

DESCRIPTIONS OF MAIN PROCESSES

This Annex contains the descriptions of the main processes determining POP environmental behavior used in the participating models.

C.1. Gas/particle partitioning

EVN-BETR and UK-MODEL

The gas-particle partitioning is described with the help of the Finizio Aerosol Partition coefficient K_{QA} . It's dependence on the octanol-air partition coefficient K_{oa} is depicted by the following formula:

$$K_{QA} = 3.5 \cdot K_{oa}$$

The fugacity capacity of the bulk air compartment can then be written as the sum of the gaseous and particle-bound chemical fraction:

$$(1 - \text{particles in air volume fraction}) \cdot Z_{air} + (\text{particles in air volume fraction}) \cdot K_{QA} \cdot Z_{air}$$

where $Z_{air} = 1/(R \cdot T)$ is the fugacity capacity in air;

T - corrected environmental temperature for annual mean of 9°C;

R - gas constant = 8.314 Pa·m³/mol K;

Particles in air volume fraction = $2 \cdot 10^{-11}$;

$K_{oa} = K_{ow} / K_{aw}$ - 51616649 for PCB 153 at the averaged ambient temperature T ;

Averaged ambient temperature = 9°C (base temperature).

CliMoChem

cited from [Scheringer et al., 2003]

The gas/particle partitioning is calculated as follows [Finizio et al., 1997]:

$$K_{partair} = 0.55 \cdot \lg \left(\frac{K_{ow}}{K_h} \right) - 8.23$$

This equation is used to calculate the fraction Phi, which indicates the particle-bound fraction of the substance. Phi-values range from 0-1.

$$\lg k_{partair} = K_{partair} + 6 = 0.55 \cdot \lg \left(\frac{K_{ow}}{K_h} \right) - 2.23 \quad \text{in (m}^3/\text{g)}$$

$$Phi = \frac{k_{partair} \cdot tsp}{(1 + k_{partair} \cdot tsp)}$$

Parameter	Description	Numeric value	Reference
tsp	Total suspended particles	$86 \cdot 10^{-6} \text{ g/m}^3$	Bennett et al. [2001] only mentioned
Phi	particle-bound fraction of substance	between 0-1	
K_h	Henry's law constant	depending on substance, See Chapter 3 and Annex B	
K_{ow}	Octanol/water partitioning coefficient	depending on substance, See Chapter 3 and Annex B	

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When K_{oa} is not available as input:

$$K_{qa} = 6 \cdot 10^6 / P_{ls},$$

where K_{qa} is dimensionless particle/gas partition coefficient and P_{ls} is liquid vapour pressure. Final partitioning is calculated with TSP and density of aerosol particles in fugacity format. Vapour pressure is temperature corrected when the temperature is different from 25 °C.

When K_{oa} is available as input:

$$K_{qa} = y \cdot K_{oa} / (\rho / 1000),$$

where, K_{qa} is dimensionless particle/gas partition coefficient, y is organic matter mass fraction, and ρ is the density of aerosol particles.

(Note: G-CIEMS model can calculate V/P partitioning from only molecular weight (for preliminary assessment purpose) or from K_{oa} . Two output 1 and 2 is presented in Chapter 4 as G-CIEMS-1 and G-SIEMS-2).

DEHM-POP

The gas-particle partitioning is calculated using the absorption model:

$$\phi = \frac{K_p TSP}{(K_p TSP + 1)},$$

where ϕ is the fraction of compound sorbed to particles, K_p is gas-particle partitioning coefficient, and TSP is the total suspended particulate matter [e.g. *Falconer and Harner, 2000*]. K_p is calculated using the K_{oa} approach:

$$\log K_p = m_r \log K_{oa} + \log f_{om} - 11.91,$$

where m_r is a constant expected to have a value close to +1 for equilibrium partitioning, K_{oa} is the octanol-air partitioning coefficient, f_{om} is the fraction of organic matter in the particles, and 11.91 is a constant determined by the intercept $br = \log f_{om} - 11.91$ [*Finizio et al., 1997, Falconer and Harner, 2000*].

The temperature dependent K_{oa} is calculated using the expression:

$$K_{oa}(T) = K_{oa}(T_{ref}) \exp\left(\frac{\Delta U_{oa}}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right),$$

where ΔU_{oa} is the internal energy of phase transfer, R is the universal gas constant, T is the temperature and $K_{oa}(T_{ref})$ is the value of K_{oa} at the reference temperature T_{ref} [*Beyer et al., 2002*].

SimpleBox

cited from [*Brandes et al., 1996*]

Air-aerosol partition coefficients are usually not known. However, some information is frequently available on the fraction of the chemical that occurs in association with the aerosol phase. SimpleBox uses this information for the computations. A value for the fraction of the chemical that is associated with the aerosol phase, $FRass_{aerosol}$, can be entered directly, or estimated on the basis of the chemical's vapor pressure, according to *Junge* [1977]. In this equation, the sub-cooled liquid vapour pressure should be used. For solids, a correction is applied according to *Mackay* [1991]:

If $MELTINGPOINT < TEMPERATURE_{[S]}$ (substance is liquid):

$$FRass_{aerosol[S]} = \frac{CONST \cdot \theta}{VAPORPRESSURE(T) + CONST \cdot \theta}$$

If $MELTINGPOINT > TEMPERATURE_{[S]}$ (substance is solid):

$$FRass_{aerosol[S]} = \frac{CONST \cdot \theta}{VAPORPRESSURE(T) \cdot e^{6.79 \cdot (1 - \frac{MELTINGPOINT}{TEMPERATURE_{[S]}})} + CONST \cdot \theta}$$

with $FRass_{aerosol[S]}$ - fraction of the chemical in air that is associated with aerosol particles at scale S [-] (A);

$VAPORPRESSURE(T)$ - vapor pressure of the chemical at temperature T at scale S [Pa] (A);

$MELTINGPOINT$ - melting point of the chemical [K] (A);

$CONST$ - constant [Pa·m] (C);

θ - surface area of aerosol phase [$m_{aerosol}^2/m_{air}^3$] (C);

$TEMPERATURE_{[S]}$ - temperature at the air-water interface at scale S [K] (A).

with the product $CONST \cdot \theta$ set equal to 10^{-4} Pa.

CAM/POPs

In the CAM/POPs model, the process of POP partitioning between the gas and particulate phases in atmosphere is based on Junge-Pankow adsorption model [Junge, 1977; Pankow, 1987] POP fraction Φ adsorbed on the atmospheric aerosol particles is given by:

$$\Phi = \frac{c \cdot \Theta}{P_L^0 + c \cdot \Theta}$$

where, Φ - fraction of POPs adsorbed on aerosol particles;

Θ - aerosol surface area available for adsorption, m^2 aerosol/ m^3 air;

P_L^0 - liquid-phase saturation vapour pressure of pure compound, Pa;

c - parameter that depends on the thermodynamics of the adsorption process and surface properties of the aerosol (Pa · cm).

Junge's proposed value of the parameter c is 17.2 Pa · cm [Pankow, 1987; Falconer et al., 1994; Bidleman et al., 1998].

The liquid vapour pressure, P_L^0 , are derived from:

$$\log_{10} P_L^0 = \frac{m}{T} + b,$$

where the slope (m) and the intercept (b) are estimated to calculate liquid vapour pressure of POPs with changing air temperature [Falconer et al., 1995; Harner et al., 1996]. Temperature dependence of P_L^0 for each congener can be seen in Table C.1.

Table C.1. Liquid vapour pressure of PCBs as a function of air temperature

	PCB-153	PCB-180
slope, m	4775	5042
intercept, b	12.85	13.03

Aerosol surface area, Θ , is calculated by multiplying aerosol number density by its wet surface area.

MSCE-POP

In the **current model version (MSCE-POP 1)** the characterization of POP partitioning between the gas and particulate phase of a pollutant is performed using subcooled liquid vapour pressure p_{ol} (Pa). According to the Junge-Pankow adsorption model [Junge, 1977; Pankow, 1987] POP fraction φ adsorbed on the atmospheric aerosol particles equals to:

$$\varphi = \frac{c \cdot \theta}{p_{ol} + c \cdot \theta}$$

where c is the constant depending on thermodynamic parameters of adsorption process and on properties of aerosol particle surface. It assumed $c = 0.17$ Pa·m [Junge, 1977] for background aerosol;

θ is the specific surface of aerosol particles, m²/m³. Assumed $\theta = 1.5 \cdot 10^{-4}$ [Whitby, 1978].

The temperature dependence of p_{ol} (Pa) is parameterized in the model by:

$$p_{ol} = p_{ol}^0 \cdot e^{-a_P \left(\frac{1}{T} - \frac{1}{T_0} \right)},$$

where $T_0 = 283.15$ K is the reference temperature, T (K) is the ambient temperature, p_{ol}^0 is p_{ol} value at reference temperature, and a_P is the coefficient of temperature dependence. The values of p_{ol}^0 and a_P for considered PCB congeners used in the model are presented in Table C.2.

Table C.2. Coefficients of p_{ol} temperature dependence for three PCB congeners used in MSCE-POP model

Congener	p_{ol}^0	a_P
PCB-28	$6.43 \cdot 10^{-3}$	9383
PCB-153	$9.69 \cdot 10^{-5}$	10995
PCB-180	$1.67 \cdot 10^{-5}$	11610

At present the work on modification of the description of gas aerosol partitioning within MSCE-POP model is ongoing. The approach using the octanol-air partitioning coefficient absorption model presented in [Falconer and Harner, 2000] is tested. Under this approach POP fraction φ adsorbed on the atmospheric aerosol particles is calculated as:

$$\varphi = \frac{K_p \cdot TSP}{1 + K_p \cdot TSP}$$

where K_p is the particle-gas partitioning coefficient and TSP is the total suspended particle concentration ($\mu\text{g} \cdot \text{m}^{-3}$). The constant K_p is calculated for PCBs via K_{oa} by the following regression equations [Falconer and Harner, 2000]:

$$\log K_p = \log K_{oa} + \log f_{om} - 11.91, \quad (\text{experimental version - MSCE-POP 2})$$

where K_{oa} is the octanol/air partitioning coefficient and f_{om} is the fraction of organic matter in the atmospheric aerosol involved in partitioning.

The temperature dependence of K_{oa} is parameterized in the model by:

$$K_{oa} = K_{oa}^0 \cdot e^{-a_K \left(\frac{1}{T} - \frac{1}{T_0} \right)},$$

where K_{oa}^0 is K_{oa} value at reference temperature, and a_K is the coefficient of temperature dependence.

The values of K_{oa}^0 and a_K for considered PCB congeners used in the model are presented in Table C.3.

Table C.3. Coefficients of K_{oa} temperature dependence for three PCB congeners used in MSCE-POP model

Congener	K_{oa}^0	a_K
PCB-28	$5.78 \cdot 10^8$	8731
PCB-153	$3.64 \cdot 10^{10}$	10811
PCB-180	$2.07 \cdot 10^{11}$	10442

C.2. Dry deposition of the particulate phase

EVN-BETR and UK-MODEL

The intermedia transport of chemicals is described using D-values (mol/Pa·h), which represent how fast advective and reactive/degradation processes are occurring. In the case of the air to surface exchange, the D-value defining dry particle deposition is:

$$D_{air-surface} = \text{Surface Area} \cdot \text{Particles in air volume fraction} \cdot V_q \cdot Z_{air} \cdot K_{QA}$$

Knowing these values can help calculate the flux of a chemical entering a region and, thus, its amount in the compartment under study.

Surface area - compartment specific;

Particles in air volume fraction - $2 \cdot 10^{-11}$;

V_q - dry deposition velocity = 10.8 m/h.

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cited from [Scheringer et al., 2003]

Dry deposition to baresoil^a, water, vegetation-covered soil^b

$$\frac{dC_{gas}}{dt} = -Phi \left(v_{dry} \cdot \left(\frac{A_i}{V_{gas}} \right) \right) \cdot C_{gas}$$

Parameter	Description	Numeric Value	Reference
C_{gas}	concentration of substance in gaseous phase		
Phi	particle-bound fraction of the substance (see C.1.)	between 0-1	
v_{dry}	deposition rate	260 m/d	[Mackay and Paterson, 1991]
A_i	Area, i = baresoil, water, vegetation-covered soil	variable	
V_{gas}	Volume of gaseous phase	variable	

^aIf the year consists of exactly four seasons with varying temperatures, v_{dry} for deposition to baresoil is changing taking into account that in the cold season the atmosphere is more stable and the deposition rate therefore is smaller. The spring and fall values are interpolations between the summer and winter values. v_{dry} changes as follows [Wania and McLachlan, 2001]:

season	$v_{dry} =$
winter	$v_{dry} / 2$
spring	$v_{dry} / 1.5$
summer	v_{dry}
fall	$v_{dry} / 1.5$

^bIf the year consists of exactly four seasons with varying temperatures, v_{dry} for deposition to vegetation-covered soil is changing taking into account that in the cold season the atmosphere is more stable and the deposition rate therefore is smaller. The spring and fall values are interpolations between the summer and winter values. v_{dry} changes as follows [Wania and McLachlan, 2001]:

season	$v_{dry} =$
winter	$v_{dry} / (2 \cdot \text{VegGrass} + 5 \cdot \text{VegCon} + 3 \cdot \text{VegDec})$
spring	$v_{dry} / (1.5 \cdot \text{VegGrass} + 2.5 \cdot \text{VegCon} + 2 \cdot \text{VegDec})$
summer	v_{dry}
fall	$v_{dry} / (1.5 \cdot \text{VegGrass} + 2.5 \cdot \text{VegCon} + 2 \cdot \text{VegDec})$

The vegetation cover consists of three types: Grass, Coniferous Forest and Deciduous Forest. The variables VegGrass, VegCon and VegDec describe the fraction of the vegetation-covered soil occupied by the different cover types. Their numeric value is between 0-1 and depends on the climatic zone.

