# 6.05 MODELING OF PARTICULATE MATTER IN THE GREATER ATHENS AREA BY REMSAD MODEL

*Eleni Athanasopoulou, Elisavet Bossioli and Maria Tombrou*
Laboratory of Meteorology, Division of Applied Physics, Department of Physics, National and Kapodistrian University of Athens, Athens, Greece

## INTRODUCTION

Athens is a densely populated area surrounded by hills, so as a result $PM_{10}$ measurements show exceedances of the proposed European limits. Many studies in the Greater Athens Area (GAA) atmosphere focus on measurements of $PM_{10}$ and their composition (e.g. Chaloulakou et al, 2003; Prosmitis et al., 2003; Eleftheriadis et al., 1998; Siskos et al., 2000), but a few modeling approaches have been made (e.g. Spyridaki, A. and M. Lazaridis, 2003; Sotiropoulou et al., 2004).

This study involves the determination of $PM_{10}$, $PM_{2.5}$ (and their chemical constituents) and $PM_{coarse}$ concentrations in the GAA, using the three-dimensional, eulerian model REMSAD (ICF Consulting, 2002). The photochemical mechanism used is the micro-CB-IV (Gery et al., 1989), the MARS-A algorithm (Binkowski F.S. and U. Shankar, 1995) is implemented for the formation of the secondary inorganic PM in the atmosphere, while the secondary organic aerosol formation is simulated by the Pankow approach (Griffin et al., 1999).

From the experimental studies, the measurements in the framework of the MEDCAPHOT-TRACE experiment (Eleftheriadis et al., 1998) were the only appropriate and available for comparison purposes, as they are chemically analysed for specific days. An additional advantage for using these data is the absence of the construction activity for the Olympic games during this period, which would induce additional particle loading, that could not be easily simulated.

## NUMERICAL DOMAIN AND DATA

The simulation domain on which the PM concentrations are estimated is 164km x 134km (2km x 2Km). The days that are chosen for the atmospheric simulation of the GAA is the 14th & 15th of September 1994. The temperature in the centre of Athens, during the selected days of simulation varied from 20$^{o}$C to 34$^{o}$C, the relative humidity ranged from about 30% to 60%, the wind speed didn't reach 6m/s and the wind direction was around 270deg (from SW to NW) after 12:00am. Suppan et al. (1998) found these days to be characterized by strong sea breeze circulation (15/09: typical sea breeze), which combined with the poor ventilation in the area, are responsible for the occurrence of pollution episodes (Ziomas et al., 1995a).

The meteorological fields and the surface characteristics of the simulation domain that are required for REMSAD are provided by MM5 (Anthes et al., 1978), the transportation and the point emissions are provided by the Ministry of the Environment, $NH_3$ biogenic emissions where calculated by Sotiropoulou et al. (2003) and the rest biogenic emissions are based on calculations that are extensively analysed by Bossioli et al (2004). The absence of information on the size and chemical speciation of the emitted aerosols (necessary input data for REMSAD) was overcome by making approximations based on literature (CARB, 2003; Bolzacchini et al., 2003; Prosmitis et al., 2003).

## REPRESENTATION AND RESULTS

In order to evaluate REMSAD, measured data for gaseous and particulate concentrations are compared with the estimated values. The average daily values available for the 14th and 15th of September 1994 refer to nitric acid ($HNO_3$), nitrogen dioxide ($NO_2$), sulphur dioxide ($SO_2$), sulphate ($SO_4^{-2}$), nitrate ($NO_3^-$) and ammonium ($NH_4^+$). Figure 1 presents the comparison between measurements and calculations.

