Proceedings of the
44th IEEE Conference on Decision and Control, and
the European Control Conference 2005
Seville, Spain, December 12-15, 2005

Design and validation of a multiphase 3D model to simulate tropospheric pollution

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Abstract— **Secondary pollutant production and removal are non linear processes, driven by precursor emissions, solar radiation and meteorological conditions. The study of these processes and the evaluation of the impact that suitable emission control strategies can have in a certain domain, require the implementation of deterministic mathematical models solving chemical/transport differential equation systems.**

This work presents the Transport and Chemical Aerosol Model (TCAM) and its validation over a Northern Italy domain, performed processing yearly simulations concerning 1999.

The model assessment analysis underlines that the model is adequately reliable to describe the atmospheric chemistry in a complex domain and that it can be used to estimate the impact of secondary pollution control strategies.

I. INTRODUCTION

Literature studies focus on the non-linearity of the cause-effect relationships between precursor emissions and secondary pollutant (aerosols and ozone) concentrations [1] [2] [3] [4] [5]. Multiphase models allow to simulate the physical-chemical processes involving secondary pollutants in atmosphere and to assess the effectiveness of emission control strategies. Detailed three-dimensional multiphase models, describing the processes involved in the formation and removal of pollutants in atmosphere by means of non linear differential equation systems, are generally run for short episodes due to the high computational costs. However, in the last decade the attention of researcher has been addressed to long term simulation as the WHO (World Health Organization) established limits for exposure indicators (mean concentration and exceedance days). The development of long term multi-phase models must take into account (1) the need of stable and efficient numerical schemes solving differential equation system describing the involved phenomena, (2) the large amount of input data required by the model and (3) the difficult in formalization of pollutant accumulation and removal processes in different meteorological regimes (winter/summer period).

This work presents the design and the development of the TCAM (Transport and Chemical Aerosol Model) and its validation over a Northern Italy domain. The model is part of the GAMES (Gas Aerosol Modelling Evaluation System) integrated modelling system [6] that also includes (1) the emission pre-processor POEM-CDII, addressed to the estimation of emission fields, (2) the CALMET meteorological model [7], which generates the meteorological input driving TCAM and (3) a pre-processors which provides initial and boundary conditions required by TCAM (Figure 1). The validation of the modelling system has been performed in the frame of CityDelta-CAFE project (6^{th} EU Environmental Action Programme) [8] .

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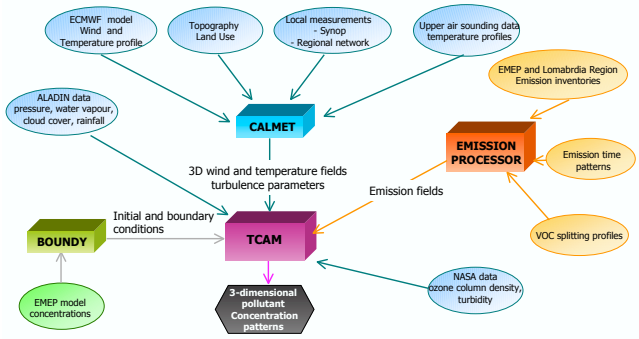

Fig. 1. Scheme of GAMES modelling system

II. MODEL DESCRIPTION

TCAM (Transport and Chemical Aerosol Model) is a multiphase three-dimensional Eulerian grid model, in terrain-following co-ordinate system. The model formalizes the physical and chemical phenomena involved in the formation of secondary air pollution in heterogeneous phase. The pollutant evolution is computed solving, for each cell of the computational domain, the following mass-balance equation:

$$\frac{\partial C_i}{\partial t} = T_i + R_i + D_i + S_i \qquad (1)$$

where:

- C_i is the concentration of species i [$g\ m^{-3}$];
- T_i is the transport/diffusion term;
- R_i the heterogeneous chemical term;
- D_i include the wet and the dry deposition;
- S_i is the emission term.