Dry deposition to vegetation

$$\frac{dC_{gas}}{dt} = -Phi \left(v_{dry} \cdot \left(\frac{A_{veg}}{V_{gas}} \right) \right) \cdot C_{gas}$$

Parameter	Description	Numeric Value
C_{gas}	concentration of substance in gaseous phase	
Phi	particle-bound fraction of the substance (see C.1.)	between 0-1
v_{dry}	deposition rate	variable, depending on climatic zone*
A_{veg}	Area of vegetation (identical with Area of vegetation-covered soil)	variable
V_{gas}	Volume of gaseous phase	variable

* - the model contains three types of vegetation. For each type, the deposition rate (v_{dry}) is different (see table below). Depending on the composition of a climatic zone, v_{dry} is calculated as follows:

$$v_{dry_i} = fraction_{grass_i} \cdot v_{dry_{grass}} + fraction_{dec_i} \cdot v_{dry_{dec}} + fraction_{con_i} \cdot v_{dry_{con}}$$

Parameter	Description	Numeric Value	Reference
v_{dry_i}	deposition rate in climatic zone i		
$v_{dry_{grass}}$	deposition rate to grass	55.92 m/d	<i>Horstmann and McLachlan [1998]</i> <i>Möller [2002]</i>
$v_{dry_{dec}}$	deposition rate to deciduous forest	447.6 m/d	
$v_{dry_{con}}$	deposition rate to coniferous forest	43.2 m/d	
$fraction_{grass_i}$	fraction of grass of total vegetation in climatic zone i	variable	
$fraction_{dec_i}$	fraction of deciduous forest of total vegetation in climatic zone i	variable	
$fraction_{con_i}$	fraction of coniferous forest of total vegetation in climatic zone i	variable	

Because of increased stability of the atmosphere in the spring, fall and winterseason, the deposition rates $v_{dry_{grass}}$, $v_{dry_{dec}}$ and $v_{dry_{con}}$ are divided by 3 for the winterseason and by 2 for the spring and fall seasons (given that the year consists of exactly four seasons with varying temperature [Wania and McLachlan, 2001]).

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$$F = v_{Dep} \cdot (TSP/\rho) \cdot C_{particle}$$

Where F is mass flux of compound for this chemical, v_{Dep} is dry deposition velocity of particles, TSP is particulate concentration of weight/volume dimension, ρ is density of aerosol particles, $C_{particle}$ is compound volumetric concentration in particles. Same value is used on all land and water surfaces.

DEHM-POP

The dry deposition of particulate phase is calculated as a flux given by the atmospheric concentration times a deposition velocity [Christensen, 1997]. The deposition velocity is highly dependent on the meteorological conditions and the surface properties. The size of the particles is assumed to be 1 μ m [Christensen, 1997].

For unstable conditions in the atmosphere (when $L < 0$, i.e. at day time with clear sky), the deposition velocity is calculated using:

$$v_d = \frac{u^*}{a} \left(1 + \left(\frac{-300}{L} \right)^{(2/3)} \right),$$

where u^* is the surface friction velocity, a is a constant depending on the surface properties, and L is the Monin-Obukhov length.

For stable conditions in the atmosphere (when $L > 0$, i.e. at night time with clear sky), the deposition velocity is calculated using:

$$v_d = \frac{u^*}{a}.$$

The surface friction velocity is calculated using:

$$u^* = \frac{0.35 \cdot U}{\ln(10) \cdot z},$$

where U is the wind speed and z is the roughness length which depends on the properties of the surface, and varies seasonally.

The Monin-Obukhov length is calculated using:

$$L = \frac{(u^*)^3 \cdot T}{0.35 \cdot g \cdot \left(\frac{-H_d}{c_p \rho} \right)},$$

where T is the temperature, g is the gravitational constant ($g = 9.82$), H_d is the heat flux, c_p is the specific heat at constant pressure, and ρ is the air density. L is positive (stable atmosphere) when the heat flux is negative (night time clear sky) and negative (unstable atmosphere) when the heat flux is positive (day time clear sky).

SimpleBox

cited from [Brandes et al., 1996]

Value for the deposition mass transfer coefficients $DRYDEP_{aerosol}$ may be obtained by means of:

$$DRYDEP_{aerosol[S]} = AEROSOLDEPRATE_{[S]} \cdot FRass_{aerosol[S]}$$

with $DRYDEP_{aerosol[S]}$: mass transfer coefficient for dry deposition of aerosol-associated chemical at scale S [m_{air}/s] (D);

$AEROSOLDEPRATE_{[S]}$ - deposition velocity of the aerosol particles at scale S with which the chemical is associated [m/s] (A);

$FRass_{aerosol[S]}$: fraction of the chemical in air that is associated with aerosol particles at scale S [-] (A).

Deposition mass flows of the chemical depend on the rate of dry aerosol deposition. Deposition velocities of aerosols vary greatly with the size of the particles. As chemicals may be associated with particles of a specific size, the deposition velocities depend also on the chemical. The values given are typical values, to be used as a starting point:

$$AEROSOLDEPRATE_{[S]} = 0.1 \text{ cm/s}$$

with $AEROSOLDEPRATE_{[S]}$: deposition velocity of the aerosol particles with which the chemical is associated at scale S [m/s] (A)

CAM/POPs

Removal of POPs particles is coupled with the dry deposition of aerosols in the CAM model. The dry deposition flux can be written as:

$$F_d = -v_d \cdot C_p,$$

where v_d is the deposition velocity and C_p is the particle concentration [Gong et al. 2003].

Dry deposition flux of POPs gas is written as:

$$F_d = -v_d \cdot C_g,$$

where the dry deposition velocity of gas, v_d , is calculated in CAM model [Gong et al. 2003].

MSCE-POP

Dry deposition to grass and bare soil

According to model of [Sehmel, 1980], deposition flux over grass is calculated as

$$F = C_p \cdot (A_{soil} u_*^2 + B_{soil}) z_0^{C_{soil}},$$

where as above u_* is the friction velocity;

z_0 is the surface roughness, mm;

$A_{soil} = 0.02$, $B_{soil} = 0.01$, $C_{soil} = 0.33$.

Dry deposition to forest

According to model of [Ruijgrok et al., 1997], deposition flux over forest is calculated as

$$F = C_p \cdot E \frac{u_*^2}{u_h},$$

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

u_* is the friction velocity, m/s;

$E = \alpha u_*^\beta (1 + \gamma \exp((RH - 80)/20))$, $\alpha = 0.048$, $\beta = 0.3$ and $\gamma = 0.25$, $RH=80$.

Dry deposition to seawater

According to model of [Lindfors et al., 1991], deposition flux over seawater is calculated as:

$$F = C_p \cdot (A_{sea} u_*^2 + B_{sea}),$$

where u_* is the friction velocity, m/s;

$A_{sea} = 0.15$, $B_{sea} = 0.013$

Similar to DEHM-POP model values of deposition flux depend on meteorological conditions (friction velocity u_*). Therefore, in the results of calculation experiments we present the range of obtained values of the flux together with its value at average environmental parameters.

C.3. Wet deposition

EVN-BETR and UK-MODEL

In a similar way as for the dry particle deposition, wet scavenging is defined as the result of:

$$D_{air-surface} = Q \cdot \text{Surface Area} \cdot \text{Particles in air fraction} \cdot K_{QA} \cdot U_R \cdot Z_{air}$$

In the case of deposition in vegetation, the percentage of rain interception due to vegetation is taken into account.

U_R - rain rate = 8.84×10^{-5} m/h;

Q - Rain Scavenging ratio = 200000;

Or Snow Scavenging Ratio = 1000000

CliMoChem

cited from [Scheringer et al., 2003]

Wet deposition from gaseous phase to baresoil and water

$$\frac{dC_{gas}}{dt} = -(1 - \Phi) \left(v_{rain} \cdot \left(\frac{A_i}{V_{gas}} \right) \cdot \frac{1}{K_h} \right) \cdot C_{gas}$$

Parameter	Description	Numeric value	Reference
C_{gas}	concentration of substance in gaseous phase		
Φ	particle-bound fraction of the substance (see C.1.)	between 0-1	
v_{rain}	global annual average precipitation	$2.33 \cdot 10^{-3}$ m/d	Mackay and Paterson, 1991
A_i	area, i = baresoil, water	variable	
V_{gas}	volume of gaseous phase	variable	
K_h	Henry's law constant	depending on substance, compare substance property sheets, See Chapter 3 and Annex B.	

Wet deposition from gaseous phase to vegetation-covered soil

$$\frac{dC_{gas}}{dt} = -(1 - \Phi) \left(v_{rain} \cdot \left(\frac{A_{vsoil}}{V_{gas}} \right) \cdot \frac{1}{K_h} \right) \cdot (1 - f_{rt}) \cdot C_{gas}$$

Parameter	Description	Numeric value	Reference
C_{gas}	concentration of substance in gaseous phase		
Φ	particle-bound fraction of the substance (see C.1.)	between 0-1	
v_{rain}	global annual average precipitation	$2.33 \cdot 10^{-3}$ m/d	Mackay and Paterson, 1991
A_{vsoil}	area of vegetation-covered soil	variable	
V_{gas}	volume of gaseous phase	variable	
K_h	Henry's law constant	depending on substance, compare substance property sheets See Chapter 3 and Annex B.	
f_{rt}	fraction of rain falling on vegetation (leaves etc)	depending on vegetation type and season*	Horstmann and McLachlan, 1998; Wania et al., 2000

* - for deciduous and coniferous forest, the f_{rt} -value is 0.35 for the summer season, for grass, the f_{rt} -value is 0.12 for the summer season. In the winter season, the value is at 10% of the summer season, in spring and fall season, the value is at the linear interpolation value between summer and winter season. Because the composition of the vegetation varies with the climatic zones, the contributions of grass, coniferous and deciduous forest to the overall f_{rt} -value of a specific climate zone differ and are proportional to the fraction of the respective vegetation type in a climatic zone.

Wet deposition from gaseous phase to vegetation

$$\frac{dC_{gas}}{dt} = -(1 - \Phi) \left(v_{rain} \cdot \left(\frac{A_{vsoil}}{V_{gas}} \right) \cdot \frac{1}{K_h} \right) \cdot f_{rt} \cdot C_{gas}$$

Parameter	Description	Numeric value	Reference
C_{gas}	concentration of substance in gaseous phase		
Φ	particle-bound fraction of the substance (see C.1.)	between 0-1	
v_{rain}	global annual average precipitation	$2.33 \cdot 10^{-3}$ m/d	Mackay and Paterson, 1991
A_{vsoil}	area of vegetation (= area of vegetation-covered soil)	variable	
V_{gas}	volume of gaseous phase	variable	
K_h	Henry's law constant	depending on substance, compare substance property sheets, See Chapter 3 and Annex B.	
f_{rt}	fraction of rain falling on vegetation (leaves etc)	depending on vegetation type and season*	Wania et al., 2000

* - for deciduous and coniferous forest, the f_{rt} -value is 0.35 for the summer season, for grass, the f_{rt} -value is 0.12 for the summer season. In the winter season, the value is at 10% of the summer season, in spring and fall season, the value is at the linear interpolation value between summer and winter season. Because the composition of the vegetation varies with the climatic zones, the contributions of grass, coniferous and deciduous forest to the overall f_{rt} -value of a specific climate zone differ and are proportional to the fraction of the respective vegetation type in a climatic zone.

Wet deposition from particulate phase to bare soil and water

$$\frac{dC_{gas}}{dt} = -Phi \left(v_{rain} \cdot scav_{ratio} \cdot \left(\frac{A_i}{V_{gas}} \right) \right) \cdot C_{gas}$$

Parameter	Description	Numeric value	Reference
C_{gas}	concentration of substance in gaseous phase		
Phi	particle-bound fraction of the substance (see C.1)	between 0-1	
v_{rain}	global annual average precipitation	$2.33 \cdot 10^{-3}$ m/d	<i>Mackay and Paterson, 1991</i>
$scav_{ratio}$	scavenging ratio: the air volume scavenged by the falling rain is scavratio-times greater than the rainwater volume	$2 \cdot 10^5$	<i>Mackay and Paterson, 1991</i>
A_i	area, i = baresoil, water	variable	
V_{gas}	volume of gaseous phase	variable	

Wet deposition from particulate phase to vegetation-covered soil

$$\frac{dC_{gas}}{dt} = -Phi \left(v_{rain} \cdot scav_{ratio} \cdot \left(\frac{A_{vsoil}}{V_{gas}} \right) \right) \cdot (1 - f_{rt}) \cdot C_{gas}$$

Parameter	Description	Numeric value	Reference
C_{gas}	concentration of substance in gaseous phase		
Phi	particle-bound fraction of the substance (see C.1)	between 0-1	
v_{rain}	global annual average precipitation	$2.33 \cdot 10^{-3}$ m/d	
$scav_{ratio}$	scavenging ratio: the air volume scavenged by the falling rain is scavratio-times greater than the rainwater volume	$2 \cdot 10^5$	<i>Mackay and Paterson, 1991</i>
A_{vsoil}	area of vegetation-covered soil (= area of vegetation)	variable	
V_{gas}	volume of gaseous phase	variable	
K_h	Henry's law constant	depending on substance, compare substance property sheets, See Chapter 3 and Annex B	
f_{rt}	fraction of rain falling on vegetation (leaves etc)	depending on vegetation type and season*	<i>Wania et al., 2000</i>

* - for deciduous and coniferous forest, the f_{rt} -value is 0.35 for the summer season, for grass, the f_{rt} -value is 0.12 for the summer season. In the winter season, the value is at 10% of the summer season, in spring and fall season, the value is at the linear interpolation value between summer and winter season. Because the composition of the vegetation varies with the climatic zones, the contributions of grass, coniferous and deciduous forest to the overall f_{rt} -value of a specific climate zone differ and are proportional to the fraction of the respective vegetation type in a climatic zone.