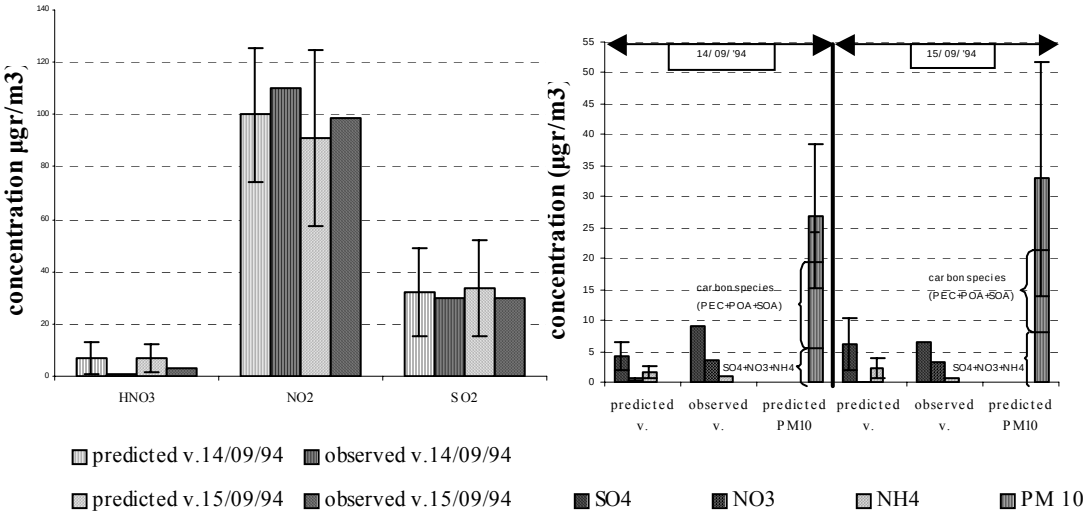


*Figure 1. Observed (Eleftheriadis et al., 1998) and predicted (REMSAD) mean daily values of gaseous (a) and particulate (b) pollutants at an urban/traffic station (Patission ave.) in Athens, for 14 &15/09/1994. The standard deviation of REMSAD concentrations is based on the hourly-calculated values.*

The comparisons for $HNO_3$ and $NO_3^-$ seem to be problematic, with the measured values being underestimated and overestimated, respectively. According to measurements at Ispra, within the framework of the EMEP (Lazaridis et al., 2001), apart from $HNO_3$ conversion to ammonium sulphate by ammonia, $HNO_3$ is also absorbed onto alkaline aerosol particles. Correspondingly, Eleftheriadis et al (1998) underlies that in the GAA, marine calcium carbonate acts as a neutralizing agent for $HNO_3$ with simultaneous formation of aerosol $NO_3^-$ (in the coarse fraction of PM). As REMSAD does not include the above chemical reaction, this is the most likely explanation for the observed differences.

$NO_2$ and $SO_2$ are calculated with great accuracy (mean absolute normal gross error: 8.6%, 9.5%, respectively), accepted by the Quality Objective of the European Directive (accuracy 50% for the annual averaged values for $PM_{10}$ and the daily average values for other pollutants; the accuracy for $PM_{10}$ daily averages is not yet defined, European Community, 1999).

The predicted $SO_4^{-2}$ concentration for the 15th of September is slightly underestimated, but on the 14th it seems to be a great underestimation. Particulate $SO_4^{-2}$ shows two peaks, one in the coarse mode associated with sea salt and one in the fine mode (Finlayson and Pitts, 2000). Since REMSAD does not simulate the creation of seaborne (coarse) aerosols, an underestimation of the predicted (fine) concentrations is expected.

Finally, $NH_3$ daily average concentrations are compared with those calculated by UAM-AERO for the 25th of May 1990 (Pilinis et al., 1993) and the measurements by Kirkitsos and Sikiotis (1993), which both refer to the Athens City Centre. The predicted value by REMSAD

is 2.15μgr/$m^3$ (st. dev.=1.76μgr/$m^3$), very close to the UAM-AERO calculations (2.48 μgr/$m^3$) and to the 24-h mean measured value of $NH_3$ concentration during March and April of 1989 (2.39μgr/$m^3$). Therefore, it is concluded that since the basic constituent of particulate $NH_4^+$ is well estimated, $NH_4^+$ overestimation has only to do with the inclusion of $SO_4^{-2}$ and $NO_3^-$ concentrations, as calculated by REMSAD (total $NH_4^+ = [NH_4]_2SO_4 + NH_4NO_3$).

As it is illustrated in figure 1, $SO_4^{-2}$ is the main constituent of the inorganic fraction of PM followed by $NH_4^+$ and $NO_3$. This was also observed by Eleftheriadis et al. (1998) and Siskos et al. (2001) for the GAA, suggesting that secondary aerosol formation arising from primary gaseous emissions is an important source of inorganic aerosols.

The sum of the calculated carbon particulate species is a big portion of $PM_{10}$ and complies with the aerosol characterization of PM inside the EMEP framework (Lazaridis et al., 2002). The main constituent of the calculated particulate carbon is primary organic aerosols (POA), followed by primary elemental carbon (PEC) and secondary organic aerosols (SOA). The sum of the organic aerosols is the majority of carbon species, which is characteristic of urban areas (Lazaridis et al., 2002) and the predominance of the organic fraction is also measured by Scheff and Valiozis (2003) and Prosmitis et al. (2003) and indicates the importance of vehicle emissions in the GAA.

