

# A Modelling Study of the Photochemical and Particulate Pollution Characteristics above a Typical Southeast Mediterranean Urban Area

Kiriaki-Maria Fameli, Vasiliki D. Assimakopoulos, Vasiliki Kotroni

**Abstract**—The Greater Athens Area (GAA) faces photochemical and particulate pollution episodes as a result of the combined effects of local pollutant emissions, regional pollution transport, synoptic circulation and topographic characteristics. The area has undergone significant changes since the Athens 2004 Olympic Games because of large scale infrastructure works that lead to the shift of population to areas previously characterized as rural, the increase of the traffic fleet and the operation of highways. However, few recent modelling studies have been *performed* due to the lack of an accurate, updated emission inventory. The photochemical modelling system MM5/CAMx was applied in order to study the photochemical and particulate pollution characteristics above the GAA for two distinct ten-day periods in the summer of 2006 and 2010, where air pollution episodes occurred. A new updated emission inventory was used based on official data. Comparison of modeled results with measurements revealed the importance and accuracy of the new Athens emission inventory as compared to previous modeling studies. The model managed to reproduce the local meteorological conditions, the daily ozone and particulates fluctuations at different locations across the GAA. Higher ozone levels were found at suburban and rural areas as well as over the sea at the south of the basin. Concerning PM<sub>10</sub>, high concentrations were computed at the city centre and the southeastern suburbs in agreement with measured data. Source apportionment analysis showed that different sources contribute to the ozone levels, the local sources (traffic, port activities) affecting its formation.

**Keywords**—Photochemical modelling, urban pollution, greater Athens area, MM5/CAMx.

## I. INTRODUCTION

THE GAA, located at the centre of the Eastern Mediterranean Basin, often faces episodic PM and O<sub>3</sub> levels especially during spring and summer, due to the anthropogenic and natural sources and prevailing atmospheric conditions that favor photochemical production of secondary pollutants and the long range transport of polluted air masses from Europe and N. Africa, [1]. According to [2], Athens is amongst the ten most polluted European cities. It has been estimated that inhabitants inhale 1.25- 2.78 µg PM<sub>10</sub> per kg of PM in the air [3]. Experimental campaigns aiming to investigate O<sub>3</sub> and PM levels and important parameters have

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taken place in the past, e.g. [4]-[6], [13]. The local sources (traffic, navigation and small combustion) dominate over the formation of particulates and ozone levels, while the pollution character across the GAA is quite uniform regarding the former pollutant [7]. However, only a few modeling studies have been performed due to the inexistence of an updated emission inventory, e.g., [8]-[10], [12]. According to their results the combination of local sources and particular weather conditions lead to the build-up of high O<sub>3</sub> and PM levels. Reference [11] revealed the role of sea-salt emissions and aerosol re-suspension rates from vehicle movement to the air quality of the GAA.

The purpose of the current work is to present results from numerical simulations with the MM5/CAMx modeling system for two typical photochemical and particulate pollution episodes that occurred in the summers of 2006 and 2010 in Athens and the GAA. The mild synoptic conditions that occurred favored the development of local circulation systems that led to poor emissions dispersion. In this respect the new emission inventory was constructed for the GAA in order to fill the existing data gap that hindered the detailed modeling study of the photochemical and particulate pollution characteristics.

## II. METHODOLOGY

### A. Study Area Characteristics

The GAA (Fig. 1) features a complex topography that includes the Athens Basin (covering an area of 450 km<sup>2</sup> with approx. 4million inhabitants), surrounded by mountains to the east, north and west and the sea to the southwest. Outside the basin there exist the Thriassion Plain to the west (mainly an industrial zone) and the Mesogia Plain to the east, a rural and suburban rapidly developing area due mainly to infrastructure works such as new highways and the Athens International Airport. The topographical features in combination with the local pollution sources (traffic, central heating, industries, shipping) and the prevailing weather conditions (sea-breeze cells, strong temperature inversions, low wind) that impede ventilation, lead to pollution episodes in the summer.

