

Chapter 1

MSCE-POP MODEL DESCRIPTION

This chapter is devoted to the description of MSCE-POP model developed by MSC-E for the evaluation of environment pollution by persistent organic pollutants (POPs). POPs are a group of toxic, persistent, and semivolatile chemicals capable to be accumulated in environmental compartments and in biological chains. A unique feature of POPs is their ability for re-emission. To evaluate long-range transport and deposition of POPs multi-compartment approach is required. For the description of atmospheric transport and deposition of POPs the MSCE-POP model uses the same modules for advective transport and turbulent diffusion of pollutants within the atmosphere as the MSCE-HM model. The POP deposition processes from the atmosphere to underlying surface are described on the basis of an approach similar to MSCE-HM model. For the description of POP exchange with and accumulation in main environmental compartments the atmospheric module of MSCE-POP model is complemented with additional modules for soil, seawater, and vegetation.

MSCE-POP model is being developed for several purposes:

- evaluation of atmospheric transport and deposition of POPs on regional (EMEP) scale;
- evaluation of spatial distribution of POPs in the atmosphere, soil, vegetation, and seawater;
- evaluation of transboundary transport of POPs;
- evaluation of POP partitioning between main environmental compartments;
- assessment of temporal and spatial trends;
- projection of future levels of POP contamination and trends under various emission scenarios;
- estimation of long-range transport potential and overall persistence of new potential POPs;
- study of environment pollution by POPs on the basis of monitoring/modelling approach.

1.1. The structure of MSCE-POP model

MSCE-POP model is a three-dimensional Eulerian multi-compartment model operating within the geographical scope of EMEP region with a spatial resolution $50 \times 50 \text{ km}^2$. The model considers main environmental compartments (atmosphere, soil, seawater, vegetation) and includes basic processes describing POP emission, long-range transport, deposition, degradation, and gaseous exchange between the atmosphere and the underlying surface (Fig. 1.1). MSCE-POP model domain covers practically the whole troposphere, upper layer of soil of 20 cm, and seawater compartment within the model grid. The horizontal dimensions of model domain are confined by the EMEP grid and described in [Travnikov and Ilyin, 2005].

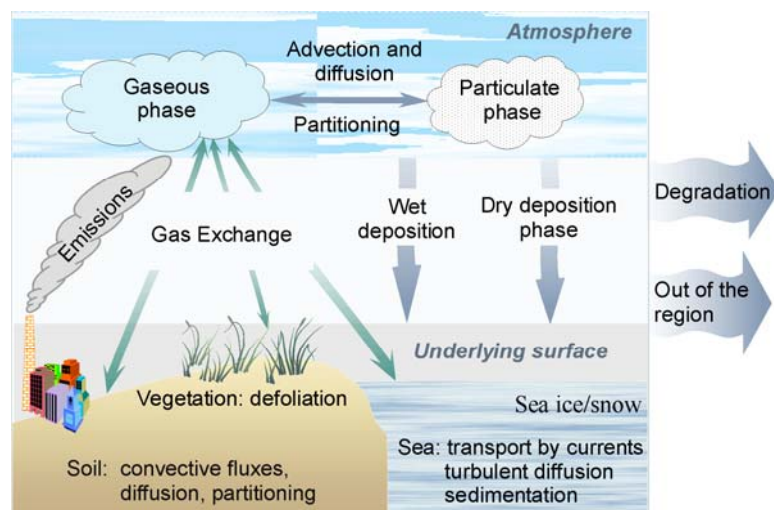


Fig. 1.1. The scheme of processes included into the MSCE-POP model

1.1.1. Compartments and basic processes

Current version of the model considers partitioning of POPs between the following environmental compartments: the atmosphere, soil, seawater, vegetation, and forest litter (Fig. 1.1). Selection of compartments and processes is based on current understanding of their importance with regard to the description of POP dispersion and accumulation in the environment.

The following processes affecting the long-range transport of POPs are included in the model:

Atmosphere:

- advective transport and turbulent diffusion;
- partitioning between the gaseous and particulate phase;
- wet and dry deposition of POP in particulate and gaseous phase to the underlying surface;
- degradation.

Vegetation:

- gaseous exchange with the atmosphere;
- degradation;
- defoliation and transfer to upper soil layer.

Soil:

- gaseous exchange with the atmosphere;
- partitioning in soil between the gaseous, solid and liquid phases;
- vertical transport due to convective water fluxes, diffusion, and bioturbation;
- degradation.

Seawater:

- gaseous exchange with the atmosphere;
- advective transport by sea currents and turbulent diffusion;
- partitioning between the dissolved and particulate phase;
- sedimentation;
- degradation.

1.1.2. Input and output information

An inclusion of additional environmental compartments, comparing to MSCE-HM model, increases the amount of input data required for modelling. Along with meteorological and emission data the MSCE-POP model uses information on soil and vegetation properties, data on sea currents, and physical-chemical properties of considered POPs (Fig. 1.2). A brief description of model input information is given in Section 1.8.

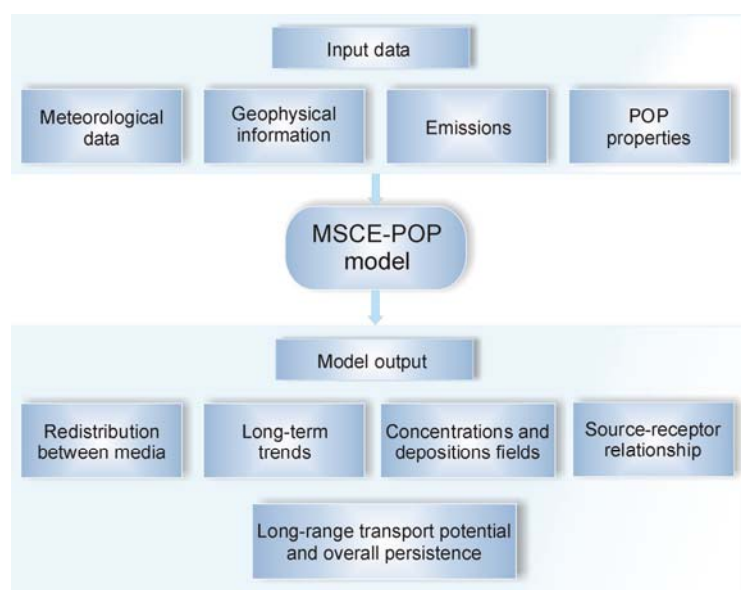


Fig. 1.2. Input and output data of the MSCE-POP multicompartment model

MSCE-POP model provide the following output information:

- spatial distribution of deposition and concentrations of POPs in environmental media;
- source-receptor relationships;
- long-term trends of POP content in main environment compartments;
- distribution of POPs between environmental media;
- long-range transport potential and overall persistence.

Hemispheric version of MSCE-POP model

Regional version of MSCE-POP model is complemented also by hemispheric one. Hemispheric version has been developed for the domain covering entire Northern Hemisphere with a spatial resolution $2.5^{\circ} \times 2.5^{\circ}$. This version of the model is similar to the regional one with regard to model structure, environmental compartments, and basic processes describing POP transport and fate. One of its distinct features is further elaborated seawater compartment module, which takes into account POP exchange between the atmosphere and sea ice compartment and sea ice dynamics. More detailed description of MSCE-POP hemispheric model can be found in [Shatalov *et al.*, 2003].

The hemispheric model is used for calculations of POP transport and accumulation on hemispheric scale, for evaluation of pollution of European region by remote sources, for evaluation of intercontinental transport, for assessing of pollution of remote regions like, for example, the Arctic region.

1.2. The atmospheric compartment

The atmospheric part of MSCE-POP model domain is defined similar to MSCE-HM model [Travnikov and Ilyin, 2005]. The processes included are the following: advection, turbulent diffusion, partitioning of a pollutant between the gaseous and particulate phase, wet and dry deposition of both phases to the underlying surface, and degradation. As it was mentioned above MSCE-HM and MSCE-POP models share the same description of advective transport and turbulent diffusion of pollutants within the atmosphere. The description of dry and wet deposition of POPs in particulate phase within the MSCE-POP model is in general similar to the approach used in MSCE-HM model [Travnikov and Ilyin, 2005].

1.2.1. Gas/particle partitioning

Characterization of POP partitioning between the gaseous and particulate phase is performed 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 adsorbed on atmospheric aerosol particles equals to:

$$\varphi = \frac{c \cdot \theta}{p_{OL} + c \cdot \theta}, \quad (1.1)$$

where c is the constant dependant on the thermodynamic parameters of the adsorption process and on the properties of aerosol particle surface; it is assumed $c = 0.17 \text{ Pa} \cdot \text{m}$ [Junge, 1977] for background aerosol;

θ is the specific surface of aerosol particles, m^2/m^3 .

The spatial distribution and temporal variations of aerosol specific surface were kindly provided by Dr. Sunling Gong (Canada). Parameter p_{OL} is pollutant-dependent and depends greatly on temperature. Coefficients of p_{OL} temperature dependencies used in model parameterisation for the selected POPs are presented in Annex A (A.1. "Subcooled liquid vapour pressure").

1.2.2. Dry deposition of the particulate phase

Dry deposition flux of the particulate phase F_{dry}^P (ng/m²/s) is a product of dry deposition velocity V_d (m/s) and air concentration C_P (ng/m³) of a pollutant in the particulate phase taken at an air reference level coinciding with the middle of the lowest atmospheric layer:

$$F_{dry}^P = V_d C_P, \quad (1.2)$$

The dry deposition velocity V_d from the reference level z_a is calculated according to the resistance analogy using the equation:

$$V_d = (R_a + 1/V_d^{surf})^{-1}, \quad (1.3)$$

where R_a is the aerodynamic resistance for turbulent transport of a pollutant from z_a to z_b , s/m;

z_b is the height of the surface layer, m;

V_d^{surf} is the surface dry deposition velocity from the surface layer height z_b .

Aerodynamic resistance R_a is calculated using the following equation (See [Tsyro and Erdman, 2000]):

$$R_a = \frac{0.74}{\kappa u_*} \left[\ln \left(\frac{z_a}{z_b} \right) - \psi_h \left(\frac{z_a}{L} \right) + \psi_h \left(\frac{z_b}{L} \right) \right], \quad (1.4)$$

where $\kappa = 0.4$ is the van Karman constant;

u_* is the friction velocity, m/s;

ψ_h is the similarity function for heat.

The values of deposition velocity to the underlying surface V_d^{surf} are calculated in different way for different types of underlying surface, namely, for sea, soil and forest separately.

Sea. Velocity of dry deposition to sea (V_d^{sea} , $z_b = 10$ m) is calculated using the equation:

$$V_d^{sea} = A_{sea} u_*^2 + B_{sea}, \quad (1.5)$$

where A_{sea} and B_{sea} are the constants dependant on the effective diameter of particle-carriers of a considered pollutant;

u_* is the friction velocity, m/s;

(regression equation obtained by *M.Pekar* [1996] from [*Lindfors et al.*, 1991] data).

Soil. Velocity of dry deposition over land (V_d^{land} , $z_b = 1$ m) is given as follows:

$$V_d^{land} = (A_{soil} u_*^2 + B_{soil}) z_0^{C_{soil}}, \quad (1.6)$$

where as above u_* is the friction velocity;

z_0 is the surface roughness, mm;

A_{soil} , B_{soil} , C_{soil} are the constants dependant on effective diameters of particle-carriers of considered POP;

(regression equation obtained by *M.Pekar* [1996] from [*Sehmel*, 1980] data).