The chemical and physical phenomena occur simultaneously in atmosphere but solving 1 for each domain cell would be too time and memory expensive [9].

To solve 1, TCAM implements a split operator technique allowing to separately treat the horizontal transport, the vertical phenomena (including transport-diffusion, emissions and deposition) and the chemistry, using the relation:

$$C_i^{n+1} = A_{xy}A_zA_cA_cA_zA_{xy}C_i^n \tag{2}$$

where C_i^n is the concentration of species i at time step n, A_{xy}, A_z and A_c are the horizontal transport, the vertical transport and the chemistry operators respectively. At each time step the three modules are executed for an half-time step and next they are re-executed in reverse order for the remaining half-time step [10]. This approach ensures second order accuracy in time. The time step is chosen before the simulation and satisfies the Courant condition [11]: $v\frac{\delta t}{\delta x} \leq 1$ where v is the maximum value of the mean wind velocity during the simulation, δt is the time step and δx is the dimension of the horizontal grid cells.

The three operators are defined by the systems:

$$\begin{aligned}
\left[\frac{\partial C_i}{\partial t}\right]_{horiz} &= -v_x\frac{\partial C_i}{\partial x} - v_y\frac{\partial C_i}{\partial y} + K_{xx}\frac{\partial^2 C_i}{\partial^2 x} + \\
&\quad + K_{yy}\frac{\partial^2 C_i}{\partial^2 y} \\
\left[\frac{\partial C_i}{\partial t}\right]_{vert} &= -v_z\frac{\partial C_i}{\partial z} + \frac{\partial}{\partial z}\left(K_{zz}\frac{\partial C_i}{\partial z}\right) + \\
&\quad + S_i - D_i \\
\left[\frac{\partial C_i}{\partial t}\right]_{chem} &= P_i(C) - L_i(C)C_i
\end{aligned} \tag{3}$$

where:

- C_i is the concentration of i species [$g\ m^{-3}$];
- v_x, v_y and v_z are the wind components [$m\ s^{-1}$];
- D_i and S_i are the deposition and emission terms;
- K_{xx}, K_{yy}, K_{zz} are the diffusion coefficient along the x, y and z direction [$m^2\ s^{-1}$];
- P_i [$g\ m^{-3}\ s^{-1}$] and L_i [s^{-1}] are the production and removal terms due to chemical reactions.

A. Horizontal advection/diffusion module

A module based on a finite difference scheme using Chapeau functions [12] has been implemented in TCAM to solve the horizontal transport system of both gas and aerosol species. Such scheme enables computationally efficient transport with mass conservation and suppression of negative concentrations. A non linear Forester filter [13] has been added to the transport solver to decrease numerical noise sometimes leading to negative concentrations. The module requires the lateral turbulent diffusivities K_{xx} and K_{yy} for both gas and aerosol species, which depend on Pasquill-Gifford stability classes [14].

B. Vertical advection/diffusion module

TCAM implements a terrain following co-ordinates system, allowing the application of the model on complex terrain domain. The vertical co-ordinates Z [m] of a generic point (x,y) in the terrain following system is defined as:

$$Z(x,y) = z(x,y) - h(x,y) \tag{4}$$

where z(x,y) [m] and h(x,y) [m] are the height of the point and the height of the terrain above sea level respectively.

The vertical component of the wind needs to be corrected to take into account the vertical transport due to horizontal components that can cause a mass displacement among the grid levels. The corrected wind velocity V_z [$m\ s^{-1}$] is obtained as:

$$V_z = v_z - v_x\frac{\delta h}{\delta x} - v_y\frac{\delta h}{\delta y} \tag{5}$$

where v_z is the physical wind velocity on z direction.

The vertical turbulent diffusion generally dominates the vertical transport of the pollutants [15]. The computation of K_{zz} is performed taking into account the meteorological parameters: the Monin-Obukhov length, the mixing height, the friction velocity and the convective velocity [7] [15]. The choice of the integration scheme is performed on the basis of the value of the vertical turbulent diffusivity coefficient K_{zz}: for high values, a fully implicit scheme is used, otherwise (stable classes, usually during the night), an explicit Cranck-Nicholson scheme is performed [16].

