

EXPAH - ACTION 4.5: Integration of PAHs
atmospheric processes within FARM model

Authors
C. Silibello

Riferimento
ARIANET R2012.01

February 2012

1	Introduction.....	2
2	FARM overview	3
2.1	Model formulation	4
2.2	Coordinates and grid system.....	5
2.3	Transport and diffusion.....	6
2.4	Gas-phase chemistry.....	6
2.4.1	Photolysis rates	6
2.5	Aerosol processes	7
2.5.1	Nucleation	10
2.5.2	Coagulation	10
2.5.3	Gas/particle mass transfer	10
2.6	Pollutants removal	10
2.6.1	Dry deposition	11
2.6.2	Precipitation scavenging	11
2.7	In-cloud chemistry: aqueous phase SO ₂ oxidation	12
3	FARM upgrade	13
3.1	Gas-phase chemistry.....	13
3.2	Mercury in-cloud chemistry.....	14
3.3	Gas-aerosol partitioning	15
3.4	Deposition processes	16
4	Preliminary test of the upgraded version of FARM.....	18
5	Conclusions.....	22
	Aknowledgents	22
	Bibliography	23

1 Introduction

The United Nation Economic Commission for Europe (*UNECE*), set up in 1947 to promote pan-European economic integration, signed in 1979 the Convention on Long-range Transboundary Air Pollution (*CLRTAP*) with the aim to protect the human environment against air pollution and to gradually reduce and prevent air pollution, including long-range transboundary air pollution. The Convention entered into force in 1983 and over the past 30 years has been extended by 8 Protocols that target pollutants such as sulphur, nitrogen oxide, persistent organic pollutants, volatile organic compounds, ammonia and toxic heavy metals. The protocol on persistent organic pollutants (POPs) considers following substances: PAHs, Dioxins/furans and Hexachlorobenzene. PAHs are a group of chemicals released during the incomplete burning of oil, coal, gas, and other organic materials such as trees during forest fires. Significant sources of PAHs include domestic combustion, vehicles, production sites of metals, coke and asphalt, and power stations. Because PAHs are actually a group of over 100 different chemicals, for the purposes of emission inventories (and modeling) the following four indicator compounds has been considered by the protocol: benzo(a)pyrene (B[a]P); benzo(b)fluoranthene (B[b]F); benzo(k)fluoranthene (B[k]F) and indeno (1,2,3-cd) pyrene (I_P).

With the establishment of the CLRTAP, the European Monitoring and Evaluation Programme (*EMEP*), set-up in 1977 to follow the needs for investigation and evaluation of the long-range transport of air pollution over Europe, became an integrated part of this Convention. The EMEP activities are carried out in four EMEP centres responsible for following activities:

1. Chemical Coordinating Centre (**CCC**): measurements;
2. Meteorological Synthesizing Centre – West (**MSC-W**): modeling of acidifying compounds, ozone and particulate matter;
3. Meteorological Centre – East (**MSC-E**): modeling of heavy metals (Cd, Pb, Hg) and selected persistent organic pollutants (PCB, PAH, HCB, PCDD/Fs, g-HCH);
4. Centre for Integrated Assessment Modelling (**CIAM**): Integrated Assessment Modelling.

The numerical models of HM and POPs airborne transport and deposition, developed by MSC-E, have been considered in order to extend the capabilities of the Chemical Transport Model (CTM) FARM (Flexible Air quality Regional Model) to these pollutants and to fulfill the modeling requirements for the EXPAH project. In particular, the implementation of PAHs atmospheric reactions processes within the FARM model, has been one of the expected results of action 4.5 of the EXPAH project.

In the following sections we will describe the CTM FARM (section 2), its upgrade in order to include PAHs transformation processes (section 3) and an example of the application of the updated version of FARM over the Italian peninsula (section 4).

2 FARM overview

FARM (Flexible Air quality Regional Model, Gariazzo *et al.*, 2007; Silibello *et al.*, 2008) is a three-dimensional Eulerian model that accounts for the transport, chemical conversion and deposition of atmospheric pollutants. The following processes and features are included in FARM:

- emission of pollutants from area and point sources, with plume rise calculation and mass assignment to vertical grid cells;
- three-dimensional transport by advection and turbulent diffusion;
- transformation of chemical species by gas-phase chemistry, with flexible mechanism configuration;
- aerosol processes;
- dry removal of pollutants dependent on local meteorology and land-use;
- wet removal through precipitation scavenging processes;
- possibility of one- or two-way nesting with an arbitrary number of computational grids
- interface with a complete modelling system for multiscale air quality simulations.

The flow of data needed and produced by FARM is outlined in Figure 1.

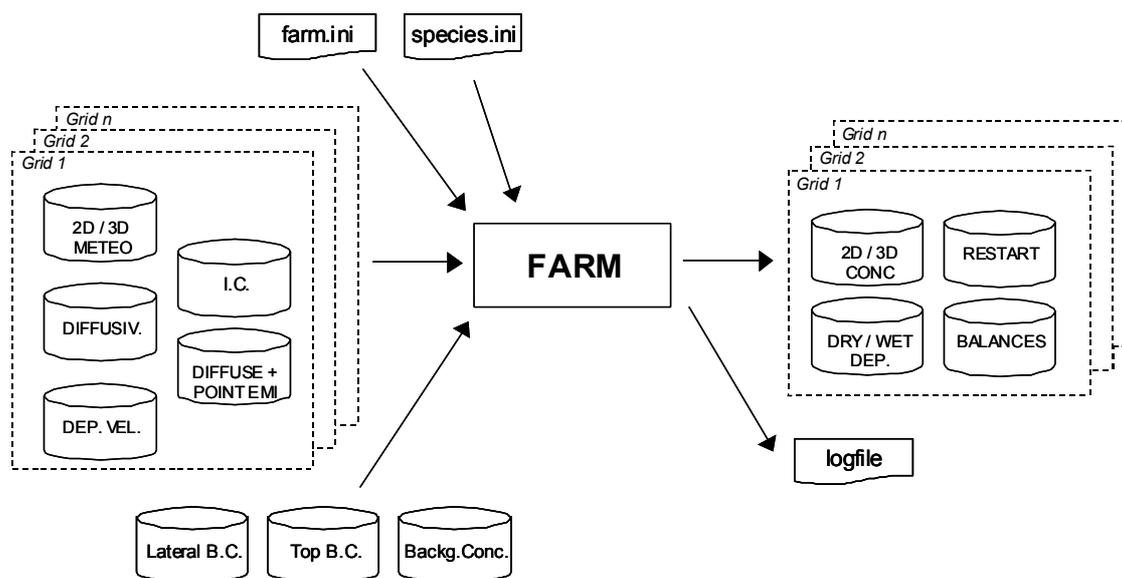


Figure 1 Outline of FARM data flow.

For each simulation grid, a set of input files must be provided, in the form of time-varying (generally hourly based) data archives:

- 3D and 2D meteorological fields (three components of wind, air temperature, pressure, relative humidity, cloud cover, precipitation);
- 3D fields of turbulent horizontal and vertical diffusivities;
- dry deposition velocities fields, for each chemical species;
- fluxes of emitted species, from point and 2D/3D diffuse sources;
- 3D initial concentrations for each chemical species;

- for the master grid time-varying (e.g. hourly) or climatological lateral and top boundary concentrations for each chemical species.

Model configuration and run parameters are assigned through:

- a general initialization file (farm.ini);
- a species initialization file (species.ini).

Output files produce by FARM are:

- a log file, reporting on model setup and run phases;
- for each simulation grid:
 - a restart file;
 - a file containing 2D and 3D time-dependent concentrations of selected species in gas and aerosol phases;
 - two files, containing respectively time-dependent dry and wet deposition fluxes;
 - a file containing balances over the whole calculation grid of selected species, detailing formation and destruction pathways due to different processes.

