

1.07 A FOUR MODEL INTERCOMPARISON CONCERNING CHEMICAL MECHANISMS AND NUMERICAL INTEGRATION METHODS

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INTRODUCTION

In the frame of CityDelta Project four different atmospheric chemistry-transport models, CALGRID (*Yamartino, R.J. et al.*, 1991), STEM (*Silibello, C. et al.*, 2001), CAMx (*ENVIRON International Corporation*, 2004) and TCAM (*Decanini, E. and M. Volta*, 2003) have been applied to 1999 summer season over a 300x300 km² domain situated in Northern Italy. The validation phase shows that all the models ensure good agreement with data. To better understand the behaviour of the different models, a sensitivity analysis has been carried out with regard to the performances of chemical mechanisms and numerical integrators. The sensitivity analysis has been performed with regard to ozone and NO₂ and considering mean values and frequency distribution. The analysis has been carried out comparing the results obtained with 4 chemical mechanisms (SAPRC 90/99, CBIV 90/99) and 3 different numerical integrators (QSSA, IEH, CMC).

THE PHOTOCHEMICAL MODELS

CALGRID

The photochemical model CALGRID is an Eulerian three-dimensional model for gas phase simulations. It implements an advection-diffusion scheme in terrain-following co-ordinates with vertical variable levels. The CALGRID chemical module implements the SAPRC90 (*Carter, W.P.L.*, 1990) and the CB4 (*Gery, M. et al.*, 1989) mechanisms. The QSSA (Quasy Steady State Approximations) algorithm solves the kinetic equations (*Hessvedt, E. et al.*, 1978).

STEM-FCM

STEM-FCM (*Silibello, C. et al.*, 2001) is an Eulerian three-dimensional photochemical model. It implements an accurate advection-diffusion scheme in terrain-following co-ordinates, with variable vertical spacing, and can take into account chemical transformations and deposition processes of both gas and aerosol species. The model uses SAPRC-90 mechanism (*Carter, W.P.L.*, 1990), including 54 chemical species and 129 reactions. As for the kinetic equations integration, STEM-FCM implements the IEH solver (*Sun, P. et al.*, 1994). Finally aerosol treatment is based on a size-resolved multicomponent aerosol module (*Wexler, A.J. et al.*, 1994).

CAMx

The Comprehensive Air quality Model with extensions (CAMx) is a publicly available computer modelling system for the integrated assessment of photochemical and particulate air pollution over many scales ranging from urban to super-regional (*Environ Corporation*, 2004). CAMx provides the option to use two different chemical mechanisms: Carbon Bond IV (CBM-IV) version 1999 (modified to model for ozone and fine / coarse PM, using RADM mechanism for aqueous phase chemistry, ISORROPIA for inorganic sulphate-nitrate-ammonium chemistry, SOAP semi-volatile scheme for secondary organic aerosols) and SAPRC version 1999. About the chemistry solver, the CAMx user can choose either IEH (Implicit-Explicit Hybrid) solver or a fast efficient solver developed by ENVIRON and

referred as CMC. CMC is based on an “adaptive-hybrid” approach and results in about a ten-fold speedup in the chemistry solution. The two approaches give similar results during the day and differ during night-time (in this case IEH is more accurate than CMC). During the phase I of CityDelta intercomparison, CAMx was applied to simulate ozone concentrations over the Milan area using CMC solver and SAPRC99 chemical mechanism.

TCAM

The Transport Chemical Aerosol Model is an Eulerian three-dimensional multiphase model. It implements the advection-diffusion scheme derived by CALGRID code. The model implements the Flexible Chemical Mechanism (FCM) interface for mechanisms based both on lumped molecule (SAPRC90, SAPRC97, COCOH97) and on lumped structure (CB-IV) approaches. The TCAM model solves the mass balance equations by means of a splitting operator. It integrates, for each simulation hour, the horizontal transport, the vertical transport and the chemistry for an half time step and then performs the same calculations in the reverse order for the remaining half. The gas phase chemistry is solved implementing the IEH algorithm (*Sun, P. et al.*, 1994) which treats separately both the slow and the fast reacting species. The former ones are solved by means of an explicit second order method, the latter by means of the implicit scheme LSODE (*Hindmarsh, A.*, 1975).

Simulation setup

The four photochemical models have been applied over the Milan area defined in the frame of CityDelta intercomparison (300 x 300 km²). The simulations concerned the 1999 six summery months hourly concentrations of ozone and NO₂.

The emission, meteorological, initial and boundary condition data set, collected by JRC for the CityDelta project (<http://rea.ei.jrc.it/netshare/thunis/citydelta/>), have been processed to provide suitable input fields to the models. Table 1 shows the model configurations analysed in this paper, showing the chemical mechanism and the numerical solver.

Table 1. The model configurations.

