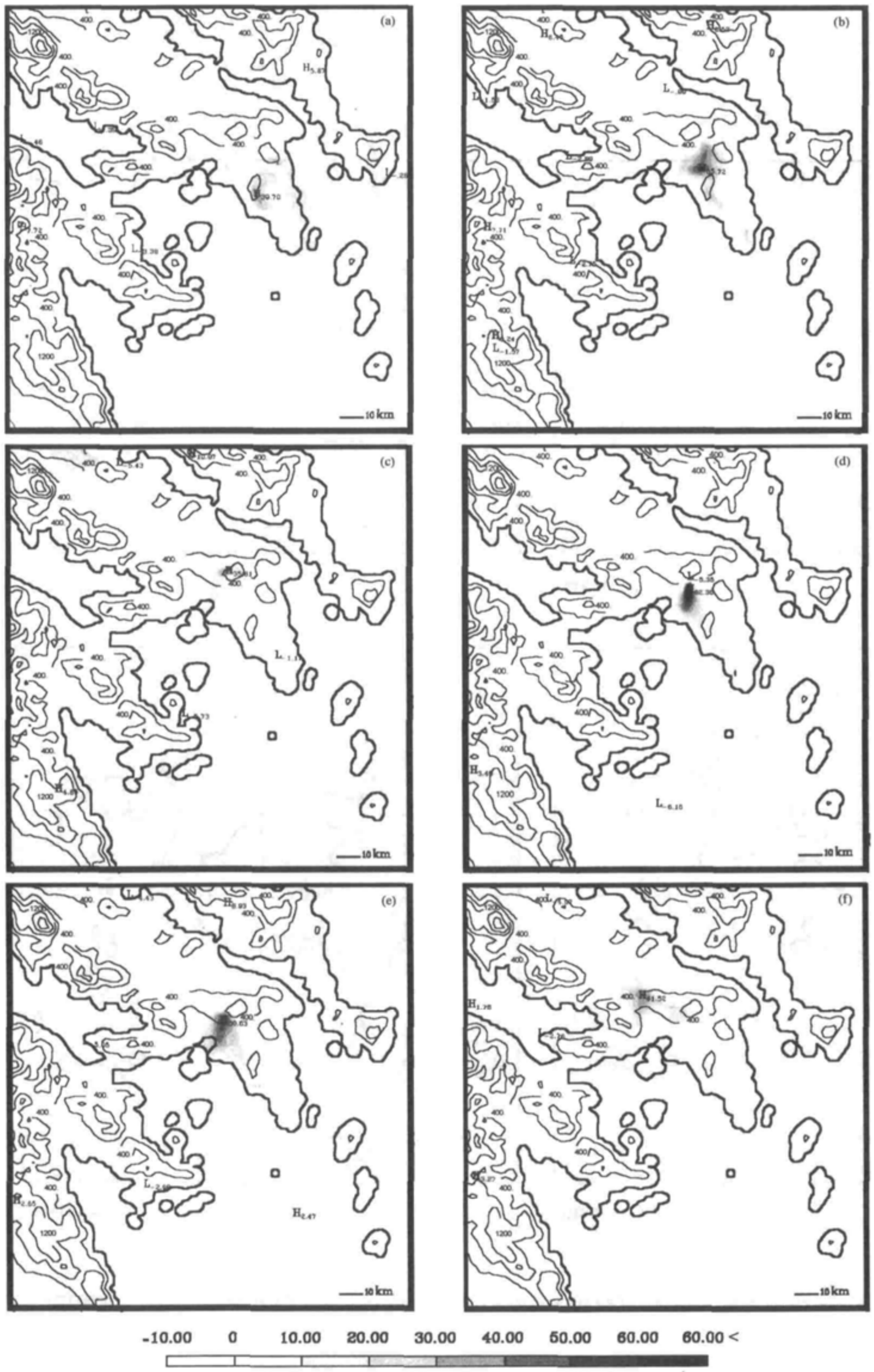

Fig. 4. Differences in calculated ozone concentrations by scenarios (A) and (B). Concentration contours are plotted in 10 ppb intervals. Topography contours are plotted every 400 m. a) 1200 UTC, 7/7/1994, b) 1400 UTC, 7/7/1994, c) 2000 UTC, 7/7/1994, d) 1100 UTC, 8/7/1994, e) 1400 UTC, 8/7/1994, f) 2000 UTC, 8/7/1994.

UTC (Fig 4d) over this area while later on (1400 UTC) these differences reduce to 60 ppb (Fig. 4e).

Later on during the late afternoon and the evening ozone which has been previously produced over the GAA has been transported by the prevailing south-easterly flow over the NW Thriassion Plane. As a result the maximum differences during the evening (2000 UTC) are evident over the NW part of the Thriassion Plane (Fig. 4f). It should be mentioned that no significant differences of the predicted ozone by both scenarios have been found over remote areas.

During the night, the predicted concentrations were identical. This fact is due to the transport of the polluted air masses outside the domain due to the prevailing NW flow. The travelling time of the air masses inside the model domain under the prevailing meteorological conditions is a critical parameter which should be taken into account for the selection of the domain size.

The comparison of the ozone concentrations calculated by the two different scenarios, revealed that differences over urban and industrial areas were higher during 8 July. In addition, the maximum differences between the two scenarios occur earlier. This result may be attributed to the transport of air masses enriched in isoprene towards Attica, during the morning hours of 8 July. This suggestion is supported by the near surface wind field predicted by RAMS. It should be mentioned also that possible changes of the propagation pattern of the boundaries inside the model domain due to changes in the wind field from 7 to 8 of July were found to affect significantly the simulated ozone levels (Varinou et al., 1998).

5 Concluding remarks

The simulations performed in the frame of this study, illustrate the importance of the biogenic emissions in the simulated air quality in the vicinity of anthropogenic emissions and the areas affected by them. The difference between various emission scenarios (with and without the biogenic emissions implemented) followed for ozone calculations suggests that the biogenic VOC emissions must be taken into account.

Meteorology was found to play an important role when isoprene emissions are used. In the case of considerable regional/mesoscale forcing the role of biogenic emissions on the photochemical activity over certain areas was found to be significant, mainly due to the transport of air masses enriched with isoprene from remote areas. This suggests that uncertainties in the simulated meteorological fields may result to a modification of the simulated ozone concentrations in areas of concern. For this reason, the improvement of the emission inventory must be accompanied by a realistic representation of the meteorological parameters.

In addition, the travelling time from the lateral boundaries (especially the inflow regions) of the model domain towards the area of interest must be considered. This is critical because of the propagation of imposed boundary values over the area of interest and must be taken into account for the definition of the size of the model domain. Sensitivity tests with different domain configurations are strongly recommended.

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