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# EMISSION SOURCES AND THEIR EFFECT ON MAXIMUM OZONE CONCENTRATIONS OVER GREECE

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## ABSTRACT

The purpose of this study is to investigate the impact of the anthropogenic emissions from maritime transport and from Greece's neighboring countries on the maximum ground-level $O_3$ concentrations over Greece during the summer period when enhanced photochemical $O_3$ production is favored. The photochemical model Urban Airshed Model (UAM-V) coupled with the meteorological model MM5 was used to address this issue.

**Key Words :** Anthropogenic Emissions, Ozone, Photochemical Modeling

## 1. INTRODUCTION

Ozone is of concern because of its adverse effects both on human health and on ecosystems. As a secondary pollutant, it is not emitted directly, but is generated in the atmosphere through complex series of chemical reactions initiated by absorption of solar energy [Seinfeld and Pandis, 1998]. Its generation is typically favored in high-pressure, stagnant atmospheric systems at locations with substantial concentrations of oxides of nitrogen (NOx) and volatile organic compounds (VOCs). Both NOx and VOCs originate either from anthropogenic source sectors, e.g. the industrial and the transport sector, or from biogenic sources. Both anthropogenic and biogenic sources play roles in $O_3$ formation and accumulation. While the impact of biogenic emissions on surface $O_3$ has been more thoroughly examined by many studies (Roselle et al., 1991; Pierce et al., 1998; Varinou et al., 1999; Tao et al., 2003), the role of anthropogenic emission sources in the production of ground-level $O_3$ has not been extensively investigated.

Greece is situated at the Eastern Mediterranean which is an area characterized by enhanced regional levels of $O_3$, especially during the summer months, as a result of both the long-range transport in the area of significant $O_3$ and $O_3$ precursors' amounts from continental Europe and the high levels of solar radiation in combination with the local anthropogenic and biogenic $O_3$ precursors' emissions (Zerefos et al., 2002; Kouvarakis et al., 2002). Increased $O_3$ concentrations over Greece have been measured both on urban and regional scale (Kourtidis et al., 2002; Ziomas et al., 1998). The greater part of Greece is surrounded by maritime areas. Sea transport

activities are an important emission source of the area. In addition Greece is neighboring with other Balkan countries significantly heterogeneous not only in environmental but also in economic and social aspects.

The principle purpose of this work is to assess the effect of the emissions from sea transport and from Greece's neighboring countries on the ground-level $O_3$ concentrations over Greece using the air quality model Urban Airshed Model (UAM-V) coupled with the meteorological model MM5. The study domain covers Greece, Albania, FYROM, western Turkey, southern Serbia and Montenegro and the greater part of Bulgaria. We base the modeling on a 2000 summer period, and select the absolute maximum hourly $O_3$ concentrations for in depth analysis.

## 2. MODELS AND DATA USED

The UAM-V model is a 3-D regional 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 (SAI, 1999). The basis for the model is the atmospheric diffusion or species continuity equation. The major processes that the model simulates which also affect $O_3$ levels are: 1) the spatial and temporal distribution and the composition of emissions of NOx and VOCs, 2) the spatial and temporal variations in the wind fields, the temperature and the solar insolation, 3) the dynamics of the boundary layer, 4) the loss of $O_3$ and $O_3$ precursors by dry and wet deposition, 5) the ambient background of VOCs, NOx, and other species and 6) the chemical reactions involving VOC, NOx, and other important species. The UAM-V program employs an extension of version IV of the Carbon Bond Mechanism (CB-IV) for solving chemical kinetics which is called CB-IV-TOX.

