

## ASSIMILATION OF NUMERICAL STUDY OF THE DISTRIBUTION OF OZONE ABOVE THE GREATER ATHENS AREA (GAA)

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### ABSTRACT

Air pollution is considered to be a critical environmental problem of large urban areas posing a threat to human health because of elevated concentrations of pollutants such as O<sub>3</sub>, NO<sub>x</sub>, VOCs and PM. In the past decades the GAA has experienced rapid expansion of the urban grid. Thus, the current study aims to examine the distribution of ozone above the GAA, with the help of the photochemical model CAMx, and assess the contribution of multiple geographical source areas, boundary and initial conditions to ozone formation. Results showed that the transport of primary and secondary pollutants can affect the air quality of the receptor area. Many pollution episodes reported to ground stations are often due to the development of a local circulation system (sea breeze) that disperses intense pollutant emissions. Moreover, the boundary and initial conditions used in numerical studies play a significant role to the ozone formation.

### 1. INTRODUCTION

Photochemical pollution is one of the most important environmental issues in the Greater Athens Area (GAA). The increase in population and the expansion of the urban grid to the east at areas previously covered by low vegetation are now replaced by new towns, have led to an increase in anthropogenic emissions. The complex terrain - the Athens basin is surrounded by mountains on three sides and the Saronic Gulf on the south - in combination with local meteorological conditions (sea breeze) have often led to the development of pollution episodes in the summer. Since a great part of the population lives under poor air quality conditions the numerical and experimental study of air pollution characteristics of the GAA has attracted the interest of many researchers, (Kalabokas et al. 2012, Mavroidis et al. 2011, Bossioli et al. 2007, Hatzianastassiou et al. 2007, Martilli et al. 2003). Moreover, ozone is a complex pollutant to manage due to its dependence on various parameters such as meteorology, local emissions and chemical interactions with other pollutants. It is of great importance though to study not only the distribution of ozone above an urban area but also to examine the source-receptor relationship (Wang et al. 2009, Passerini et al. 2011, Dunker et al. 2002) and reveal the parameters that lead to high ozone concentrations in certain areas.

The purpose of the present work is to study the dispersion of ozone and its precursors (NO<sub>x</sub> and VOCs) above the GAA as well as the influence of the source area distribution and the initial and boundary conditions to ozone formation. Thus, the characteristics of photochemical pollution in Athens may be quantified making the design of measures for sources that have significant contribution to high ozone levels possible.

### 2. METHODOLOGY

The photochemical simulations were performed with CAMx v4.40, an Eulerian photochemical model that simulates the emission, dispersion, chemical reaction and removal of pollutants in the troposphere by solving the pollutant continuity equation for each chemical species on a system of nested three-dimensional grids. At each time step, the continuity equation is replaced by a splitting method that calculates the contribution of each process (emission, dispersion, chemical reaction and removal) to the change of each cell's concentration which is then carried at the center of each cell volume.

For the present study, two nested grids were used (Fig.1) having a spatial resolution of 15 and 5 km. The fine grid (29 x 29 cells) covered the GAA, Boeotia, part of NE Peloponnesus and NE Evoia Island. The simulation period lasted 3 days, from 00.00 UTC on June 17<sup>th</sup>, 2006 until 24.00 UTC on June 19<sup>th</sup>, 2006. High air pollution concentrations were measured in the GAA during the above period due to the development of a local circulation system (sea breeze). The meteorological fields used in CAMx were produced by the mesoscale meteorological model MM5, having an updated land use field as input. Hourly gridded emissions from the EMEP Center were used for the coarse grid, the projection of which changed to Lambert Conformal Conic with the application of ERDAS Imagine. For the fine grid an emission inventory dated back to 2000 was used that included hourly emission profiles for pollutants SO<sub>2</sub>, NO<sub>x</sub>, CO, NH<sub>3</sub>, NMVOCs, PM<sub>10</sub> and

PM<sub>2.5</sub> for point, line and area sources divided in 10 different SNAP-categories (SNAP Level 1). The Carbon Bond IV chemical mechanism was used.

