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Introduction

To continue studies on the behaviour of POPs in the atmosphere and other environment compartments MSC-E and involved experts focus their effort on the following POPs: benzo(a)pyrene (B(a)P), lindane, polychlorinated biphenyls (PCB), and hexachlorobenzene (HCB). These substances were recommended by the EMEP workshop on HM and POP [Moscow, 1996].

The main task of this study is to review and analyse mechanisms of POP migration and transformation and assess parameters needed for long-range transport modelling.

1 POP EMISSION TO THE ATMOSPHERE

1.1 Sources of POP emissions to the atmosphere

Polycyclic aromatic hydrocarbons (PAH), of which the best known is benzo(a)pyrene, enter the atmosphere primarily during combustion of different kinds of fuel and waste [Rovinsky *et al.*, 1988; Wilbert *et al.*, 1992]. The sources of POP emissions to the atmosphere can be located both near the ground surface (house heating, land transportation) and at the elevation of dozens of meters (stacks of industrial enterprises and boiler works) or even several kilometres (aircraft). The height at which PAH are released, along with size distribution of particles on which they are sorbed, are most important parameters determining a possible scale of their atmospheric transport.

Polychlorinated biphenyls (PCBs) are widely used as dielectrics in resistors and transformers, as additions to car fuel, as lubricants and in production of plastics and carbon-free tracing paper. After the environmental hazardness of PCBs became evident, their production has been cut down and their application has been significantly reduced. Yet, today the world inventory of PCBs is estimated at 1.2 million tonnes, with about one third of them circulating in the environment [Duursma and Carroll, 1996].

Hexachlorobenzene (HCB) was earlier widely used as a pesticide and an industrial chemical. At present, however, the main source of HCB emissions to the atmosphere is unintentional generation of HCB admixtures in production of organochlorine compounds such as perchloroethylene, trichloroethylene and chlorinated benzenes. Besides, some pesticides contain HCB impurities and when they are produced emissions of HCB to the atmosphere can occur [Wilbert *et al.*, 1992].

Lindane (gamma isomer of hexachlorocyclohexane, γ -HCH) is an effective agent for control of many pests. It is applied during sowing and germination of agricultural plants, for treating forest plantations and gardens, to control locust and spraying cotton plants, beet roots and potatoes during the growing season and for other purposes. It is used as dust, granules, oil solutions, emulsions and suspensions by spraying, surface application or plowing in soil [Gruzdev, 1987]. By estimation, in the 80s 5900 tonnes per year of lindane was used in the world and 4000 tonnes - in the 90-s [Li *et al.*, 1996].

The part of lindane released directly to the atmosphere is dictated by the way of application and is the highest with spraying or dispersing from aircraft. The fate of the pesticide is then determined by the size of particles in which it is incorporated. The characteristic drift distance of pesticide particles with aircraft application is several kilometers, but the major part of compounds such as γ -HCH can evaporate while the aerosol remains in the atmosphere and thus it will be able to be transported over longer distances.

In conclusion it should be mentioned that whereas estimates of total emissions of POP to the environment from different sources, even though rather rough, are available in the literature, data on the state of substances in the emissions (ratio of gaseous and aerosol components, particle size

distribution and chemical nature of aerosol particles, distribution of POP in particle volume) are very scarce and they are not properly classified. The situation is more or less clear only with lindane and HCB, which can be considered, with a good accuracy, as entering the atmosphere in the gaseous phase.

1.2 Volatilization from soil and water surfaces

1.2.1 Vaporization from soil

Due to modern methods of analysis of persistent organic compounds in the environment it has become possible to monitor partitioning dynamics of any chemical applied in the environment and to establish the basic pathways of its losses. According to *J.Plimmer* [1992] pesticides losses due to volatilization to the atmosphere may be 40-80% of quantity applied depending on pesticide physicochemical characteristics, environmental conditions and application mode.

1.2.1.1 Field investigations of pesticides volatilization from the underlying surface

Experimental studies of the persistent pesticides behavior in "atmosphere-underlying surface" system have been carried out for a long time [*Malakhov*, 1983; *White et al.*, 1977; *Taylor et al.*, 1976; *Parmele et al.*, 1972; *Taylor et al.*, 1977; *Cooper et al.*, 1990; *Harper et al.*, 1976; *Harper et al.*, 1983; *Terner et al.*, 1977; *Majewski et al.*, 1989; *Ross et al.*, 1990; *Majewski et al.*, 1991].