Wet deposition from particulate phase to vegetation

$$\frac{dC_{gas}}{dt} = -Phi \left(v_{rain} \cdot scav_{ratio} \cdot \left(\frac{A_{vsoil}}{V_{gas}} \right) \right) \cdot f_{rt} \cdot C_{gas}$$

Parameter	Description	Numeric value	Reference
C_{gas}	concentration of substance in gaseous phase		
Phi	particle-bound fraction of the substance (see C.1.)	between 0-1	
v_{rain}	global annual average precipitation	$2.33 \cdot 10^{-3}$ m/d	
$scav_{ratio}$	scavenging ratio: the air volume scavenged by the falling rain is scavratio-times greater than the rainwater volume	$2 \cdot 10^5$	<i>Mackay and Paterson, 1991</i>
A_{vsoil}	area of vegetation (= area of vegetation-covered soil)	variable	
V_{gas}	volume of gaseous phase	variable	
K_h	Henry's law constant	depending on substance, compare substance property sheets, See Chapter 3 and Annex B	
f_{rt}	fraction of rain falling on vegetation (leaves etc)	depending on vegetation type and season*	<i>Wania et al., 2000</i>

* - for deciduous and coniferous forest, the f_{rt} -value is 0.35 for the summer season, for grass, the f_{rt} -value is 0.12 for the summer season. In the winter season, the value is at 10% of the summer season, in spring and fall season, the value is at the linear interpolation value between summer and winter season. Because the composition of the vegetation varies with the climatic zones, the contributions of grass, coniferous and deciduous forest to the overall f_{rt} -value of a specific climate zone differ and are proportional to the fraction of the respective vegetation type in a climatic zone.

G-CIEMS

$$F = R_{rain} \cdot C_{air} / H + (TSP/\rho) \cdot Q \cdot C_{particle},$$

where F is total mass flux by this process, R_{rain} is rain rate, C_{air} is gaseous concentration of chemical, H is Henry's law constant, TSP is particulate concentration, ρ is density of particles, Q is scavenging ratio of particles, and $C_{particle}$ is volumetric chemical concentration in particles.

Same Q value is assumed over all land and water surfaces.

DEHM-POP

The wet deposition is given as a flux calculated as the product between the air concentration and a scavenging ratio [Christensen, 1997]. Different scavenging ratios are used for in-cloud scavenging and below-cloud scavenging. It is assumed that air pollution is scavenged more efficient in the clouds than below the clouds. The below cloud scavenging rate at a given height σ is given by:

$$W(\sigma) = \frac{\Lambda_{bc} P_a(\sigma)}{H \rho_w},$$

where Λ_{bc} is the below cloud scavenging coefficient, P_a is the total precipitation at the level, H is an effective thickness for scavenging ($H = 1000$ m), and ρ_w is the density of water. The in cloud scavenging rate at a given height σ is given by:

$$W(\sigma) = \frac{\Lambda_c P(\sigma)}{H \rho_w},$$

where Λ_c is the below cloud scavenging coefficient, P_a is the is the total precipitation created inside the cloud layer. The used scavenging ratios are: $\Lambda_{bc} = 100000$ and $\Lambda_c = 700000$.

The total amount of pollutant scavenged by the wet deposition is then dependent on the actual height of the formation of the precipitation, and on the vertical concentration profile.

SimpleBox

cited from [Brandes et al., 1996]

Value for the deposition mass transfer coefficient *WASHOUT* may be obtained by means of:

$$WASHOUT_{[S]} = RAINRATE_{[S]} \cdot SCAVratio_{[S]}$$

with $WASHOUT_{[S]}$ - mass transfer coefficient for wet atmospheric deposition at scale S [$m_{air} \cdot s^{-1}$] (D);
 $RAINRATE_{[S]}$ - rate of wet precipitation at scale S [$m_{rain} \cdot s^{-1}$] (A);
 $SCAVratio_{[S]}$ - scavenging ratio (quotient of the total concentration in rainwater and the total concentration in air) of the chemical at scale S [-] (A).

The scavenging ratio may be known from measurements or estimated:

$$SCAVratio_{[S]} = \frac{1 - FRass_{aerosol[S]} + FRass_{aerosol[S]} COLLECTeff_{[S]}}{K_{air-water[S]}}$$

with $SCAVratio_{[S]}$ - scavenging ratio (quotient of the total concentration in rainwater and the total concentration in air) of the chemical at scale S [-] (A);
 $FRass_{aerosol[S]}$ - fraction of the chemical in air that is associated with aerosol particles at scale S [-] (A);
 $K_{air-water[S]}$ - air-water equilibrium distribution constant at scale S [$mol \cdot m_{air}^{-3} / mol \cdot m_{water}^{-3}$] (A);
 $COLLECTeff_{[S]}$ - aerosol collection efficiency at scale S [-] (A),

The first term represents an estimate of the (equilibrium) distribution between rain water in air and the gas phase of air. The second term represents the scavenging of aerosol particles by rain droplets. The proportionality constant of $2 \cdot 10^5$ is taken from Mackay [1991].

Deposition mass flows of the chemical depend on the rate of wet precipitation. Collection efficiencies of aerosols vary greatly with the size of the particles. As chemicals may be associated with particles of a specific size, the collection efficiencies depends also on the chemical. The values given are typical values, to be used as a starting point:

$$COLLECTeff_{[S]} = 2 \cdot 10^5$$

with $COLLECTeff_{[S]}$ - aerosol collection efficiency at scale S [-] (A).

Table C4. RAINRATE of the scales

Scale	RAINRATE, mm/y
Regional	700
Continental	700
Moderate	700
Arctic	250*
Tropic	1300*

* - from Wania and Mackay [1995]

CAM/POPs

The precipitation scavenging of POPs particles by falling rain or snow is coupled with the wet removal of aerosols in the CAM model.

The particulate wet deposition flux, F_p , can be written as:

$$F_p = (-\Psi_{rain\ or\ snow} h) C_p,$$

where h is the falling distance, C_p is the particulate phase POPs concentration, ψ is the scavenging rate for rain or snow [Gong et al. 1997].

The gas phase POPs are assumed to be in quasi-steady equilibrium with the rain drop. The air-water equilibrium coefficient, K_{aw} , is a dimensionless partition coefficient that can be derived from Henry's Law constant, H ($\text{Pa} \cdot \text{m}^3/\text{mol}$) [Seinfeld, 1986].

$$K_{aw} = H / (R \cdot T)$$

and, $H = H_0 \exp(a(1/T_0 - 1/T))$,

where T is the temperature (K) and R is the gas constant ($8.314 \text{ Pa} \cdot \text{m}^3/\text{mol} \cdot \text{K}$ or J/mol/K), H_0 is the value at the reference temperature T_0 , and a is a parameter of temperature dependence.

	PCB-153	PCB-180
H_0	2.43	1.01
T_0	298 °K	298 °K
a	3.4E+3	3.4E+3

The net wet deposition flux, F_w , is then written as:

$$F_w = (-p / K_{AW}) \cdot C_G$$

where p is the precipitation rate, usually reported in mm/h and C_G is the gas phase POPs concentration.

MSCE-POP

Wet deposition of particulate phase

The values of concentration in precipitation are given by the formula:

$$C_w^s = W_p C_a^p,$$

where C_a^p - the particle bound phase concentration in the air surface layer, ng/m³;
 C_w^s - the suspended phase concentration in precipitation water, ng/m³;
 $W_p = 1.5 \cdot 10^5$ - the dimensionless washout ratio for the particulate phase.

Wet deposition of gaseous phase

$$C_w^d = W_g C_a^g,$$

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

C.4. Gaseous exchange between atmosphere and soil

EVN-BETR and UK-MODEL

Air-soil diffusion

$$D_{air-soil} = (Soil\ Area \cdot Z_{air}) / [(Z_{air} / (MTC_{as} \cdot Z_{air} + MTC_{sw} \cdot Z_{water})) + 1 / MTC_{sabl}]$$

where Average soil depth = 10 cm;
Soil Area = $8.36 \cdot 10^{12}$ m²;
 $Z_{water} = Z_{air} / K_{AW} = 543$ mol/m³ Pa;
 MTC_{as} - soil air-phase diffusion transport velocity = 0.04 m/h;
 MTC_{sw} - soil water-phase diffusion transport velocity = 1×10^{-5} m/h;
 MTC_{sabl} - soil air boundary layer transport velocity = 1 m/h.

Air-soil rain dissolution

$$D_{air-soil} = Soil\ Area \cdot U_R \cdot Z_{water}$$

CliMoChem

cited from [Scheringer et al., 2003]

Diffusion from atmosphere to baresoil and vegetation-covered soil

$$\frac{dC_{gas}}{dt} = -(1 - Phi) \left\{ \frac{1}{v_{gasS}} + \frac{1}{vG + \frac{vL}{K_h} + \frac{vS}{\frac{K_h}{regc \cdot rhoom \cdot foc \cdot K_{ow}}}} \right\}^{-1} \cdot \frac{A_i}{V_{gas}} \cdot C_{gas}$$

Parameter	Description	Numeric Value	Reference
C_{gas}	concentration of substance in gaseous phase		
Φ	particle-bound fraction of the substance (see C.1)	between 0-1	
v_{gasS}	transfer velocity on the interface soil-atmosphere: air over soil	24 m/d	<i>Mackay and Paterson, 1991; Jury et al., 1983</i>
v_G	transfer velocity on the interface soil-atmosphere: air filled pores	calculation see below	
v_L	transfer velocity on the interface soil-atmosphere: water filled pores	calculation see below	
v_S	transfer velocity on the interface soil-atmosphere: sorbed phase	calculation see below	
f_{oc}	fraction of organic matter in soil: different for different types of soil.	baresoil: 0.02 vegetation-covered soil: variable, calculation see below	assumed
$regc$	regression coefficient from equation $K_{oc}=regc \cdot K_{ow}$, where K_{oc} is the partitioning coefficient of organic carbon and water	0.35 L/kg	<i>Seth et al., 1999</i>
ρ_{hum}	density of organic matter	2.5 kg/L	<i>Seth et al., 1999</i>
A_i	Area, i=bare soil, vegetation-covered soil	variable	
V_{gas}	Volume of gaseous phase	variable	
K_h	Henry's law constant	depending on substance compare substance property sheets, See Chapter 3 and Annex B.	
K_{ow}	Octanol/water partitioning coefficient	depending on substance compare substance property sheets, See Chapter 3 and Annex B.	

Analogous to the procedure in subsection C.3, the parameter v_{gasS} is changed if the year consists of exactly four seasons with varying temperatures (compare tables below).

bare soil:

season	$v_{gasS} =$
winter	$v_{gasS}/2$
spring	$v_{gasS}/1.5$
summer	v_{gasS}
fall	$v_{gasS}/1.5$

vegetation-covered soil:

season	$v_{gasS} =$
winter	$v_{gasS}/(2 \cdot VegGrass + 5 \cdot VegCon + 3 \cdot VegDec)$
spring	$v_{gasS}/(1.5 \cdot VegGrass + 2.5 \cdot VegCon + 2 \cdot VegDec)$
summer	v_{gasS}
fall	$v_{gasS}/(1.5 \cdot VegGrass + 2.5 \cdot VegCon + 2 \cdot VegDec)$

The vegetation cover consists of three types: Grass, Coniferous Forest and Deciduous Forest. The variables VegGrass, VegCon and VegDec describe the fraction of the vegetation-covered soil occupied by the different cover types. Their numeric value is between 0-1 and depend on the climatic zone.

Calculation of v_G , v_L , v_S [*Jury et al., 1983*].