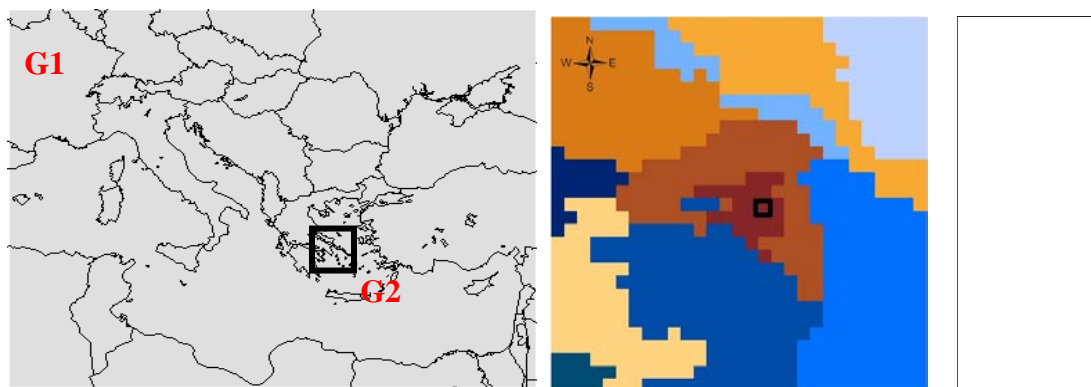


Figure 1. Coarse grid (G1) and fine grid (G2) (left); the 11 source areas used in OSAT for the fine grid, the receptor cell is marked in black (right).

In order to estimate the contributions of multiple source areas to ozone formation the Ozone Source Apportionment Technology (OSAT) tool was selected, that employs multiple tracer species to track the fate of O<sub>3</sub> precursor emissions (NO<sub>x</sub> and VOC). These tracers are affected by chemical reactions, transport, diffusion, local emissions and deposition within the normal CAMx simulation domain and allow for ozone formation from multiple “source groupings” to be tracked. In this study, separate source groupings were defined in terms of geographical areas and initial and boundary conditions. A source area map having each country as a different source region was created for the coarse grid, (Fig. 1). The fine grid was divided into 11 source regions: GAA urban area (region 28), rest part of Attica (region 29), Boeotia (region 30), Evoia island (region 31), Aegean sea (region 32), South Euvoic Gulf (region 33), Aegean sea (region 34), Saronic Gulf (region 35), NE Peloponnesus (region 36), Argolic Gulf (region 37), Corinthian Gulf (region 38).

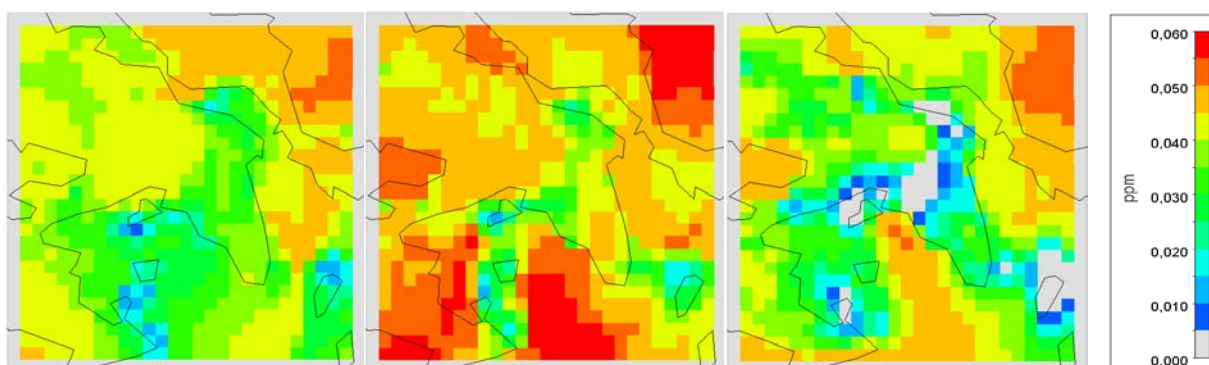


Figure 2. Spatial distribution of surface ozone concentrations at 7.00 UTC - left, 13.00 UTC – middle, and 18.00 UTC - right on June 19<sup>th</sup>.

### 3. RESULTS

Fig. 2 presents the spatial distribution of surface ozone concentrations at 7.00 UTC, 13.00 UTC and 18.00 UTC on June 19<sup>th</sup>, 2006. CAMx managed to reproduce the typical (expected) diurnal variation of O<sub>3</sub>. Early in the morning background concentrations dominated above the GAA and the surrounding areas while after sunrise the intense solar radiation driven photochemistry lead to the consequent ozone formation. The dispersion of primary pollutants, emitted mainly in the center of the GAA, at the eastern suburbs of Athens and the Saronic Gulf where they arrive as secondary pollutants early in the afternoon when the sea breeze is strongest, resulted in high values of O<sub>3</sub>. Comparison of model results with measurements provided by the Greek Ministry of Environment revealed a satisfactory agreement especially for the urban and suburban background stations in Nea Smirni and Ag.Paraskeui (Fig.3). However, CAMx didn't manage to reproduce the high values of ozone that were reported to urban traffic stations sited at the eastern suburbs of the GAA.