2.1 Model formulation

FARM is a three-dimensional Eulerian model. Physical and chemical process influencing the concentration fields within the modelling domain are described by a system of partial differential equations (PDE). Each of them expresses the time dependency of the *i*-th gas-phase average species concentration c_i within each grid cell volume as the sum of the contributions given by all the physical and chemical processes operating on that volume. For a single-phase atmosphere (e.g. gas) this system has the form:

$$\frac{\partial c_i}{\partial t} = -u \frac{\partial c_i}{\partial x} - v \frac{\partial c_i}{\partial y} - w \frac{\partial c_i}{\partial z} + K_{xx} \frac{\partial^2 c_i}{\partial x^2} + K_{yy} \frac{\partial^2 c_i}{\partial y^2} + \frac{\partial}{\partial z} \left(K_{zz} \frac{\partial c_i}{\partial z} \right) + S_i + C_i + R_i$$

where u , v and w are the components of wind velocity vector, K_{xx} , K_{yy} and K_{zz} , the diagonal components of the diffusivity tensor, S_i the source term, C_i the gas-phase reaction term and R_i the removal term due to deposition processes (dry and wet). In FARM the lateral diffusivities are assumed space independent i.e. $K_{xx}=K_{yy}=K_H$ and coherently $K_{zz}=K_V$

The numerical integration of the above system of PDEs is performed by a method that splits the multi-dimensional problem into time dependent one-dimensional problems, which are then solved sequentially over the time step Δt (operator splitting). According to this technique, the time evolution of the *i*-th chemical species over the time step Δt is then computed as follow:

$$c_i(\mathbf{x}, t + \Delta t) = L_x(\Delta t)L_y(\Delta t)L_z(\Delta t)L_c(\Delta t)c_i(\mathbf{x}, t)$$

where L_x , L_y are advection-diffusion operators along the two horizontal axes, L_z is the vertical operator taking into account transport, diffusion, source injection and dry deposition processes in the adopted coordinates system and L_c the operator containing all chemical conversion terms. These operators take the following expressions:

$$L_x c_i = m^2 \frac{\partial(\frac{uc_i}{m})}{\partial x} - m \frac{\partial}{\partial x} \left[m K_H \frac{\partial c_i}{\partial x} \right]$$

$$L_y c_i = m^2 \frac{\partial(\frac{vc_i}{m})}{\partial y} - m \frac{\partial}{\partial y} \left[m K_H \frac{\partial c_i}{\partial y} \right]$$

$$L_z c_i = \frac{\partial(wc_i)}{\partial z} - \frac{\partial}{\partial z} \left[K_V \frac{\partial c_i}{\partial z} \right] + m^2 \frac{E_i}{\partial x \partial y \partial z} + R_i$$

$$L_c c_i = C_i = P_i + D_i c_i$$

where P_i e D_i represent production and destruction terms due to gas-phase chemical reactions, E_i is the emission term from point and diffusion sources and m is the map scale factor (e.g. the ratio of the length of a path on the map to the length of the path that it represents on the earth).

2.2 Coordinates and grid system

The FARM 3D computational mesh is structured as follows.

In the horizontal directions, the following metric coordinate systems can be adopted:

- UTM (Universal Transverse Mercatore);
- polar stereographic;
- latitude/longitude;
- mercator.

In the vertical direction, terrain-following coordinates are adopted (see Figure 2), with curved top and levels parallel to ground: $Z(x, y) = z - h(x, y)$ where $h(x, y)$ represent the topography.

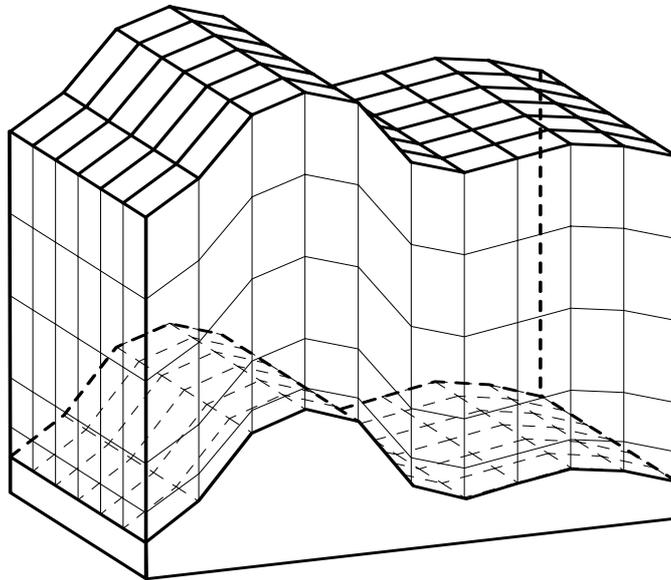


Figure 2 Example of a modelling domain in Z terrain following coordinate system.

2.3 *Transport and diffusion*

Partial differential equations involved in horizontal and vertical advection-diffusion operators are solved in FARM using the schemes employed in CALGRID model (Yamartino *et al.*, 1992).

Horizontal advection-diffusion operators are solved using a finite elements method based on Blackman cubic polynomials (Yamartino, 1993). In Yamartino's scheme, the coefficients of a cell-centered cubic polynomial are constrained in order to maintain high-accuracy and low-diffusion characteristics and to avoid undesirable negative concentrations. In addition, a filter is used for filling in undesired short wavelength minima.

The numerical integration of the vertical diffusion equation is performed using a hybrid method employing a hybrid semi-implicit Crank-Nicholson / fully implicit scheme (Yamartino *et al.*, 1992).

2.4 *Gas-phase chemistry*

FARM model can be configured with different gas-phase chemical schemes, according to user and problem needs. This is accomplished through the use of KPP chemical pre-processor (KPP, Kinetic Pre-Processor: Damian *et al.*, 2002; Sandu *et al.*, 2003; Daescu *et al.* 2003): starting from a symbolic description of a given chemical mechanism, this allows the preparation of mechanism-specific files and subroutines to be linked to the rest of the code, avoiding the long hand-coding phase, that is prone to errors and difficult to debug. Once prepared, mechanism-specific files and subroutines are then employed in FARM, allowing its use virtually with any chemical mechanism. The gas-phase chemical mechanism that has been upgraded in order to include PAHs chemistry is SAPRC-99 (Carter, 2000), that includes the treatment of gas-phase atmospheric reactions of volatile organic compounds (VOCs) and nitrogen oxides (NO_x) and can be used to simulate photochemical processes that lead to the formation of ozone and secondary organic aerosols in the lower troposphere. The equations describing the chemical mechanism are generally highly complex and nonlinear, forming a stiff system of ordinary differential equations (ODEs). These equations are solved in FARM by means of the following methods included in KPP: Rosenbrock (Sandu *et al.* 2003) and LSODE (Radhakrishnan and Hindmarsh, 1993).

2.4.1 **Photolysis rates**

Photolysis reaction rates appearing in photodissociation reactions vary diurnally depending on the solar zenith angle. Two approaches can be used in FARM to estimate photolysis rates:

1. a simple method that uses look-up tables to calculate the rate constants for photolysis reactions. Photolysis rates are computed and adjusted according to local solar zenith angle using an empirical formula based on Peterson (1976) data;
2. the Tropospheric Ultraviolet-Visible Model (TUV, Madronich 1989), a state-of-the-art radiation transfer model widely used by the scientific community to calculate spectral irradiance, spectral actinic flux, and photodissociation rates (J-values).

Since the second approach is more time consuming than the previous one some strategies have been adopted to save computer time:

1. in case of nested grid TUV model is run only for the master grid; photodissociation rates at finer grids are interpolated from master grid values;

2. TUV model can be called few times in one hour instead of at each time step;
3. a limited number of wavelength can be used (e.g. "Fast TUV").

When using TUV the user can provide optional files containing albedo and total column ozone expressed in Dobson unit. A pre-processor has been developed to process OMI Daily gridded files (available at <ftp://toms.gsfc.nasa.gov/pub/omi/data/Level3e/ozone/>) that provides the extraction of daily fields over the studied area and, eventually, the interpolation of missing data.

In presence of a cloud layer, a cloud factor is used to estimate the effects of this layer on the actinic flux and consequently on photochemical reactions. Two methods are implemented to estimate this factor.

With the first method, the cloud factor α^k is estimated at each level k as follow:

- a. above cloud top (clear sky): $\alpha^k = 1$;
- b. immediately above cloud top: $\alpha^k = 1.3$ (increase due to albedo);
- c. inside and below cloud: $\alpha^k = 1 - 0.55 TCC^{1.75}$ (Kaiser and Hill, 1976).

The second method (Chang *et al.*, 1987) is based on cloud characteristics: coverage, optical properties (optical depth and transmissivity).

Below cloud following formula is adopted::

$$\alpha^k = 1 + TCC[1.6t_r \cos(\theta) - 1]$$

where θ is the solar zenith angle and t_r is the cloud transmissivity computed using following relationship:

$$t_r = \frac{5 - e^{-\tau_{cloud}}}{3 + 3\tau_{cloud}(1 - f)}$$

where f is the *scattering phase function asymmetry factor* set to 0.86 and τ_{cloud} is the cloud optical depth that is estimated using Stephens (1978) formula:

$$\log(\tau_{cloud}) = 0.2633 + 1.7095 \ln[\log(W)]$$

where W [g m^{-3}] is the liquid water path.