Forest. Velocity of dry deposition to a forest (V_d^{forest} , $z_b = 20$ m), (adapted by L.Erdman [Tsyro and Erdman, 2000] from [Ruijgrok et al., 1997]):

$$V_d^{forest} = E \frac{u_*^2}{u_h}, \quad (1.7)$$

where u_h is the wind speed at forest height $h = z_b$;

$$E = \alpha u_*^\beta (1 + \gamma \exp((RH - 80)/20)) \quad (1.8)$$

is the total collection efficiency for particles within the forest canopy and α , β and γ are the experimental coefficients, depending on effective diameters of particles-carriers.

In the current model version it is assumed that the relative humidity of air (RH) is 80% of the average. Wind speed at forest height u_h (m/s) is calculated using the following equation:

$$u_h = \frac{u_*}{\kappa} \left[\ln \left(\frac{z_b - d_0}{z_0} \right) - \psi_m \left(\frac{z_b - d_0}{L} \right) + \psi_m \left(\frac{z_0}{L} \right) \right], \quad (1.9)$$

where $\kappa = 0.4$ is the van Karman constant;

$d_0 = 15$ m is zero-plane displacement;

$z_0 = 2$ m is the roughness length;

L is the Monin-Obukhov parameter;

ψ_m is the universal correction function for the atmospheric stability for momentum.

Two types of forest are distinguished in the model: deciduous forest and coniferous forest. It is assumed that dry deposition velocities to forest are calculated by Eq. (1.7) for deciduous forests during the vegetative period (from May to September). For the remaining time, dry deposition velocities for areas covered by deciduous forests are calculated as for soil Eq. (1.6). For areas covered by coniferous forests dry deposition velocities are calculated by Eq. (1.7) throughout the year.

The amount of pollutant deposited to forest is distributed between soil and leaves/needles in accordance with the distribution coefficient K_{vs} , which is pollutant-dependent.

The coefficients A_{sea} , B_{sea} , A_{soil} , B_{soil} , C_{soil} , α , β and γ , as well as the distribution coefficient K_{vs} between soil and leaves/needles for forests, are a part of model parameterization for a particular chemical. Their values for the selected POPs are given in the Annex A. (A.3. "Dry deposition velocities over land, sea, and forest").

1.2.3. Wet deposition

Wet deposition of POPs in gaseous and particulate phase is distinguished in the MSCE-POP model. Making an 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:

$$W_T = W_g (1 - \varphi) + W_P \varphi, \quad (1.10)$$

where W_g is the washout ratio of the POP gaseous phase;

W_P is the washout ratio of a substance associated with aerosol particles;

φ is the substance fraction associated with aerosol particles in the atmosphere.

For the description of gaseous phase scavenging with precipitation, the instantaneous equilibrium between the gaseous phase in the air and the dissolved phase in precipitation is assumed:

$$C_w^d = W_g C_a^g, \quad (1.11)$$

where C_w^d is the dissolved phase concentration in precipitation water, ng/m³;
 C_a^g is the gaseous phase concentration in air, ng/m³;
 $W_g = 1/K'_H$ is the dimensionless washout ratio for the gaseous phase;
 K'_H is the dimensionless Henry's law constant.

The Henry's law constant (K'_H) is temperature dependant. Temperature dependence and its parameters for selected POPs can be found in *Annex A* (A.2. "Henry's law constant and air/water partition coefficient").

For the description of particle bound phase scavenging with precipitation, the washout ratio determined experimentally is used:

$$C_w^s = W_p C_a^p, \quad (1.12)$$

where C_a^p is the particle bound phase concentration in the air surface layer, ng/m³;
 C_w^s is the suspended phase concentration in precipitation water, ng/m³;
 W_p is the dimensionless washout ratio for the particulate phase.

The W_p is a parameter specific for each POP which values can be found in *Annex A* (A.4. "Washout ratio").

1.2.4. Degradation in air

Degradation process of POPs in the atmosphere is considered as the gas-phase reaction of pollutants with hydroxyl radicals and all other reactions are neglected. The degradation process in the atmosphere is described by the equation of the second order:

$$\frac{dC}{dt} = -k_{air} \cdot C \cdot [OH], \quad (1.13)$$

where C is the pollutant concentration in air (gaseous phase), ng/m³;
 $[OH]$ is the concentration of OH radical, molec/cm³;
 k_{air} is the degradation rate constant for air, cm³/(molec·s).

In the MSCE-POP model for some of considered POPs the degradation rate constant due to reaction with OH-radical in the atmosphere is taken to be temperature dependent. Temperature dependence of degradation rate constant of the gas-phase reaction with OH-radical is described using Arrhenius equation (see *Annex A*, A.5 "Degradation rate constants in environment media"). OH radical concentrations in the atmosphere vary substantially depending on many factors (latitude, cloudiness, day time, season, some atmospheric properties, etc.). Data on temporal and spatial variations of OH radical concentrations are described in [Travnikov and Ilyin, 2005].

The process of degradation of POPs associated with particles is not included in the model due to lack of information on this topic.

1.2.5. Gaseous exchange with underlying surface

The gaseous exchange of POPs between the atmosphere and underlying surface (soil, vegetation, and seawater) is described in the MSCE-POP model on the basis of the resistance analogy. Description of this process is given below in sections devoted to corresponding media, namely, soil, vegetation, and seawater.

1.3. Soil compartment

The soil module is based on the model developed by *C.M.J. Jacobs and W.A.J. van Pul* [1996]. The soil compartment is represented by upper 20 cm soil layer which is separated into seven horizontal sub-layers of different thickness, namely, $\Delta z_i = 0.1, 0.3, 0.6, 1, 2, 5$ and 11 cm.

In the current version of the model the following processes are included: partitioning of the pollutant between various phases in soil, vertical transport due to diffusion and convective water fluxes, bioturbation, gaseous exchange with the atmosphere, and the degradation.