The meteorological model MM5 was used to produce the hourly meteorological fields necessary for the implementation of the UAM-V model. The Mesoscale Model MM5 is a limited-area, nonhydrostatic, terrain-following sigma-coordinate model designed to simulate or predict mesoscale and regional-scale atmospheric circulation (Grell et al., 1994). Using the capability of MM5 for multiple nesting, the model run with the option of two way nesting for two domains (figure 1). The large domain, covering the South-Eastern Mediterranean, was consisted of 55 x 55 grid points having 30km x 30km spatial resolution. The finer domain, covering the study area, was consisted of 115 x 115 grid points having 10km x 10km spatial resolution. Simulations starting at 18:00 UTC and ending after 78 hours were performed in order to produce meteorological data for a time period extending from 11 June 2000 to 31 July 2000. MM5 simulations were initialised and developed lateral boundary conditions using NCEP Global Analyses. Both of the domains had the same vertical structure consisted of 33 $\sigma$ levels.

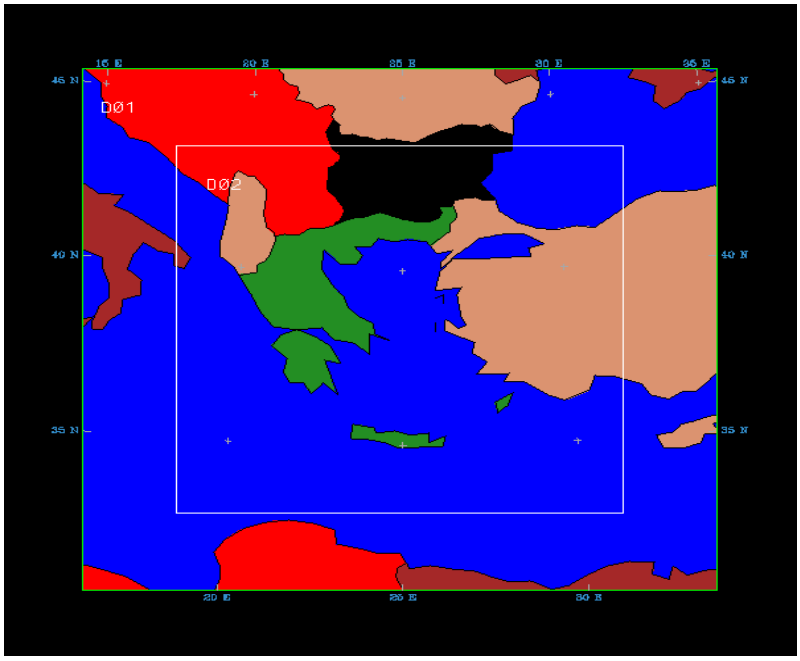


Figure 1. MM5 modeling domains.

The gridded, hourly, and speciated biogenic and anthropogenic emissions data used as input data to the photochemical model were based on an emission inventory compiled for the Balkan Region having high spatial and temporal resolution (Symeonidis et al., 2004; Poupkou et al., 2004). Following the methodology of the EMEP/CORINAIR emission inventory guidebook (EMEP/CORINAIR Guidebook, 2002), typical diurnal biogenic emission variations of isoprene and monoterpenes, emitted from different land use types (forests, shrub species and agricultural crops) extracted from satellite data, were calculated for every month of the year with spatial resolution of 10km x 10km. Using the top-down methodology on reported emission data of the years 1994-2000 (Ritter, 1997; EMEP/MSC-W, 2002), annual emission fields of NOx, NMVOCs and CO for different anthropogenic emission source sectors such as the transport sector, the industrial sector and the central heating sector were estimated with spatial resolution of 10km x 10km. More detailed was the transport sector emission inventory for Greece calculated using methodologies of the EMEP/CORINAIR emission inventory guidebook (EMEP/CORINAIR Guidebook, 2002). The anthropogenic annual emission data were temporally disaggregated in order to get seasonal and diurnal emission variations.