Above cloud top following formula is adopted:

$$\alpha^k = 1 + TCC\gamma_i(1 - t_r) \cos(\theta)$$

where γ_i is a factor ranging from 0.7 to 1.3 depending on chemical species (in FARM is set to 1.) Inside cloud a linear interpolation of above/below cloud factors is performed.

With both methods, no correction of photolysis rates is performed for τ_{cloud} values lowed than 5.

2.5 Aerosol processes

As in the case of gas-phase chemistry, FARM model can be configured with two aerosol modules: *AERO3*, as implemented in the Community Multiscale Air Quality (CMAQ) modeling system, and the simpler mass model *AERO0*, as implemented in EMEP Eulerian Unified model. Since we have upgraded the *AERO3* module in order to include the partitioning of PAHs between gas and aerosol phases, in the following sections it will be described extensively.

The *AERO3* aerosol module treats particles dynamic and their interaction with gas-phase species as implemented in the U.S. EPA Community Multiscale Air Quality (CMAQ) modeling system (Binkowski, 1999).

The aerosol model is coupled with the gas-phase chemical model and it is invoked after every gas-phase calculation allowing the use of updated gas-phase precursors concentrations. Aerosol variables are transported using same time steps and algorithms used for gas-phase species. The implemented aerosol module follows the so-called Whitby approach (1978) by which particles are described by a superposition of lognormal distributions called modes defined as:

$$n(\ln D) = \frac{N}{\sqrt{2\pi \ln \sigma_g}} \exp \left[-\frac{1}{2} \left(\frac{\ln \frac{D}{D_g}}{\ln \sigma_g} \right)^2 \right]$$

where N is the number concentration [m^{-3}], D the particle diameter, D_g the median diameter, and σ_g the standard deviation of the distribution. The aerosol size distribution is characterized by three modes: the Aitken mode ($D_g < 0.1 \mu\text{m}$), the accumulation mode ($0.1 \mu\text{m} < D_g < 2.5 \mu\text{m}$) and the coarse mode ($D_g > 2.5 \mu\text{m}$). $\text{PM}_{2.5}$ is given by the sum of Aitken and accumulation modes while PM_{10} is given by the sum of the three modes. The k^{th} moment of the distribution is defined as:

$$M_k = \int_{-\infty}^{\infty} D^k n(\ln D) d(\ln D)$$

with the solution:

$$M^k = ND_g^k \exp \left[\frac{k^2}{2} (\ln \sigma_g)^2 \right]$$

M^0 is the total number of aerosol particles within the mode suspended in a unit volume of air (N), M^2 is proportional to the total particulate surface area within the mode suspended in a unit volume of air (π is the constant of proportionality) and M^3 is proportional to the total particulate volume within the mode suspended in a unit volume of air ($\pi/6$ is the constant of proportionality). Given C_i^n , C_j^n and C_c^n the mass concentration [$\mu\text{g m}^{-3}$] of the n^{th} species respectively in Aitken, accumulation and coarse modes, M^3 is determined as follows:

$$M_{i,j,c}^3 = \sum_{n=1}^{n_{\max}} \frac{C_{i,j,k}^n}{\frac{\pi}{6} \rho_{i,j,k}^n}$$

where $\rho_{i,j,c}^n$ is the average density of the n^{th} species in the three modes [kg m^{-3}]. For Aitken and accumulation modes are considered eighth aerosol species: sulfate, ammonium, nitrate, anthropogenic secondary organics, primary organics, secondary biogenic organics, elemental carbon and unspecified anthropogenic compounds; and three species for the coarse mode: anthropogenic, marine, and soil-derived aerosols. Aerosol particle are assumed to be internally mixed, i.e. all particles in the same mode have the same composition.

The conservations equation used to predict the aerosol size distribution are similar to those used for gas-phase species, i.e.:

$$\frac{\partial M_{i,j,c}^k}{\partial t} = -u \frac{\partial M_{i,j,c}^k}{\partial x} - v \frac{\partial M_{i,j,c}^k}{\partial y} - w \frac{\partial M_{i,j,c}^k}{\partial z} + K_H \frac{\partial^2 M_{i,j,c}^k}{\partial x^2} + K_H \frac{\partial^2 M_{i,j,c}^k}{\partial y^2} + \frac{\partial}{\partial z} \left(K_{zz} \frac{\partial M_{i,j,c}^k}{\partial z} \right) + S_{i,j,c}^k + A_{i,j,c}^k + R_{i,j,c}^k$$

where u , v and w are the components of wind velocity vector, K_H , and K_{zz} the horizontal and vertical diffusivities, the index k means the k^{th} moment of the aerosol size distribution (for $k=3$ the aerosol species concentrations in the three modes are actually considered), the indexes i, j, c refer respectively to Aitken, accumulation and coarse modes, $S_{i,j,c}^k$ the source term, $A_{i,j,c}^k$ the chemical-physical processes considered by the aerosol module and $R_{i,j,c}^k$ the removal term due to dry deposition processes. The numerical integration of the above equations is performed, as done for the gas-phase species, using the *operator splitting technique*.

Following formulas are used by the module to diagnose D_g and σ_g from N , M^2 and M^3 :

$$\ln^2 \sigma_g = \frac{1}{3} (2 \ln M^3 + 3 \ln N) - \ln M^2$$

$$D_g^3 = \frac{M^3}{N \exp\left(\frac{9}{2} \ln^2 \sigma_g\right)}$$

Nucleation and growth of existing particles by condensable material (vapor) condensation are the two pathways for increasing the total aerosol mass. Aerosol growth by condensation occurs in two steps: the production of condensable material (performed by the gas-phase chemical module) and the condensation and evaporation of ambient volatile species on aerosols. Particle collision and coagulation are the main processes that alter the aerosol size distribution. In the following figure a schematic representation of nucleation, condensation and coagulation processes is shown.

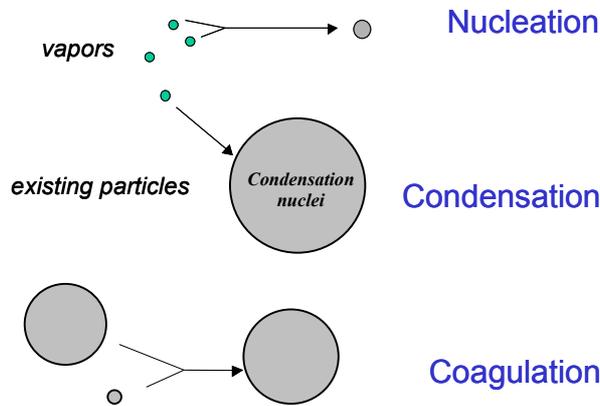


Figure 3 Dynamic aerosol processes.

The thermodynamic equilibrium of condensable inorganic and organic species between the gas and the aerosol phases and following chemical reactions within aerosols are responsible for the chemical composition of aerosols. Except for nucleation, where only inorganic compounds are considered, all aerosol dynamics processes include both inorganic and organic compounds. In the following sections the above processes are briefly described.

2.5.1 Nucleation

The most important process for the formation of secondary aerosol particles is the homogeneous nucleation in the sulfuric acid-water system. It is calculated by the method given in Kulmala *et al.*, 1998.

2.5.2 Coagulation

Following Whitby *et al.*, 1991 and Binkowski and Shankar, 1995 the representation of coagulation is performed assuming that the distributions remain log-normal during the process of coagulation and considering only the effects caused by Brownian motion. Intra- and inter-modal coagulation within and between Aitken and accumulation modes are considered. The mathematical formulation for the coagulation process can be found in the above references.

2.5.3 Gas/particle mass transfer

Atmospheric aerosol are particles composed of water, inorganic salts, insoluble materials (dust, crustal material), organics and trace metals. An important mechanism that influences the chemical composition of airborne aerosol is the partitioning of chemical compounds (water, ammonia, nitric acids, organics, etc.) between the gas and particulate phases that requires an analysis of the thermodynamic properties of aerosols. Since in common situation such volatile compounds in the gas and particulate phases are assumed to be in equilibrium (exceptions are found for coarse particles and cool environments), thermodynamic equilibrium models are commonly used to describe partitioning processes.

The calculation of the distribution of ammonia/ammonium, nitric acid/nitrate, sulfate and water between the gas and aerosol phases is performed by ISORROPIA model (Nenes *et al.*, 1998) depending on total (i.e. gas + aerosol) sulfate, ammonia and nitrate concentrations, relative humidity and temperature.