C. Dry and Wet deposition

Dry deposition is an important removal process, acting on all pollutant and it is characteristic of lower level of atmosphere. Due to the surface retain capability upon gas molecules and solid particles, it is mostly influenced by roughness, composition and type, amount and physiological state of the vegetation and atmospheric parameters (stability, turbulence intensity) and pollutant properties. The phenomenon is described by the equation [18]:

$$F_i = C_i \cdot v_{di} \tag{6}$$

where F_i [$g\ m^{-2}\ s^{-1}$] is the removed pollutant flux, C_i is the concentration of the i species near the terrain and v_{di} [$m\ s^{-1}$] is the deposition velocity. The deposition velocity for gas species is calculated as:

$$v_{di} = (r_a + r_d + r_c)^{-1} \tag{7}$$

where r_a [$s\ m^{-1}$] is related to atmospheric turbulence, r_d [$s\ m^{-1}$] depends on molecular and brownian diffusion and r_c [$s\ m^{-1}$] takes into account the capability of the terrain to retain the gas molecules.

The deposition velocity for aerosol species is defined as:

$$v_{di} = (r_a + r_d + r_a r_d v_g)^{-1} + v_g \tag{8}$$

where r_a and r_d are defined previously, and v_g [$m\ s^{-1}$] is the gravitational component of the deposition velocity.

Wet deposition (of both gas and aerosol species) is described by the equation [18]:

$$F_i = -\Lambda \cdot C_i \tag{9}$$

TABLE I
CHEMICAL MECHANISM IMPLEMENTED IN TCAM MODEL

Mechanism	Approach	No. Active Species	No. Reactions
SAPRC-90 [20]	Lumped Molecule	54	128
SAPRC-97 [21]	Lumped Molecule	82	184
COCOH-97 [24]	Lumped Molecule	95	187
CBIV-90 [19]	Lumped Structure	32	81

where Λ [$m\ s^{-1}$] is the scavenging coefficient determined separately for gases and particulates. For gases, two components are calculated: (1) the uptake of ambient gas concentration into falling precipitation, which can occur within and below clouds, and (2) the collection by precipitation of cloud droplets containing dissolved gas species. For particles, separate in-cloud and below-cloud scavenging coefficients are determined. Within clouds, all aerosol mass is assumed to exist in cloud droplets (all particles are activated as condensation nuclei), so scavenging is due to the efficient collection of cloud droplets by precipitation. Below clouds, dry particles are scavenged by falling precipitation with efficiency depending on particle size.

D. Gas phase chemical module

A full mathematical description of the atmospheric chemistry is not possible because of the complexity of the large amount of reactions involving primary and secondary compounds. Air quality models implement simplified atmospheric chemistry by means of condensed chemical mechanisms [17]. Two approach could be used [19]:

- in the lumped structure approach, organic compounds are split into smaller reaction elements based on the types of carbon bonds in each species;
- in the lumped molecule approach, organic compounds are grouped taking into account similar chemical and kinetic characteristics.

TCAM allows the simulation of gas chemistry using either lumped structure or lumped molecule approach (Table I).

Once the chemical mechanism has been defined in terms of reactions (R) and species (S), the kinetic equations to be solved over each cell of the computational domain have the following form:

$$\begin{aligned}\frac{dC_i(t)}{dt} &= P_i(C,t) - L_i(C,t)C_i \\ &= \sum_{j\in Q(i)} \left(k_j \prod_{\substack{k\in rc(j)\\ k\neq j}} C_k(t) \right) + \\ &- \sum_{j\in R(i)} \left(k_j \prod_{\substack{k\in rc(j)\\ k\neq j}} C_k(t) \right) C_i(t) \qquad (10)\end{aligned}$$

where $i = 1,\ldots n_{act}$, n_{act} is the number of active species, C is the concentration vector, k_j is the kinetic constant of reaction j, $P(i)$=$\{j \in R/$ the species i is a product of reaction $j\}$, $Q(i)$=$\{j \in$ R/ the species i is a reactant of reaction $j\}$, $rc(j)$=$\{i \in S/\ i$ is a reactant of reaction $j\}$. The inclusion of photochemistry into the grid-based model constitutes a severe numerical challenge as the resulting system is characterized by eigenvalues ranging over 10 orders of magnitude.