When calculating the v_i -value, the corresponding D_i -value must be used (eg. for calculating v_G , the D_G -value is used):

$$v_i = \frac{D_i}{\frac{h_{soil}}{2}} \cdot \left[\frac{K_h}{regc \cdot \rho_{hum} \cdot f_{OC} \cdot K_{ow} (1 - frac_{wsoil} - frac_{airsoil}) + frac_{wsoil} + frac_{airsoil} \cdot K_h} \right]$$

Parameter	Description	Numeric value	Reference
v_i	vG, vS, vL		
DG	diffusion coefficient in soil air pores	$8.0469 \cdot 10^{-3} \text{ m}^2/\text{d}$ (calculation see below)	
DL	diffusion coefficient in soil water pores	$3.10885 \cdot 10^{-6} \text{ m}^2/\text{d}$ (calculation see below)	
DS	diffusion coefficient in soil sorbed phase	$5.5 \cdot 10^{-7} \text{ m}^2/\text{d}$	<i>Elzein and Balesdent, 1995</i>
h_{soil}	height of soil	0.1 m	
$regc$	regression coefficient from equation $K_{oc} = regc K_{ow}$ where K_{oc} is the partitioning coefficient of organic carbon and water	0.35 L/kg	<i>Seth et al., 1999</i>
$rhoom$	density of organic matter	2.5 kg/L	<i>Seth et al., 1999</i>
$frac_{wsoil}$	part of water in soil	0.3	<i>Scheringer, 1996</i>
$frac_{airsoil}$	part of air in soil	0.2	<i>Scheringer, 1996</i>
f_{oc}	fraction of organic matter in soil: different for different types of soil.	baresoil: 0.02 vegetation-covered soil: variable, calculation see below	assumed
K_h	Henry's law constant	depending on substance, compare substance property sheets, See Chapter 3 and Annex B.	
K_{ow}	Octanol/water partitioning coefficient	depending on substance, compare substance property sheets, See Chapter 3 and Annex B.	

$$DG = 0.43 \cdot \left(\frac{frac_{airsoil}^{\frac{10}{3}}}{(frac_{airsoil} + frac_{wsoil})^2} \right)$$

$$DL = 0.000043 \cdot \left(\frac{frac_{wsoil}^{\frac{10}{3}}}{(frac_{airsoil} + frac_{wsoil})^2} \right)$$

Calculation of the fraction of organic matter (f_{oc}) in the vegetation covered soil

The model contains three types of vegetation. For each type, the f_{oc} is different (see table below). Depending on the composition of a climatic zone, f_{oc} is calculated as follows:

$$f_{oc_i} = fraction_{grass_i} \cdot f_{oc_{grass}} + fraction_{dec_i} \cdot f_{oc_{dec}} + fraction_{con_i} \cdot f_{oc_{con}}$$

Parameter	Description	Numeric value	Reference
f_{oc_i}	fraction of organic matter in vegetation-covered soil in climatic zone i		
$f_{oc_{grass}}$	fraction of organic matter in grass covered soil	0.19	<i>Meijer et al., 2002</i>
$f_{oc_{dec}}$	fraction of organic matter in deciduous forest covered soil	0.71	
$f_{oc_{con}}$	fraction of organic matter in coniferous forest covered soil	0.55	
$fraction_{grass_i}$	fraction of grass of total vegetation in climatic zone i	variable	
$fraction_{dec_i}$	fraction of deciduous forest of total vegetation in climatic zone i	variable	
$fraction_{con_i}$	fraction of coniferous forest of total vegetation in climatic zone i	variable	

Diffusion from baresoil and vegetation-covered soil to the atmosphere

$$\frac{dC_{gas}}{dt} = \frac{K_h}{regc \cdot rhoom \cdot f_{oc} \cdot K_{ow}} \cdot \left(\frac{1 - \frac{tsp}{rho_{part}} + k_{partair} \cdot rho_{part} \cdot \frac{tsp}{rho_{part}}}{1 - frac_{airsoil} - frac_{wsoil} + frac_{airsoil} \cdot \frac{K_h}{regc \cdot rhoom \cdot f_{oc} \cdot K_{ow}} \cdot \frac{frac_{wsoil}}{regc \cdot rhoom \cdot f_{oc} \cdot K_{ow}}} \right) \cdot \left[\frac{1}{v_{gasS}} + \frac{1}{vG + \frac{vL}{K_h} + \frac{vS}{\frac{K_h}{regc \cdot rhoom \cdot f_{oc} \cdot K_{ow}}}} \right]^{-1} \cdot \frac{A_i}{V_{gas}} \cdot C_{soil}$$

For explanation of the grey part in the formula see subsection 1.

Parameter	Description	Numeric value	Reference
C_{gas}	concentration of substance in gaseous phase		
C_{soil}	concentration of substance in soil		
$regc$	regression coefficient from equation $K_{oc} = regc K_{ow}$, where K_{oc} is the partitioning coefficient of organic carbon and water	0.35 L/kg	Seth et al., 1999
ρ_{oom}	density of organic matter	2.5 kg/L	Seth et al., 1999
tsp	total suspended particles	$86 \cdot 10^{-6}$ g/m ³	Bennett et al., 2001, only mentioned
ρ_{hpart}	density of aerosols	$2 \cdot 10^6$ g/m ³	http://www.mpi-hd.mpg.de/dustgroup/~graps/earth/properties.html
$k_{partair}$	$k_{partair} = 0.55 \lg (K_{ow}/K_h) - 2.23$ (compare with 1)	in m ³ /g	Finizio et al., 1997
$frac_{airsoil}$	part of air in soil	0.2	Scheringer, 1996
$frac_{wsoil}$	part of water in soil	0.3	Scheringer, 1996
f_{oc}	fraction of organic matter in soil: different for different types of soil.	baresoil: 0.02 vegetation-covered soil: variable, calculation see subsection 1	assumed
A_i	Area, i = baresoil, vegetation-covered soil	variable	
V_{gas}	volume of gaseous phase	variable	
K_h	Henry's law constant	depending on substance compare substance property sheets, See Chapter 3 and Annex B.	
K_{ow}	octanol/water partitioning coefficient		

G-CIEMS

Typical formulation as that uses two thin-film theory of intermedia diffusion, with restricted diffusion for soil-side mass transfer. Air-side mass transfer coefficient is calculated as the ratio of molecular diffusivity and diffusion path length for air and the thickness of assumed air-side stagnant layer. Soil-side mass transfer coefficient is calculated by molecular diffusivity and effective diffusion path length for cavity air in soil, which is calculated by Millington-Quirk equation.

$$B_{ae} = B_a \cdot v_a^{10/3} / (v_a + v_w)^2$$

Where B_{ae} is effective diffusivity, B_a is molecular diffusivity in air, v_a is volumetric air content in soil, v_w is volumetric water content in soil. Effective mass transfer for soil side is calculated by combining this effective diffusivity with diffusion path length in soil. Total diffusive exchange process is calculated by combining effective mass transfer process in soil and normal mass transfer process in air-side.

Bulk soil compartment is assumed to be in equilibrium for chemical among soil organic matter, cavity air and cavity water. Soil concentration in our model is calculated as theoretical dry-base concentration assuming all content in bulk soil matrix is concentrated onto dry soil particles.

DEHM-POP

The air/soil gas exchange, $F_{exc,s}$ is given by:

$$F_{exc,s} = v_e (C_a / \rho_a - C_s / H_{s/a}),$$

where v_e is the exchange velocity, C_a is the concentration in the lowermost atmospheric layer, C_s is the concentration in the soil, ρ_a is the density of air at the measured height, and $H_{s/a}$ is the partitioning coefficient between soil and soil air. v_e is given by:

$$v_e = \frac{D_G^{air} a^{10/3} (1-l-a)^{-2} + D_L^{water} l^{10/3} (1-l-a)^{-2} H_{w/a}}{0.5 z_s},$$

where D_G^{air} is the air diffusion coefficient, D_L^{water} is the liquid diffusion coefficient, l and a is the water and air fractions in soil respectively, z_s is the soil depth, and $H_{w/a}$ is the dimensionless Henry law constant [Strand and Hov, 1996].

The partitioning between the soil air and the soil itself is given by:

$$H_{s/a} = \rho_b f_{OC} K_{OC} H_{w/a} + l H_{w/a} + a,$$

where ρ_b is the density, f_{OC} is the organic carbon fraction, and K_{OC} is the organic carbon partitioning coefficient [Strand and Hov, 1996]. K_{OC} is calculated as: $K_{OC} = 0.41 \cdot K_{OW}$ [Mackay, 1999], where K_{OW} is the temperature dependent octanol-water partitioning coefficient given by:

$$K_{OW}(T) = K_{OW}(T_{ref}) \exp\left(\frac{\Delta U_{OW}}{R}\right) \left(\frac{1}{T_{ref}} - \frac{1}{T}\right),$$

where T is the temperature, T_{ref} is the reference temperature $T_{ref} = 298.15$ K, R is the molar gas constant ($R = 8.314$ J/mol K), and ΔU_{OW} is the energy of the phase transfer from octanol to water [Beyer et al., 2002].

Values used for the three modelled PCB congeners are [Beyer et al., 2002]:

PCB 153:	$K_{OW}(T_{ref}) = 5.62 \cdot 10^6$	$\Delta U_{OW} = -17.5 \times 10^3$ J/mol
PCB 28:	$K_{OW}(T_{ref}) = 5.13 \cdot 10^5$	$\Delta U_{OW} = -18.4 \times 10^3$ J/mol
PCB 180:	$K_{OW}(T_{ref}) = 1.54 \cdot 10^7$	$\Delta U_{OW} = -8.27 \times 10^3$ J/mol

The water air partitioning coefficient (the dimensionless Henry's law coefficient) is assumed temperature dependent and is given by:

$$H_{w/a} = \exp\left(-\frac{\Delta H_H}{RT} + \frac{\Delta S_H}{R}\right),$$

where T is the temperature, R is the molar gas constant, ΔH_H is the enthalpy (the slope when $H_{w/a}$ is plotted against $1/T$) and ΔS_H is the entropy of the phase change from the dissolved phase to the gas phase (the intercept when $H_{w/a}$ is plotted against $1/T$) [Bamford et al., 2000]. ΔH_H and ΔS_H are determined from laboratory experiments.

Values used for the three modelled PCB congeners are [Bamford et al., 2000]:

PCB 153:	$\Delta H_H = 66.1 \times 10^3$ J/mol and	$\Delta S_H = 190$ J/(mol K)
PCB 28:	$\Delta H_H = 32.5 \times 10^3$ J/mol and	$\Delta S_H = 74$ J/(mol K)
PCB 180:	$\Delta H_H = 143.6 \times 10^3$ J/mol and	$\Delta S_H = 447$ J/(mol K)

The soil concentrations assuming equilibrium in the modelling experiments are found by setting the flux equal to zero and isolating:

$$F_{exc,s} = v_e (C_a / \rho_a - C_s / H_{s/a}) = 0 \Rightarrow (C_a / \rho_a - C_s / H_{s/a}) = 0 \Rightarrow C_s = C_a H_{s/a} / \rho_a.$$

SimpleBox

cited from [Brandes et al., 1996]

Values for the overall mass transfer coefficients for gas absorption and volatilization may be estimated using the classical two-film resistance model. In the case of transport across the air-soil interface, the soil-side of the interface is treated as a pair of parallel resistances (air phase and water phase of the soil). The following equations may be used:

$$GASABS_{soil[S]} = \frac{kasl_{air[S]} \cdot kasl_{soilair[S]} + kasl_{air[S]} \cdot kasl_{soilwater[S]} / K_{air-water[S]}}{kasl_{air[S]} + kasl_{soilair[S]} + kasl_{soilwater[S]} / K_{air-water[S]}} - (1 - FRass_{aerosol[S]})$$

with $GASABS_{soil[S]}$ - overall mass transfer coefficient for gas absorption across the air-soil interface, referenced to air at scale S [$m_{air} \cdot s^{-1}$] (D);

$kasl_{air[S]}$ - partial mass transfer coefficient at the air-side of the air-soil interface at scale S [$m_{air} \cdot s^{-1}$] (A);

$kasl_{soilair}[S]$ - partial mass transfer coefficient at the soilair-side of the air-soil interface at scale S [$m_{air} \cdot s^{-1}$] (A);
 $kasl_{soilwater}[S]$ - partial mass transfer coefficient at the soilwater-side of the air-soil interface at scale S [$m_{water} \cdot s^{-1}$] (A);
 $K_{air-water}[S]$ - air-water equilibrium distribution constant at scale S [$m_{water}^3 \cdot m_{air}^{-3}$] (A);
 $FRass_{aerosol}[S]$ - fraction of the chemical in air that is associated with aerosol particles at scale S [-] (A).

And, since the quotient of the mass transfer coefficients for gas absorption and volatilization is equal to the volume-based intermedia partition coefficient:

$$VOLAT_{soil\ i}[S] = \frac{GASABS_{soil\ i}[S]}{1 - FRass_{aerosol}[S]} \cdot \frac{K_{air-water}[S]}{K_{soil\ i-water}[S]}$$

with $VOLAT_{soil\ i}[S]$ - overall mass transfer coefficient for volatilization across the air-soil interface, referenced to soil at scale S [$m_{soil} \cdot s^{-1}$] (D);
 $GASABS_{soil\ i}[S]$ - overall mass transfer coefficient for gas absorption across the air-soil interface, referenced to air at scale S [$m_{air} \cdot s^{-1}$] (D);
 $FRass_{aerosol}[S]$ - fraction of the chemical in air that is associated with aerosol particles at scale S [-] (A);
 $K_{air-water}[S]$ - air-water equilibrium distribution constant at scale S [$m_{water}^3 \cdot m_{air}^{-3}$] (A);
 $K_{soil\ i-water}[S]$ - soil i-water equilibrium distribution constant at scale S [$m_{water}^3 \cdot m_{soil}^{-3}$] (A);

The partial mass transfer coefficients at the air-soil interface may be derived using the reasoning suggested by Mackay *et al.* [1992].

According to this reasoning, the value for the air side may be taken equal to the value at the air-water interface:

$$kasl_{air} = kaw_{air}$$

with $kasl_{air}$ - partial mass transfer coefficient at the air-side of the air-soil interface [$m_{air} \cdot s^{-1}$] (A);
 kaw_{air} - partial mass transfer coefficient at the air-side of the air-water interface [$m_{air} \cdot s^{-1}$] (A).