The calculation of secondary organic aerosol (SOA) is based on the absorptive partitioning model of Pankow, 1994 that was extended by Odum *et al.*, 1996. Input to the model includes the concentrations of reacted ROG's, the total (gas + aerosol) concentration of each semi-volatile organic compound and the concentrations of primary and secondary organic aerosols. Gas/aerosol equilibrium is established only after the organic gas concentration reaches the threshold value defined in Schell *et al.*, 2001. Until this threshold value is reached, organic vapors are allowed to partition to the aerosol phase only when a semi-volatile organic compound exceeds its effective saturation vapor pressure, in the manner described by Pandis *et al.*, 1992. Once the organic gas/aerosol equilibrium has been established, gas and aerosol-phase concentrations of each condensable species are calculated iteratively using a globally convergent variation of Newton's method as described in Schell *et al.*, 2001. The model treats anthropogenic and biogenic precursors separately and is interfaced with the gas-phase mechanism implemented in FARM.

2.6 Pollutants removal

Wet and dry deposition are the ultimate paths by which trace gases and particles are removed from the atmosphere. Dry deposition is the transport of pollutants from the atmosphere onto surfaces in the absence of precipitations; wet deposition, instead, refers to scavenging processes

by which pollutants are captured by hydrometeors and consequently delivered to the Earth's surface (Seinfeld and Pandis, 1998).

2.6.1 Dry deposition

For many compounds, dry deposition is at least as important as wet deposition as a removal process. In FARM the flux of pollutant material to the surface (Φ) is treated as a first-order removal mechanism, where the flux of a pollutant to the surface is the product of a characteristic deposition velocity and its concentration in the "surface layer" (i.e., the lowest model layer): $\Phi = -v_{d,i}c_i$.

The deposition velocity depends in general from surface properties (i.e. presence and type of vegetation, etc.), the meteorology of the lowest layer of the atmosphere and the chemical species involved. The mass removed in this way from the atmosphere is then cumulated on the ground on the cells of calculation grid, constituting the dry deposition.

The dry deposition term is always active in FARM, as a boundary condition for the vertical transport-diffusion operator. Gridded hourly fields of deposition velocities for each gas-phase chemical species subject to deposition must be supplied to the code. They can be computed on the basis of land-use and meteorological data using SURFPRO (SURface-atmosphere interFace PROCessor), a pre-processor implementing a multi-resistance 'big leaf' scheme (Arianet, 2005).

Using the AERO3 aerosol module, the rate of dry deposition of particles is computed for the zeroth and third moment following the approach described in Binkowski, 1999. Gridded deposition velocities, for the k^{th} moment, are internally computed using updated values of k^{th} moment of the lognormal size distribution and micrometeorological parameters (aerodynamic resistance, friction velocity and convective velocity scale) provided by SURFPRO.

2.6.2 Precipitation scavenging

The parameterization of wet deposition follows EMEP (2003) approach, including in-cloud and below-cloud scavenging of gas and particles. The in-cloud scavenging of a soluble component of concentration C is computed as:

$$\Delta C_{wet} = -C \frac{W_{in} \cdot P}{\Delta z \cdot \rho_w}$$

where P is the precipitation rate ($\text{kg m}^{-2} \text{s}^{-1}$), Δz is the scavenging depth (assumed to be 1000 m), ρ_w is the water density (1000 kg m^{-3}) and W_{in} is the in-cloud scavenging ratio.

Below-cloud scavenging of gases is computed by means of a similar relationship:

$$\Delta C_{wet} = -C \frac{W_{sub} \cdot P}{\Delta z \cdot \rho_w}$$

where W_{sub} is the sub-cloud scavenging ratio. In case of particles, below-cloud scavenging is computed by means of Scott (1979) relationship:

$$\Delta C_{wet} = -C \frac{A \cdot P}{V_{dr}} \bar{E}$$

where $A = 5.2 \text{ m}^3 \text{ Kg}^{-1} \text{ s}^{-1}$ is an empirical coefficient (a Marshall-Palmer size distribution is assumed for rain drops), V_{dr} is the raindrop fall speed (assumed to be 5 m s^{-1}) and \bar{E} is the size-dependent collision efficiency of aerosols by the raindrops. Scavenging ratios and collection efficiencies used in precipitation scavenging are given in Table 1

Table 1 Scavenging ratios and collection efficiencies used in precipitation scavenging calculation.

Component	$W_{in} (* 10^6)$	$W_{sub} (* 10^6)$	\bar{E}
SO ₂	0.3	0.15	-
HNO ₃	1.4	0.5	-
NH ₃	1.4	0.5	-
H ₂ O ₂	1.4	0.5	-
HCHO	0.1	0.03	-
SO ₄	1.0	-	0.1
NO ₃	1.0	-	0.1
NH ₄	1.0	-	0.1
PM _{fi}	1.0	-	0.1
PM _{co}	1.0	-	0.4

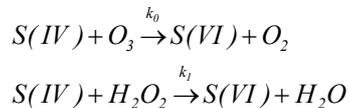
The mass removed from the atmosphere is then cumulated on the ground on the cells of calculation grid, constituting the wet deposition. The scavenging module is invoked between the L_z and L_c operators.

2.7 In-cloud chemistry: aqueous phase SO₂ oxidation

Due to the efficiency of sulphate production in solution, in presence of a cloud layer a simplified aqueous phase mechanism is included, taking into account S(IV) ($= [SO_2 \cdot H_2O] + [HSO_3^-]$) oxidation paths due to aqueous-phase ozone and hydrogen peroxide, leading to the production of sulfate inside cloud layer. In the calculations the closed system assumption for the gas phase is adopted (gas-phase partial pressures decrease with time as material is depleted from the gas-phase). Considering this approach the aqueous phase concentration of a species A is given by:

$$[A(aq)]_{closed} = \frac{H_A p_A^0}{1 + H_A w_L R T}$$

where p_A^0 is the partial pressure of the species A in the gas-phase, w_L the cloud liquid water mixing ratio, R the universal gas constant and T the temperature. According to Seinfeld and Pandis, 1998 following rate expressions for sulfate formation S(VI) due to the oxidation of S(IV) by $(O_3)_{aq}$ and $(H_2O_2)_{aq}$ are considered:



where $k_0 = 2.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $k_1 = 3.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

3 FARM upgrade

In this section we will describe the upgrade activity on FARM model in order to include PAHs chemistry and to extend its capabilities in order to fulfil both EXPAH requirements and the indication of EU Directive on ambient air quality and cleaner air for Europe (Directive 2008/50/EC) implemented by the Italian legislation with the D.L. 155. Since both the Directive and the D.L explicitly refer to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, the CTM has been upgraded in order to include also these pollutants. The upgrade follows the approaches implemented in the numerical models of HM and POPs developed by MSC-E (Gusev *et al.*, 2005). The following species have been included in the updated version of FARM:

- Gas-phase:
 - benzo(a)pyrene (B[a]P);
 - benzo(b)fluoranthene (B[b]F);
 - benzo(k)fluoranthene (B[k]F);
 - indeno(1,2,3-cd)pyrene (I_P);
 - elemental mercury (Hg⁰);
 - oxidised mercury or divalent gaseous mercury (HgO);
- aerosol-phase:
 - Aitken (I) and accumulation (J) modes benzo(a)pyrene (AB[a]PI, AB[a]PJ);
 - Aitken (I) and accumulation (J) modes benzo(b)fluoranthene (AB[b]FI, AB[b]FJ);
 - Aitken (I) and accumulation (J) modes benzo(k)fluoranthene (AB[k]FI, AB[k]FJ);
 - Aitken (I) and accumulation (J) modes indeno(1,2,3-cd)pyrene (AI_PFI, AI_PJ);
 - Aitken (I) and accumulation (J) modes mercury (AHgI, AHgJ);
 - accumulation mode marine (ASEASJ);
 - accumulation mode soil-derived (ASOILJ);
 - accumulation mode lead (APbJ);
 - accumulation mode arsenic (AAsJ);
 - accumulation mode cadmium (ACdJ);
 - accumulation mode nickel (ANiJ).

Two aerosol species in the accumulation model associated to sea-salts (ASEASJ) and dust (ASOILJ) have been considered in order to better discriminate the contribution of natural and anthropogenic sources on particulate matter simulated concentrations. In the following sections the upgrade of the gas-phase chemical mechanism and the aerosol module will be described.

3.1 Gas-phase chemistry

Degradation process of PAHs in the atmosphere is considered as the gas-phase reaction of these pollutants with hydroxyl radical and all other reactions are neglected. As for mercury, reactions with hydroxyl radical, ozone, gas-phase nitrate and hydrogen peroxide have been included. In following Table 2 the list of gas-phase reactions involving PAHs and mercury, added to the SAPRC99

chemical mechanism, is presented. It has to be noted that the oxidised mercury (HgO) is not resolved by a specific compound in this mechanism.