### B. Description of F.E.I.-GREGAA

The new detailed GAA emission inventory, called F.E.I. - GREGAA (Flexible Emission Inventory for Greece and the GAA), was developed for the period 2006-2010 on a spatial scale of 6x6km<sup>2</sup> for Greece and 2x2km<sup>2</sup> for the GAA, respectively and on a temporal scale of 1 h. It was constructed

following the EMEP/EEA Emission Inventory Guidebook 2009 and 2013 for 10 emission sources categories (SNAP levels) for SO<sub>2</sub>, NO<sub>x</sub>, CO, PM<sub>10</sub>, PM<sub>2.5</sub>, NMVOCs, VOCs, NH<sub>3</sub> and CO<sub>2</sub>. Annual emissions were calculated for each source category from accurate, analytical data such as the traffic fleet, airplane fleet etc. The spatial and temporal allocation of total annual emissions was fulfilled using appropriate proxy values for each source category, such as degree of urbanization, population density, land use, road types and seaways. Moreover, an updated land use [14] and temporal coefficients (yearly, monthly, daily and hourly profiles) were constructed for the road transport [15] and the aviation sectors. The inventory is flexible as it allows for the study of the temporal and spatial characteristics of each source type through case studies, the inclusion of other pollutants and the update with contemporary data. It can also be used in applications with photochemical models and contribute to quantitative and qualitative conclusions concerning the type of sources that contribute to the air quality of the GAA.



Fig. 1 Map of the GAA (depicted by the white line) and the location of the monitoring stations

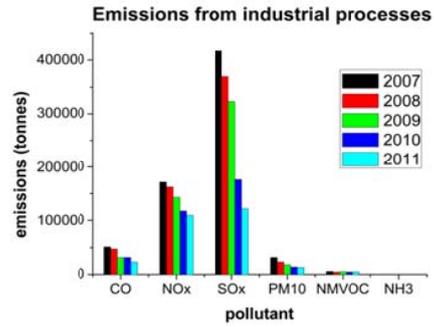


Fig. 3 Annual emission of pollutants from SNAP category 7

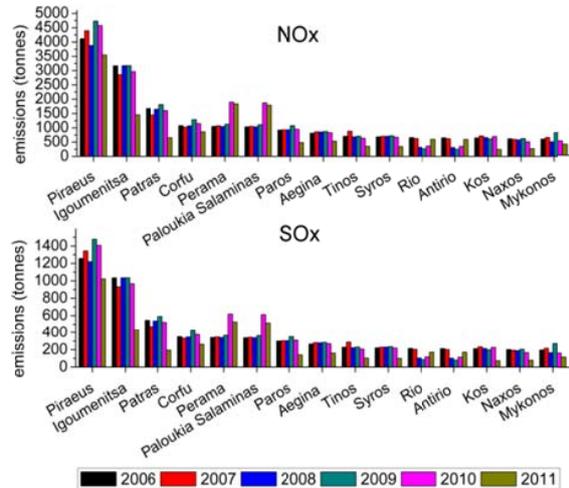


Fig. 4 Annual emission of pollutants from SNAP category 7

In Figs. 2-4 one may observe the annual variations of the pollutants emitted in the GAA from road transport, industries and shipping, which constitute the most important pollution sources for the GAA and those that form the air quality status. A clear reduction of CO and VOC-NMVOC amounts emitted is observed as a result of the financial crisis and the new technology engine cars introduced to the market. Similar conditions are also evidenced for industries. Regarding the shipping sector (Piraeus being the biggest port on the south west of the GAA) emissions of NO<sub>x</sub> and SO<sub>x</sub> fluctuate and do not show a clear trend.

*C.MM5/CAMx Modeling System-Initial and Boundary Conditions*

The simulations were performed with the aid of the Comprehensive Air quality Model with extensions CAMx v6.1 [16]. CAMx is a widely used 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. For the present study, three nested grids were used (Fig. 5) having a spatial resolution of 18×18, 6×6 and 2x2 km<sup>2</sup> covering Europe, Greece and the GAA, respectively. The simulation periods lasted 10 and 7 days each (including a two-day spin up