The algorithm implemented in TCAM to integrate 10 is the Implicit-Explicit Hybrid (IEH) solver [22], that divides all the species in fast and slow ones, according to their reaction velocity.

The system of fast species is solved by means of the implicit Livermore Solver for Ordinary Differential Equations (LSODE) [23] [22]. It implements the Adams method (predictor-corrector) in the non-stiff case [16], and the Backward Differentiation Formula method in the stiff case [16].

E. Emission injection

TCAM has been developed to consider both point and areal emission sources for gas and particulate matter. The areal emission fluxes have to be specified for each ground level cell of the domain at each time step, while the point emissions are assigned for the cells where the sources are localized. The emission data have the same chemical details of the condensed mechanisms implemented in the TCAM chemical module. The particulate matter emissions are described considering 6 chemical species (organic carbon, elementary carbon, SO_4=, NO_3-, H_2O and others, including the heavy metals and the undefined compounds), and size bins ranging from 0 to 11.4 μm.

F. Aerosol Module

The aerosol module implemented in TCAM is coupled with the COCOH-97 gas phase chemical mechanism [26]. The aerosol module describes aerosols by means of a fixed-moving approach. A generic particle is represented with an internal core containing the non volatile material, like elemental carbon, crustal and dust. The dimension of the core of each size class is established at the beginning of the simulation on the basis of a logarithmic distribution and it is held constant during the simulation. The volatile material is supposed to reside in an outer shell of the particle whose dimension is evaluated by the module at each time step on the basis of the total mass and of the total number of suspended particles. Both shell and core fractions are suppose to be internally mixed. The aerosol module describes the dynamics of 21 chemical compounds split in 10 size bins, so that the prognostic variables of the module are 210. The inorganic species are twelve (H_2O, SO_4=, NH_4+, Cl-, NO_3-, Na+, H+, SO_2(aq), H_2O_2(aq), O_3(aq), elemental carbon and other), while the organic species are 9, namely a generic primary and 8 classes of secondary organic species. TCAM describes the most relevant aerosol processes: the condensation, the evaporation [18], the nucleation [25] of H_2SO_4 and the aqueous oxidation of SO_2 [18].

III. MODEL VALIDATION

A. Model Setup

The model has been applied to a 300x300 km^2 area located in the Northern Italy and centered on the Milan metropolitan area (Figure 2). The area is characterized by complex terrain and by high industrial and urban emission and by a close road net.

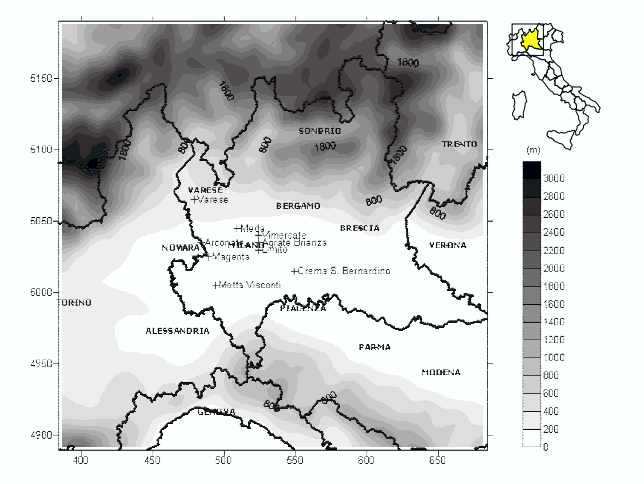

Fig. 2. Simulation domain topography (m.a.s.l.)