Table 2 Gas/phase PAHs and mercury reactions $ARR(A,B)=Ae^{-B/T}$ where T is the temperature in K

Reaction	Reaction rate [cm ³ molec ⁻¹ s ⁻¹]	Reference
B[a]P + OH → products	5 10 ⁻¹¹	Meylan and Howard, 1993
B[b]F + OH → products	1.86 10 ⁻¹¹	
B[k]F + OH → products	5.36 10 ⁻¹¹	
I_P + OH → products	6.447 10 ⁻¹¹	
Hg ⁰ + O ₃ → 0.5HgO + 0.5HgAER	ARR(2.11 10 ⁻¹⁸ , 1256.5)	Xie <i>et al.</i> , 2008; Jung <i>et al.</i> , 2009; HgAER (condensable mercury) from CMAQ
Hg ⁰ + OH → 0.5HgO + 0.5HgAER	3.1 10 ⁻²⁰ (298 K)	
Hg ⁰ + H ₂ O ₂ → HgO	7.7 10 ⁻¹⁴	
Hg ⁰ + H ₂ O ₂ → HgO	8.5 10 ⁻¹⁹	
Hg ⁰ + NO ₃ → HgO + NO ₂	4 10 ⁻¹⁵	

3.2 Mercury in-cloud chemistry

In presence of a cloud layer the exchange of soluble compound between gas and aqueous phases is considered. In the following Table 3, the aqueous-phase chemical equilibria and kinetic reactions involving mercury included in the aqueous phase chemical mechanism are reported. This approach has been derived from the version 4.3 of CAMx model (ENVIRON, 2006). Since chlorine chemistry has not been included in the current implementation of SAPRC99 chemical mechanism, very low values have been considered for HCl and Cl₂, respectively 1 and 10⁻³ ppb.

Table 3 Aqueous-phase chemical equilibria and kinetic reactions involving mercury (OCI and OCI⁻ come from the dissolution and subsequent dissociation of molecular chlorine (Cl₂)).

Gas-liquid equilibria
$Hg^0_{(g)} \leftrightarrow Hg^0_{(aq)}$
$HgO_{(g)} \leftrightarrow HgO_{(aq)}$
Aqueous-phase chemical equilibria
$HgCl_{2(aq)} \leftrightarrow Hg^{2+} + 2Cl^-$
$Hg(OH)_{2(aq)} \leftrightarrow Hg^{2+} + 2OH^-$
$Hg^{2+} + SO_3^{2-} \leftrightarrow HgSO_3$
$HgSO_3 + SO_3^{2-} \leftrightarrow Hg(SO_3)_2^{2-}$
Aqueous Kinetic Reactions
$Hg^0_{(aq)} + O_{3(aq)} \rightarrow Hg^{2+}_{(aq)}$
$Hg^0_{(aq)} + OH_{(aq)} \rightarrow Hg^{2+}_{(aq)}$
$HgSO_{3(aq)} \rightarrow Hg^0_{(aq)}$
$Hg^{2+}_{(aq)} + HO_{2(aq)} \rightarrow Hg^0_{(aq)}$
$Hg^0_{(aq)} + HOCl_{(aq)} \rightarrow Hg^{2+}_{(aq)}$
$Hg^0_{(aq)} + OCl_{(aq)} \rightarrow Hg^{2+}_{(aq)}$
Adsorption of Hg(II) on PM (Seigneur <i>et al.</i>, 1998)
$Hg(II)_{(aq)} \leftrightarrow H(II)_{(p)}$

3.3 Gas-aerosol partitioning

As stated by Finizio *et al.* 1987, there is some debate whether the POPs partitioning between the gaseous and particulate phase (sorption process) is adsorption or absorption or both. When particulate is mainly constituted by mineral material, simple physical adsorption will dominate the sorption process, while absorption process seems to be relevant when particulate matter contains organic matter from primary emissions and from the formation of secondary aerosols (Pankow, 1994).

The adsorption process to mineral surfaces is represented using the Junge-Pankow model (Junge, 1977; Pankow, 1987) based on subcooled liquid vapour pressure p_{OL} (Pa). According to this model the POP fraction φ^{ad} adsorbed on tropospheric aerosol particles equals to:

$$\varphi^{ad} = \frac{c \cdot \theta}{(p_{OL} + c \cdot \theta)}$$

where: c is the constant dependant on the thermodynamic parameters of the adsorption process and on the properties of aerosol particle surface and θ is the specific surface of aerosol particles [$\text{m}^2 \text{m}^{-3}$]. A value of 0.17 [$\text{Pa} \cdot \text{m}$] is assumed for the parameter c (Junge, 1977).

Pankow [1994] has proposed that absorption of gas-phase compounds into an organic film coating particles gives an important contribution to the overall particle-gas partitioning processes. The gas-particle partitioning K_p [$\text{m}^3 \mu\text{g}^{-1}$] is defined as follows:

$$K_p^{OC} = \frac{C_p}{C_g \cdot TSP}$$

where TSP is the concentration of suspended particulate material [$\mu\text{g m}^{-3}$], C_p and C_g respectively the particulate-associated and gaseous concentration of a given semi-volatile organic chemical (SOC) [ng m^{-3}]. The octanol-air partition coefficient K_{OA} is a valuable direct descriptor of semi-volatile organic chemicals. The relation of K_p^{OC} to K_{OA} is (Finizio *et al.*, 1997):

$$K_p^{OC} = \frac{10^{-9} K_{OA} f_{om} \gamma_{OCT} M_{OCT}}{\rho_{OCT} \gamma_{om} M_{om}}$$

where f_{om} is the fraction of the particle mass that consist of absorbing organic matter, ρ_{OCT} is the density of octanol (820 kg m^{-3}), γ_{OCT} and γ_{om} the activity coefficient of the chemical respectively in octanol and in the organic matter, M_{OCT} and M_{om} the molecular mass respectively of octanol and

the organic matter phase [g mol^{-1}]. With the assumptions that $\frac{\gamma_{OCT}}{\gamma_{om}}$ and $\frac{M_{OCT}}{M_{om}} \approx 1$ (Harner *et al.*,

1999) the previous relation becomes:

$$K_p^{OC} \approx \frac{10^{-9} K_{OA} f_{om}}{\rho_{OCT}}$$

In a similar way, the partitioning coefficient for absorption of POPs into aerosol water can be given by Aulinger *et al.*, 2007:

$$K_p^{aq} \approx \frac{10^{-9} K_{WA} f_w}{\rho_{wa}}$$

where f_w is the fraction of the particle mass that consist of water. The fraction $\varphi^{ab,OC}$ absorbed into organic aerosol particles is given by:

$$\varphi^{ab,OC} = \frac{C_p}{C_p + C_g} = \frac{K_p^{OC} \cdot TSP}{1 + K_p^{OC} \cdot TSP}$$

and similarly the fraction $\varphi^{a,aq}$ absorbed on aerosol water is then given by:

$$\varphi^{ab,aq} = \frac{C_P}{C_P + C_G} = \frac{K_p^{aq} \cdot TSP}{1 + K_p^{aq} \cdot TSP}$$

In FARM model, the fraction of POPs sorbed on tropospheric aerosol particles is computed following the approach proposed in Aulinger *et al.*, 2007. Since in the aerosol module AERO3 two modes actually contains organic matter and water, respectively Aitken and accumulation modes, the particulate forms of PAHs were introduced in these modes. The concentration of the compound that is bound to aerosols in each mode is calculated with:

$$a_i = \varphi_i (a_i + g)$$

where a_i is the particulate concentration of the compound in mode i ($i=I,J$ e.g. Aitken and accumulation), g is the gaseous concentration and φ_i is the particulate fraction of the compound in mode i due to the sum of three different sorption processes: adsorption (ad), absorption into organic carbon (ab,OC), and absorption into aerosol water (ab,aq):

$$\varphi_i = \varphi_i^{ad} + \varphi_i^{ab,OC} + \varphi_i^{ab,aq}$$

Because the constraint of mass consistency must hold, g can be replaced by means of the total concentration of the compound c_{tot} : $g = c_{tot} - a_I - a_J$. Above equations lead to a system of two linear equations for Aitken (I) and accumulation modes (J):

$$\begin{aligned} a_I &= \varphi_I (a_I + g) = \varphi_I (a_I + c_{tot} - a_I - a_J) = \varphi_I (c_{tot} - a_J) \\ a_J &= \varphi_J (a_J + g) = \varphi_J (a_J + c_{tot} - a_I - a_J) = \varphi_J (c_{tot} - a_I) \end{aligned}$$

or in matrix form:

$$\begin{bmatrix} 1 & \varphi_I \\ \varphi_J & 1 \end{bmatrix} \cdot \begin{bmatrix} a_I \\ a_J \end{bmatrix} = c_{tot} \cdot \begin{bmatrix} \varphi_I \\ \varphi_J \end{bmatrix}$$

that has solutions for particulate concentrations in each mode:

$$\begin{aligned} a_I &= c_{tot} \cdot \varphi_I \cdot \frac{1 - \varphi_J}{1 - \varphi_I \varphi_J} \\ a_J &= c_{tot} \cdot \varphi_J \cdot \frac{1 - \varphi_I}{1 - \varphi_I \varphi_J} \end{aligned}$$

The gaseous concentration g can then be calculated using above relationship. Finally, as proposed in Aulinger *et al.*, 2007, the absorption into aerosol water is considered when the aerosol can be treated as wet. This occurs when the ratio of aerosol water to ammonium sulfate exceeds the solubility of ammonium sulfate, which is considered the major compound in mineral aerosols. In this condition, all inorganic ions are dissolved and no adsorption to inorganic material can take place.

