# NUMERICAL MODELING OF AN AIR POLLUTION EPISODE OF OZONE IN THE WESTERN MEDITERRANEAN AREA

Salvador R., Stein A.F., Diéguez J.J., and Millán M.
Centro de Estudios Ambiéntales del Mediterráneo (CEAM), Valencia, Spain
salvador@ceam.es, astein@ceam.es, jjaime@ceam.es, millan@ceam.es

## ABSTRACT

European directives regarding air pollution mandate to inform the population when pollutant levels reach specific threshold values. Analysis of the air quality network in the Valencia Community has shown that the human health protection threshold for ozone (120 μg/m3 8-hour average) has been systematically exceeded almost every day between March and September. Moreover, the vegetation protection threshold (AOT40 18000 μg/m3) has also been surpassed. Since 1999, heuristic models, and more recently photochemical ones, have been applied to analyze such ozone exceedances. In particular, an ozone episode that took place during the period of August 13-15, 2000 in the Eastern Spanish coast, including the Catalonian and Valencia communities, has been examined. In this study, we analyze the dispersion and photochemical formation processes that cause high ozone concentrations using modeling tools. Numerical simulations have been carried out using the MM5 meteorological model and the CMAQ photochemical simulation, independently. Both models make use of the nested grid capabilities to include interactions between different scales that are involved. Taking into account that the qualities of meteorological simulations as well as the simulated emissions play a crucial role in the proper representation of ozone formation processes, a comparison between meteorological observations and predicted wind and temperature fields has been performed. This complex and comprehensive exercise including simulation of emissions, meteorology and photochemistry constitutes the first implementation of modeling nesting capabilities applied to the Western Mediterranean area.

## INTRODUCTION

A very extensive set of experimental and historical data, including meteorological and air quality measurements, resulting from various EC sponsored projects (MECAPIP, RECAPMA, SECAP, BEMA, and RECAB) [1], is available at the eastern Spanish coast. Analysis of the experimental data and the Air Quality Network (AQN) during the last 10 years, have revealed the main pollutant dynamics characteristics in this region. The AQN has also given information about the spatial-temporal distribution of pollutant concentrations at surface level. As a result of this research, atmospheric pollution in the Valencia Community (VC) has been related to significant concentrations of photochemical pollutants such as ozone at the regional level, which systematically exceeds the target value for protection of human health set out in Directive 2002/03/EC.

An ozone episode that took place during the period of August 13-15, 2000 in the Eastern Spanish coast, including the Catalonian and Valencia communities, has been examined. In this study, the dispersion and photochemical formation processes that give rise to high ozone concentrations have been analyzed using modeling tools. In order to understand the observed spatial and temporal variations in ozone levels, the Community Multiscale Air Quality (CMAQ) [2] modeling system with meteorological fields obtained from PSU/NCAR Mesoscale Model System (MM5) [3] has been utilized to simulate air quality in this area.

## MONITORING NETWORK

In the VC, the coastal distribution of urban centers and industrial areas, i.e. the main emissions sources, confined by a geographic situation and a complex topography that favor the development of mesoscale circulations, guarantees the presence of pollutants throughout the entire territory. Figure 1 shows the geographical location of the AQN for the region under study. Monitoring sites present different pollutants patterns depending on relative position with respect to the emission sources, distance to the coast, and altitude [4].

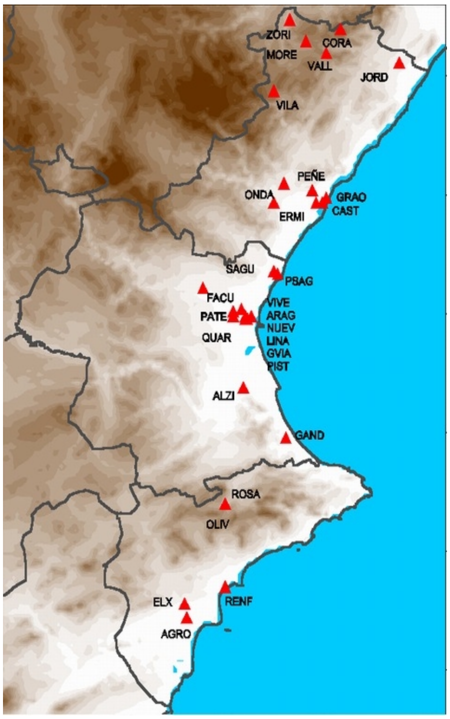


Figure 1. Monitoring sites of the Air Quality Network of Valencia Community.