The domain has been horizontally divided into 5x5 km^2 grid cells and vertically in 11 levels ranging from 20 to 3900 meters above ground level. The 1999 simulation has been performed.

The input data are provided to the model by meteorological, emission and boundary condition pre-processors processing data shared by JRC-IES during CityDelta exercise [8]. In particular:

- emission fields have been estimated by means of POEM-CDII pre-processor starting from local inventory, covering the Lombardia Region and EMEP (European Monitoring and Evaluation Programme) emission data [29]. Temporal profiles, chemical characterization and PM size distribution have been provided by EMEP [29].
- Boundary conditions have been defined from the outputs of the Unified EMEP model [28]. The EMEP concentration fields, available on a 3 hour basis over a grid with 50 km horizontal resolution and 20 vertical levels of growing thickness up to 15.000 m a.s.l., have been linearly interpolated in space and time.
- Meteorological fields (wind, mixing height, humidity and temperature) have been calculated by CALMET meteorological model, merging ALADIN prognostic model fields [27] and local measurement.

B. Stability Analysis

The model in the heterogeneous configuration describes the evolution of 305 state variables. Therefore, an analytic stability analysis of the system cannot be performed. The stability of the model has been assessed by means of the simulation method, in the frame of CityDelta project, forcing the system with different input patterns.

C. Performance Indexes

The validation has been performed with regard to O_3 and $PM10$ (particles with diameter lower or equal to 10 μm) concentration series, using the following statistical indexes:

- Calculated and Observed mean concentrations over the period;
- Normalized Mean Square Error over the period:

$$NMSE = \frac{1}{N}\frac{\sum_{t=1}^{N}(C^{mod}(t)-C^{obs}(t))^2}{\sum_{t=1}^{N}(C^{obs}(t))^2} \qquad (11)$$

- Correlation Coefficient:

$$CORR = \frac{\sum_{t=1}^{N}(C^{mod}(t)-\bar{C}^{mod})(C^{obs}(t)-\bar{C}^{obs})}{\sqrt{\sum_{t=1}^{N}(C^{mod}(t)-\bar{C}^{mod})^2\sum_{t=1}^{N}(C^{obs}(t)-\bar{C}^{obs})^2}} \qquad (12)$$

where $C^{mod}(t)$ and $C^{obs}(t)$ are the calculated and observed concentration at the time t respectively, $\bar{C}^{mod}$ and $\bar{C}^{obs}$ are the mean concentration of species and N is the number of valid data.

D. Gas phase results

In Figure 3 the mean ozone concentration distribution is presented. The map shows that the highest concentrations are computed in the valleys on the north of the domain, due to breezes that transport the Milano metropolitan area plume. In high NOx emission areas, such as the surrounding of the main cities of the domain (Milano, Brescia and Bergamo) the concentration are lower, because of the reaction of NO with ozone to form NO_2. The validation of the model for what the ozone is concerned has been carrying out comparing observed and calculated hourly concentrations in the summer period (April-September) in 9 monitoring stations. The model is able to reproduce the mean concentration both during 24 hours and light hours (Table II). In terms of NMSE (Table III), the model shows a good agreement (0.15-0.20) in particular during day-light hour (8-19), when high concentration levels are reached. The correlation coefficient (Table III) confirms the good agreement of the simulations with measured data. The coefficient is above 0.7 in Magenta and Arconate stations. The high mean concentration station of Varese is the only one with correlation coefficient below 0.6.