3.4 Deposition processes

As for deposition processes, the dry deposition flux of the PAHs in the gas-phase species is not considered while the deposition velocity v_d of the particulate phase is the same of that considered for the fine aerosol components by AERO3 module.

Wet deposition of PAHs in gaseous and particulate phase is distinguished in FARM model. Making the assumption that the pollutant does not redistribute between dissolved and particulate phase

within a raindrop, total dimensionless ratio W_T for a substance washout with precipitation is determined by the following equation:

$$W_T = W_G(1 - F) + W_P F$$

where: W_G is the washout ratio of the PAHs gaseous phase, W_P is the washout ratio of a substance associated with aerosol particles and F is the substance fraction associated with aerosol particles in the atmosphere. In-cloud and below-cloud scavenging ratios and collision efficiency of aerosols by the raindrops, for PAHs, are given in following Table 4.

Table 4 Scavenging ratios and collection efficiencies used in precipitation scavenging calculation for PHAs.

Component	$W_{in} (* 10^6)$	$W_{sub} (* 10^6)$	\bar{E}
PAHs (gaseous)	0.1	0.03	-
PAHs (particulate)	1.0	-	0.1

4 Preliminary test of the upgraded version of FARM

In order to test the upgraded version of FARM, a simulation over the Italian peninsula has been performed. The simulation refers to 1st February 2005. Meteorological fields have been produced by RAMS prognostic models; emissions come from the integration of different dataset: over the Italian peninsula from the Italian inventory, while for the surrounding regions are from EMEP-MSC-E and EMEP-MSC-W respectively for PAHs and HMs and for the other pollutants. As for boundary conditions we have used results from larger scale simulations performed by EMEP-MSC-E and EMEP-MSC-W models respectively for PAHs and HMs and for the other pollutants. Meteorological fields produced by RAMS model were processed by SURFPro module in order to produce 2D and 3D fields needed by FARM: dry deposition velocities, vertical and horizontal diffusivities, cloud fields (e.g.: coverage, base and top height, water content), natural emissions and micrometeorological parameters used to estimate dry deposition of aerosols (e.g.: aerodynamic resistance, friction velocity and convective velocity scale). In the following Figures are reported ground level daily mean concentration fields for a representative set of pollutants computed by this version of FARM model.

The analysis of Figure 4 evidences that biggest portion of atmospheric B(a)P is bound to aerosols and particularly to the accumulation mode. This is due to the nature of this pollutant: B(a)P is poorly volatile and highly affinitive to octanol, which represents organic carbon.

As for Mercury, the analysis of Figure 5 evidences that biggest portion of atmospheric mercury remains in the gas-phase and that in the aerosol phase the accumulation mode represent the major fraction.

As for the other pollutants (nitrogen oxides, VOCs, ozone, radicals, PM) the analysis of concentration fields produced by the previous version FARM and the upgraded version does not evidences significant differences. As an example, in the Figure 6 are presented the daily averaged concentrations of ozone, nitrogen dioxide, hydroxyl radical (OH) and PM_{2.5} produced by the upgraded version of FARM.

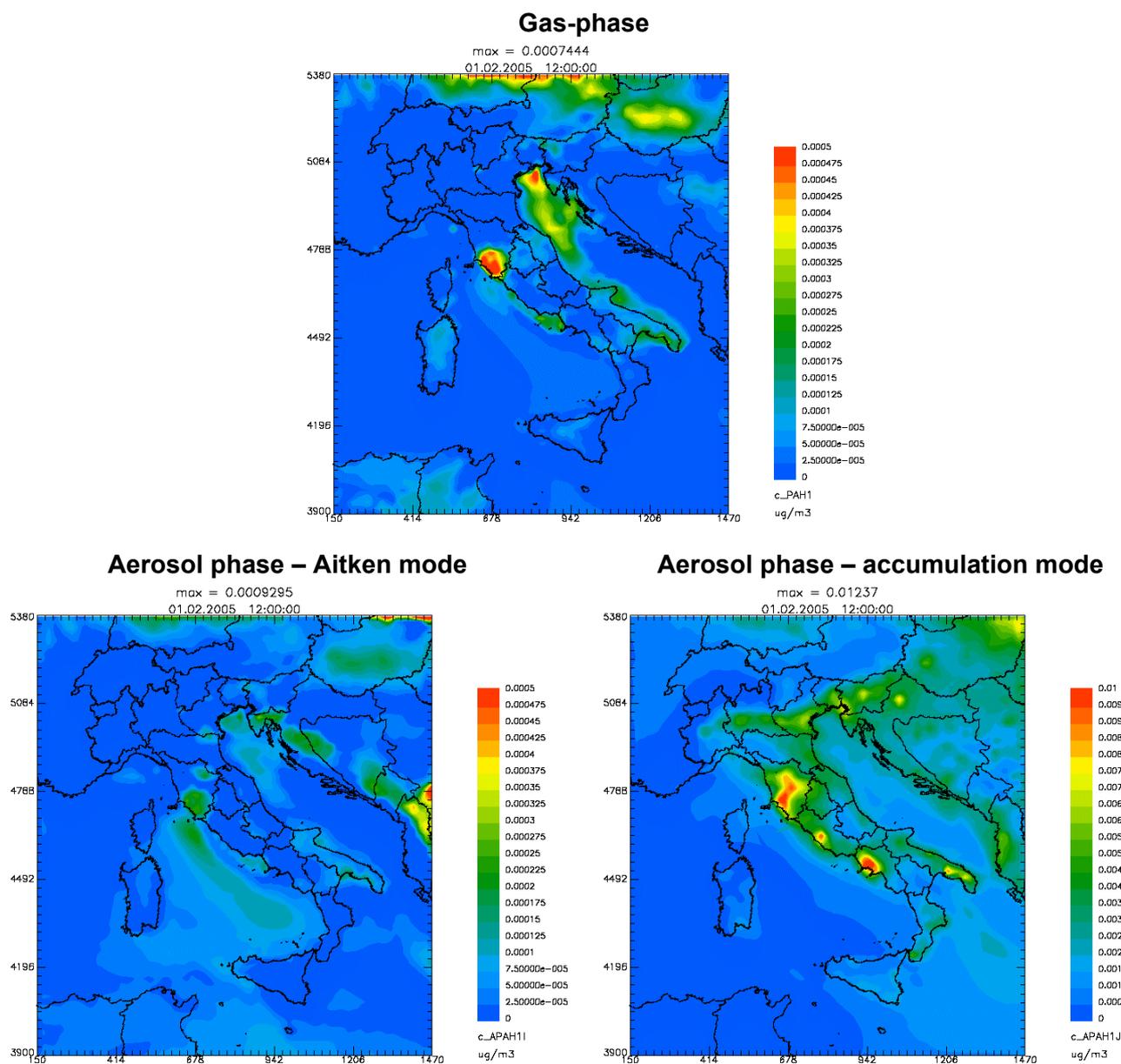


Figure 4 Ground level daily mean concentration fields (1st February 2005) of B[a]P in gas and aerosol phases computed by FARM model.