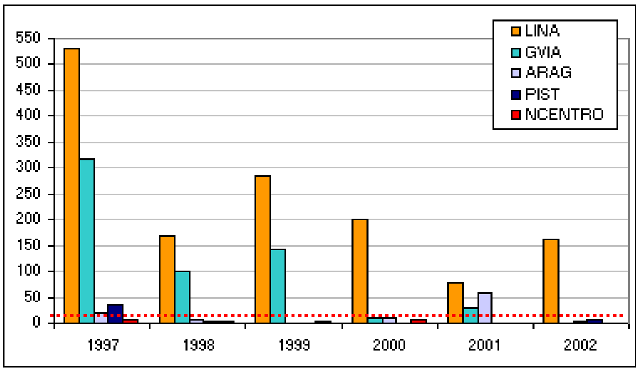


Figure 2a. Number of exceedances of the $NO_2$ 1h-limit value for human health protection (200 µg/m$^3$ ): 18 times

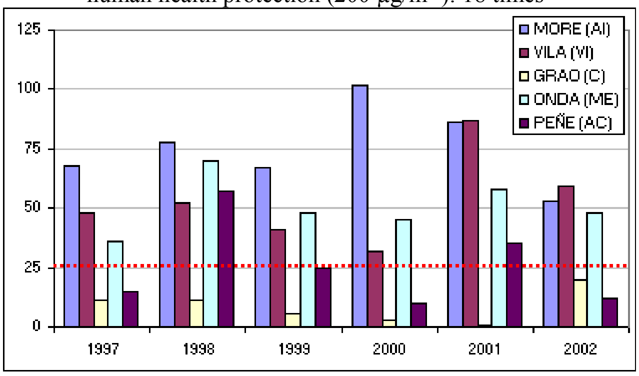


Figure 2b. Number of exceedances of the $O_3$ 8h-average target value for human health protection (120 µg/m$^3$ ): 25 times

Taking as reference the latest European directives (1999/30/CE for $SO_2$, $NO_x$, PM10 and Pb, 2000/69/CE for CO and $C_6H_6$, and 2002/3/CE for $O_3$), figure 2b shows a significant number of $O_3$ exceedances at all site types except the urban ones. Conversely, $NO_x$ exceedances are only significant at urban sites with high traffic density. Indeed, the number of exceedences of the $NO_2$ hourly limit value shows a decreasing tendency over the last six years (figure 2a). This is not the case, however, for tropospheric ozone (figure 2b). For this secondary pollutant, the human health protection threshold was exceeded systematically and almost every day between March and September at the following three station types: Mountain top (More), upper-valley floor (Vila) and valley floor (Onda) [4].

## MODEL DESCRIPTION

### Meteorological Model

The non-hydrostatic MM5 v3.5 model [3] has been used to simulate the meteorological pattern. The simulation has been initialized at 00UTC 13 August 2000 and run through 1800 UTC 16 August 2000 (Figure 3). Four nested grids have been used with 2, 6, 24, and 72 km

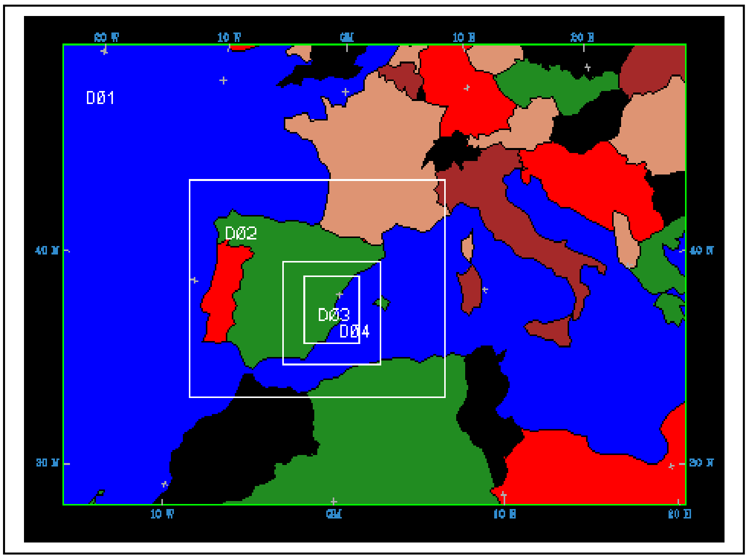


Figure 3. MM5 grid configuration.

horizontal resolution and a variable vertical resolution ranging from 0 to 15 km, with 10 m on the first level. The Kain and Fritsh scheme has been used to parameterize cumulus convection for grids one and two since there is not available cumulus parameterization schemes for grid resolution on the order of 10 km or less. The PBL scheme is that of the Mellor and Yamada as used in the Eta model. The four grids run parameterized microphysics processes using a simple ice scheme. A cloud-radiation scheme that accounts for long- and short-wave interaction with clear air and cloud has been utilized. Moreover, a soil model simulates temperature at five layers (1,2,4,8, 16 cm) using a vertical diffusion equation.