E. Aerosol phase results

PM10 highest mean concentration values are estimated in the central region of the domain (Pianura Padana), that includes the intense emission urban areas of Milano, Brescia and Bergamo. The validation of PM10 simulated patterns has been performed processing computed and measured daily mean concentration during 1999 in 4 stations (Limito, Meda, Vimercate, Magenta) located in the surrounding of Milano urban area. The mean concentrations (Table IV) are well simulated in the Vimercate and Magenta stations. The

TABLE II

COMPUTED (MOD) AND MEASURED (OBS) O_3 HOURLY MEAN CONCENTRATION OVER THE PERIOD ($\mu g\, m^{-3}$)

Station	Mean			
	0-23		8-19	
	Mod	Obs	Mod	Obs
Urban				
Agrate Brianza	57.40	59.73	90.08	84.41
Limito	58.56	63.60	90.55	90.16
Meda	64.94	72.95	93.71	96.68
Vimercate	56.28	65.64	89.51	86.45
Magenta	64.94	58.95	92.79	85.70
Suburban				
Arconate	61.30	77.20	89.79	110.40
Varese Vid.	75.03	81.46	93.44	97.74
Rurali				
Crema	79.85	59.58	97.91	83.53
Motta	74.61	77.40	93.60	106.61

TABLE III

SIMULATION PERFORMANCE INDEXES CONCERNING O_3 HOURLY CONCENTRATION

Station	CORR	NMSE	
	0-23	0-23	8-19
Urban			
Agrate Brianza	0.66	0.37	0.22
Limito	0.69	0.32	0.19
Meda	0.64	0.31	0.20
Vimercate	0.63	0.38	0.20
Magenta	0.70	0.28	0.19
Suburban			
Arconate	0.72	0.34	0.23
Varese Vidoletti	0.55	0.19	0.16
Rural			
Crema S. Bernardino	0.59	0.34	0.19
Motta Visconti	0.62	0.22	0.15

differences between mean computed and observed concentrations are higher in Limito and Meda. In these stations, the performances are worse in the winter season, when the aerosol is mainly primary, suggesting that the disagreement could be due to emission estimation. The NMSE index (Table V) confirms that the performances of the model are more adequate in summer-season than in winter one. This fact indicates that the model is able to reproduce the complex relationships between gas and aerosol phases, that in summer time are particularly intense. The good performances of the model are confirmed by the correlation indexes, showing high values in all the stations.

F. Computational details

The yearly simulation has been performed on a PC Pentium IV, 3.2 GHz CPU, 512 MB RAM. In this configuration, the computation time is about 1h and 45 min for 24 simulated hours.

IV. CONCLUSION

This paper presents the description and the validation of TCAM model, designed to simulate the physical-chemical transformations of primary and secondary pollutants in the troposphere. TCAM treats gas and aerosol phase pollutants, and considers the main processes involving them, such as transport/diffusion, wet and dry deposition, chemical reactions in both gas and aqueous phases, condensation/evaporation and nucleation. The validation analysis, performed in the frame of CityDelta modelling exercise, shows a good agreement with measured data, both for O_3 and PM. This fact is explained by the detailed representation of the processes and by the efficient implemented numerical solvers. The results suggest that the model is adequate to describe the atmospheric chemistry in a complex domain and that it can be integrated in a Decision Support System to assess the impact of secondary pollution control strategies.

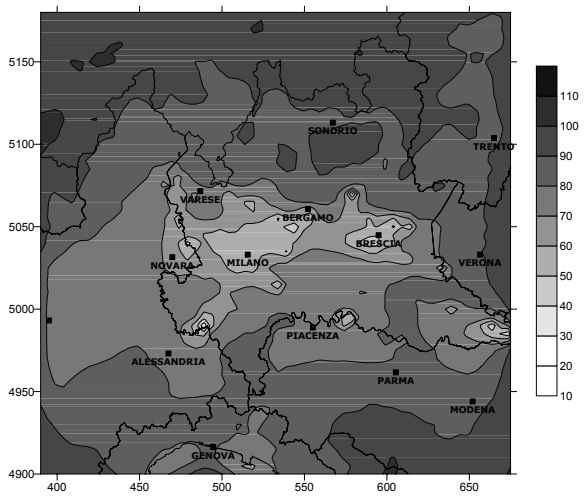

Fig. 3. Ozone summer mean concentration ($\mu g\, m^{-3}$)