1.3.1. Partitioning in soil

Several phases of POPs within the soil are considered in the model: gaseous phase, dissolved phase, phase sorbed on the dissolved organic carbon, and phase sorbed on organic carbon within the solid soil fraction (Fig. 1.3). To take into account the dynamic character of the redistribution between POP sorbed on solid organic carbon and other POP phases in soil, total content of solid organic carbon (OC) was split into two separate fractions: easily accessible and potentially accessible [Vassilyeva and Shatalov, 2002]. It is assumed that the equilibrium between all POP phases except sorbed on potentially accessible soil OC fraction is established instantaneously.

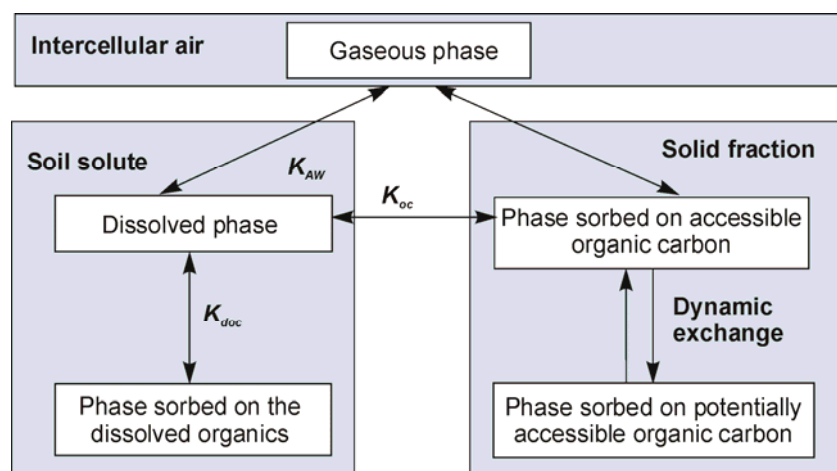


Fig. 1.3. POP fractions in soil, exchange processes and partitioning coefficients

The process of partitioning between these phases is governed by the following three partitioning coefficients:

- Air/water partitioning coefficient (K_{AW} , dimensionless):

$$K_{AW} = \frac{K_H}{RT} \quad (1.14)$$

where K_H is the air-water Henry's law constant, Pa·m³/mol;
 T is soil temperature, K;
 $R = 8.314$ J/(mol·K) is the universal gas constant.

- Organic carbon/water partitioning coefficient K_{oc} , m³/kg.
- Dissolved organic carbon/water partitioning coefficient K_{doc} , dm³/kg.

For the Henry's law constant in the dimensionless form (K'_H), temperature dependence determined by the Eq. (A.3) (*Annex A*) is assumed, where coefficients K_{H0} and a_H are pollutant-dependant.

The other two partitioning coefficients are calculated via the octanol/water partitioning coefficient K_{OW} of a pollutant in question by the following regression equations:

$$K_{OC} = 0.41 K_{OW} \text{ [Karikhoff, 1981]} \quad (1.15)$$

$$\text{and } \log K_{doc} = 0.98 \log K_{OW} - 0.39 \quad \text{for PAHs} \quad (1.16)$$

$$\log K_{doc} = 0.93 \log K_{OW} - 0.54 \quad \text{for PCBs} \quad (1.17)$$

[Poershman and Kopinke, 2001].

The latter relation obtained for a number of POPs with wide range of K_{OW} can also be used for other POPs (PCDD/Fs, HCB, γ -HCH) [Vassilyeva and Shatalov, 2002]. Values of K_{OW} and K_{OC} used in model parameterization are given in *Annex A* (A.6 "Octanol-water partition coefficient", A.7 "Organic carbon-water partition coefficient").

Following [Jacobs and van Pul, 1996], we express total POP concentration in soil C_T (ng/m³) via concentrations C_s (ng/kg), C_g (ng/m³), C_d (ng/m³) and C_{doc} (ng/m³) of solid, gaseous, dissolved and sorbed on dissolved organics fraction by the equation:

$$C_T = \rho_s C_s + \alpha_w (C_d + C_{doc}) + \alpha_a C_g, \quad (1.18)$$

where ρ_s is the bulk density of solid soil material, kg/m³;
 α_w is the volumetric water content of the soil;
 α_a is the volumetric air content of the soil.

Relations between concentrations in different POP phases in soil are as follows:

$$C_g = K_{aw} C_d, \quad (1.19a)$$

$$C_{doc} = c_{doc} K_{doc} C_d, \quad (1.19b)$$

$$C_s = f_{oc} K_{oc} C_d, \quad (1.19c)$$

where f_{oc} is the fraction of organic carbon in soil,
 c_{doc} is the concentration of dissolved organic carbon in soil solute (mobile fraction, kg/L).

The fraction f_{oc} of organic carbon varies widely depending on soil type (from 0.1 to 30% in Europe). The value of c_{doc} was chosen for calculations using the assumption that the fraction f_{doc} of soil organic carbon contained in mobile soil solute is about 0.5% of total organic carbon content in soil. This leads to the dissolved organic matter concentration in soil solute of about 170 mg/L at fraction f_{oc} of soil organic carbon equal to 5%. This value agree with that obtained by measurements (see [Vassilyeva and Shatalov, 2002]).

From formulas (1.18), (1.19 a-c) we obtain:

$$C_T = R_l C_l = R_s C_s = R_g C_g, \quad (1.20)$$

where $C_l = C_d + C_{doc} = C_d (1 + c_{doc} K_{doc})$ is the POP concentration in soil solute, and soil partitioning coefficients R_l , R_s and R_g are calculated by:

$$R_l = \alpha_w + (\rho_s f_{oc} K_{oc} + \alpha_a K_{aw}) / (1 + c_{doc} K_{doc}), \quad (1.21a)$$

$$R_s = R_l (1 + c_{doc} K_{doc}) / (f_{oc} K_{oc}), \quad (1.21b)$$

$$R_g = R_l (1 + c_{doc} K_{doc}) / K_{aw}. \quad (1.21c)$$

The exchange between a pollutant sorbed on easily accessible (C_0) and on potentially accessible (C_1) solid OC fractions is assumed to be a process of first order:

$$\begin{aligned} \frac{dC_0}{dt} &= k(C_1 + C_0) \\ \frac{dC_1}{dt} &= k(C_0 + C_1) \end{aligned} \quad (1.22)$$

where mass transfer coefficient k is chosen in such a way that the characteristic time for the exchange process equals to 1 year. The fraction f_{acc} of easily accessible fraction was assumed to be 30%.