**Emissions**

Emission calculations have been performed to account for primary pollutants released from sources located in two different domains, the first domain covering the Iberian Peninsula and the second one the VC. Sources corresponding to the Iberian Peninsula have been estimated based on EMEP emissions inventory. On the other hand, a high-resolution emission inventory has been developed for this VC region, including the estimation of biogenic and road-traffic emissions [5]. These emission sources have been calculated with a 1-h temporal and 1 $km^2$ horizontal resolution using a bottom-up approach for primary pollutants ($NO_X$, NMVOCs, $SO_2$, CO and PM); and were built into a Geographical Information System (GIS).

**Photochemical Model**

The CMAQ model version 4.22 has been implemented using the pierce-wise parabolic method (PPM) for advection, K-theory parameterization for vertical diffusion, Carbon Bond IV (CB-IV) chemistry mechanism, and quasi-steady state approximation (QSSA) gas-phase reaction solver. Meteorological output data from MM5 has been linked to CMAQ utilizing the Meteorological Chemistry Interface Processor (MCIP). Two nested grids have been defined, a coarse grid with 24 km horizontal resolution (50x46 cells) covering the Iberian Peninsula and a fine grid with 4 km horizontal resolution (172x108 cells) encompassing the VC. The number of vertical layers is 15.

## CASE STUDY

Meteorological conditions corresponding to the 13-15 August 2000 episode feature a weak pressure gradient along with a relative low-pressure development in the southern part of the peninsula (Iberian Thermal Low). Under these synoptic conditions and induced by the local characteristics of the terrain, mesoscale flow features, such as land and sea breezes, mountain wind and topographic injection, develop. This episode is characterized by occurrence of unusual late night ozone levels during August 14th at inland monitoring stations in the northern part of the VC domain (e.g. Morella). In contrast, the coastal stations show the typical daily oscillation with maximum values during middle of day (e.g. Puerto Sagunto).

Evolution of the wind field and ozone pattern distributions at the fine grid is presented in figure 4. The results show that the nocturnal cooling of inland ground surface has led to the development of down-slope flow of mountain ranges and valley winds. At this time, domain maximum values of $O_3$ are simulated nearby inland stations (mountain-top), in qualitative agreement with the AQN. At this location, flow sinking brings reservoir layer to surface level. At coastal sites, the high $NO_x$ emissions and the absence of photolysis have led to low $O_3$ values. Under these conditions, $O_3$ is depleted through a reaction with NO emitted mainly from road traffic.  After sunrise, land surface has warmed up initiating the onset of sea breeze and up-slope flows. At this time, ozone levels start to rise due to fumigation of pollutants from the reservoir layers over the sea and photochemical production of freshly emitted precursors over the coast. In mid-afternoon, polluted air masses rich in $O_3$, while still producing photochemical oxidants, are pushed further inland and orographycally injected into reservoir layers [4].