Figure 2 presents, for each of the 3 anthropogenic pollutants, percentage emission contributions by geographical area of the study domain. The different geographical areas that are separately being examined are the continental parts of the countries included in the study domain and the maritime area considered as a whole. NOx emissions from maritime transport activities represent about 34% of the annual total anthropogenic NOx emissions and are comparable to NOx emissions of continental Greece which have a percentage contribution of almost 29%. NOx emissions of continental western Turkey have an 18% share in overall NOx emissions. Summing

NOx emissions of all other geographical areas we calculate a 19% contribution to NOx emissions total. NMVOCs emitted from continental Greece and western Turkey respectively account for 47% and 35% of the annual total anthropogenic NMVOCs emissions while less important is the contribution of the rest of the geographical areas to NMVOCs emissions. Most significant are the CO amounts emitted from continental Greece and western Turkey each one representing 36% of the total CO emissions. CO emissions of the continental part of Bulgaria included in the area of study have a 17% share in the overall CO emissions.

It can be pointed out that sea transport activities at the maritime area of the study domain are an important NOx emission source. Pollutants' emissions from the rest geographical areas other than Greece seem to be less significant compared to emissions of continental Greece. The only exception is western Turkey representing pollutants' emissions which, despite the fact that in some cases are less than those of Greece, they can be however considered comparable. It is worth noticing that the contribution of the other countries than Greece to the total pollutants' emissions might be underestimated since these emissions are poorly reported.

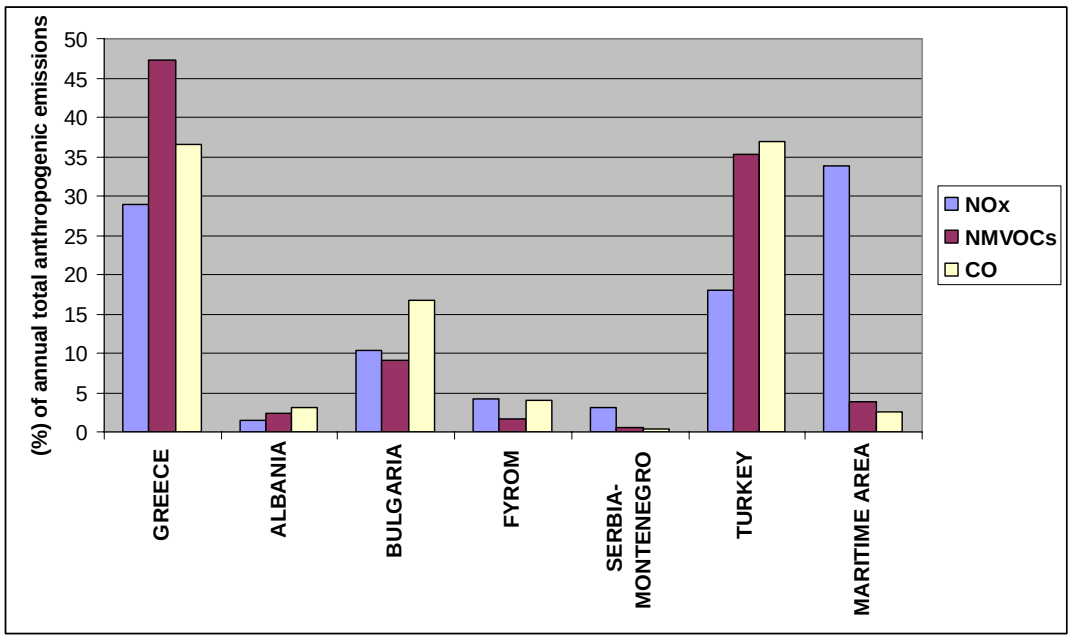


Figure 2. Percentage emission contributions by geographical area of the study domain.