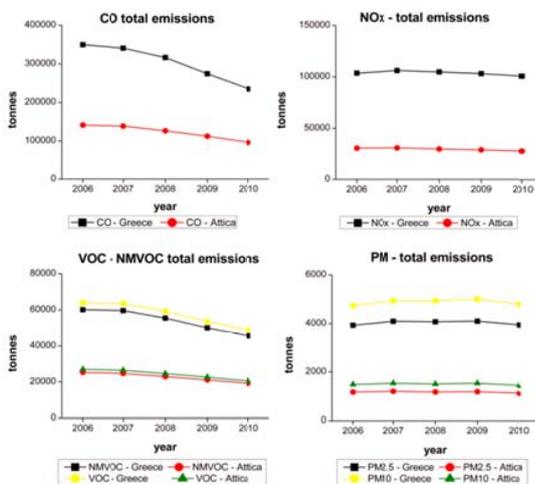


Fig. 2 Annual emission of pollutants from SNAP category 7

period), from 00.00 UTC on 10/6/2010 to 24.00 UTC on 20/6/2010 and from 00.00 UTC 30/7/2006 to 24.00UTC 5/8/2006. Both periods were selected because of the relatively weak southerly flow that led to increased O<sub>3</sub> and particulate pollution levels. The necessary meteorological inputs (temperature, wind, pressure, humidity, and cloud/rain) for CAMx, were produced by the Mesoscale Meteorological Model MM5 using an updated land use field. Hourly gridded emissions from the EMEP (European Monitoring and Evaluation Program for the long range transmission of air pollutants) 50 × 50 km<sup>2</sup> database were used for the coarse grid adapted to the 18 × 18 km<sup>2</sup>.



Fig. 5 The system of nested grids used for the CAMx simulations

The Carbon Bond (CB05)-CF mechanism was used to describe the chemical transformation of gaseous and aerosol species. The initial and boundary conditions were assumed to be invariant for the coarse grid having the value of 50 ppb for O<sub>3</sub>, 0.1ppb for NO<sub>x</sub>, 200ppb for CO and 1.5 ppb for SO<sub>2</sub> provided by the literature. The first two days of the simulation were used as a spin up period in an attempt to minimize the effects from initial and boundary conditions on the computed results.

#### D. Meteorological and Air Quality Conditions

Both periods selected for the modeling study shared common meteorological conditions that lead to O<sub>3</sub> and PM episodes. During the ten day simulations mild synoptic conditions prevailed because of the presence of a high barometric pressure system above Greece, which receded the following days allowing higher south-southwesterly winds. Meteorological data from ground stations of the National Observatory of Athens showed that the wind direction shifted from the northeasterly direction at night-time to northwesterly after sunrise and turned to south-southwesterly after 12.00 LST when the sea-breeze cell developed reaching the inner most areas of the Athens Basin at 14.00 LST with a wind speed of approximately 4m/s. After 21.00 LST when the solar radiation had ceased the wind turned to northwesterly direction signaling the land breeze circulation. The ambient temperature ranged from 19 to approximately 36°C during

both periods. According to the air pollution monitoring network operated by the Ministry of Environment the O<sub>3</sub> levels exceeded the population information threshold of 180µg/m<sup>3</sup> at the northeastern suburban stations (e.g. Marousi) and were on the order of 160 µg/m<sup>3</sup> at the southern suburban station of Nea Smyrni during both periods. PM<sub>10</sub> concentrations were also quite high exceeding the 50µg/m<sup>3</sup> limit value (not shown here).

### III. RESULTS AND DISCUSSION

Regarding the meteorological field simulation results by MM5, the model managed to reproduce the development of the sea breeze circulation quite satisfactorily while presenting good agreement with the measured wind speed at the Thissio site in the centre of Athens. The results from the 13<sup>th</sup> and 14<sup>th</sup> of June 2010 are shown indicatively here (Fig. 6).

Comparison of CAMx results from both periods with measurements revealed a satisfactory agreement with the stations of the monitoring network. In general, the model managed to reproduce the daily ozone variation and the afternoon peak concentrations recorded. As can be seen in Fig. 7 for the 13<sup>th</sup> of June at 6.00 LST before photochemical activity commences the ozone levels maintain background values (approx. 40ppb) and seem to be almost uniform across the GAA. However, at 9.00 LST during the morning rush hour and the solar radiation intensity increase O<sub>3</sub> levels begin to rise at the northeastern suburbs and the Saronic Gulf. By 15.00 LST, maximum concentrations appear above the Mesogia Plain, the northeastern and southern suburbs and the Saronic Gulf, which agree with the experimental findings of other researchers [17]. The O<sub>3</sub> plume penetrated the interior of the basin with the aid of the sea breeze mechanism and reached even the most remote stations. It can be seen that the ozone plume is able to penetrate deep into the GAA and reach the northernmost monitoring stations (18.00LST). The sea breeze cell of the Mesogia Plain that develops in parallel with the Saronic Gulf one pushes the high ozone plume towards the southwest (21.00LST).