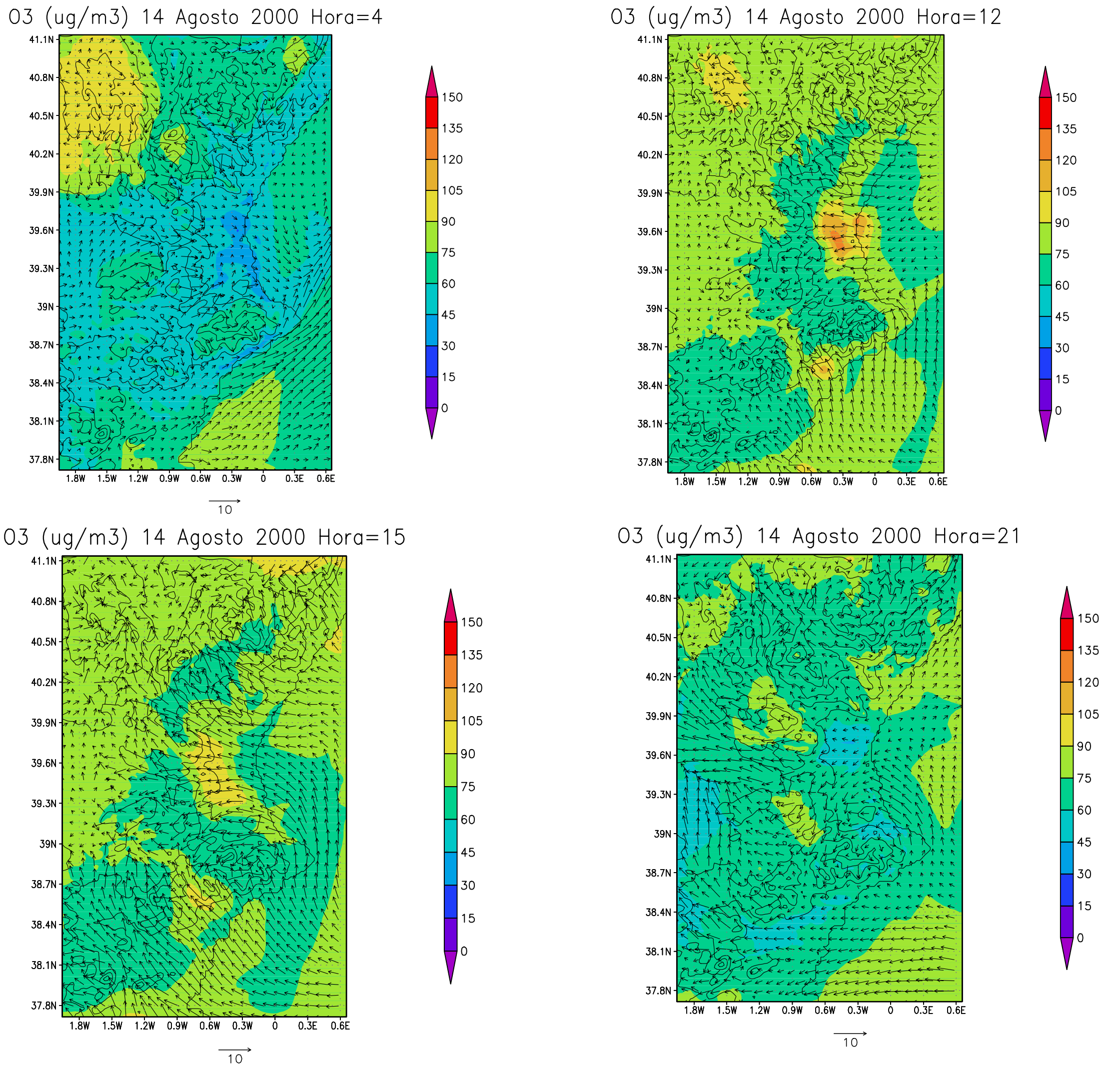


Figure 4. Horizontal distribution of ozone and wind field in the first layer of the fine domain at 4,12,15,21 UTC August 14th 2000.

## MODEL PERFOMANCE EVALUATION

Meteorological data, such as temperature, wind speed and direction calculated by MM5 have been compared with measured values. As can be inferred from Figure 5, the meteorological model underestimates temperature, but the trend is still well reproduced. Reproduction of wind speed at Zorita and Onda stations is good. Additionally, the model captures the sea breeze arriving later at Morella station in August 14th. On the other hand, ozone levels measured at 6 monitoring stations have been compared with CMAQ model outputs (Figure 6). CMAQ reproduces the main qualitative features of the temporal evolution of ozone. Good quantitative representation of the patterns is observed for stations located on the central and southern portions of the VC domain (Puerto Sagunto, Paterna, and Renfe). However, the model tends to underpredict the ozone levels at stations (Onda, Zorita, and Morella) influenced by industrial sources that have not been included among the emission estimates.