TABLE IV

COMPUTED (MOD) AND MEASURED (OBS) PM10 DAILY MEAN CONCENTRATION OVER THE PERIOD ($\mu g\, m^{-3}$)

Station	Mean					
	Year		Summer		Winter	
	Mod	Obs	Mod	Obs	Mod	Obs
Limito	68.82	52.29	50.74	38.62	87.10	66.11
Meda	51.37	62.74	41.70	41.36	61.14	84.23
Vimercate	62.87	59.11	48.60	49.55	77.29	68.88
Magenta	52.78	52.86	42.15	40.38	63.53	65.20

REFERENCES

[1] Meng Z., Dabdub D., Seinfeld J.H. Chemical coupling between atmospheric ozone and particulate matter. *Science*, 277:116-119, 1997.

[2] Kleinman L.I., Daum P.H., Lee J.H., Lee Y., Nunnermacker L.J., Springston S.R., Newman L. Dependance of ozone production on NOx and Hydrocarbons in the troposphere. *Geophysic Resource Letters*, 24(18):2299-2302, 1997.

[3] Sillman S. The relation between ozone, NOx and Hydrocarbons in Urban and polluted rural environments. *Atmospheric Environment*, 33:1821-1845, 1999.

[4] Jenkin M.E., Clemitshaw K.C. Ozone and other secondary photochemical pollutants: chemical porcesses governing their formation in the planetary boundary layer. *Atmospheric Environment*, 34:2499-2527, 2000.

TABLE V

SIMULATION PERFORMANCE INDEXES CONCERNING PM10 DAILY CONCENTRATION

Station	CORR	NMSE		
	Year	Year	Summer	Winter
Limito	0.67	0.29	0.21	0.29
Meda	0.52	0.48	0.22	0.53
Vimercate	0.60	0.22	0.11	0.27
Magenta	0.58	0.27	0.15	0.30

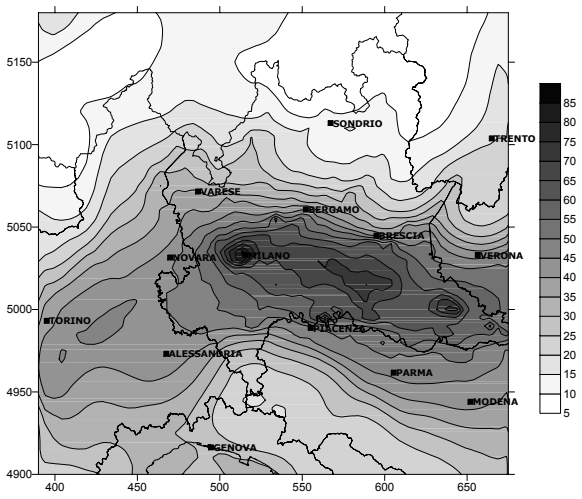

Fig. 4. PM10 mean yearly concentration ($\mu g\ m^{-3}$)

[5] Nguyen K., Dabdub D. NOx and VOC control and its effects on the formation of aerosols. *Aerosol Science and Technology*, 36:560-572, 2002.

[6] Volta M. , Finzi G. GAMES, a new comprehensive gas aerosol modelling system. *Environmental Modelling and Software*, 2005, doi: 10.1016/j.envsoft.2004.06.012.

[7] Scire J.S., Insley E.M., Yamartino R.J. Model Formulation and User's Guide for the CALMET Meteorological Model. Technical Report A025-1, California Air Resources Board, Sacramento, CA, 1990.

[8] Thunis P. , Cuvelier C. *Air Pollution Modeling and Its Application*, chapter CITYDELTA: a European modelling inter-comparison to predict air quality in 2010. Kluwer Academic/ Plenum Publishers, 2004.