Model	Chemical Mechanism	Numerical solver
STEM	SAPRC 90	IEH
CALGRID	SAPRC 90	QSSA
CAMx	SAPRC 99	CMC
CAMx	CB-IV 99	CMC
TCAM	CB-IV 90	IEH

SIMULATION DISCUSSION

Simulation results present a good agreement with data in terms of mean ozone concentration values for all the models (Figure 1). Concerning the frequency distribution, even if the shapes of the measured and simulated value curves are very similar, the models, with the exception of TCAM, overestimates frequencies of concentration in the range 30-70 ppb and underestimates frequencies outside these bounds (Figure 2).

The analysis of mean ozone concentration maps shows low concentration in the Milan Metropolitan area and high values in foothill zones in the North and in the South of the domain (Figure 3). This could be due to the fact that the wind directions are biased by the mountain-valley breeze regimes, driving Milan plume north-eastwards forced by Alps, and southwards forced by Appennini.

The comparison between the model results has been performed analysing the following points:

- **Models using SAPRC mechanisms (CALGRID-STEM-CAMxSAPRC99):** Even if the mean daily ozone concentration are very similar (Figure 1), IEH integrator (STEM) ensures better performances than QSSA (CALGRID), even requiring higher computational time. CMC integrator implemented in CAMx has performances comparable to IEH only during the day, but heavily underestimates ozone concentration during the night. Frequency analysis (Figure 2) confirms that QSSA is not able to reproduce the higher concentration values. This could be explained by the fact that solver implements an explicit algorithm working as a low-pass filter, unable to follow strictly high gradient in the dynamic of the phenomenon.
- **Models implementing the IEH integrator (STEM-TCAM):** Mean values are very close during night-time, but during the day TCAM concentration are always higher than STEM ones (Figure 1). Frequency analysis shows that TCAM overestimates frequencies of concentration higher than 70 ppb, probably caused by the high reactivity of the CBIV90 mechanism (Figure 2).
- **Models implementing the CMC integrator (CAMx):** During the day, mean concentration calculated using SAPRC99 mechanism are higher than values calculated by means of CBIV99. On the contrary, during the night, the behaviour is closer, and in some cases CBIV99 seems to be more reactive than SAPRC99 (Figure 1). Frequency analysis shows that the two versions of the model have the same distribution for the concentration lower than 70 ppb, but outside this range the frequencies calculated with SAPRC99 mechanism are higher.

In conclusion, the analysis suggests that: (1) all the models used in the comparison are able to reproduce the ozone production in the simulation domain; (2) the integrator algorithms have a deep impact over the simulated peak concentration; (3) the chemical schemes mainly differ in diurnal and nocturnal pollutant dynamics simulation.

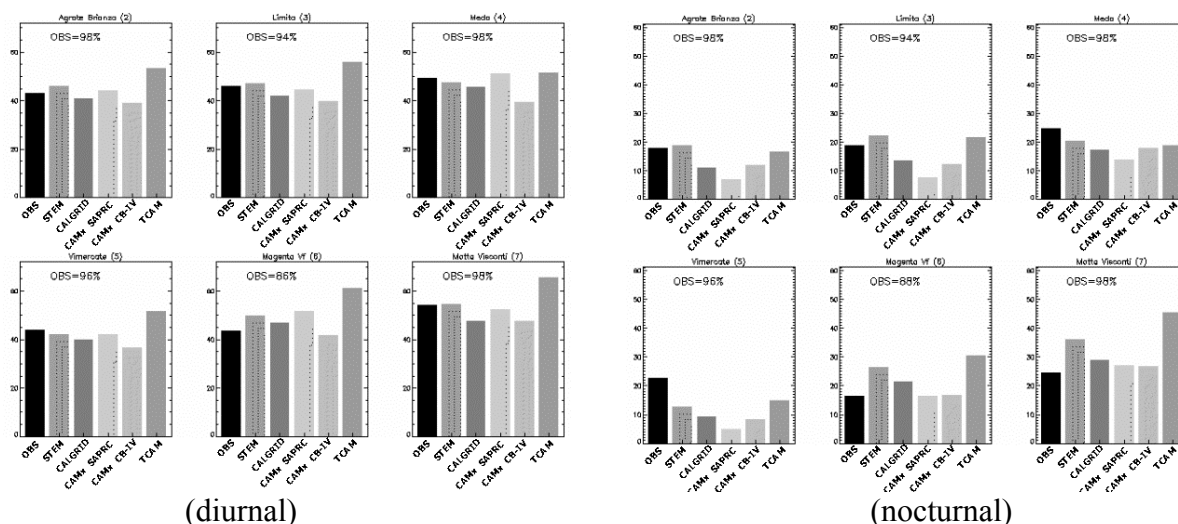


Figure 1. Diurnal (8a.m.–8p.m.) and nocturnal (8p.m.–8a.m.) mean ozone concentrations over six months measured and performed by STEM, CALGRID, CAMx (SAPRC99), CAMx (CB-IV), TCAM models for selected monitoring stations.