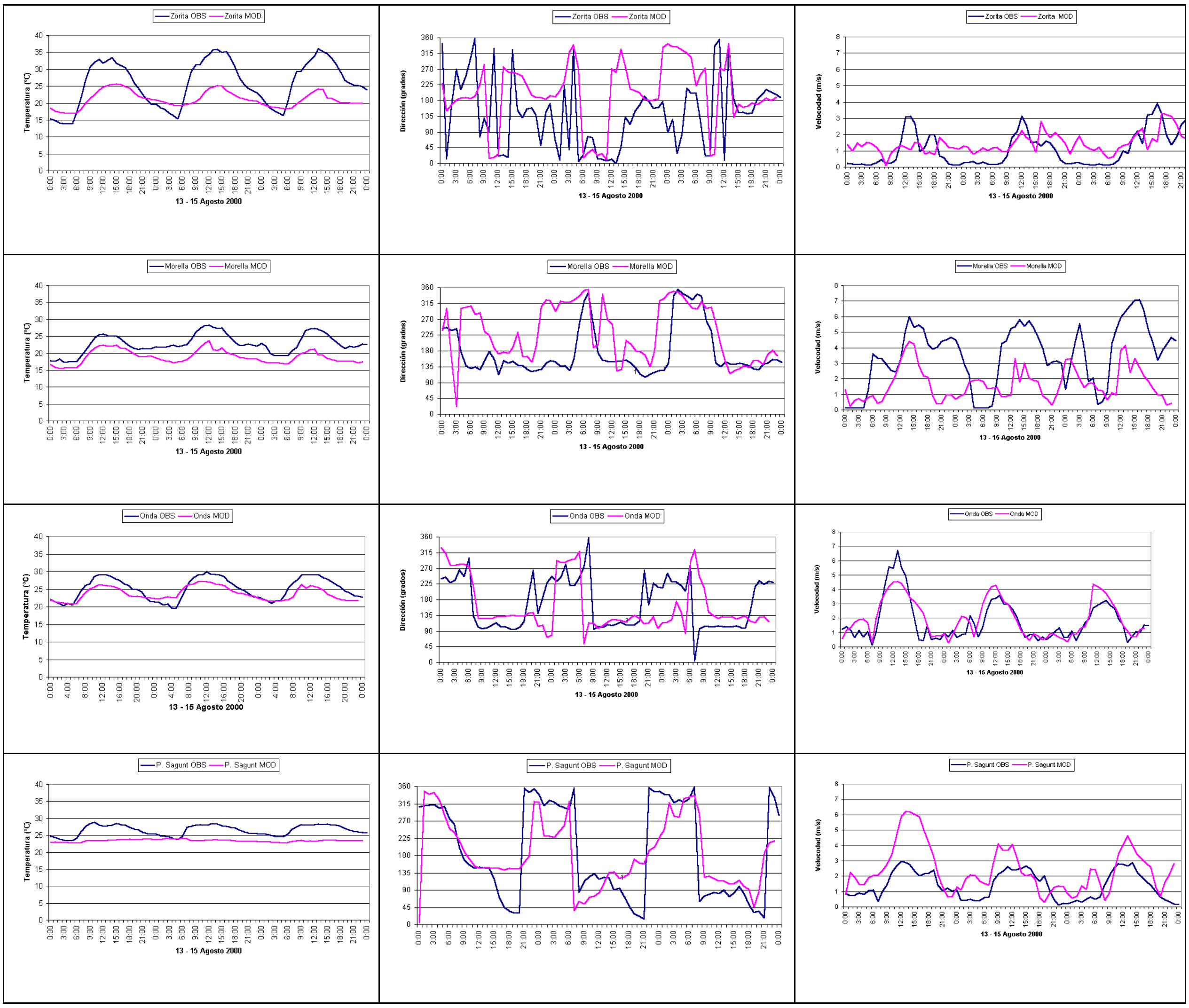


Figure 5. Comparison of the measured (blue) and simulated (red) temperature, wind speed and direction at four station representative of mountain top (Zorita and Morella) and coastal site (Onda and Port Sagunt) .