[9] Bastrup-Birk A., Brandt J., Uria I., Zlatev Z. Studying Cumulative Ozone Exposures in Europe During a Seven-Year Period. Internal Report, National Environmental Research Institute, Roskilde, Denmark, 1996.

[10] Marchuk G.I. *Methods of Numerical Mathematics*. Springler, New York, 1975.

[11] Yamartino R.J., Scire J.S., Carmichael G.R, Chang Y.S. The CALGRID Mesoscale Photochemical Grid Model - I. Model Formulation. *Atmospheric Environment*, 26A(8):1493–1512, 1992.

[12] Pepper D.W., Kern C.D., Long P.E. Modelling the Dispersion of Atmospheric Pollution Using Cubic Splines and Chapeau Functions. *Atmospheric Environment*, 13:223–237, 1979.

[13] Forester C.K. Higher Order Monotonic Convection Difference Schemes. *Journal of Computational Physics*, 23:1–22, 1977.

[14] Pasquill F. *Atmospheric Diffusion, 2nd Edition*. Halsted Press of John Wiley & Sons, New York, 1974.

[15] Holtslag A.A.M., Nieuwstadt F.T.M. Scaling the Atmospheric Boundary Layer. *Boundary Layer Meteorology*, 36:201–209, 1986.

[16] Wille D.R. New Stepsize Estimators for Linear Multistep Methods. Numerical Analysis Report 247, inst-MCCM, March 1994.

[17] Dodge M.C. Chemical Oxidant Mechanisms for Air Quality Modelling: Critical Review. *Atmospheric Environment*, 34:2103–2130, 2000.

[18] Seinfeld J.H., Pandis S.N. *Atmospheric Chemistry and Physics*. John Wiley & Sons, 1997.

[19] Gery M.W, Whitten G.Z., Killus J.P. A Photochemical Mechanism for Urban and Regional-Scale Computer Modeling. *Journal of Geophysical Research*, 94:12925–12956, 1989.

[20] Carter W.P.L. A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic Compounds. *Atmospheric Environment*, 24A:481–518, 1990.

[21] Carter W.P.L., Luo D., Malkina I.L. Environmental Chamber Studies for Development of an Updated Photochemical Mechanism for *VOC* Reactivity Assessment. Technical report, California Air Resources Board , Sacramento (CA), 1997. Final Report.

[22] Chock D.P., Winkler S.L., Sun P. A Comparison of Stiff Chemistry Solvers for Air Quality Modeling, June 1994. *Air & Waste Management Association* 87^{th} *Annual Meeting*, June 1994.

[23] Hindmarsh A.C. LSODE and LSODEI, Two New Initial Value Ordinary Differential Equation Solvers. *ACM-SIGNUM Newsletter*, 15(4):10–11, 1975.

[24] Durlak S. K., Baumgardner D. Examination of the evolution of urban plumes using MAPS (Model for Aerosol Process Studies) *11th Joint Conference on the Applications of Air Pollution Meteorology with the Air and Waste Management Association.* Long Beach, CA, January 9-13 2000.

[25] Jaecker-Voirol A., Mirabel P. Heteromolecular Nucleation in the Sulfuric Acid-Water System. *Atmospheric Environment*, 23:2053–2057, 1989.

[26] Wexler A.S., Seinfeld J.H. Second-Generation Inorganic Aerosol Model. *Atmospheric Environment*, 25A:2,731–2,748, 1991.

[27] Bubnova R., Horanyi A., Malardel S. International project ARPEGE/ALADIN. *EWGLAM Newsletter*, 22: 117130, 1993.

[28] Simpson D. , Fagerli H. , Jonson J.E. , Tsyro S. , Wind P. Transboundary acidification, eutrophication and ground level ozone in Europe - part I: Unified EMEP model description. Technical Report 1/2003, EMEP MSC-W, 2003.

[29] Vestreng V. , Adams M. , Goodwin J. Inventory Review 2004. Emission data reportedd to CRLTAP and under the NEC Directive. Technical report, EMEP/EEA Joint Review Report, 2004.