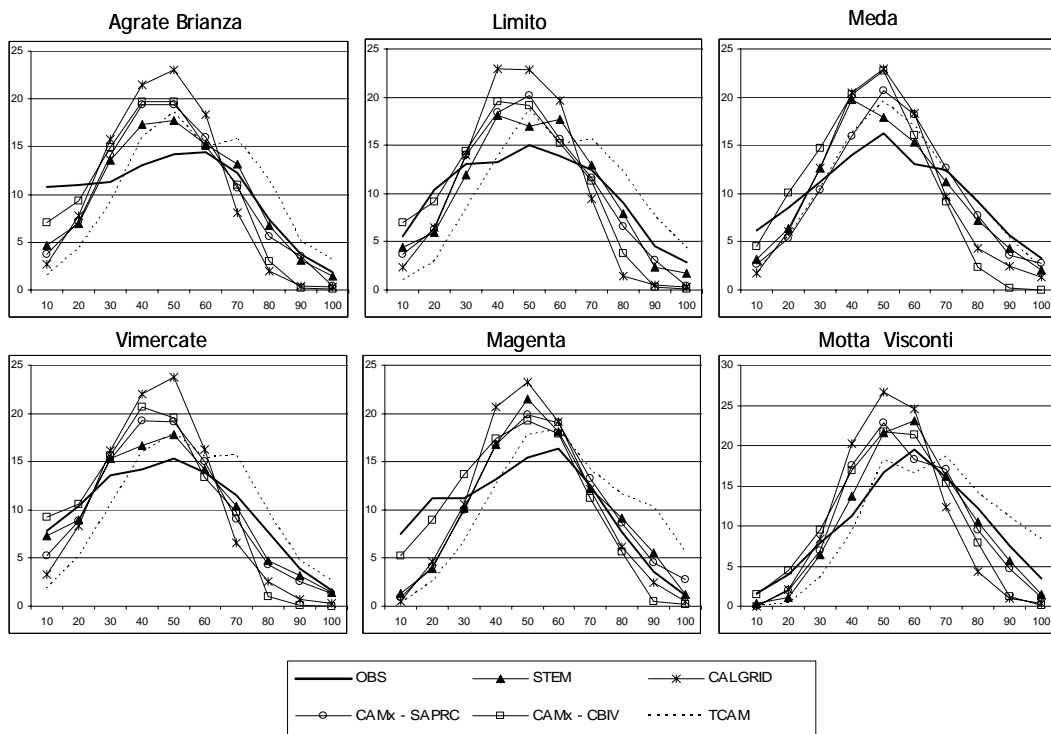


Figure 2. Diurnal Frequency analysis concerning ozone concentration during the simulation period.

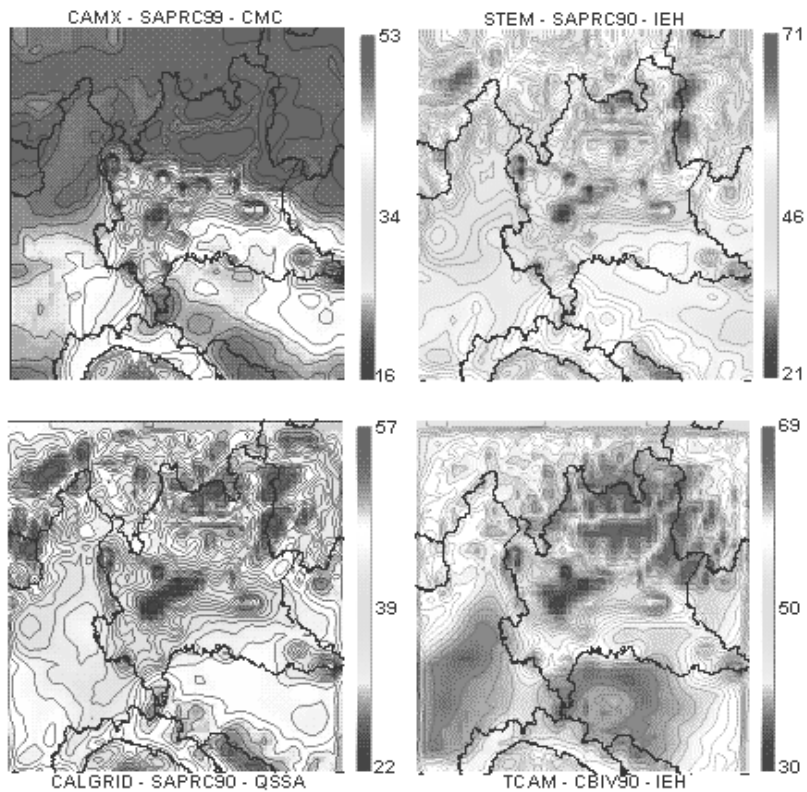


Figure 3. Ozone spatial distribution in the domain area.

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