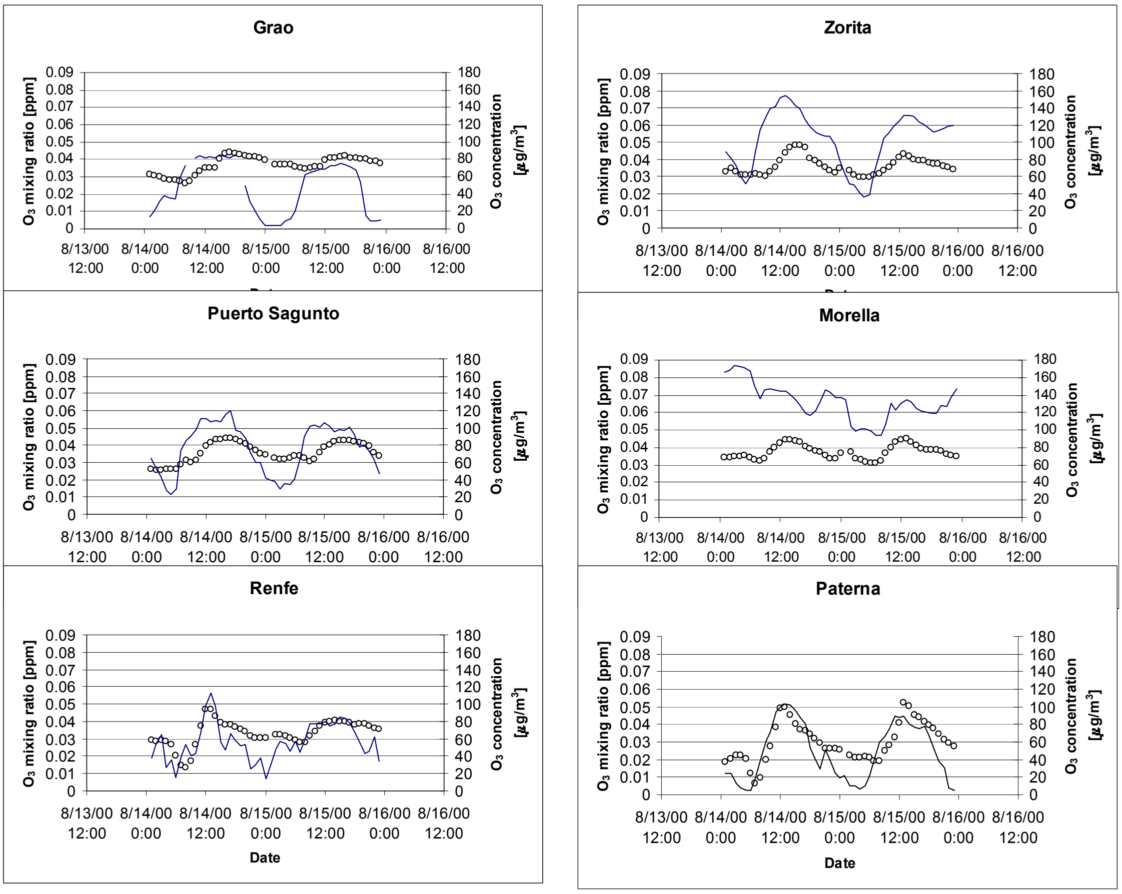


Figure 6. Comparison of measured (line) and modeled (circles) hourly ozone concentrations as a function of time for some representative stations in the Valencia community.

## CONCLUSIONS

An ozone episode influenced by a weak pressure gradient is qualitatively well reproduced by the combination of a meteorological model (MM5) and a state of the art photochemical model (CMAQ) giving information of polluted airmass origin. Some discrepancies between observation and simulation can be attributed the lack of accurate description of the industrial emissions in the area while others are still to be determined. Future work includes a sensitivity analysis of meteorological and emission input data to determine the sources of error.

**Acknowledgements**

The work is funded by the CICYT of the Spanish Ministry for Science and Technology- CONMED project: REN2000-1020-C02-02/CLI and BANCAIXA also supported the work. We would also like to thank Prof. J. M. Baldasano and O. Jorba for his continuous support during the development of the project.

## REFERENCES

[1] M. Millán, R. Salvador, E. Mantilla, and G. Kallos, 1997: Photooxidant dynamics in the Mediterranean basin in summer: Results from Eurpean reserarch projects, *J. Geophysical. Researcher.,* 102, D7,8811-8823.

[2] EPA, 1999. Science Algorithms of the EPA MODELS-3 Community Multiscale Air Quality (CMAQ) modeling system, Rep. EPA/600/R-99/030, Off. Of Res. And Dev., Washington, D.C.

[3].Dudhia, J., 1993: A non-hydrostatic version of the Penn State-NCAR mesoscale model: Validation tests and simulation of an Atlantic cyclonic and cold front. *Monthly Weather Review* 121, 1493-1513.

[4] Millán,M.M.; Mantilla,E.; Salvador,R.; Carratalá,A.; Sanz,M.J. (2000). Ozone cycles in the western Mediterranean basin: Interpretation of monitoring data in complex coastal terrain. *Journal of Applied Meteorology* 39, 487-508.

[5].Arévalo, G., R. Salvador, S. Gassó and J.M. Baldasano: High Resolution Emission Inventory of Valencia Community (Spain) for Year 2000. Submitted at Twelfth International Conference on Modelling, Monitoring and Management of Air Pollution 2004. 30 June-2 July, Rhodes, Greece