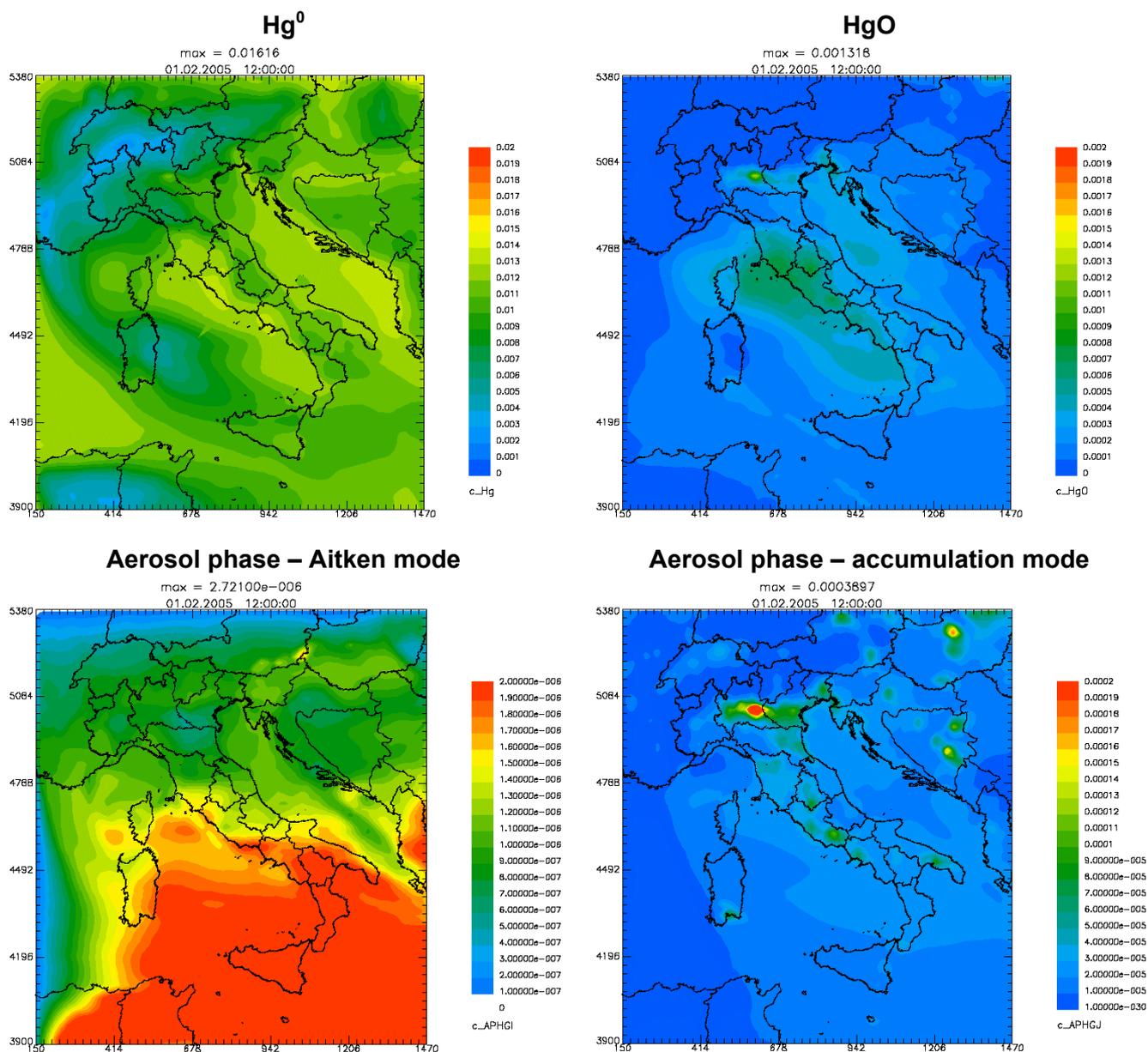


Figure 5 Ground level daily mean concentration fields (1st February 2005) of Hg in gas and aerosol phases computed by FARM model.

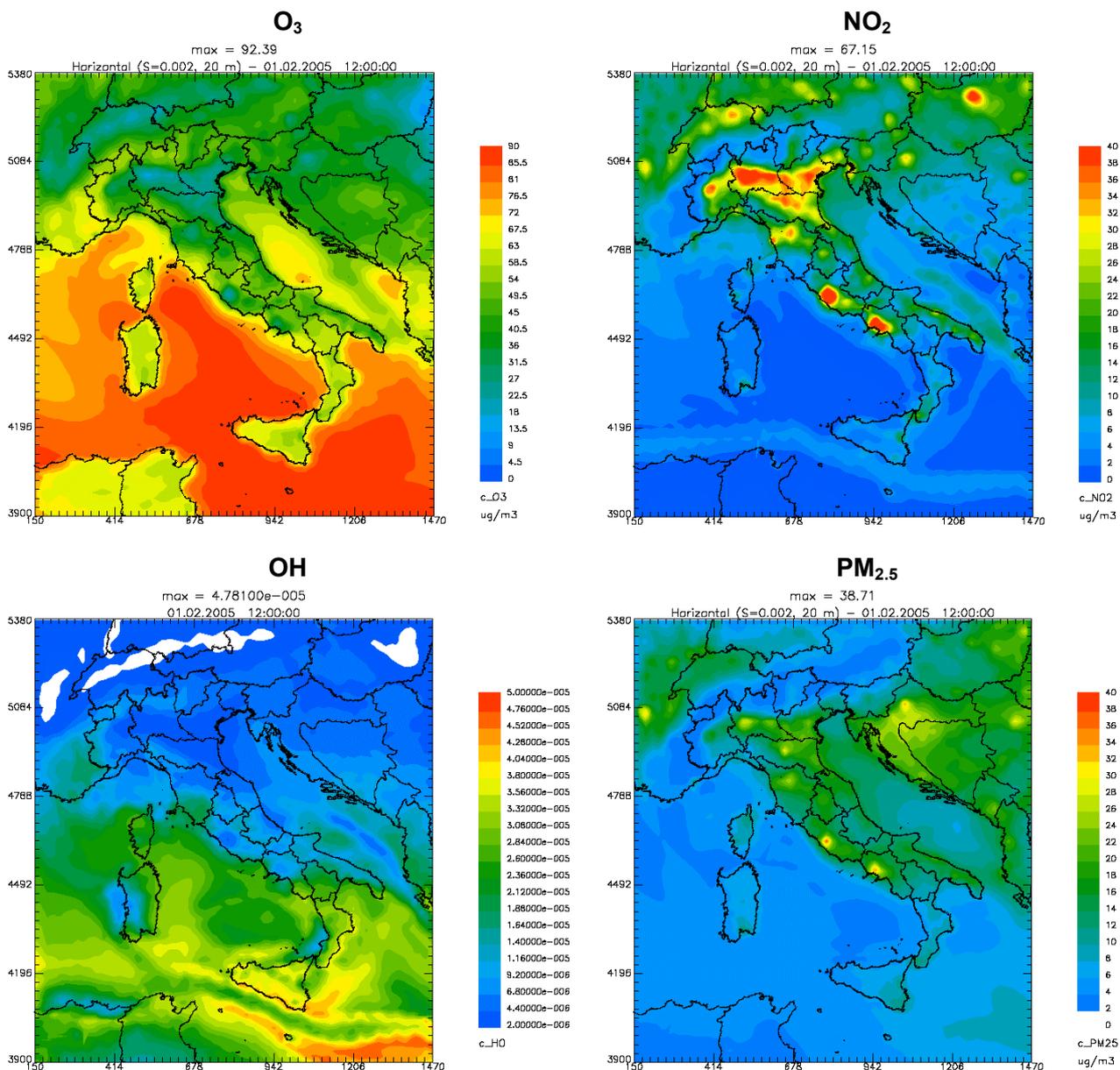


Figure 6 Ground level daily mean concentration fields (1st February 2005) for a representative set of pollutants computed by FARM model.

5 Conclusions

According to the CLRTAP protocol on POPs the following four indicator compounds has been considered for PAHs: benzo(a)pyrene (B[a]P); benzo(b)fluoranthene (B[b]F); benzo(k)fluoranthene (B[k]F) and indeno(1,2,3-cd)pyrene (I_P).

In order to include these PAHs in FARM model and to extend its capabilities to fulfil the requirements of the EU Directive on ambient air quality and cleaner air for Europe (Directive 2008/50/EC) we have upgraded the current version of FARM, implementing the SAPRC99 gas-phase chemical mechanism and the AERO3 aerosol module by:

- adding to SAPRC99 reactions of PAHs with hydroxyl radical and reactions of mercury, considered by the EU Directive, with hydroxyl radical, ozone, gas-phase nitrate and hydrogen peroxide);
- including into AERO3:
 - a partitioning mechanism for PAHs on the basis of the approach proposed in Aulinger *et al.*, 2007 that consider both adsorption and absorption (by organic aerosol and water) processes. According to the AERO3 module, the particulate form of these PAHs has been considered in Aitken and accumulation modes;
 - a condensation mechanism of unspecified mercury compounds on aerosol. This mechanism has been derived from CMAQ in which the particulate form of mercury has been considered in Aitken and accumulation modes;
 - two aerosol species in the accumulation model associated to sea-salts and soil in order to better discriminate the contribution of natural and anthropogenic sources on particulate matter simulated concentrations;
 - four HMs considered by the Directive in the accumulation mode: e.g. lead; arsenic; cadmium; and nickel.

