Atmospheric transport

The model description of mercury atmospheric transport is based on the three-dimensional advection-diffusion equation adapted to the (σ–p) coordinate [see e.g. *Jacobson*, 1999]:

$$\frac{\partial}{\partial t}(q_i p_s) = -\nabla_H \cdot (q_i p_s \mathbf{V}_H) - \frac{\partial}{\partial \sigma}(q_i p_s \dot{\sigma}) + \frac{\partial}{\partial \sigma}\left[K_z \frac{g^2 \rho^2}{p_s^2} \frac{\partial}{\partial \sigma}(q_i p_s)\right] + C_i + S_i - R_i \tag{1}$$

Here $q_i = c_i/\rho$ is mixing ratio of i^{th} mercury species;

c_i and ρ are the mercury species volume concentration and the local air density;

$\dot{\sigma} = d\sigma / dt$ is the vertical scalar velocity in the σ–p coordinate;

∇_H and $\mathbf{V}_H$ denote vectors of horizontal divergence operator and horizontal wind velocity respectively;

K_z is the vertical eddy diffusion coefficient; and g is the gravitational acceleration.

In Eq. (1) we omitted horizontal components of eddy diffusion because of the coarse horizontal grid resolution. The local air density ρ is coupled with air temperature T_a and surface pressure p_s through the equation of state:

$$\rho = \frac{\sigma p_s}{R_a T_a}, \tag{2}$$

where R_a is the humid air gas constant.

The first two terms on the right hand side of Eq. (1) describe horizontal and vertical advection of a pollutant in the atmosphere. The third term represents vertical eddy diffusion, the fourth considers species mutual chemical transformations (C_i), and the last two terms describe bulk pollutant sources (S_i) and removal processes (R_i). Eq. (1) is solved by means of the time-splitting technique [*Yanenko*, 1971; *Marchuk*, 1975; *McRae et al.*, 1982]. Following this method, Eq. (1) is decomposed into several separate sub-equations describing different physical and chemical processes, which are solved successively during each time step.

Advection

In spherical coordinates the sub-equation of Eq. (1) describing horizontal advection has the following form:

$$\frac{\partial}{\partial t}(q_i p_s) = -\frac{1}{R_E \cos\varphi}\left[\frac{\partial}{\partial \lambda}(q_i p_s V_\lambda) + \frac{\partial}{\partial \varphi}(q_i p_s V_\varphi \cos\varphi)\right] \tag{3}$$

where λ and φ are the geographical longitude and latitude;

R_E is the Earth radius;

V_λ and V_φ are zonal and meridional components of the wind velocity respectively.

Moreover, the former term in the square brackets describes the zonal advective transport, while the latter term represents the meridional one.

Eq. (3) is numerically solved using Bott flux-form advection scheme [*Bott*, 1989a; 1989b]. This scheme is mass conservative, positive-definite, monotone, and is characterized by comparatively low artificial diffusion [see e.g. *Dabdub and Seinfeld*, 1994]. In order to reduce the time-splitting error in strong deformational flows the scheme has been modified according to [*Easter*, 1993]. The original

Bott scheme has been derived in the Cartesian coordinates. To apply the scheme to the transport in spherical coordinates it has been modified taking into account peculiarities of the spherical geometry. Detailed description of the Bott advection scheme in the spherical coordinates is presented in [*Travnikov*, 2001].

The vertical advection part of Eq. (1) is written as follows:

$$\frac{\partial}{\partial t}(q_i p_s) = -\frac{\partial}{\partial \sigma}(q_i p_s \sigma) \,. \tag{4}$$

This one-dimensional advection equation is solved using the original Bott scheme generalized for a grid with variable step $\Delta\sigma$.

Mass consistency

A very important issue for any air quality model is the mass consistency. It means that off-line fields of wind and surface pressure supplied by the meteorological pre-processor should satisfy the continuity equation:

$$\frac{\partial p_s}{\partial t} + \nabla_H \cdot (p_s \mathrm{V}_H) + \frac{\partial}{\partial \sigma}(p_s \sigma) = 0 \,. \tag{5}$$

In the terms of an air quality model it implies that the model maintain a uniform mass mixing ratio field of an inert tracer [*Odman and Russel*, 2000]. It can be exactly realized only if the air quality model and a meteorological model supplying input data have the same discretization, i.e. grid structure, time step, and finite-difference formulation. However, many transport models (including considered one) have the discretization different from that used in the weather prediction model (WPM) supplying the data. Besides, time resolution of the off-line meteorological data (6 hours for the model involved) is often considerably lower than the model time resolution (10-30 minutes) defined by the numerical stability of the explicit scheme. It requires temporal interpolation of the meteorological data. All mentioned above can lead to a considerable mass inconsistency and the uniform tracer field cannot be maintained. A possible approach to adjust the input meteorological fields to the model discritization is derivation of vertical wind velocity σ from the continuity Eq. (5) at each time step [*Odman and Russel*, 2000].