Mass transfer in the soil air phase is treated as molecular diffusion in the gas phase of a porous solid medium, characterized by an effective diffusivity of $10^{-3} m^2 \cdot hr^{-1}$ and a diffusion path length of 5 cm. This leads to:

$$kasl_{soilair} = 5.56 \cdot 10^{-6} m / s^{-1}$$

with $kasl_{soilair}$ - partial mass transfer coefficient at the soilair-side of the air-soil interface [$m_{air} \cdot s^{-1}$] (A).

Mass transfer in the soil water phase is similarly treated as molecular diffusion in the water phase of a porous solid medium, characterized by an effective diffusivity of $10^{-7} m^2 \cdot hr^{-1}$ and a diffusion path length of 2 cm, leading to:

$$kasl_{soilwater} = 5.56 \cdot 10^{-10} m \cdot s^{-1}$$

with $kasl_{soilwater}$ - partial mass transfer coefficient at the soilwater-side of the air-soil interface [$m_{water} \cdot s^{-1}$] (A).

CAM/POPs

The exchange process depends on the balance between two transfer processes: the chemical transfer between deep soil layers and surface soil, and the exchange of the chemical vapour between the soil surface and the atmosphere.

PCBs move through the soil by advective diffusion. Quantitatively, it is given by Fick's Law. The rate of change of concentration of PCBs in the soil is simplified as:

$$\frac{\partial C_G}{\partial t} = D_{ES} \frac{\partial^2 C_G}{\partial z^2}$$

where C_G is the gaseous phase concentration in soil and D_{ES} (m^2/s) is the effective diffusivity of the chemical in the soil matrix. The effective diffusivity will be written as a function of K_{SA} and K_{AW} assuming that the porosity is not equal to zero and the water body still contains soil particles. The expression may be simplified as:

$$D_{ES} = \frac{\left[\left(\frac{a^{10/3}}{\phi^2} \right) \cdot D_{PCBair} + \left(\frac{\theta^{10/3}}{\phi^2} \right) \cdot \frac{D_{PCBwater}}{K_{AW}} \right]}{K_{SA} + a + \frac{\theta}{K_{AW}}}$$

where a is the volumetric air content (m^3 air/ m^3 soil), θ is the volumetric water content (m^3 water/ m^3 soil), and ϕ is the porosity (volume pore space/volume soil), $D_{PCB,air}$ is the air-side POPs diffusion coefficients in the soil matrix, $D_{PCB,water}$ is the water-side POPs diffusion coefficients in the soil matrix.

$D_{PCB,air}$ ($cm^2/s \cdot 10^{-2}$)

Congener	T = 0 °C	T = 5 °C	T = 10 °C	T = 15 °C	T = 20 °C	T = 25 °C
PCB153	4.12	4.26	4.39	4.53	4.67	4.81
PCB180	3.99	4.12	4.25	4.38	4.52	4.65

$D_{PCB,water}$ ($cm^2/s \cdot 10^{-6}$)

POPs	T = 0 °C	T = 5 °C	T = 10 °C	T = 15 °C	T = 20 °C	T = 25 °C
PCB153	2.55	3.00	3.50	4.05	4.65	5.30
PCB180	2.45	2.89	3.36	3.89	4.47	5.10

K_{sa} is the soil-air partition coefficient (volume air/volume soil).

$$K_{sa} = \frac{K_{sw}}{K_{aw}} = 0.411 \cdot f_{OC} \cdot \rho_b \cdot K_{oa} \quad \text{and, } \rho_b = \rho_{soil} \cdot (1 - \phi)$$

where ρ_b is the bulk soil density (in kg/L), ρ_{soil} is soil density (kg/L), f_{OC} is the mass fraction of organic carbon present in the particulate matter in soil (kg organic carbon /kg soil).

K_{oa} is the octanol-air partition coefficient.

$$\log_{10} K_{oa} = a/T + b$$

$$a = -529 - 19.25 \log P \quad \text{and} \quad b = 8.2995 - 0.95 \log P$$

where T is temperature (K), P is vapour pressure, and a and b are parameters depended on vapour pressure of POPs.

MSCE-POP

Partitioning. The scheme of exchange processes used in the model is displayed in Fig.C1.

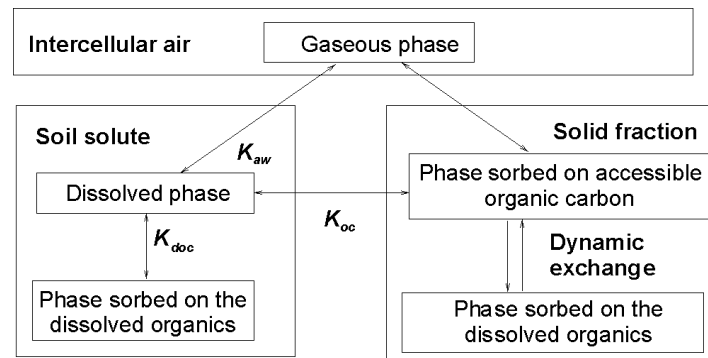


Fig.C1. Scheme of POP processes in soil used in MSCE-POP model

The total volume concentration in soil C is expressed as the sum of the concentration C^0 of a pollutant in gaseous, dissolved, sorbed on dissolved organics, and sorbed on accessible part of solid soil fraction phases and concentration C^1 of a pollutant sorbed on deep (potentially accessible) soil solid matter. It is supposed that all phases except for that sorbed on potentially accessible soil solids are in the instantaneous equilibrium with one another. Following [Jacobs and van Pul, 1996], the concentration C^0 , ng/m³ is then expressed via mass concentration C_s of a pollutant absorbed by the soil matter, ng/kg, volume concentration C_d of a pollutant dissolved in the soil water, ng/m³, volume concentration C_{doc} of a pollutant sorbed on the dissolved organics, ng/m³, and gas-phase volume concentration C_g of a pollutant in the soil air, ng/m³:

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

where $\rho_s = 1350$ - bulk density of solid soil material, kg/m³;

$\alpha_w = 0.3$ - volumetric water content of the soil;

$\alpha_a = 0.2$ - volumetric air content of the soil.

The concentration in each phase may be represented by C^0 using soil partitioning coefficients R_s , R_d and R_g :

$$C = R_s C^s = R_d C^d = R_g C^g,$$

where $R_d = \alpha_w + (\rho_s f_{oc} K_{oc} + \alpha_a K_H) / (1 + c_{doc} K_{doc})$;

$$R_s = R_d (1 + c_{doc} K_{doc}) / (f_{oc} K_{oc});$$

$$R_g = R_d (1 + c_{doc} K_{doc}) / K_H;$$

f_{oc} is the fraction of organic carbon in soil;

K_H is the dimensionless Henry's law constant (see above),

K_{oc} is the organic carbon distribution coefficient;

K_{doc} is dissolved organic carbon/water partitioning coefficient.

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:

$$K_{oc} = 0.41 \cdot K_{ow}$$

[Karikhoff, 1981], and

$$\log K_{doc} = 0.98 \log K_{ow} - 0.39 \quad \text{for PAHs}$$

$$\log K_{doc} = 0.93 \log K_{ow} - 0.54 \quad \text{for PCBs}$$

[J.Poershman and F.D.Kopinke, 2001]. The latter relation obtained for a number of POPs with wide range of K_{ow} can be also used for other POPs (PCDD/Fs, HCB, γ -HCH) [Vasilieva and Shatalov, 2002].

The exchange of a POP between easily accessible and potentially accessible OC fractions is assumed to be a process of first order:

$$\frac{dC^0}{dt} = k(C^1 - C^0)$$

$$\frac{dC^1}{dt} = k(C^0 - C^1)$$

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

Vertical transport. The migration of a pollutant over the vertical profile in soil is assumed to be due to diffusion and transport with convective water flux J_w . The corresponding equation is:

$$\frac{\partial C}{\partial t} + \frac{J_w}{R_d} \frac{\partial C}{\partial z} = D_E \frac{\partial^2 C}{\partial z^2} - k_{soil} C$$

where D_E is the effective gas-liquid diffusion coefficient, m^2/s ,
 k_{soil} is the degradation rate constant for soil, s^{-1} .

The coefficient D_E is determined by the following equation:

$$D_E = \frac{\xi_g D_g}{R_g} + \frac{\xi_l D_l}{R_d} + D_b,$$

where D_g, D_l are the molecular diffusion coefficient for gas and liquid;

$\xi_g = a^{10/3} / \phi^2$, $\xi_l = \theta^{10/3} / \phi^2$ are gas and liquid tortuosity factors;

ϕ is the porosity of soil (assumed $\phi = 0.5$);

D_b is effective diffusion coefficient due to bioturbation (assumed $D_b = 6 \cdot 10^{-12}$, [McLachlan et al., 2002]).

Liquid flux J_w is supposed to be equal to precipitation intensity h_p , m/c during rain events and has opposite direction (upward) for certain period after rain events. This period is chosen to be 5 days as model assumption. Preliminary estimations show low model sensitivity to this parameter. The value of the upward flux is chosen in such a way that 60% of precipitation amount is evaporated to the atmosphere (evaluated on the basis of data from [Atmosphere Handbook, 1991]).

Gaseous exchange with the atmosphere. The gaseous exchange between soil and the atmosphere is parameterized using resistance analogy.

The gaseous flux of POP from the atmosphere into the soil is driven by the difference between atmospheric gas concentration C_a^g at the air reference level (z_a - equal to half of the height of the lower atmospheric layer) and the soil gas-phase concentration C_s^g at the soil reference level at depth $z_s = \Delta z_1/2$ (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. C.2).

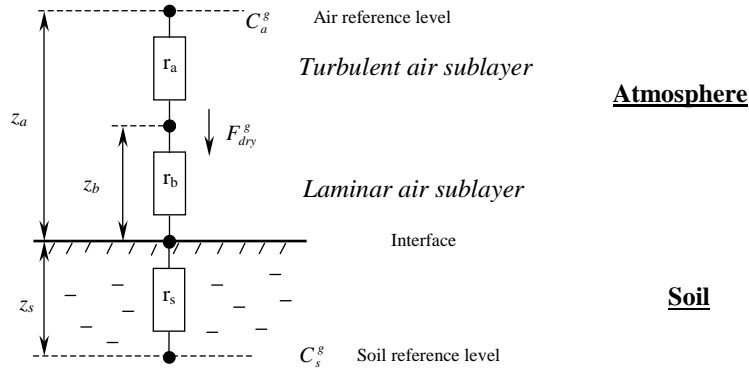


Fig. A2. Resistance scheme used for the description of gaseous exchange between soil and the atmosphere

- Turbulent air sublayer resistance r_a , s/m that is the resistance to transporting through turbulent air sublayer (from z_a to z_b . The latter is laminar sublayer height);
- Laminar surface air sublayer resistance r_b , s/m that is the resistance to transporting through laminar surface air sublayer (z_b) to the interface;
- Surface soil resistance r_s , s/m that is the resistance to transporting from surface soil interface to the soil reference level (z_s).

Hence, the formula for atmosphere/soil flux is:

$$F_{dry}^g = \frac{C_a^g - C_s^g}{r_a + r_b + r_s},$$

where r_a is atmospheric resistance, and:

$$C_s^g = \frac{C(z_1) (2D_E / \Delta z_1 - qJ_w / R_d)}{R_g (2D_E / \Delta z_1 + pJ_w / R_d)}$$

$$r_s = \frac{1}{R_g (2D_E / \Delta z_1 + pJ_w / R_d)}$$

$$r_b = \frac{2}{\kappa u_*} \left(\frac{Sc}{Pr} \right)^{2/3},$$

where Pr = 0.71 - Prandtl number;

Sc = n/D_a - Schmidt number;

$n = 1.5 \cdot 10^{-5}$ - kinematic viscosity of air, m²/s;

D_a - the molecular diffusion coefficient of the pollutant in air, m²/s;

D_E - the molecular diffusion coefficient of the pollutant in air, m²/s;

J_w - the convective water flux equal to mean annual precipitation intensity, m/c;

R_d - the soil partitioning coefficient, see 2.16 above, dimensionless;

u_* - the friction velocity, m/s;

$p = 1$ and $q = 0$ for downward water flux and $p = 0$ and $q = 1$ for upward water flux.

C.5. Gaseous exchange between atmosphere and seawater

EVN-BETR and UK-MODEL

Air-Water Diffusion

$$D = \text{Sea Area} / [(1 / (MTC_{\text{air}} \cdot Z_{\text{air}})) + (1 / (MTC_{\text{sea}} \cdot 0.8 \cdot Z_{\text{water}}))]$$

where Average Seawater depth = 87.5 m;

Sea Area = $5.63 \cdot 10^{12}$ m²;

MTC_{air} - air side air-sea transport velocity = 30 m/h;

MTC_{sea} - sea side air-sea transport velocity = 0.03 m/h.

Rain Dissolution to Water

$$D = \text{Sea Area} \cdot \text{Rain Rate} \cdot Z_{\text{water}}$$

CliMoChem

cited from [Scheringer et al., 2003]

Diffusion from atmosphere to seawater

$$\frac{dC_{\text{gas}}}{dt} = -(1 - \Phi) \cdot \left(\frac{V_{\text{gasW}} \cdot V_{\text{water}}}{K_h \cdot V_{\text{gasW}} + V_{\text{water}}} \right) \frac{A_{\text{water}}}{V_{\text{gas}}} \cdot C_{\text{gas}}$$

Parameter	Description	Numeric value	Reference
C_{gas}	concentration of substance in gaseous phase		
Φ	particle-bound fraction of substance (see C.1)	between 0-1	
V_{gasW}	transfer velocity on the interface atmosphere-water: air over water	72 m/d	Mackay and Paterson, 1991
V_{water}	transfer velocity on the interface atmosphere-water: in water	0.72 m/d	
A_{water}	Area of water	variable	
V_{gas}	Volume of gaseous phase	variable	
K_h	Henry's law constant	depending on substance compare substance property sheets, See Chapter 3 and Annex B.	