The upgraded version of FARM model has been then applied to a one day test case (the simulation refers to 1st February 2005) covering the Italian peninsula. The analysis of this preliminary simulation evidences that the largest portion of atmospheric B(a)P is bound to aerosols and particularly to the accumulation mode. As for mercury, viceversa, its biggest portion remains in the gas-phase and the accumulation mode represent the major fraction in the aerosol phase. For the other pollutants (nitrogen oxides, VOCs, ozone, radicals, PM), the analysis of concentration fields produced by the previous and the upgraded version of FARM does not evidences significant differences.

Aknowledgents

We thank Dr. Armin Aulinger and Dr. Volker Matthias of Institute of Coastal Research, Helmholtz-Zentrum Geesthacht, for providing us the routines used for partitioning and heterogeneous degradation of B[a]P used in this work.

Bibliography

- ARIANET (2005) SURFPRO (SURface-atmosphere interFace PROcessor) User's guide – Version 2.2. Arianet report R2005.11.
- Aulinger, A., Volker M., Quante M. (2007) Introducing a Partitioning Mechanism for PAHs into the Community Multiscale Air Quality Modeling System and Its Application to Simulating the Transport of Benzo(a)pyrene over Europe. *Journal of Applied Meteorology and Climatology*, **46**, 11, 1718-1730.
- Binkowski, F. S. (1999) The aerosol portion of Models-3 CMAQ. In Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. Part II: Chapters 9-18. D.W. Byun, and J.K.S. Ching (Eds.). EPA-600/R-99/030, National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC, 10-1-10-16.
- Binkowski, F.S., Shankar, U. (1995) The regional particulate matter model, 1. mode description and preliminary results. *J. Geophys. Res.*, **100**, 26191-26209.
- Carter, W.P.L. (2000) *Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment*. Final Report to California Air Resources Board, Contract 92-329 and 95-308, SAPRC, University of California, Riverside, CA.
- Chang, J.S., Brost, R.A., Isaksen, I.S.A., Madronich, S., Middleton, P., Stockwell, W.R., Walcek, C.J. (1987) A three-dimensional eulerian acid deposition model: physical concepts and formulation. *J. Geophys. Res.*, **92** (D12), 14681-14700.
- Daescu, D., Sandu, A., Carmichael, G.R. (2003) Direct and Adjoint Sensitivity Analysis of Chemical Kinetic Systems with KPP: II -- Validation and Numerical Experiments'. *Atmos. Environ.*, **37**, 5097-5114.
- Damian, V., Sandu, A., Damian, M., Potra, F., Carmichael, G.R. (2002): The Kinetic PreProcessor KPP -- A Software Environment for Solving Chemical Kinetics'. *Computers and Chemical Engineering*, **26**, 11, 1567-1579.
- EMEP (2003) *Transboundary acidification, eutrophication and ground level ozone in Europe*. EMEP Status Report 2003, Norwegian Meteorological Institute, August 2003.
- ENVIRON (2006) CAMx user's guide comprehensive air quality model with extensions version 4.30.
- Finizio, A., Mackay, D., Bidleman, T., Harner, T. (1997) Octanol-Air Partition Coefficient as a Predictor of Partitioning of Semi-Volatile Organic Chemicals to Aerosols. *Atmos. Environ.*, **31**, 2289-2296.
- Gariazzo, C., Silibello, C., Finardi, S., Radice, P., Piersanti, A., Calori, G., Cucinato, A., Perrino, C., Nussio, F., Cagnoli, M., Pelliccioni, A., Gobbi, G.P., Di Filippo, P. (2007) A gas/aerosol air pollutants study over the urban area of Rome using a comprehensive chemical transport model. *Atmos. Environ.*, **41**, 7286-7303.
- Gusev, A., Mantseva, E., Shatalov, V., Strukov, B. (2005) Regional Multicompartment Model MSCE-POP. EMEP/MSCE-E Technical Report 5/2005.
- Jung, G., Hedgecock, I. M., Pirrone, N. (2009) ECHMERIT V1.0 – a new global fully coupled mercury-chemistry and transport model. *Geosci. Model Dev.*, **2**, 175-195.
- Junge, C.E. (1977) Basic considerations about trace constituent in the atmosphere is related to the fate of global pollutant. In: Fate of pollutants in the air and water environment. Part I, I.H. Suffet (ed.) *Advanced in Environ. Sci. Technol.*, **8**, Wiley-Interscience, New York.
- Kaiser, J.A.C., Hill, R.H. (1976) Irradiance at sea. *J. Geophys. Res.*, **81**, 395.
- Kulmala, M., Laaksonen, A., Pirjola, L. (1998) Parameterization for sulphuric acid/water nucleation rates. *J. Geophys. Res.*, **103**, 8301-8307.

- Madronich, S. (1989) Photodissociation in the atmosphere 1. Actinic flux and the effect of ground reflections and clouds. *J. Geophys. Res.*, **92**, 9740-9752.
- Meylan, W.M., Howard, P.H. (1993) Computer estimation of the atmospheric gas-phase reaction rate of organic compounds with hydroxyl radicals and ozone. *Chemosphere*, **26**, 2293-99.
- Nenes, A., Pandis, S.N., Pilinis, C. (1998) ISORROPIA: A new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols. *Aquat. Geoch.*, **4**, 123-152.
- Odum, J. R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R. C., Seinfeld, J. H. (1996) Gas/particle partitioning and secondary organic aerosol yields. *Environ. Sci. Technol.*, **30**, 8, 2580-2585.
- Pandis, S. N., Harley, R. A., Cass, G. R., Seinfeld, J. H. (1992) Secondary organic aerosol formation and transport. *Atmos. Environ.*, **26A**, 13, 22669-2282.
- Pankow, J. F. (1994) An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmos. Environ.*, **28**, 2, 185-188.
- Pankow, J.F. (1987) Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. *Atmos. Environ.*, **21**, pp.2275-2283.
- Peterson, J.T (1976) Calculated actinic fluxes (290-700nm) for air pollution photochemistry applications. EPA-600/4-76-025.
- Radhakrishnan, K., Hindmarsh, A. (1993) Description and use of LSODE, the Livermore solver for differential equations. NASA reference publication 1327.
- Sandu, A., Daescu, D., Carmichael G.R. (2003) Direct and Adjoint Sensitivity Analysis of Chemical Kinetic Systems with KPP: I -- Theory and Software Tools'. *Atmospheric Environment*, **37**, 5083-5096.
- Schell, B., Ackermann, I. J., Hass, H., Binkowski, F. S., Abel, A. (2001) Modeling the formation of secondary organic aerosol within a comprehensive air quality modeling system. *J. Geophys. Res.*, **106**, D22, 28275-28293.
- Scott, B.C. (1979) Parametrization of sulphate removal by precipitation. *J. Appl. Met.*, **17**, 11379-11389.
- Seinfeld, J.H., Pandis, S. N. (1998) *Atmospheric Chemistry and Physics*. John Wiley&Sons, Inc.
- Silibello, C., Calori, G., Brusisca, G., Giudici, A., Angelino, E., Fossati, G., Peroni, E., Buganza, E. (2008) Modelling of PM₁₀ Concentrations Over Milano Urban Area Using Two Aerosol Modules. *Environmental Modelling and Software*, **23**, 333-343.
- Stephens, G.L. (1978) Radiation profiles in extended water clouds. II.: Parameterization schemes, *J. Atmos. Sci.*, **35**, 2123-2132.
- Whitby, E. R., McMurry, P. H., Shankar, U., Binkowski, F. S. (1991) Modal Aerosol Dynamics Modeling. Rep. 60013-91/020, AREAL, U.S. EPA, Research Triangle Park, NC, (NTIS PB91-161729/AS).
- Whitby, K.T. (1978) The physical characteristics of sulfur aerosols. *Atmos. Environ.*, **12**, 135-159.
- Xie, Z.Q., Sander, R., Poschl, U., Slemr, F. (2008) Simulation of atmospheric mercury depletion events (AMDEs) during polar springtime using the MECCA box model. *Atmospheric Chemistry and Physics*, **8**, 7165-7180,
- Yamartino, R.J. (1993) Nonnegative, conserved scalar transport using grid-cell-centered, spectrally constrained Blackman cubics for applications on a variable-thickness mesh. *Mon. Wea. Rev.*, **121**, 753-763.
- Yamartino, R.J., Scire, J.S., Carmichael, G.R., Chang, Y.S. (1992) The CALGRID mesoscale photochemical grid model - I. Model formulation. *Atmos. Environ.*, **26A**, 8, 1493-1512.