In the majority of studies for determination of pesticide flux to the atmosphere by data on measured concentrations the gradient method based on the similarity theory for the atmospheric boundary layer has been used. Recently Theoretical-Profile-Shape method (TPS) was proposed [*Wilson et al.*, 1982] for determination of the evaporating substance flux to the atmosphere from the round area source. In the works of *M.Majewski et al.* [1989; 1991] this method has been compared with the gradient one. Fluxes calculated by these methods showed that TPS method gives average flux values approximately 20% - 30% higher than calculated by the gradient measurements.

In all experiments influence of a daily variation of the atmospheric turbulent characteristics on pesticide fluxes and concentrations in the atmosphere boundary layer is pointed out. At distinct daily variation of the atmospheric meteorological characteristics the values of chemical concentrations measured in the day time are many times less than those measured at night. This difference can be as high as fifty times [*White*, 1977], although in the majority of studies it does not exceed one order of magnitude. The greatest fluctuations of pesticide concentrations in the atmosphere are observed during the first several days after application and their amplitude decreases with time. Absolute values of pesticide concentrations in atmosphere also decrease with time after application.

Analysis of a daily fluctuation of a chemical flux in the atmosphere has shown, that its maximum values, as a rule, are observed at daytime, and the flux value correlates with the module of wind velocity and soil temperature. However, sometime fluxes and concentrations decrease at the day time and increase at night [*Malakhov et al.*, 1983; *Harper et al.*, 1976; *Ross et al.*, 1990; *Majewski et al.*, 1991]. *L.Harper L.A. et al.* [1976] connect such flux behaviour in the atmosphere with intensive drying of the upper soil layer in the day time (volumetric moisture content in the upper 0.5 cm soil layer in the day time reached 0.01). Soil overdrying results in decreasing of chemical concentrations in the vapor phase [*Valsaraj and Thibodeaux*, 1992]. The amplitude of daily flux fluctuations, as a rule, decreases with time after application. Absolute values of the pesticide flux from soil to the atmosphere decrease as well.

A. Taylor et al. [1977] investigated the influence of the meteorological element daily fluctuations on volatilization of pesticides applied on vegetation. Amount of applied pesticides was large and at a level close to height of the vegetation the vapor phase concentration was close to saturation for a long time. In this case the chemicals volatilization is defined only by the meteorological conditions. In this experiment the chemical flux and concentration in the atmosphere correlated with increase of wind velocity and temperature.

Therefore the investigations of pesticides volatilization under field conditions show, that the pesticides volatilization depends on the turbulent characteristics of the atmospheric boundary layer and the processes occurring with them in the upper soil layer.

1.2.1.2 Phenomenological approaches to the description of pesticides volatilization

The most simple models [*Kearney and Sheets*, 1964; *Beesman and Deming*, 1974] of pesticides losses from soil and from plant surface as the result of volatilization describe this process by the first order kinetic equation, that dependence can be expressed as:

$$C_{\dot{0}}(t) = C_{\dot{0}0} \exp(-\lambda t), \quad (1.1)$$

where $C_{\dot{0}}(t)$ - pesticide concentration in soil at the moment of time t ,

$C_{\dot{0}0}$ - initial chemical concentration in soil;

λ - constant describing the volatilization rate.

Equation (1.1) parameter values are supposed to be determined from the experimental data on the dynamics of pesticide content in soil or layer of vegetation. Under real conditions simple exponential dependence is usually insufficient. *M. Hoskins* [1961] and *F. Phillips* [1971] proposed to describe pesticide volatilization from soil by the following expression:

$$C_{\dot{0}}(t) = C_{\dot{0}1} \exp(-\lambda_1 t) + C_{\dot{0}2} \exp(-\lambda_2 t), \quad (1.2)$$

which point on the existence of the two independent volatilization rates λ_1 and λ_2 ; $C_{\dot{0}1}$ and $C_{\dot{0}2}$ are specific concentrations of a POP.