Diffusion from seawater to atmosphere

$$\frac{dC_{\text{gas}}}{dt} = (1 - \text{Phisusp}w) \cdot \left(\frac{\left(1 - \frac{tsp}{\rho_{\text{part}}}\right) \cdot \frac{1}{R \cdot T} + \frac{tsp}{\rho_{\text{part}}} \cdot k_{\text{partair}} \cdot \rho_{\text{part}} \cdot \frac{1}{R \cdot T}}{\left(1 - \text{sea}_{\text{part}}\right) \cdot \frac{1}{K_{\text{hmin}} \cdot R \cdot T_w} + \text{sea}_{\text{part}} \cdot \frac{1}{K_{\text{hmin}} \cdot R \cdot T_w} \cdot \text{fossusp} \cdot \text{regc} \cdot \rho_{\text{hoom}} \cdot K_{\text{owmin}}}} \right) \cdot \left(\frac{V_{\text{gasW}} \cdot V_{\text{water}}}{K_h \cdot V_{\text{gasW}} \cdot V_{\text{water}}} \right) \cdot \frac{A_{\text{water}}}{V_{\text{gas}}} \cdot C_{\text{water}}$$

Parameter	Description	Numeric value	Reference
C_{gas}	concentration of substance in gaseous phase		
$\text{Phisusp}w$	waterparticle-bound fraction of substance	calculation see below	
tsp	total suspended particles (in gaseous phase)	$86 \cdot 10^{-6} \text{ g/m}^3$	Bennett et al., 2001, only mentioned
ρ_{part}	density of aerosols	$2 \cdot 10^6 \text{ g/m}^3$	http://www.mpi-hd.mpg.de/dustgroup/~graps/earth/properties.html
R	universal gas constant	$8.3145 \text{ J/mol}\cdot\text{K}$	
T	Temperature	variable	
k_{partair}	$k_{\text{partair}} = 0.55 \lg(K_{\text{ow}}/K_h) - 2.23$ (compare with 1)	in m^3/g	Finizio et al., 1997
T_w	Temperature	variable, minimum at 270 K	
fossusp	global mean organic part of sea particles	0.3	Wania and Mackay, 1995
regc	regression coefficient from equation $K_{\text{oc}} = \text{regc} K_{\text{ow}}$, where K_{oc} is the Partitioning coefficient of organic carbon and water	0.35 L/kg	Seth et al., 1999
ρ_{hoom}	density of organic matter	2.5 kg/L	Seth et al., 1999
sea_{part}	volume fraction of particles in seawater	$5 \cdot 10^{-8}$ for latitudes 90-81 degrees 10^{-7} for latitudes 81-72 degrees $5 \cdot 10^{-7}$ for latitudes 72-0 degrees	Wania and Mackay, 1995
V_{gasW}	transfer velocity on the interface atmosphere-water: air over water	72 m/d	Mackay and Paterson, 1991
V_{water}	transfer velocity on the interface atmosphere-water: in water	0.72 m/d	
A_{water}	Area of water	variable	
V_{gas}	Volume of gaseous phase	variable	
K_{owmin}	Octanol/water partitioning coefficient, where T_w is used for calculation of temperature dependence	depending on substance compare substance property sheets, See Chapter 3 and Annex B.	
K_{hmin}	Henry's law constant, where T_w is used for calculation of temperature dependence		
K_h	Henry's law constant		

Calculation of $\text{Phisusp}w$

$$\text{Phisusp}w = \frac{\text{fossusp} \cdot \text{regc} \cdot \rho_{\text{hoom}} \cdot K_{\text{ow}} \cdot \text{seapart}}{(1 + \text{fossusp} \cdot \text{regc} \cdot \rho_{\text{hoom}} \cdot K_{\text{ow}} \cdot \text{seapart})}$$

Parameter	Description	Numeric Value	Reference
$\text{Phisusp}w$	waterparticle-bound fraction of substance		
fossusp	global mean organic part of sea particles	0.3	Wania and Mackay, 1995
regc	regression coefficient from equation $K_{\text{oc}} = \text{regc} K_{\text{ow}}$, where K_{oc} is the partitioning coefficient of organic carbon and water	0.35 L/kg	Seth et al., 1999
ρ_{hoom}	density of organic matter	2.5 kg/L	Seth et al., 1999
sea_{part}	volume fraction of particles in seawater	$5 \cdot 10^{-8}$ for latitudes 90-81 degrees 10^{-7} for latitudes 81-72 degrees $5 \cdot 10^{-7}$ for latitudes 72-0 degrees	Wania and Mackay, 1995
K_{ow}	Octanol/water partitioning coefficient	depending on substance, compare substance property sheets, See Chapter 3 and Annex B.	

G-CIEMS

Typical formulation as that uses two thin-film theory of intermedia diffusion. Air-side and water-side mass transfer coefficient are calculated as the ratio of molecular diffusivity and diffusion path length for air and water. Same molecular diffusivity and diffusion path length are assumed on all water surfaces.

(Note: Gaseous fluxes using diffusive transportation module in our model is applied to the data in the Input data table in this calculation.)

DEHM-POP

The gaseous exchange between atmosphere and water is determined by a similar expression as for the gaseous exchange between atmosphere and soil:

$$F_{exc,o} = v_e (C_a - C_o / H_{w/a}),$$

where v_e is the exchange velocity, C_a is the concentration in the lowermost atmospheric layer, C_o is the concentration in the ocean, and $H_{w/a}$ is the partitioning coefficient between water and air (the dimensionless Henry's law constant). The exchange velocity is dependent on the wind speed and it is derived using the two-film layer resistance method.

SimpleBox

cited from [Brandes et al., 1996]

Values for the overall mass transfer coefficients for gas absorption and volatilization may be estimated using the classical two-film resistance model. In the case of transport across the air-water interface, the overall transfer coefficients follow from summation of the resistances at the water- and air sides of the interface. The following equations may be used:

$$GASABS_{water\ i[S]} = \frac{kaw_{air[S]} \cdot kaw_{water[S]}}{kaw_{air[S]} \cdot K_{air-water[S]} + kaw_{water[S]}} \cdot (1 - FRass_{aerosol[S]})$$

- with
- $GASABS_{water\ i[S]}$ - overall mass transfer coefficient for gas absorption across the air-water interface, referenced to air at scale S [$m_{air} \cdot s^{-1}$] (D);
 - $kaw_{air[S]}$ - partial mass transfer coefficient at the air-side of the air-water interface at scale S [$m_{air} \cdot s^{-1}$] (A);
 - $kaw_{water[S]}$ - partial mass transfer coefficient at the water-side of the air-water interface at scale S [$m_{water} \cdot s^{-1}$] (A);
 - $K_{air-water[S]}$ - air-water equilibrium distribution constant at scale S [$m_{water}^3 \cdot m_{air}^{-3}$] (A);
 - $FRass_{aerosol[S]}$ - fraction of the chemical in air that is associated with aerosol particles at scale S [-] (A).

And, since the quotient of the mass transfer coefficients for gas absorption and volatilization is equal to the volume-based intermedia partition coefficient:

$$VOLAT_{water\ i[S]} = \frac{GASABS_{water\ i[S]} \cdot K_{air-water[S]} \cdot FRdisslvd_{water\ i[S]}}{1 - FRass_{aerosol[S]}}$$

- with
- $VOLAT_{water\ i[S]}$ - overall mass transfer coefficient for volatilization across the air-water interface, referenced to water at scale S (D);
 - $GASABS_{water\ i[S]}$ - overall mass transfer coefficient for gas absorption across the air-water interface, referenced to air at scale S [$m_{air} \cdot s^{-1}$] (D);
 - $FRass_{aerosol[S]}$ - fraction of the chemical in air that is associated with aerosol particles at scale S [-] (A);
 - $K_{air-water[S]}$ - air-water equilibrium distribution constant at scale S [$m_{water}^3 \cdot m_{air}^{-3}$] (A);
 - $FRdisslvd_{water(i)[S]}$ - dissolved fraction of water column i at scale S [-] (A).

A value for the partial mass transfer coefficient at the air-side of the air-water interface may be derived from the equation [Schwarzenbach et al., 1993]:

$$kaw_{air} = 0.01 \cdot (0.3 + 0.2 \cdot WINDSPEED_{[S]}) \cdot \left(\frac{0.018}{MOL\ WEIGHT} \right)^{0.4355}$$

- with
- kaw_{air} - partial mass transfer coefficient at the air side of the air-water interface [$m_{air} \cdot s^{-1}$] (A);

$WINDSPEED_{[S]}$ - average windspeed at 10 m above the surface at scale S [$m \cdot s^{-1}$] (A);
 $MOL\ WEIGHT$: - molecular weight of the chemical [$kg \cdot mol^{-1}$] (A);
0.018 - molecular weight of water (C).

For the partial mass transfer coefficient at the water side of the air-water interface, the equation of [Schwarzenbach et al., 1993] may be used:

$$k_{aw_{water}} = 0.01 \cdot (0.004 + 0.00004 \cdot WINDSPEED_{[S]}) \cdot \left(\frac{0.032}{MOLWEIGHT} \right)^{0.4047}$$

with $k_{aw_{water}}$ - partial mass transfer coefficient at the water-side of the air-water interface [$m \cdot water \cdot s^{-1}$] (A);
 $WINDSPEED_{[S]}$ - average windspeed at 10 m above the surface at scale S [$m \cdot s^{-1}$] (A);
 $MOL\ WEIGHT$ - molecular weight of the chemical [$kg \cdot mol^{-1}$] (A);

CAM/POPs

The air concentration above water, C_G , can be solved as:

$$C_G(t) = C_W \cdot K_{AW} + (C_{GO} - C_W \cdot K_{AW}) \exp(-K_{TA} \cdot t / h)$$

where C_{GO} is the initial air concentration, C_W is the water concentration, h is the height (m), t is the time. The equation is used in air-water surface flux calculations. K_{AW} has been shown in the Section 3, K_{TA} overall air side mass transfer coefficient, (m/s).

$$K_{TA} = 1 / (1 / K_A + K_{AW} / K_W)$$

where K_A (air-side), K_W (water-side) are mass transfer velocity [Mackay et al., 1983; Schwarzenbach et al., 1993]:

$$K_A = 10^{-3} + 4.62 \cdot 10^{-4} \cdot (6.1 + 0.63 u_{10})^{0.5} u_{10} [SC_{pcb,air}]^{-0.67} \quad (m/s)$$

$$K_W = [2.5 \cdot (0.5246 + 1.6256 \cdot 10^{-2} \cdot T + 4.9946 \cdot 10^{-4} \cdot T^2) + 0.3 u_{10}^2] \cdot (SC_{pcb,water} / 660)^{-1/2} \quad (cm/h)$$

where the temperature, T , is in $^{\circ}C$, and the surface wind velocity at reference height of 10m, u_{10} , is in m/s. $SC_{pcb,air}$, $SC_{pcb,water}$ are Schmidt numbers.

MSCE-POP

For POP flux through the sea surface the following expression is used [Strukov, 2001].

$$F_z|_{z=0} = \alpha_1 (c_{ga} / K_{HR}(T) - c_d) ((1 - \alpha_2) D_\mu / \delta + \alpha_2 K_{HR} h_f),$$

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_{ga} and c_d - POP gas-phase and dissolved concentration in the surface atmosphere, ng/m^3 ;

$K_{HR}(T)$ - Henry's law constant depending on temperature, dimensionless;

$D_\mu = 5.14 \cdot 10^{-10}$ - molecular diffusion coefficient in water, m^2/s ;

$\delta_0 = 4 \cdot 10^{-5}$ - surface molecular layer depth at zero wind speed, m;

U_a - wind speed absolute value near the surface, m/s;

$h_f = 8 \cdot 10^{-3}$ - foam settling rate on the sea surface, m/s;

α_1 - coefficient introduced for the description of surface sea area expansion due to wave disturbance;

α_2 - describes the relative sea surface area covered with foam at strong wind.

More detailed description of these processes is given in [Strukov et al., 2000].

C.6. Gaseous exchange between atmosphere and vegetation

EVN-BETR and UK-MODEL

Air-Vegetation Diffusion

The vegetation side vegetation-air transport velocity (Veg_airMTC) is calculated according to *Cousins et al.* [2001].

$$D = 1/((1/(Veg\ Area \cdot Veg_airMTC \cdot Z_{veg})) + (1/(Veg\ Area \cdot Air_VegMTC \cdot Z_{air})))$$

where: Veg_area - vegetation area = $8.36 \cdot 10^{12} \text{ m}^2$;

Veg_airMTC - vegetation side air-vegetation transport velocity = 10.8 m/h;

Air_VegMTC - air side air-vegetation transport velocity = 9 m/h;

Z_{veg} - fugacity capacity in vegetation = 462 mol/m³ Pa.

Air-Vegetation Rain Dissolution

$$D = Veg\ Area \cdot Rain\ Rate \cdot Z_{air} \cdot Foliage_rain$$

where Foliage_rain - fraction of rain intercepted by foliage = 0.1.