1.3.2. Vertical transport in soil and exchange with the atmosphere

The migration of a pollutant over the vertical profile in soil is assumed to be due to diffusion and transport with the convective water flux J_w (equal to mean annual precipitation intensity h_p , m/c). The corresponding equation is:

$$\frac{\partial C_T}{\partial t} = \frac{\partial}{\partial z} \left(D_E \frac{\partial C_T}{\partial z} - V_E C_T \right). \quad (1.23)$$

In the latter formula the effective diffusion coefficient D_E is given by:

$$D_E = \frac{\xi_g D_a}{R_g} + \frac{\xi_l D_w}{R_l} + D_b. \quad (1.24)$$

where ξ_g and ξ_l are gas and liquid tortuosity factors;

$$\xi_g = a_a^{10/3} / \phi^2; \quad \xi_l = a_w^{10/3} / \phi^2;$$

ϕ is the porosiry of the soil;

D_a and D_w are molecular diffusion coefficients in air and water;

D_b is bioturbation coefficient, $D_b = 6 \cdot 10^{-12} \text{ m}^2/\text{s}$ [McLachlan et al., 2002].

Bioturbation in the description of POP behavior in soil is treated as additional diffusion process and is based on the paper [McLachlan *et al.*, 2002].

The effective solute velocity V_E is defined as:

$$V_E = J_w / R_l \quad (1.25)$$

At this stage the convective water flux J_w is assumed to be the same as the precipitation rate. Dynamic character of convective water flux will be taken into account later. In current version of MSCE-POP model the description of vertical transport of POPs in soil is rather simplified. This approach is used since the model is aimed at calculation of monthly and annual averages of POP concentrations and fluxes. For the description of POP vertical transport with upward water fluxes it is supposed that during some period T_{inv} (inverse flux period) after each precipitation event an upward water flux takes place. This flux is supposed to be constant in time. Its value is chosen in such a way that the amount of water transported by this flux to soil surface during the inverse flux period constitutes certain fraction f_{inv} of the amount fallen down during the precipitation event. The parameter f_{inv} is chosen to be 0.6 (60%) since the fraction of evaporated water from land is estimated as 60% from total precipitation amount on the average over Europe [Atmosphere Handbook, 1991].

To complete the description of POP vertical transport in soil, it is necessary to write down the expression of fluxes through upper and lower boundaries of the soil calculation domain.

The flux F_{as} at the atmosphere/soil interface is given by the following equation:

$$F_{as} = \frac{C_a - C_T / K_{as}}{R_a + R_b + R_s}, \quad (1.26)$$

where C_a is air concentration;

K_{as} is effective air/soil distribution coefficient.

This parameterization is based on the resistance analogy. The gaseous flux of POP from the atmosphere to the soil is driven by the difference between atmospheric gas concentration C_a at the air reference level z_a (equal to half the height of the lowest model atmospheric layer) and gaseous phase concentration C_T in soil at the reference level $z_s = \Delta z_1 / 2$ (Δz_1 – is the upper soil layer thickness). In the course of pollutant transport from the air reference level to the soil reference level it overcomes three resistances (see Fig. 1.4).

- Turbulent air sublayer resistance R_a , s/m is the resistance to transport through the turbulent air sublayer (from z_a to z_b).
- Laminar surface air sublayer resistance R_b , s/m is the resistance to transport through the laminar surface air sublayer (z_b) to the interface;
- Surface soil resistance R_s , s/m, is the resistance to transport from the surface soil interface to the soil reference level (z_s).

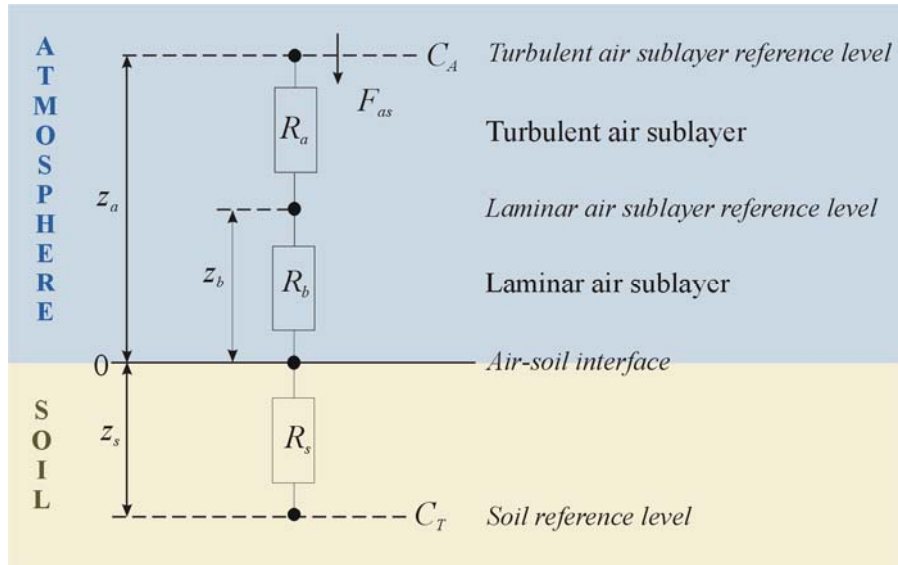


Fig. 1.4. Resistance scheme used for the description of gaseous exchange between the atmosphere and the soil

The resistance of upper soil layer r_s and effective air/soil distribution coefficient K_{as} are given by:

$$R_s = \frac{1}{R_g \left(\frac{2D_E}{\Delta z_1} + pV_E \right)}, \quad K_{as} = \frac{1}{r_s \left(\frac{2D_E}{\Delta z_1} + qV_E \right)} \quad (1.27)$$

where Δz_1 is the thickness of the upper layer of the soil calculation grid;

$p = 1, q = 0$ for downward water flux ($V_E > 0$) and $p = 0, q = 1$ for upward water flux ($V_E < 0$).