There are also approaches allowing to estimate pesticide flux in the atmosphere on the basis of a known flux of a model substance [*Hartley*, 1969; *Spenser et al.*, 1974]. This approach is based on the assumption that fluxes of different substances under other equal conditions depend only on saturated vapor pressures and the gas phase diffusion coefficients of these substances. In this approach the water flux from soil to the atmosphere is used to determine the flux of pesticide evaporating from soil to the atmosphere.

1.2.1.3 Physico-mathematical models of POPs volatilization from soil

As a rule, surfaces polluted by POPs have relatively large areas. It allows to consider only vertical POPs migration in soil, assuming horizontal uniformity of pollutant distribution and soil properties. Therefore in physico-mathematical models of POPs behavior in soil their migration is described by one-dimensional convective-diffusion equation in sorbing medium (downward direction is taken as positive):

$$\frac{\partial C_{\dot{0}}}{\partial t} + \frac{\partial J_T}{\partial z} + Q_r = 0 \quad (1.3)$$

where $\tilde{N}_{\dot{0}}$ is total POP concentration in soil;

J_T is total vertical POP flux;

Q_r is a term, describing POP dissipation in soil.

The POP degradation is usually described by the first order kinetic equation [Borsilov *et al.*, 1991].

In general, POP in soil can be in solid, liquid, dissolved, gaseous and sorbed states [Borsilov *et al.*, 1991]. The last three phases are considered here. Total POP concentration in soil can be presented as [Jury *et al.*, 1983]:

$$C_0 = \rho C_s + \theta C_w + (g - \theta) C_a, \quad (1.4)$$

where ρ is the soil bulk density,

θ is a volumetric soil moisture content,

g is soil porosity,

C_s, C_w, C_a are concentrations in sorbed, liquid and vapor phase, respectively.

Since POP transport in soil occurs in liquid and vapor phases, the transport mechanisms are molecular diffusion and convection. Therefore total POP flux in soil can be written as:

$$J_T = -\theta D_w \frac{\partial C_w}{\partial z} + V_w C_w - (g - \theta) D_a \frac{\partial C_a}{\partial z}, \quad (1.5)$$

where D_w and D_a are the porous media POP diffusion coefficients in the soil solution and in the air, correspondingly;

V_w is Darcy flux of soil solution.

Chemical convective transport in the vapor phase is caused by a gradient of vapor pressure as a result of soil temperature change with depth. *Y.Cohen et al.* [1988] studied the influence of daily soil temperature fluctuations on the chemical transport rate in soils at low moisture content. Numerical modelling of this process shows that the contribution of the convective component to vapor phase flux of a chemical in soil is small.

Inhomogeneity of porous medium results in so-called hydrodynamic dispersion [Ber *et al.*, 1971], consisting of additional diffusional dilution of the moving admixture. At low soil solution flow rates (< 0.06 m/day) this phenomenon can be neglected [Scott, 1983].

As can be seen from (1.5), POP mobility in soil depends on how it is distributed between phases. Sorption of hydrophobic POP occurs in basic on soil organic matter [Karickhoff, 1979; Karickhoff, 1986], though sorption on soil mineral fractions also takes place, especially at low soil moisture content [Valsaraj and Thibodeaux, 1992]. Some POP have ability to irreversible sorption [Borsilov *et al.*, 1991], for examples triazines.

Since characteristic time of the concentration change in soil for the majority of POPs is more than characteristic times of sorption and desorption, the instantaneous sorption equilibrium can be assumed. In linear approximation dependence between sorbed and dissolved POP phases can be presented as [Karickhoff, 1986; Farmer and Letey, 1974]:

$$C_s = K_p C_w, \quad (1.6)$$

where K_p - partition coefficient.

This relations is used for the description of POP reversibly sorbed fraction, while irreversible sorption can be accounted by as an additional degradation process [Borsilov *et al.*, 1991]. The equilibrium distribution between dissolved and vapor phases is described by the Henry law.

$$C_w = K_H C_a, \quad (1.7)$$

where K_H is the Henry law constant.