For the exact mass conservation it is important to apply to solution of Eq. (5) the same numerical scheme used for species advection description. The solution is performed in two steps:

Step 1. Solution of the horizontal constituent of the air continuity equation for p_s using Bott advection scheme:

$$\frac{\partial p_s}{\partial t} = -\nabla_H \cdot (p_s \mathrm{V}_H) \,. \tag{6}$$

For the initial condition the surface pressure at the beginning of the time step $(p_s)_t$ is used. As a result a tree-dimensional distribution of the intermediate pressure $(p_s)_{t+\Delta t/2}$ = f(x,y,Δ) is obtained.

Step 2. Solution of the vertical constituent of the air continuity equation for the vertical velocity:

$$\frac{\partial p_s}{\partial t} = -\frac{\partial}{\partial \sigma}(p_s \sigma) \,. \tag{7}$$

The intermediate pressure $(p_s)_{t+\Delta t/2}$ from the Step 1 is used as the initial condition; and the surface pressure at the end of the time step $(p_s)_{t+\Delta t}$ = f(x,y) interpolated from the input data is considered as a final condition. The vertical velocity is derived from Eq. (7) analytically by inversion of the Bott scheme applied for the vertical transport description.

Eddy diffusion

Vertical eddy diffusion is described by the following equation:

$$\frac{\partial}{\partial t}(q_i p_s) = \frac{\partial}{\partial \sigma}\left[K_z \frac{g^2 \rho^2}{p_s^2} \frac{\partial}{\partial \sigma}(q_i p_s)\right]. \qquad (8)$$

Vertical eddy diffusion coefficient $K_z = K_z(\lambda,\varphi,\sigma)$ is supplied by the atmospheric boundary layer module of the meteorological data preparation system. Non-linear diffusion Eq. (8) has been approximated by the second-order implicit numerical scheme in order to avoid restrictions of the time step caused by possible sharp gradients of species mixing ratio $q_i(\sigma)$. The obtained finite-difference equation is solved by means of the sweep method.

Initial and boundary conditions

The model computation domain has two boundaries: upper and equatorial. Long residence time of mercury in the atmosphere requires setting appropriate initial and boundary conditions to take into account mercury contained in the computation domain before the computations and the input fluxes of mercury through the boundaries.

According to the numerous measurements carried out for last decades [e.g. see *R.Ebinghaus et al.*, 1999] elemental mercury Hg^0 is more or less uniformly distributed over the Northern Hemisphere (background concentrations are around 1.7 ng/m^3). Vertical distribution of Hg^0 is also rather uniform [*Banic et al.*, 1999]. Therefore we prescribed uniform distribution of elemental mercury concentration at the upper boundary – 0.185 pptv (corresponding to about 1.5 ng/m^3 at 1 atm and 20°C). On the other hand, some gradient of total gaseous mercury (TGM) was observed over the ocean between the Northern and Southern Hemispheres [e.g. see *Banic et al.*, 1999]. According to *R.Ebinghaus et al.* [2001] mean concentrations of TGM over the Northern and Southern Hemispheres are 1.7 and 1.3 ng/m^3 respectively. Elemental mercury makes up the main part of TGM. Summarizing the measurement data from [*Slemr*, 1996] we set the gradient of Hg^0 to 0.05 ng/m^3/degree at the equatorial boundary. Since the residence time of other mercury species in the atmosphere is considerably shorter we neglected their input through the boundaries. Currently, only atmospheric module is adequately developed for the mercury transport description. Therefore, the lower boundary at the Earth surface is closed. The mercury fluxes through the lower boundary are indirectly considered by deposition and “natural emission and re-emission” processes.

To fill up the model domain with mercury from anthropogenic sources of different regions and continents (it is necessary for the inter-continental transport assessment) we performed a computation run for the period of one year without any boundary and initial conditions. Then we used the obtained concentrations of mercury species as initial conditions for the regular computation run. Besides, the contribution of different sources to mercury incoming through the upper boundary is assumed to be the same as at the highest atmospheric layer.