The flux at the lower boundary of soil calculation domain is assumed to be zero.

Equation (1.25) with the above boundary conditions is numerically solved by explicit scheme. The number of vertical calculation layers in the soil calculation domain and their thickness are chosen in an appropriate way. The criterion for the choice of these parameters is the stability of the value of net gaseous flux with respect to further subdivision of soil layers. As a result, 7 layers with thickness 0.1, 0.3, 0.6, 1, 2, 5 and 11 cm downwards are used.

1.3.3. Degradation in soil

The degradation process in soil is described as a first-order process by the equation:

$$\frac{dC}{dt} = -k_{soil}C, \quad (1.28)$$

where C is the pollutant concentration in soil, ng/m^3 ;

k_{soil} is the degradation rate constant for soil, s^{-1} .

The degradation rate constant k_{soil} is a part of model parameterization for a given pollutant (see Annex A (A.5. Degradation rate constants in environmental media)).

1.4. Vegetation compartment

Three types of vegetation are distinguished in the model: coniferous forest, deciduous forest, and grass. The information on vegetation types is based on the land cover data described in [Travnikov and Ilyin, 2005]. Coefficients governing exchange processes between the atmosphere and vegetation are determined separately for each of the above vegetation types. Furthermore, we consider forest litter as an intermediate medium between vegetation and soil. In essence this medium can be viewed as an upper soil layer.

1.4.1. Gaseous exchange with the atmosphere

The equation describing atmosphere/vegetation exchange has the following form:

$$\frac{dC_V}{dt} = \frac{1}{R_{tot}} (C_a^g - C_V / K_{Va}), \quad (1.29)$$

where C_a^g is the air concentration of a pollutant;
 C_V is the concentration in vegetation of a given type;
 K_{Va} is the bioconcentration factor (BCF);
 R_{tot} is the total resistance to the gaseous exchange given by the formula:

$$R_{tot} = R_a + a_V / k, \quad (1.30)$$

where R_a is the aerodynamic resistance of the turbulent atmospheric layer;
 k is the mass transfer coefficient, m/s;
 a_V is the specific surface area of vegetation, m²/m³ (assumed value is 8000, see [Duyzer and van Oss, 1997]).

The total amount of pollutant in vegetation of a given type in a certain grid cell is then expressed by the equation:

$$Q = C_V \frac{S \cdot LAI}{a_V}, \quad (1.31)$$

where S is the area covered by vegetation of a given type within a grid cell;
 LAI is the particular leaf area index for the considered type of vegetation.

Parameterization of BCF. The bioconcentration factor is determined by the following equation [McLachlan and Horstmann, 1998]:

$$K_{Va} = mK_{OA}^n, \quad (1.32)$$

where K_{OA} is the partitioning coefficient between octanol and air;
 m, n are the regression coefficients presented in Table 1.1.

Table 1.1. Regression parameters for Eq. (1.32)

	Grass [Thomas et al., 1998]	Forest [McLachlan and Horstmann, 1998]	
		Coniferous	Deciduous
m	22.91	38	14
n	0.445	0.69	0.76

While calculating BCF using Eq. (1.32) the temperature dependence of K_{OA} should be taken into account. Coefficients of K_{OA} temperature dependencies used in model parameterisation for the selected POPs are presented in *Annex A* (A.8. "Octanol-air partitioning coefficient").

Parameterization of the mass transfer coefficient k . According to [Pekar et al., 1999], the mass transfer coefficient is directly proportional to the value of K_{OA} . Hence, for the evaluation of the temperature dependence of k the following formula can be used:

$$k = k_0 \exp \left[a_K \left(\frac{1}{T} - \frac{1}{T_0} \right) \right], \quad (1.33)$$

where k_0 is the k value at the reference temperature, based on the data given in [McLachlan and Horstmann, 1998] for forests and in [Pekar et al., 1999] for grass;

a_K is the coefficient of K_{OA} temperature dependence, K.

The values of a_K for the selected POPs are given in the *Annex A* (A.8. "Octanol-air partitioning coefficient").

1.4.2. Defoliation and transport to soil from forest litter

The description of the defoliation process is also included in the model. It is assumed that part of the pollutant transported from vegetation to the forest litter is proportional to the decrease of leaf area index for deciduous forest and grass. For coniferous trees defoliation was described as a first-order process with a half-life $T_{1/2} = 2$ years.

The transmission of a pollutant from fallen leaves to the underlying soil is described as a first order process with the half-life of about 10 years as a preliminary rough hypothesis.

1.4.3. Degradation in vegetation

There is very little data on degradation rates of considered chemicals in vegetation. For this reason, the degradation process in vegetation is not considered at present. A more detailed discussion of this question with rough estimation of degradation rates in vegetation for some POPs can be found in [Pekar et al., 1999]. On the basis of preliminary investigations, the degradation process in forest litter was introduced to the model as a first-order process with a degradation constant rate two times higher than that in soil.

1.5. Seawater compartment

This section contains a general description of the processes included in the seawater module of the current version of MSCE-POP model. The following physical processes describing POP fate in seawater compartment are considered: gaseous exchange of POPs with the atmosphere, transport of POPs by sea currents and turbulent diffusion, redistribution of POP, between the dissolved and particulate phase, sedimentation of POPs, degradation of POPs within seawater.

The seawater domain is divided into 15 vertical layers with depths of 12.5, 37.5, 65, 105, 165, 250, 375, 550, 775, 1050, 1400, 1900, 2600, 3500, 4600 metres.