For practical purposes, as a rule, uniformity and stability of soil characteristics with depth is supposed, then with the help of equations (1.6) and (1.7) equation (1.3) can be expressed as:

$$\frac{\partial C_t}{\partial t} = D_e \frac{\partial^2 C_t}{\partial z^2} - V_e \frac{\partial C_t}{\partial z} - \mu C_t, \quad (1.8)$$

where D_e is an effective diffusion coefficient, determined by the expression:

$$D_e = (K_H Da + D_w) R_w \quad (1.9)$$

and V_e is effective transport velocity of a substance:

$$V_e = \frac{V_w}{R_w} \quad (1.10)$$

μ is the additive first order POPs degradation constant in soil, and R_w is retardation factor, determined by expression: $R_w = \theta + K_p + (g-\theta)K_h$.

To finish the description of the model, it is necessary to put initial and boundary conditions. The initial conditions are set according to the problem to be solved. Considering the problem of substance losses it is convenient to write down the initial condition as:

$$\begin{aligned} C_t(z,0) &= C_{t0} \text{ at } 0 \leq z \leq l, \\ C_t(z,0) &= 0 \text{ at } z > l. \end{aligned} \quad (1.11)$$

For the bottom boundary condition at $z \rightarrow \infty$ the obvious condition of the solution limitation $C_t(z = \infty, t) < \infty$ is used.

It is necessary to stop in more detail on the top boundary condition because the way of its specification is the basic difference of the chemical volatilization models.

It is rather obvious, that the characteristic time of mixing in the atmosphere is much less than the corresponding time in soil. Therefore steady-state vertical distribution of POP concentration in the atmosphere is rather quickly established, i.e. the atmosphere instantly reacts to concentration change in soil.

In general it is necessary to solve a problem of POP migration in soil along with its dissipation in the atmosphere. Then the conditions of solutions combination will be as follows:

$$\begin{aligned} -D_e \frac{\partial C_t}{\partial z} + V_e C_t &= E_a, & z = 0 \\ K_H C_t / R_w &= C^a, & z = 0 \end{aligned} \quad (1.12)$$

where E_a is a flux to the atmosphere,

C^a is a concentration in the air near the soil-atmosphere interface.

In such record the problem is reduced to the determination of the flux value E_a by means of the boundary concentration C^a .

Then the flux to the atmosphere can be written in the Newton form and expressed by means of difference of concentrations on the border and at some level $z = \delta$:

$$E_a = \beta_a (C^a - C^a(\delta)), \quad (1.13)$$

where β_a is a mass transfer coefficient in atmosphere, and $C^a(\delta)$, as a rule, equals to zero.

Using equation (1.13), the boundary conditions (1.12) can be written as one equation.

$$-D_e \frac{\partial C_t}{\partial z} + V_e C_t = -\beta_a K_H \frac{C_t}{R_w} \text{ at } z=0. \quad (1.14)$$

S.Zenov et al. [1990] suggested to use the analytical solution of steady-state equation of turbular diffusion on the underlying surface with the first order boundary conditions for determination of volatilizing chemical flux from a spill. The value of concentrations in the atmosphere at the boundary is suggested to be equal to saturated vapor concentrations. Along with usual shortages connected with the approximation of profiles of the turbulent atmosphere characteristics, this approach suggests that the area of the advanced turbulence extends up to the underlying ground surface. However, near the underlying ground surface there is a layer, where substance transport is determined mostly by the molecular processes. Estimations show, that the ratio of concentrations on the bottom and upper boundaries of the surface layer can be as much as one order of magnitude.

Y.Cohen and P.Ryan [1989] supposed that mass transfer coefficient in the atmosphere is completely defined by the processes in the surface atmospheric layer.

$$\beta_a = \rho u_* Da_0, \quad (1.15)$$

where ρ is air density,

u_* is dynamic velocity,

Da_0 is oversurface Dalton number.

Calculated by this formula mass transfer coefficients provided by *Y.Cohen and P.Ryan* [1989] show that they essentially exceed the field experiment values.

O.Vozhennikov and A.Burkov [1991] proposed the model which estimates chemical fluxes from the underlying surface based on the assumption about the automodelity chemical concentrations profile in the atmosphere, and the layer thickness occupied by admixture is used as automodelity scale. The expression for the mass transfer coefficient derived in this work is:

$$\beta_a = \frac{\kappa u_*}{\kappa(D_{a0}^{-1} - C_{d0}^{-1/2}) + \ln\left(\frac{\delta}{z_0}\right) - \phi\left(\frac{\delta}{L}\right)}, \quad (1.16)$$

where $\hat{\epsilon}$ is Karman constant,

Cd_0 is an oversurface layer resistance coefficient,

δ is a thickness of the layer occupied by the admixture, being function of the distance from downwind edge of the polluted area.