CliMoChem

cited from [Scheringer et al., 2003]

Diffusion from atmosphere to vegetation

$$\frac{dC_{gas}}{dt} = -(1 - Phi) \cdot v_{gasdiff} \cdot \frac{A_{veg}}{V_{gas}} \cdot C_{gas}$$

Parameter	Description	Numeric value	Reference
C_{gas}	concentration of substance in gaseous phase		
Phi	particle-bound fraction of the substance (see C.1)	between 0-1	
$v_{gasdiff}$	diffusion rate from atmosphere to vegetation	variable, depending on climatic zone*	
A_{veg}	Area of vegetation (identical with Area of vegetation-covered soil)	variable	
V_{gas}	Volume of gaseous phase	variable	

* - the model contains three types of vegetation. For each type, the diffusion rate ($v_{gasdiff}$) is different (see table below). Depending on the composition of a climatic zone, $v_{gasdiff}$ is calculated as follows:

$$v_{gasdiff}_i = fraction_{grass}_i \cdot v_{gasdiff}_{grass} + fraction_{dec}_i \cdot v_{gasdiff}_{dec} + fraction_{con}_i \cdot v_{gasdiff}_{con}$$

Parameter	Description	Numeric value	Reference
$v_{gasdiff}_i$	deposition rate in climatic zone i		
$v_{gasdiff}_{grass}$	deposition rate to grass	85.3 m/d	Möller, 2002
$v_{gasdiff}_{dec}$	deposition rate to deciduous forest	2207.28 m/d	Möller, 2002
$v_{gasdiff}_{con}$	deposition rate to coniferous forest	673.92 m/d	Möller, 2002
$fraction_{grass}_i$	fraction of grass of total vegetation in climatic zone i	variable	
$fraction_{dec}_i$	fraction of deciduous forest of total vegetation in climatic zone i	variable	
$fraction_{con}_i$	fraction of coniferous forest of total vegetation in climatic zone i	variable	

Diffusion from vegetation to atmosphere

$$\frac{dC_{gas}}{dt} = \left(f_{lipid} \cdot \frac{K_{ow}}{K_h} \cdot \left(1 - \frac{tsp}{\rho_{part}} + k_{partair} \cdot \rho_{part} \cdot \frac{tsp}{\rho_{part}} \right) \right)^{-1} \cdot v_{gasdiff} \cdot \frac{A_{veg}}{V_{gas}} \cdot C_{veg} \cdot vegvolfactor^2$$

Parameter	Description	Numeric value	Reference
C_{gas}	concentration of substance in gaseous phase		
C_{veg}	concentration of substance in vegetation		
f_{lipid}	fraction of lipids in vegetation	variable, depending on climate zone ^a	
tsp	totalsuspended particles	$86 \cdot 10^{-6} \text{ g/m}^3$	Bennett et al., 2001, only mentioned
ρ_{part}	density of aerosols	$2 \cdot 10^6 \text{ g/m}^3$	http://www.mpi-hd.mpg.de/dustgroup/~graps/earth/properties.html
$k_{partair}$	$K_{partair} = 0.55 \lg (K_{ow}/K_h) - 2.23$ (compare with 1)		Finizio et al., 1997
$v_{gasdiff}$	diffusion rate from atmosphere to vegetation	variable, depending on climatic zone ^b	
A_{veg}	Area of vegetation (= Area of vegetation-covered soil)	variable	
V_{gas}	Volume of gaseous phase	variable	
$vegvolfactor$	factor taking into account the different vegetation volumes for different seasons	variable, depending on the climatic zone and the season*	
K_{ow}	Octanol/water partitioning coefficient	depending on substance, compare substance property sheets, See Chapter 3 and Annex B.	
K_h	Henry's law constant		

* - the model contains three types of vegetation. For each type, the fraction of lipid (f_{lipid}) is different (see table below). Depending on the composition of a climatic zone, f_{lipid} is calculated as follows:

$$flipid_i = fractiongrass_i \cdot flipid_{grass} + fractiondec_i \cdot flipid_{dec} + fractioncon_i \cdot flipid_{con}$$

Parameter	Description	Numeric value	Reference
$flipid_i$	fraction of lipids in vegetation in climatic zone i		
$flipid_{grass}$	fraction of lipids in grass	0.02	Möller, 2002
$flipid_{dec}$	fraction of lipids in deciduous forest	0.01	Möller, 2002
$flipid_{con}$	fraction of lipids in coniferous forest	0.06	Möller, 2002
$fractiongrass_i$	fraction of grass of total vegetation in climatic zone i	variable	
$fractiondec_i$	fraction of deciduous forest of total vegetation in climatic zone i	variable	
$fractioncon_i$	fraction of coniferous forest of total vegetation in climatic zone i	variable	

^b The model contains three types of vegetation. For each type, the diffusion rate ($v_{gasdiff}$) is different (see table below). Depending on the composition of a climatic zone, $v_{gasdiff}$ is calculated as follows:

$$v_{gasdiff}_i = fractiongrass_i \cdot v_{gasdiff}_{grass} + fractiondec_i \cdot v_{gasdiff}_{dec} + fractioncon_i \cdot v_{gasdiff}_{con}$$

Parameter	Description	Numeric Value	Reference
$v_{gasdiff}_i$	deposition rate in climatic zone i		
$v_{gasdiff}_{grass}$	deposition rate to grass	85.3 m/d	Horstmann and McLachlan, 1998;
$v_{gasdiff}_{dec}$	deposition rate to deciduous forest	2207.28 m/d	Möller, 2002
$v_{gasdiff}_{con}$	deposition rate to coniferous forest	673.92 m/d	
$fractiongrass_i$	fraction of grass of total vegetation in climatic zone i	variable	
$fractiondec_i$	fraction of deciduous forest of total vegetation in climatic zone i	variable	
$fractioncon_i$	fraction of coniferous forest of total vegetation in climatic zone i	variable	

Because of increased stability of the atmosphere in the spring, fall and winterseason, the deposition rates $v_{gasdiff}_{grass}$, $v_{gasdiff}_{dec}$ and $v_{gasdiff}_{con}$ are divided by 3 for the winterseason and by 2 for the spring and fall seasons [Horstmann, and McLachlan, 1998].

The winter value of the vegetation volume is set to 10% of the summer value, spring and fall values are interpolations between summer and winter value. The *vegvolfactor* is calculated weighing the volumes of the seasons with the spring volume (which is equal to the fall volume), resulting in the following values:

season	<i>vegvolfactor</i>
spring	1
summer	1.82
fall	1
winter	0.182

Exception to this calculation is the coniferous vegetation volume which is the same for all the seasons, and the vegetation volume in the equator region which is assumed to be the same for all seasons.

Because the composition of vegetation varies for different climate zones, the *vegvolfactor* is weighed with the fractions of the respective vegetation types.

G-CIEMS

Similar to air-soil processes, but different parameters values.

DEHM-POP

Vegetation is not included in the model, and we have not made any calculations for this part of the inter-comparison.

SimpleBox

cited from [Brandes *et al.*, 1996]

Diffusive transport between air and vegetation by means of gas absorption and volatilization is described by:

$$\underline{DIFF_{air-veg\ i[S]} = XCH_{air-veg\ i[S]} \cdot C_{air[S]}}$$

with $DIFF_{air-veg\ i[S]}$ - diffusive mass flow from air to vegetation *i* at scale *S* by gas absorption [$\text{mol} \cdot \text{s}^{-1}$] (I);
 $XCH_{air-veg\ i[S]}$ - transport coefficient for gas absorption by vegetation *i* at scale *S* [$\text{m}_{\text{air}}^3 \cdot \text{s}^{-1}$] (I);
 $C_{air[S]}$ total concentration in air (gas phase + aerosol phase + rain water phase) at scale *S* [$\text{mol} \cdot \text{m}_{\text{air}}^{-3}$] (S).

$$\underline{XCH_{air-veg\ i[S]} = GASABS_{veg\ i[S]} \cdot AREA_{leaves\ i[S]}}$$

with $XCH_{air-veg\ i[S]}$ - transport coefficient for gas absorption to vegetation *i* at scale *S* [$\text{m}_{\text{air}}^3 \cdot \text{s}^{-1}$] (I);
 $GASABS_{veg\ i[S]}$ - overall mass transfer coefficient for gas absorption across the air-vegetation interface, referenced to air at scale *S* [$\text{m}_{\text{air}} \cdot \text{s}^{-1}$] (D);
 $AREA_{leaves\ i[S]}$ - leaf surface area at scale *S* [-] (D).

$$GASABS_{veg\ i[S]} = (1 - FRass_{aerosol[S]}) \cdot g_{veg\ i[S]}$$

with $GASABS_{veg\ i[S]}$ - overall mass transfer coefficient for gas absorption across the air-vegetation interface, referenced to air at scale *S* [$\text{m}_{\text{air}} \cdot \text{s}^{-1}$] (D);
 $FRass_{aerosol[S]}$ - fraction of the chemical in air that is associated with aerosol particles at scale *S* [-] (A);
 $g_{veg\ i[S]}$ - conductance [$\text{m} \cdot \text{s}^{-1}$] (D).

The conductance, g_{veg} , depends on the chemical properties, plant species and environmental conditions [Trapp and Matthies, 1995]:

$$\underline{g_{veg\ i[S]} = 0.001\ m \cdot s^{-1}}$$

with $g_{veg\ i[S]}$ conductance [$m \cdot s^{-1}$] (D)

may be taken as default value.

The volatilization mass flows are obtained from:

$$DIFF_{veg\ i-air[S]} = XCH_{veg\ i-air[S]} \cdot C_{veg\ i[S]}$$

with $DIFF_{veg\ i-air[S]}$ - diffusive mass flow from vegetation i to air at scale S by volatilization [$mol \cdot s^{-1}$] (I);
 $XCH_{veg\ i-air[S]}$ - transport coefficient for volatilization from vegetation i at scale S [$m_{veg}^3 \cdot s^{-1}$] (I);
 $C_{veg\ i[S]}$ - dissolved concentration in vegetation i at scale S [$mol \cdot m_{veg}^{-3}$] (S).

$$XCH_{veg\ i-air[S]} = VOLAT_{veg\ i[S]} \cdot AREA_{leaves\ i[S]}$$

with $XCH_{veg\ i-air}$ - transport coefficient for volatilization from vegetation i at scale S [$m_{veg}^3 \cdot s^{-1}$] (I);
 $VOLAT_{veg\ i[S]}$ - overall mass transfer coefficient for volatilization across the vegetation-air interface, referenced to vegetation i at scale S [$m_{water} \cdot s^{-1}$] (D);
 $AREA_{leaves\ i[S]}$ - leaf surface area at scale S [-] (D).

$$VOLAT_{veg\ i[S]} = \frac{g_{veg\ i[S]}}{K_{leaf\ i-air[S]}}$$

with $VOLAT_{veg\ i[S]}$ - overall mass transfer coefficient for volatilization across the air-vegetation interface, referenced to vegetation at scale S [$m_{air} \cdot s^{-1}$] (D);
 $g_{veg\ i[S]}$ - conductance [$m \cdot s^{-1}$] (D);
 $K_{leaf\ i-air[S]}$ - plant tissue-air partition coefficient at scale S [$m^3 \cdot m^{-3}$] (A).

CAM/POPs

Similar to air-soil processes.

MSCE-POP

Three types of vegetation are distinguished in the model: coniferous forest, deciduous forest, and grass. Coefficients governing exchange processes between the atmosphere and vegetation are determined separately for each of the above vegetation types. Besides, we consider forest litter as an intermediate medium between vegetation and soil. The description of these media is placed in this section.

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

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

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

$$R_{tot} = R_a + a_V / k,$$

where R_a - aerodynamic resistance of turbulent atmospheric layer;
 k - mass transfer coefficient, m/s;
 a_V - specific surface area of vegetation, m^2/m^3 (assumed value is 8000, see [Duyzer and van Oss, 1997]);

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

$$Q = C_V \frac{S \cdot LAI}{a_V},$$

where S - area covered by vegetation of a given type within a grid cell;
 LAI - 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]:

$$K_{Va} = mK_{OA}^n, \quad \text{C.1.}$$

where K_{OA} - partitioning coefficient between octanol and air;
 m, n - regression coefficients presented in Table C.5.

Table C5. Parameters of regression for equation C.1

	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. C.1 the temperature dependence of K_{OA} should be taken into account. In the model it is assumed that:

$$K_{oa} = K_{oa}^0 \exp \left[a_K \left(\frac{1}{T} - \frac{1}{T_0} \right) \right],$$

where as earlier $T_0 = 283.15$ K - reference temperature;
 K_{oa}^0 - K_{oa} value at the reference temperature;
 a_K - coefficient of K_{oa} temperature dependence, K.

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

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

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.

For PCB-153:

$$K_{oa}^0 = 3.64 \cdot 10^{10} \text{ - } K_{oa} \text{ value at the reference temperature;} \\ a_K = 10811 \text{ } ^\circ\text{K - coefficient of } K_{oa} \text{ temperature dependence.}$$

C.7. Degradation processes

CliMoChem

Degradation in atmosphere

$$\frac{dC_{gas}}{dt} = -(1 - Phi) \cdot k_{gas} \cdot C_{gas}$$

Parameter	Description	Numeric value	Reference
C_{gas}	Concentration of substance in atmosphere		
Φ	particle-bound fraction of the substance (see C.1)	between 0-1	
k_{gas}	first order degradation rate in the atmosphere	depending on substance compare substance property sheets, See Chapter 3 and Annex B.	