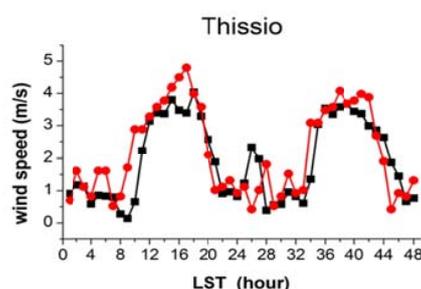


Fig. 6 Comparison of the modeled (black line) and measured (red line) wind speeds at the NOA station

The ozone episodes for both computational periods evolve in quite the same way, their levels being similar.

Concerning PM<sub>10</sub>, high concentrations were computed at the city centre (105.29 µg/m<sup>3</sup>) and the southeastern suburbs (70.25µg/m<sup>3</sup>). As can be seen by Table I, a good agreement

between the computed and measured concentrations can be seen. It was observed that the PM concentrations were more affected by the urban traffic and presented peaks during the morning and evening rush hours. The maximum concentrations appeared within the Athens basin, while at the suburbs (e.g., Lykovrisi etc) the values were significantly lower (figure not shown here). The two computational periods share common features since the meteorological conditions are the same as expected.

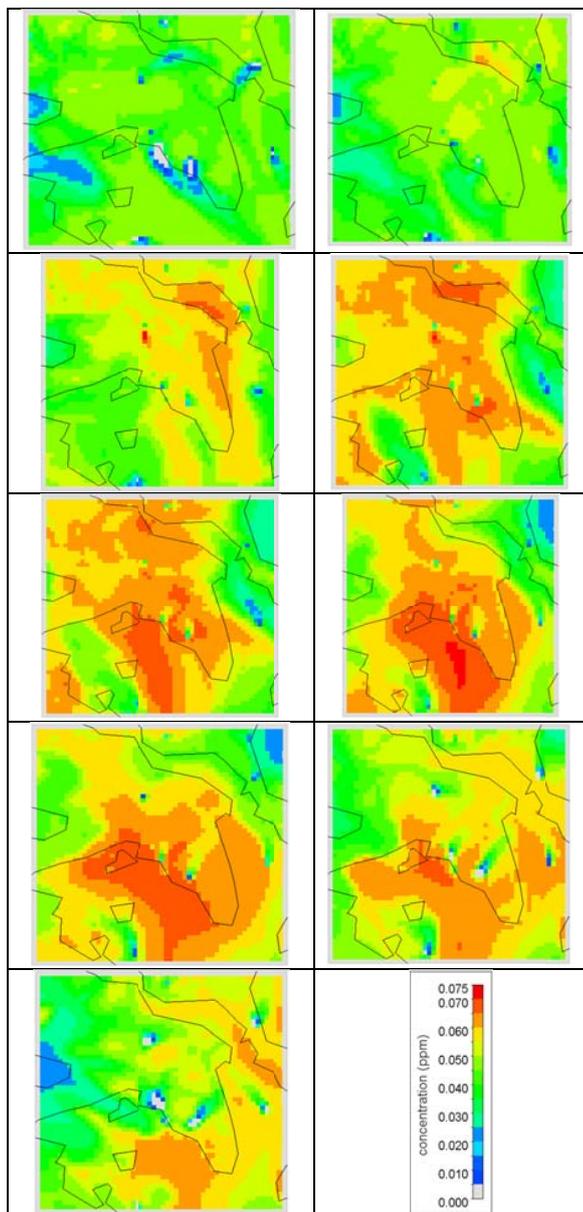
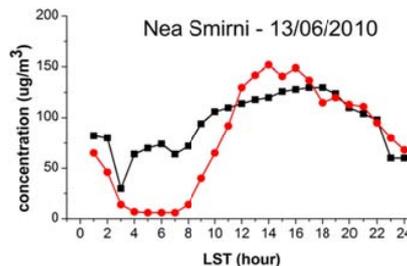
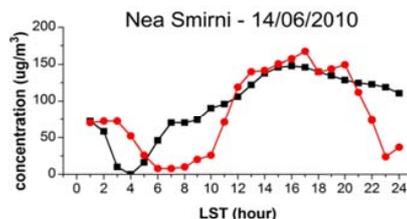