UAM-V was used to simulate ambient $O_3$ concentrations across the domain and to quantify the effect of the anthropogenic emissions from sea transport and from Greece's neighboring countries on the ground-level $O_3$ concentrations over Greece. The domain was divided into 110 rows by 110 columns with a horizontal grid resolution of 10 km. There were 5 vertical layers extending from surface to approximately 2.5 km above the ground. The vertical layers were unevenly distributed with higher resolution at the near-surface layers. The first layer height was 50 m. The analysis of the model results concerns the first layer of the model. To

run UAM-V, proper initial and boundary conditions must be prescribed. The boundary conditions used represent background atmospheric conditions. The boundary concentrations for $O_3$ were set to 40 ppb. In this study the initial conditions were set using the preconditioning technique which began with an initial guess of the species concentrations and was followed by a 3-day ‘‘spin-up’’ simulation. The final hour concentration of each species from the preconditioning run was then set as the initial conditions for the full period simulation. Successive 3-day model simulations were performed in order to calculate hourly $O_3$ concentrations for the time period of interest extending from 14 June 2000 to 31 July 2000.

The UAM-V model was implemented considering 3 different emission scenarios. According to them $O_3$ concentrations were calculated with the use of:

1. Base emission scenario: Biogenic and all anthropogenic emissions.
2. 2nd emission scenario: Biogenic and anthropogenic emissions excluding maritime transport sector emissions.
3. 3rd emission scenario: Biogenic and anthropogenic emissions excluding the anthropogenic emissions of all continental geographical areas of the study domain other than Greece.

Our study focuses in the study of spatial distribution of the differences (df) defined as:

$$df = [O_3]_{i\ emission\ scenario} - [O_3]_{base\ emission\ scenario} \qquad (i = 2nd, 3rd) \qquad (1)$$

where $[O_3]$: absolute maximum hourly $O_3$ concentration (figures 3, 4).

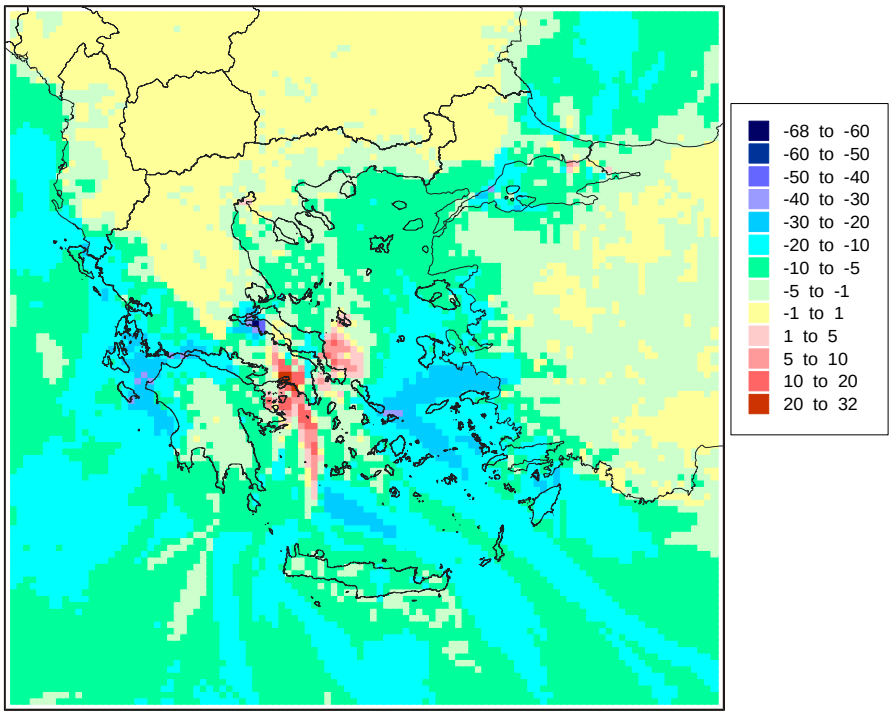


Figure 3. The impact of the maritime transport emissions on the absolute maximum hourly $O_3$ concentrations (ppb) as calculated with equation (1).