For calculations with PCBs, the degradation in the atmosphere is described as follows:

$$\frac{dC_{gas}}{dt} = -k \cdot c_{OH} \cdot C_{gas}$$

Parameter	Description	Numeric value	Reference
C_{gas}	Concentration of substance in atmosphere		
k_{gas}	second order degradation rate in the atmosphere in cm^3/s	depending on substance compare substance property sheets, See Chapter 3 and Annex B	
c_{OH}	concentration of OH-radicals in the atmosphere in $1/cm^3$	depending on temperature, calculation see below	<i>Beyer et al., 2002</i>

compare substance property sheets, See Chapter 3 and Annex B

$$c_{OH} = (0.5 + (T - 273.15) \cdot 0.4) \cdot 10^5 \text{ for } T \geq 273.15K$$

$$c_{OH} = 5 \cdot 10^4 \text{ for } T \leq 273.15K$$

Degradation in baresoil and vegetation-covered soil

$$\frac{dC_i}{dt} = -k_{soil} \cdot C_i$$

Parameter	Description	Numeric value	Reference
C_i	Concentration of substance in i, i: baresoil, vegetation-covered soil		
k_{soil}	first order degradation rate in soil	depending on substance compare substance property sheets, See Chapter 3 and Annex B	

Degradation in vegetation

$$\frac{dC_{veg}}{dt} = -k_{veg} \cdot C_{veg}$$

Parameter	Description	Numeric value	Reference
C_{veg}	Concentration of substance in vegetation		
k_{veg}	first order degradation rate	depending on substance compare substance property sheets, See Chapter 3 and Annex B	

Degradation in water

$$\frac{dC_{water}}{dt} = - \left(k_{water} + \frac{v_{partdep}}{h_{water}} \cdot \Phi_{susp} \right) \cdot C_{water}$$

Parameter	Description	Numeric value	Reference
C_{water}	Concentration of substance in water		
k_{water}	first order degradation rate	depending on substance compare substance property sheets, See Chapter 3 and Annex B	
$v_{partdep}$	velocity of particle deposition to deep sea	1.23 m/d	<i>Falkowski et al., 1998, Murray, 1992</i>
h_{water}	height of water	200 m	
Φ_{susp}	waterparticle-bound fraction of substance	calculated	

SimpleBox

cited from [Brandes et al., 1996]

Degradation in air

$$kdeg_{air[S]} = (1 - FRass_{aerosol[S]}) \cdot krad_{OH[S]}$$

- with $kdeg_{air[S]}$ - pseudo first order transformation rate constant in air at scale S [s^{-1}] (D);
 $FRass_{aerosol[S]}$ - fraction of the chemical in air that is associated with aerosol particles at scale S [-] (A);
 $krad_{OH[S]}$ - pseudo first order rate constant for reaction with OH-radicals at scale S [s^{-1}] (A).

As a default for $krad_{OH}$, it may be considered that nearly all organic chemicals show some reactivity with OH-radicals. According to Peijnenburg (personal communication), a half life of 160 days, equivalent to:

$$krad_{OH[S]} = \frac{\ln 2}{160} d^{-1}$$

- with $krad_{OH[S]}$ - pseudo first order rate constant for reaction with OH-radicals at scale S [d^{-1}] (A);
160 - maximum half-life for organic chemicals in air [d] may be taken as a minimum reactivity.

Degradation in water

A value for $kdeg_{water}$ may be obtained by means of the scaling procedure proposed by Struijs and Van den Berg [1995]. This procedure assumes that the pseudo first order rate constant for degradation in water is proportional to the concentration of bacteria in the water. The degradation rate is corrected by an empirical relationship which changes the degradation rate 50% per 10 degrees¹. The rate constant for surface water may be deduced from the rate constant observed in laboratory tests at 20 °C by scaling:

$$kdeg_{water\ i[S]} = kdeg_{test} \cdot \left(1.072^{TEMPERATURE_{[S]} - 293}\right) \cdot \frac{BACT_{water}}{BACT_{test}} \cdot FRdisslvd_{water\ i[S]}$$

- with $kdeg_{water\ i[S]}$ - pseudo first order degradation rate constant in water i at scale S [s^{-1}] (D);
 $FRdisslvd_{water(i)[S]}$ - dissolved fraction of water column i at scale S [-] (A);
 $kdeg_{test}$ - pseudo first order degradation rate constant in laboratory test [s^{-1}] (A);
 $BACT_{water}$ - concentration of bacteria in the water compartment [$cfu \cdot ml_{water}^{-1}$] (A);
 $BACT_{test}$ - concentration of bacteria in the laboratory test water [$cfu \cdot ml_{test\ water}^{-1}$] (A);
 $TEMPERATURE_{[S]}$ - temperature at scale S [K] (A).

It is further assumed in this procedure that a pseudo first order degradation rate constant may be obtained by extrapolation from the results of standard screening tests for ready biodegradability in water:

$$kdeg_{test} = \frac{\ln 2}{5} d^{-1} \text{ if } PASSreadytest = y$$
$$kdeg_{test} = \frac{\ln 2}{1000} d^{-1} \text{ if } PASSreadytest = n$$

- with $kdeg_{test}$ - pseudo first order degradation rate constant in laboratory test [d^{-1}] (A);
 $PASSreadytest$ - the result of a standard screening test; expressed as "y" if the chemical is "readily biodegradable" and "n" if the chemical is not "readily biodegradable".

For derivation of the degradation rate in water, the following default-values may be considered:

$$BACT_{test} = 4 \cdot 10^4 cfu \cdot ml^{-1}$$

¹ : the degradation rates in the EUSES-system are not temperature dependent. For a simulation of EUSES with SimpleBox 2.0 the $kdeg$ -values of EUSES must be entered.

with $BACT_{test}$ - concentration of bacteria in the laboratory test water [$\text{cfu} \cdot \text{ml}_{\text{test water}}^{-1}$] (A).

$$BACT_{\text{water}} = 4 \cdot 10^4 \text{ cfu} \cdot \text{ml}^{-1}$$

$BACT_{\text{water}}$ - concentration of bacteria in the water compartment [$\text{cfu} \cdot \text{ml}_{\text{water}}^{-1}$] (A).

Degradation in sediment

A value for $kdeg_{sed}$ may be obtained by means of the scaling procedure proposed by *Struijs and Van den Berg* [1995]. The degradation rate is corrected by an empirical relationship which changes the degradation rate 50% per 10 degrees. As with degradation in water, it is assumed that the degradation rate is related to the degradation rate constant observed in standard tests for (aerobic) ready degradability in water. Degradation in sediment is treated as disappearance from the water phase of the sediment. The concentration of bacteria, present in the pore water or at the surface of the solid phase (or both), in the sediment compartment is expressed on a pore water volume basis:

$$kdeg_{sed\ i[S]} = kdeg_{test} \cdot (1.072^{TEMPERATURE_{[S]} - 293}) \cdot \frac{BACT_{sed\ i[S]}}{BACT_{test}} \cdot FRdisslvd_{sed\ i[S]}$$

with $kdeg_{sed\ i[S]}$ - pseudo first order degradation rate constant in sediment [s^{-1}] (D);
 $kdeg_{test}$ - pseudo first order degradation rate constant in laboratory test [s^{-1}] (A);
 $BACT_{sed\ i[S]}$ - concentration of bacteria in sediment, expressed on a pore water basis [$\text{cfu} \cdot \text{ml}_{\text{pore water}}^{-1}$] (A);
 $BACT_{test}$ - concentration of bacteria in the laboratory test water [$\text{cfu} \cdot \text{ml}_{\text{test water}}^{-1}$] (A);
 $FRdisslvd_{sed\ i[S]}$ - fraction of the chemical in sediment, present in the pore water phase of the sediment [-];
 $TEMPERATURE_{[S]}$ - temperature at scale S [K] (A).

For derivation of the degradation rate in sediment, a value for $BACT_{sed}$ may be derived from:

$$BACT_{sed\ i[S]} = \frac{1.8 \cdot 10^9}{FRwater_{sed\ i[S]}}$$

with $BACT_{sed\ i[S]}$ - concentration of bacteria in sediment i, expressed on a pore water basis at scale S [$\text{cfu} \cdot \text{ml}_{\text{pore water}}^{-1}$] (A);
 $1.8 \cdot 10^9$ - concentration of bacteria reported in aerobic sediment [$\text{cfu} \cdot \text{cm}_{\text{sed}}^{-3}$];
 $FRwater_{sed\ i[S]}$ - volume fraction of the water phase of the sediment i at scale S [-] (A).

It should be noted that this procedure to derive a degradation rate constant in sediment applies only to aerobic sediments and that generally only the top few millimeters of the sediment are aerobic.

Degradation in soil

A value for $kdeg_{soil}$ may be obtained by means of the scaling procedure proposed by *Struijs and Van den Berg* [1995], in analogy with the derivation of $kdeg_{sed}$. The degradation rate is corrected by an empirical relationship which changes the degradation rate 50% per 10 degrees.

$$kdeg_{soil\ i[S]} = \frac{kdeg_{water\ i[S]} \cdot (1.072^{TEMPERATURE_{[S]} - 293})}{FRdisslvd_{water\ i[S]}} \cdot \frac{BACT_{soil\ water}}{BACT_{water}} \cdot FRdisslvd_{soil\ i[S]}$$

with $kdeg_{soil\ i[S]}$ - pseudo first order degradation rate constant in soil i at scale S [s^{-1}] (D);
 $kdeg_{water\ i[S]}$ - pseudo first order degradation rate constant in water i at scale S [s^{-1}] (D);
 $BACT_{soil}$ - concentration of bacteria in soil, expressed on a pore water basis [$\text{cfu} \cdot \text{ml}_{\text{pore water}}^{-1}$] (A);
 $FRdisslvd_{soil\ i[S]}$ - fraction of the chemical in soil i at scale S, present in the pore water phase [-];

$FR_{diss} / v_{d,water,i[S]}$	- dissolved fraction of water column i at scale S [-] (A);
$BACT_{water}$	- concentration of bacteria in the water compartment [$cfu \cdot ml_{water}^{-1}$] (A);
$TEMPERATURE_{[S]}$	- temperature at scale S [K] (A).

For derivation of the degradation rate in soil, a value for $BACT_{soil}$ may be derived from *Struijs and Van den Berg* [1995]:

$$BACT_{soil} = \frac{10^6 / 1.4}{FR_{water,soil,i[S]}}$$

with $BACT_{soil}$ - concentration of bacteria in soil, expressed on a pore water basis [$cfu \cdot ml_{pore\ water}^{-1}$] (A);
 10^6 - concentration of bacteria reported in aerobic soil [$cfu \cdot g_{soil}$];
1.4 - bulk density of soil [$kg_{soil} \cdot m_{soil}^{-3}$] (A);
 $FR_{water,soil,i[S]}$ - volume fraction water of soil i at scale S [-] (A).

It should be noted that this procedure for deriving a degradation rate constant in soil applies only to aerobic systems.

MSCE-POP

Degradation in air

The process of POP degradation in the atmosphere is viewed only as a reaction of a pollutant with hydroxyl radicals. In regional model version, this reaction is described by the equation of the first order:

$$\frac{dC}{dt} = -k_{air} \cdot C,$$

where C is the pollutant concentration in air (gaseous phase), ng/m^3 ;
 k_{air} is the degradation rate constant for air, s^{-1} .

Three different values of degradation rate constant k_{air} are used for winter, spring/autumn and summer, respectively.

In hemispheric version, the degradation process in the atmosphere is described by the equation of the second order:

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

where C is the pollutant concentration in air (gaseous phase), ng/m^3 ;
 $[OH]$ is the concentration of OH radical, $molec/cm^3$;
 k_{air} is the degradation rate constant for air, $cm^3/(molec \cdot s)$.

OH radical concentrations in the atmosphere vary substantially depending on many factors (latitude, cloudiness, day time, season, some atmospheric properties, etc.). At present, in the MSCE-POP model as a first approximation, OH radical concentrations have no diurnal variations and depend only on the season. At the latitude of $45^{\circ}N$ mean diurnal OH-radical concentration in the surface layer of 2 km depth is $2 \cdot 10^6$ molec/ cm^3 in summer, $0.8 \cdot 10^6$ molec/ cm^3 in spring and autumn and $0.09 \cdot 10^6$ molec/ cm^3 in winter at mean annual concentration $0.8 \cdot 10^6$ molec/ cm^3 [Yu Lu and Khall, 1991]. To assess the influence of this assumption rough experimental calculations are made (see Annex A). Temporal and spatial variations of this parameter will be taken into account in the model in the near future.

Temperature dependence of rate constant of the gas-phase reaction with OH-radical is taken in the form of Arrhenius equation:

$$k_{air} = A \cdot \exp(-E_a / RT),$$

where A is the pre-exponential multiplier; $cm^3/(molec \cdot s)$;

E_a is the activation energy of interaction with OH-radical in air, J/mol;

R is the universal gas constant, J/(mol · K);

T is the ambient temperature, K.

Values of parameters A and E_a depend on pollutant properties.

This equation is applied for the gaseous phase of a pollutant only. Currently the process of degradation of a pollutant associated with particles is not included in the model due to lack of information on this topic.

Degradation in soil

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

$$\frac{dC}{dt} = -k_{soil} C,$$

where C is the pollutant concentration in soil, ng/m³;

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. It is assumed, as a first approximation, that doubling of the degradation rate constant occurs with each 10K temperature increase. This temperature dependence was adapted from [Lammel, et al., 2001].

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.

Degradation in seawater

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

$$dC/dT = -k_{sea} \cdot C$$

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.