Fig. 7 Diurnal and spatial variation of ozone distribution above the GAA as computed by CAMx for 13/6/2010



(a)



(b)

Fig. 8 (a) Comparison between measured (red line) and computed (black line) hourly concentrations for 13/06/2010 and (b) for 14/06/2010

TABLE I  
COMPARISON BETWEEN MEASURED AND COMPUTED 24 HR AVERAGED PM<sub>10</sub> CONCENTRATIONS

Station	Measured	Modelled
Aristotelous	67	105.29
Ag. Paraskevi	41	49.39
Marousi	52	70.25
Lykovrisi	50	39.57
Gl. Nera	40.80	32.93
Pallini	32.43	21.89

#### IV. OSAT ANALYSIS

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 (NOx 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 inner grid was divided into 11 source regions including the areas surrounding the 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), Korinthian Gulf (region 38).

The selected receptor cell covers part of the NE suburbs of

the GAA and is located in the Mesogia Plain, where the pollution episode was more severe. It was found that the biggest part of O<sub>3</sub> precursors was emitted at the urban area of the GAA and the suburban and rural areas around it respectively (NO<sub>x</sub> contribution is about 77% while for VOCs it is 84%). Since human activity is accumulated at these areas high emissions from fossil-fuel combustion sources were expected. As can be seen in Fig. 9, 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%.

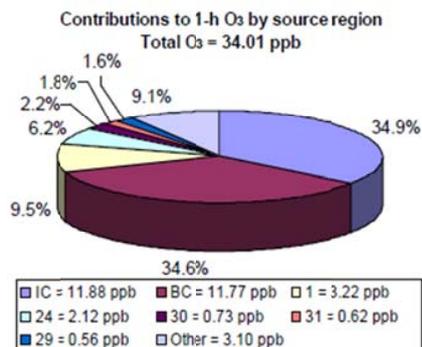


Fig. 9 Contributions to O<sub>3</sub> concentration by source region at the receptor cell on July 2006, 13.00 UTC

#### V. CONCLUDING REMARKS

The purpose of the present work is to study with the aid of the photochemical modeling system MM5/CAMx the photochemical and particulate pollution characteristics and evolution above the Greater Athens Area for two periods in the summers of 2006 and 2010, where air pollution episodes occurred, using a new updated emission inventory. The area has undergone significant changes after the 2004 Olympic Games that changed the distribution of the population, the size of the urban area and the pollution sources. However, modeling studies were quite difficult to accomplish because of the lack of an updated emission inventory. The present work used a new emission inventory constructed that covered the period 2006 to 2010 and produced some interesting results.

1. Comparison of CAMx results with measurements revealed a satisfactory agreement for the urban and rural stations. The model managed to reproduce the daily ozone variation and the afternoon peak concentrations recorded.
2. The O<sub>3</sub> plume penetrated the interior of the basin with the aid of the sea breeze mechanism and reached even the most remote stations.
3. Concerning PM<sub>10</sub>, high concentrations were computed at the city centre and the southeastern suburbs.
4. Different sources contribute to the ozone levels, the local sources (traffic) accounting for approximately 60% of ozone formation.
5. The factors that lead to the formation of ozone and particulate pollution episodes in the GAA still remain the same.

6. The character and concentration levels of the photochemical and particulate pollutants have not presented a significant decrease according to the CAMx results even though on average the emissions of primary pollutants have decreased. This indicates that the simple reduction of emissions is not efficient and other sources such as transboundary pollution should be considered.
7. However, traffic and shipping emissions are the most significant sources of pollution for the GAA in the hot period of the year where central heating systems do not operate.
8. FEI-GREGAA the new emission inventory constructed for the study of air quality above Athens improved the modeled results for
9. The results imply the need for more simulations during different seasons and suggest that the effective control of O<sub>3</sub> and PM precursor sources is crucial to controlling their levels.
10. The air quality management of such a complex area requires the deep understanding of the impact of all pollutant emission sources to the formed concentration levels and to the secondary products with the combined effect of meteorology.

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