The calculated $PM_{coarse}$ fraction represents about 15% of the daily average $PM_{10}$ in the GAA, which contradicts its 50% participation, according to measurements by Chaloulakou et al. (2003). It is believed that the absence from REMSAD of the wind-driven and traffic-induced resuspension and of the seaborne processes and ionic species ($Na^+$, $Cl^-$), justify the underestimation of the calculations and cannot confirm the observed contribution of road dust and seaborne aerosol to the PM regime in the Athens atmosphere (Eleftheriadis et al., 1998; Siskos et al., 2001).

Figure 2 presents the spatial distribution of $PM_{10}$ concentrations at 9:00 and 21:00 LT (14/09/94). The intense anthropogenic activity during the morning hours causes the high levels of $PM_{10}$ in the centre of Athens (about 50μgr/$m^3$), while at the Thriassion plain (industrial area) concentration reaches 80μgr/$m^3$ due to industrial activity and at the harbor of Pireas a combination of industry, marine vessels and circulation results in elevated aerosol pollution (about 80μgr/$m^3$). The contribution of the industrial activity combined with the wind fields in the GAA is more profound at the night hours and it seems to affect an extended area. The elevated $PM_{10}$ levels at night are also ascertained by data processing of hourly $PM_{10}$ concentrations measured by the National Ministry of the Environment and are attributed to the lower mixing height during these hours.

A sensitivity analysis was made, in order to assess the role of industrial emissions in the GAA. Due to the extended dispersion of the point sources in the area of interest, the industrial activity combined with the wind fields, influences the whole GAA. The $PM_{10}$ regime around the Thriassion plain is exclusively owed to the point sources, while even in the centre of Athens the role of transportation emissions on the 15th of September (typical sea breeze) is confined to 37% of the total activity.

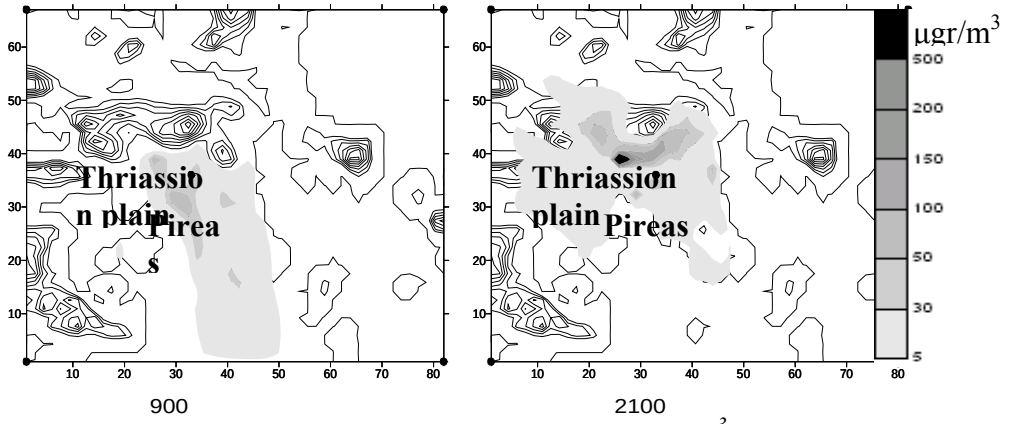


*Figure 2. Spatial distribution of $PM_{10}$ concentrations ($\mu gr/m^3$) at 9:00 and 21:00 LT (14/09/94) in the GAA. The black mark indicates the centre of Athens (Patission avenue).*

## REFERENCES

*Anthes R. A.*, 1972: The development of asymmetries in a three-dimensional numerical model of the tropical cyclone. *Mon. Wea. Rev.,* **100**, 461-476.

*Binkowski, F.S. and U. Shankar*, 1995: The regional particulate matter model, 1: model description and preliminary results. *J. of Geophysical Research*, **100**, 26191-26209.

*Bolzacchini, E., V. M.G. Gianelle, L. Perrone, G. Pozzoli, G. Mognaschi, F. Avella, D. Faedo and B. Rindone,* 2003. Speciation of $PM_{10}$ and $PM_{2.5}$ in the urban atmosphere of Milan. *Geophysical Research Abstracts*, 5.