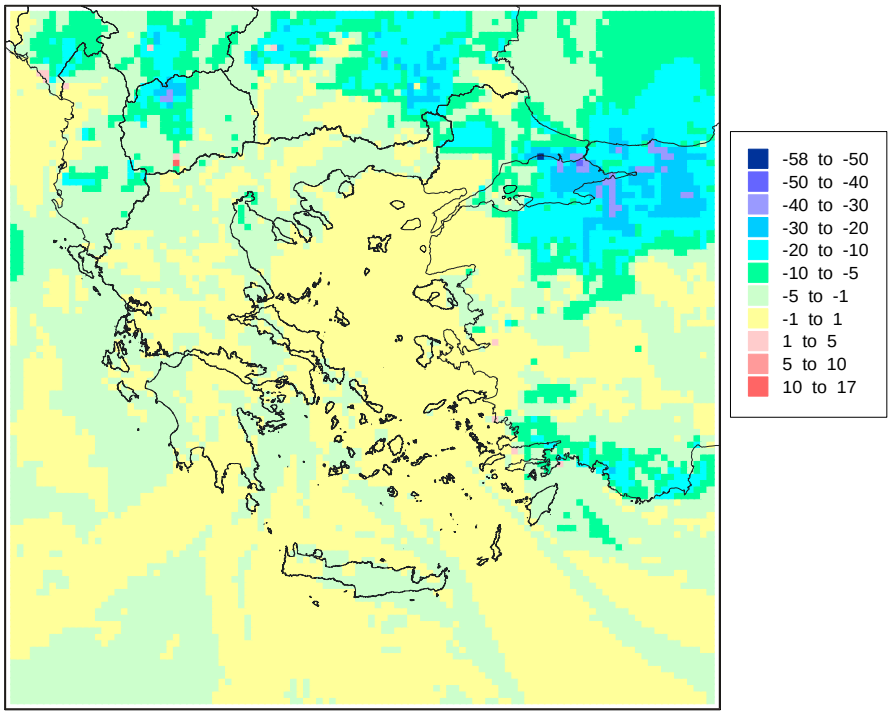


Figure 4. The impact of the anthropogenic emissions of all continental geographical areas of the study domain other than Greece on the absolute maximum hourly $O_3$ concentrations (ppb) as calculated with equation (1).

## 3. DISCUSSION - CONCLUSIONS

The influence of maritime transport emissions on the maximum $O_3$ concentrations over Greece is significant. When these emissions are not taken into account for the calculation of $O_3$ concentrations there is a general reduction of absolute maximum hourly $O_3$ levels over Greece. Over the continental part of the country $O_3$ reduction can be on the order of 20 ppb. Over maritime areas the decrease is more pronounced reaching 68 ppb. However, over the greater Athens area and the maritime region southern of the city, maximum $O_3$ levels increases are observed ranging from 10 ppb to 32 ppb. Such areas are influenced by high NOx amounts that are emitted from the sea transport activities. The elimination of these emissions prohibits $O_3$ destruction which is photochemically produced by $O_3$ precursors released in significant amounts by the emission sources of the large urban agglomeration of Athens.

Small decrease of maximum $O_3$ levels on the order of 5 ppb is estimated over Greece when continental anthropogenic emissions of all countries other than Greece are considered equal to zero. The greater area of Thessaloniki, which is a large city situated at northern Greece, is more affected since there the reduction of maximum $O_3$ levels ranges from 5 ppb to 10 ppb. Ozone concentrations are reduced over the greater part of the rest modeling domain. The reductions are larger (maximum values up to 58 ppb) over areas where large urban centers or important emission sources are

located, for example over the northern part of western Turkey, over the central Bulgaria and northern FYROM.

In conclusion, the emissions from maritime transport are estimated to have greater impact on maximum ozone levels over Greece compared to the emissions of countries neighboring with Greece. However, as emissions of Balkan countries are generally poorly reported their contribution might be underestimated. Improved emission estimations for the whole area of study are undoubtedly suggested.

## 4. ACKNOWLEDGEMENTS

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