1.5.1. Basic equation

It is assumed that POPs in the marine environment can be in dissolved state and bound to organic and inorganic fine particles. The considered mechanisms of POP transport in the marine environment involve such processes as three-dimensional advection and three-dimensional turbulent diffusion (taking into account intensive vertical mixing within the upper mixed layer), sedimentation with settling particles and degradation of different intensity depending on the type of POP and its state. The equation for the dynamics of total concentration can be written as follows:

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} + w \frac{\partial C}{\partial z} = K_H \Delta_H C + \frac{\partial}{\partial z} (K_V \frac{\partial C}{\partial z}) - v_{sed} \frac{\partial C_p}{\partial z} - k_d C, \quad (1.34)$$

where C, C_p are POP total and particulate phase concentrations;
 $(u, v, w) - x, y, z$ components of prescribed velocity field;
 Δ_H is the Laplace operator in horizontal variables;
 $K_V(z)$ and K_H are the coefficients of vertical and horizontal diffusion;
 v_{sed} is the sedimentation rate constant, which is estimated by the Stokes formula:

$$v_{sed} = \frac{g(\rho_p - \rho_w)d_p^2}{12\mu} \quad (1.35)$$

where g is gravitational acceleration, m/s^2 ;
 ρ_p is mean density of particles, kg/m^3 ;
 ρ_w is water density, kg/m^3 ;
 d_p is the diameter of seawater particles, m ;
 μ is dynamic viscosity of seawater, $kg/m.s$.

Fields of sea current velocities and the depth of the upper mixed layer are taken from the ocean dynamic model (OGCM) [Resnyansky and Zelenko, 1991; 1992; 1999]. The description of this information is given in [Strukov *et al.*, 2000].

1.5.2. Degradation in seawater

The degradation process of POPs in seawater is described as a first-order process by the equation:

$$\frac{dC}{dt} = -k_{sea} C, \quad (1.36)$$

where C is the pollutant concentration in seawater, pg/L ;
 k_{sea} is the degradation rate constant for seawater, s^{-1} .

The degradation rate constant k_{sea} is a part of model parameterization for a given pollutant (see Annex A, A.5. "Degradation rate constants in environmental media").

1.5.3. POP partitioning between different phases

POP redistribution between the dissolved phase and the phase associated with particles essentially affects the dynamics of POP concentration fields in the marine environment. Under the condition of instantaneous phase equilibrium establishment it is possible to consider that the relationship is always fulfilled:

$$c^p = k^p c^d \quad (1.37)$$

where c^p is the concentration of POP sorbed on particles;
 c^d is the concentration of POP dissolved in water;
 k^p is the partition coefficient between the particle and dissolved phase.

In its turn k^p may be estimated by the expression:

$$k^p = k_p^o K_p c_{prt} \quad (1.38)$$

where k_p^o is the fraction of organic matter in a particle;
 K_p is the equilibrium constant for sorption/desorption processes (proportional to the octanol-water coefficient K_{OW});
 c_{prt} is particle concentration.

1.5.4. POP exchange between seawater and the atmosphere

On the sea surface diffusive exchange of POP gas-phase, deposition of POP washed out by precipitation in the gas-phase, wet and dry depositions of POP associated with particles take place. The description of air-sea gaseous exchange process takes also into account the influence of surface wind speed which is parameterized following to [Sergeev *et al.*, 1979]. For POP flux through the sea surface the following expression is used:

$$F_z|_{z=0} = \alpha_1 (c_a^g / K'_H(T) - c^d) ((1 - \alpha_2) D_w / \delta + \alpha_2 K_{HR} h_f) + F_{gw} + F_{pd} + F_{pw}, \quad (1.39)$$

where: $\delta = \delta_0 \exp(-0.15 \cdot U_a)$,

$$\alpha_1 = 1.75 - 0.75 \exp(-0.18 \cdot U_a),$$

$$\alpha_2 = 1 - \exp(-0.01 \cdot U_a).$$

c_a^g is the POP gas-phase concentration in the lower layer of the atmosphere;

c^d is the dissolved POP concentration in upper layer of the sea;

$K'_H(T)$ is the dimensionless Henry's law constant depending on temperature;

D_w is the molecular diffusion coefficient in water;

δ_0 is the surface molecular layer depth at zero wind speed [Sergeev *et al.*, 1979];

U_a is the wind speed absolute value near the surface;

h_f is the foam settling rate at the sea surface [Sergeev *et al.*, 1979];

F_{gw} is the POP gas-phase flux with precipitation;

F_{pd} is the flux of POP associated with particles in the atmosphere as a result of particle dry deposition;

F_{pw} is the flux of POP associated with particles in the atmosphere as a result of particle washout with precipitation;

α_1 is the coefficient introduced for the description of surface sea area increase due to wave disturbance [Sergeev *et al.*, 1979];

α_2 describes the relative sea surface area covered with foam at strong wind [Sergeev *et al.*, 1979].

1.6. Initial conditions and influence of external emission sources

Evaluation of POP pollution levels within European region requires appropriate information on initial concentrations in the environmental compartments and influence of emission sources outside the model grid. Initial concentrations of POPs in main environmental compartments are calculated in model run using historical emissions of particular pollutant. For POPs with significant long-range potential initial concentrations can be calculated using hemispheric MSCE-POP model.

The influence of emission sources outside the model domain can be taken into account using measurement data or by the use of hemispheric MSCE-POP model. However, due to lack of available monitoring data on POP concentrations along the MSCE-POP model boundaries the influence of remote emission sources is evaluated by means of hemispheric model. For this purpose the hemispheric model is run with all hemispheric emissions excluding sources within the EMEP grid. The contribution of European emission sources to the pollution levels within the EMEP grid is obtained by means of regional MSCE-POP model.