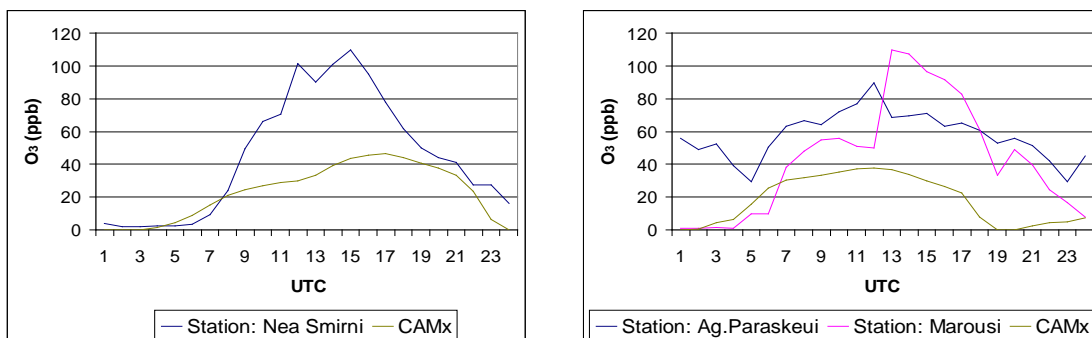


Figure 3. Diurnal variation of modeled and measured O<sub>3</sub> concentrations on June 19<sup>th</sup>, 2006.

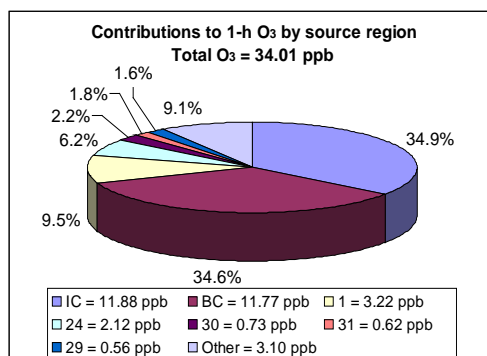


Figure 4. Contributions to O<sub>3</sub> concentration by source region at the receptor cell on 19<sup>th</sup> June 2006, 13.00 UTC.

For the present simulation CAMx ran with the grid nesting method in order to provide time varying boundary conditions for the fine grid. As for the effects associated with initial conditions the first two simulation days were used as a spin-up period so initial conditions refer to the amount of ozone formed at 24.00 UTC of 18<sup>th</sup> June, 2006. The selected receptor cell (see Fig. 1) covers part of the NE suburbs of Athens where the pollution episode was more severe as reported by the two monitoring stations at Marousi and Ag.Paraskeui which are located in this cell. Table 1 shows the top contributors by each source region to NO<sub>x</sub> and VOC concentrations at 13 UTC. It is obvious that the biggest part of O<sub>3</sub> precursors was emitted at source areas 28 and 29 which stand for the urban area of the GAA and the rest part of Attica respectively (NO<sub>x</sub> contribution is about 77% while for VOCs it is 84% for region 28). Since human activity is accumulated at these areas high emissions from fossil-fuel combustion sources were expected at region 28. As can be seen on Fig. 4, the initial and boundary conditions have a significant effect on ozone formation (IC- 34.9%; BC- 34.6%). The majority of ozone that occurred in the receptor cell was formed at neighboring areas. Total ozone contribution from regions 30 and 31 was about 4%.

Table 1. Top NO<sub>x</sub> and VOC contributors by source region to the receptor cell on 19<sup>th</sup> June, 2006 at 13 UTC.

Region	NO <sub>x</sub> (ppb)	Percent	Region	VOCs	Percent
28	20.48	77.1%	28	29.77	84.0%
29	5.07	19.1%	29	3.33	9.4%
30	0.64	2.4%	1	0.78	2.2%
33	0.20	0.7%	24	0.47	1.3%
31	0.07	0.2%	30	0.13	0.4%
Other	0.11	0.5%	Other	0.96	2.7%
<b>TOTAL</b>	<b>26.56</b>	<b>100.0%</b>	<b>TOTAL</b>	<b>35.44</b>	<b>100.0%</b>

#### 4. CONCLUDING REMARKS

Based on the simulations performed with the photochemical model CAMx v.4.40 and the tool OSAT in order to study the source apportionment and source sensitivity of ozone above the Greater Athens Area (GAA) during a pollution episode, the following conclusions could be made:

- Regarding ozone model concentrations, although values followed the expected diurnal variation they didn't reach the peaks of the measured ones.
- Meteorological conditions play a significant role to the dispersion of primary and secondary pollutants and therefore to the development of pollution episodes.
- Ozone transported from surrounding areas to the NE suburbs of the Athens basin was mainly responsible for the total amount occurred at the area and led to high values on June 19<sup>th</sup>, 2006.
- Among the factors that should be taken into consideration when studying air pollution at urban areas is the source-receptor relationship.

Further work needs to be done in order to examine which emission source regions, categories (e.g. emissions from road transport) and species when reduced would have the greatest effect in ozone concentrations.

## 5. ACKNOWLEDGEMENTS

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