*Bossioli, E., M. Tombrou and A. Dandou*, 2004: Modeling of an ozone episode in the Greater Athens Area, Greece using both UAM-V and a box model. 9th International Conference on Harmonization within atmospheric dispersion modeling for regulatory purposes. Garmisch-Partenkirchen, Germany.

*C.A.R.B.,* 2003: Assignments of Organic and PM Speciation Profiles and Fractions by SCC. California Emission Inventory Development And Reporting System (CEIDARS).

*Chaloulakou, A., P. Kassomenos, N. Spyrellis, P. Demokritou, P. Koutrakis*, 2003: Measurements of $PM_{10}$ and $PM_{2.5}$ particle concentrations in Athens, Greece. *Atmospheric Environment,* **37**, 649-60.

*Eleftheriadis, K, D. Balis, I. Ziomas, I. Colbeck and N. Manalis*, 1998: Atmospheric aerosol and gaseous species in Athens, Greece. *Atmospheric Environment,* **32**, 2183-91.

*EU Directive 999/30/EC, 1999:* Council directive relating to limit values for sulfur dioxide and oxide of nitrogen, particulate matter and lead in ambient air. Off. J. Eur. Comm. L163/50.

*Finlayson-Pitts, B. and Jr. J. N. Pitts*, 2000: Upper and lower atmosphere.

*Gery, M.W., G.Z. Whitten, J.P. Killus and M.C. Dodge,* 1989: A photochemical kinetics mechanism for urban and regional computer modeling. *J. Geophys. Res.,* **94**, 925-956.

*Griffin, R.J., D.R. Cocker III, R.C. Flagan and J.H. Seinfeld*, 1999: Organic aerosol formation from the oxidation of biogenic hydrocarbons. *J. Geophysical Research*, **104**, 3555-3567.

*ICF Consulting*, 2002: User's guide to the Regional Modeling System for Aerosols and Deposition (REMSAD).

*Kirkitsos, P.D. and D. Sikiotis, 1993:* Chemical-composition of the NH3-HNO3-H2SO4-NaCl system in the atmosphere of Athens, Greece. *Environ Monit Assess*, **28**, 61-81.

*Lazaridis, M., A. Semb, S. Larssen, A.G. Hjellbrekke., O. Hov, J.E. Hanssen, J. Schaug and K. Torseth,* 2002*:* Measurements of particulate matter within the framework of the European Monitoring and Evaluation Programme (EMEP) I. First results. *The Science of the Total Environment,* **285**, 209-235.

*Pilinis C., P. Kassomenos and G. Kallos, 1993:* Modeling of photochemical pollution in Athens, Greece. Application of the RAMS-CALGRID modelling system. *Atmos Environ*, **27B**, 353-370.

*Prosmitis A.B., E. Diapouli, A. Chaloulakou and N. Spyrellis,* 2003: Organic and elemental carbon particulate continuous field measurement in Athens urban area. 8th International Conference on Environmental Science and technology Lemnos island, Greece, 8-10 September.

*Scheff P. and C. Valiozis, 2003.* Characterization and source identification of respirable particulate matter in Athens, Greece. *Atmospheric Environment,* **24**, 203-11.

*Siskos P.A., E.B. Bakeas, I. Lioli, V.N. Smirnioudi, P. Koutrakis*, 2001: Chemical characterization of $PM_{2.5}$ aerosols in Athens-Greece. *Environ. Tech*, **22**, 687-95.

*Sotiropoulou, R.E.P., E. Tagaris and C. Pilinis,* 2004*:* The BOND project: Biogenic aerosols and air quality in Athens and Marseille greater areas. *Journal of Geophysical Research,* **109**.

*Spyridaki, A. and M. Lazaridis*, 2003: Modelling study of fine aerosol and photo oxidants during winter at the Mediterranean, 8th International Conference on Environmental Science and technology Lemnos island, Greece, 8-10 September.

*Suppan P., P. Fabian, L. Vyras and S.E. Gryning*, 1998: Ozone and peroxyacetyl nitrate mixing ratios during the MEDCAPHOT-TRACE Campaign in Athens Greece, *Atmospheric Environment* **32**, 2089-2102.

*Ziomas I., D. Melas, C. Zerefos, A.F. Bais, A.G. Paliatsos*, 1995. Forecasting peak pollutant levels from meteorological variables. *Atmospheric Environment,* **29**, 3703-3711.