1.7. Computations of transboundary fluxes

Evaluation of transboundary fluxes of POPs between European countries is carried in the same way as in the MSCE-HM model [Travnikov and Ilyin, 2005]. The transport of a pollutant from each selected emission sources is calculated separately. Similar to MSCE-HM model to avoid the uncertainties connected with non-linearity of the model all processes are computed for total mass recalculating the contribution of each emission source after each process. This approach permits to evaluate the contribution of selected emission sources (countries, regions, etc.) to annual concentrations and depositions for each model grid cell. In case of POPs mostly associated with atmospheric particles and small fraction of gaseous phase the influence of re-emission can be neglected. For POPs with significant fraction of gaseous phase an additional source corresponding to re-emission flux is introduced.

1.8. Input data for modelling

The MSCE-POP model input information includes emission data, meteorological and geophysical information, and physical-chemical properties of POPs. MSCE-POP and MSCE-HM models use the same meteorological data, land cover information, and data on OH radical content in the atmosphere. These data sets are described in MSCE-HM model description [Travnikov and Ilyin, 2005]. In addition to them MSCE-POP model requires also data on leaf area index, organic carbon content in soil, data on specific aerosol surface in air and data on sea currents.

1.8.1. Emissions of selected POPs

The preparation of emission data for modelling is made on the basis of official data submitted to the UN ECE Secretariat by countries and available expert estimates of POP emissions. The official data on POP emissions (PAHs, PCDD/Fs, PCBs, HCB and γ -HCH) for the period from 1990 to 2001 (at least for one year) were submitted by 32 Parties to the Convention. Data on other pollutants (Aldrin, Chlordane, Chlordecone, Dieldrin, Endrin, Heptachlor, Hexabromobiphenyl, Mirex, Toxaphene, DDT, PCP and SCCP) were submitted by 16 countries. It is worth to note that in recent years, the number

of countries submitting data on POP emissions and their spatial distribution over the EMEP domain increased. For countries for which official emission data were not available, expert estimates are used.

Emission data for polycyclic aromatic hydrocarbons were compiled with the usage of officially submitted data and available expert estimates of [Pacyna *et al.*, 1999; Tsibulsky *et al.*, 2001; Berdowski *et al.*, 1997; Baart *et al.*, 1995]. In the model computations seasonal variations of PAH emissions are considered in accordance with [Baart *et al.*, 1995].

Data on polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) emissions of European countries were prepared using official emissions and expert estimates of PCDD/F total emissions and their spatial distribution of [Pacyna *et al.*, 1999]. For model calculations splitting of the overall toxicity of PCDD/F mixture between different congeners was performed and spatial distributions of emissions for each congener were prepared on the basis of the data from [Pacyna *et al.*, 1999].

Emissions of polychlorinated biphenyls (PCBs) for European region are based on global emission inventory of 22 PCB congeners for the period 1930-2000 [Breivik *et al.*, 2002]. These data were redistributed into MSCE-POP model grid using the information on population density.

Information on HCB and γ -HCH emissions of European countries was compiled on the basis available official information and expert estimates of [Pacyna *et al.*, 1999]. Seasonal variations of γ -HCH emissions due to its application for agricultural purposes in spring and early summer are taken into account in modelling.

Detailed description of emission data used for modelling can be found in MSC-E/CCC technical reports 7/2002 and 4/2003 [Shatalov *et al.*, 2002; Shatalov *et al.*, 2003].

1.8.2. Physical-chemical properties of selected POPs and substance-specific parameters

Basic differences in the long-range transport of POPs mainly result from peculiarities of their physical-chemical properties and degradation rates in the main environmental media. The key characteristics required for POP modelling are the following:

- subcooled liquid vapour pressure (p_L^0);
- air-water Henry's law constant (K_H);
- washout ratio for the particulate (W_p) and gaseous phase (W_g);
- degradation rate constants for different environmental compartments;
- coefficients of partitioning between different media (octanol-water partition coefficient (K_{OW}), octanol-air partition coefficient (K_{OA}), organic carbon-water partition coefficient (K_{OC}));
- data on the distribution of low volatile POPs with particle sizes in the atmosphere;
- and molecular diffusion coefficients (D_A , D_W , m^2/s).

These physical-chemical properties were prepared for the evaluation of environmental pollution with MSCE-POP model for selected POPs, namely, PAHs (B[a]P, B[b]F, B[k]F and I_P), PCDD/Fs (17 congeners), PCBs (5 congeners), γ -HCH and HCB. The mentioned above characteristics used for modelling of considered POPs are presented below in Annex A. For some of these POPs temperature dependencies of subcooled liquid-vapour pressure, Henry's law constant, octanol-air partition coefficient and degradation rate constants are also given.

The selection of parameters was carried out on the basis of literature data on POP physical-chemical properties and measurement data. Many studies report data on experimentally determined or theoretically derived physical-chemical properties of individual POPs. At that base values of some physical-chemical properties and/or coefficients of temperature dependencies vary substantially. The scattering of the values reported can to some extent characterize the uncertainty of particular parameter.

1.8.3. Geophysical data

Leaf Area Index (LAI) data set is used for the description of POP gaseous exchange between the atmosphere and vegetation. The Leaf Area Index for a given grid cell implies the ratio between the area of leaves in this cell to its total area (m^2/m^2). The geographically resolved leaf area index data with monthly resolution was adopted from CD-ROM of NASA Goddard Space Flight Center [Sellers *et al.*, 1994, 1995] and converted to MSCE-POP model grid. Consistency of these data in relation to the land cover information was investigated by correlation analysis.

Data on sea currents were obtained from ocean general circulation model (OGCM) [Resnyansky and Zelenko, 1991; 1992; 1999]. These data describe three-dimensional structure of velocity fields in the oceanic depth and the surface mixed layer depths within the EMEP grid. The velocity fields and the upper mixed layer thickness are defined for every two days with linear interpolation of values obtained within this period of time. Description of this information can be found in MSC-E Technical Note 5/2000 [Strukov *et al.*, 2000].