ϕ is the universal function of Monin-Obukhov similarity theory,

z_0 is a roughness parameter.

As this expression shows this definition of the mass transfer coefficient includes parameters characterizing admixture transport in both oversurface and stratified boundary layer. Moreover the mass transfer coefficient is a function of the distance from the edge of a polluted area. Characteristic values of the mass transfer coefficients calculated by (1.16) are in the range $(1 \div 5) \cdot 10^{-3}$ m/s

In the model described by *V.Borsilov et al.* [1993] the soil block suggested by *W.Jury et al.* [1983] and equation (1.16) are used. The expression for mass transfer coefficient was derived assuming that for averaging time of several days and more the atmosphere can be considered as neutrally stratified and the vertical velocity profile was approximated by the power function of height. This model was

successfully used for the analysis of the field experiment with a volatile pesticide [Burkov *et al.*, 1995].

1.2.2 Volatilization from water

In water quality models volatilization is considered as a process resulting in decrease of POPs concentration in water bodies. On the other hand, volatilization from water can also be an important source of atmospheric air pollution by some POPs [Thibodeaux, 1984; Eisenreich *et al.*, 1992]. It is especially true for POPs, which direct emission into air has been significantly reduced during the last years, for example for PCBs.

S.Eisenreich *et al.* [1992] used the mass balance model to construct POPs input-output budgets in the Great Lakes. The overall input-output calculations for PCBs and B(a)P are presented in table 1.1.

Table 1.1 PCBs and B(a)P input-output budgets in the Great Lakes

Lake	Input, kg/yr.	Output, kg/yr.	% Volatilization of total output
	PCBs		
Superior	606	2190	86
Michigan	685	7550	68
Huron	636	2760	75
Erie	2520	2390	46
Ontario	2540	1320	53
B(a)P			
Superior	71.7	314	19
Michigan	208	6250	6
Huron	290	1350	31
Erie	122	3720	15
Ontario	155	1290	33

For PCBs, estimates show that the volatilization flux for some lakes is much higher than the total atmospheric deposition. For B(a)P, estimated volatilization and deposition fluxes are of the same order of magnitude for all the lakes. It means that POPs volatilization from natural waters may significantly contribute to their concentration in air.

Transfer of organic vapors at the air-water interface is often predicted from the two film diffusion model [Eisenreich *et al.*, 1992; Pivovarov, 1987; Shnoor, 1987; Mackay, 1986; Thibodeaux, 1984; Thibodeaux, 1979]. In this model the vapor fluxes in water and air at the interface may be given as (upward direction is taken as positive):

$$E_a = K_w(C_w - C_{wi}) = K_a(C_{ai} - C_a), \quad (1.17)$$

where K_w and K_a are liquid and gas mass transfer coefficients, m/day;

C_w and C_{wi} are dissolved chemical concentrations in the bulk water and at the air-water interface, mol/m³;

C_a and C_{ai} are vapor phase chemical concentrations in the bulk air and at the air-water interface, mol/m³.

The dimensional Henry's law constant relates C_{wi} to C_{ai} :

$$C_{ai} = K_H C_{wi} \quad (1.18)$$

Equations (1.16) can then be written as:

$$E_a = K_{\dot{O}}(C_w - C_a/K_H), \quad (1.19)$$

where $K_{\dot{O}}$ is an overall mass transfer coefficient, m/day;

The overall mass transfer coefficient $K_{\dot{O}}$ can be defined as follows:

$$1/K_T = 1/K_w + 1/(K_H K_a) \quad (1.20)$$

K_w and K_a values can be estimated from empirical equations derived by *D.Mackay* [1986]:

$$\begin{aligned} K_a(\text{m/s}) &= 10^{-3} + 46.2 \cdot 10^{-3} u_* Sc_a^{-0.67} \\ K_w(\text{m/s}) &= 10^{-6} + 34.1 \cdot 10^{-4} u_* Sc_w^{-0.50} \quad (u_* > 0.3) \\ K_w(\text{m/s}) &= 10^{-6} + 144 \cdot 10^{-4} u_*^{0.22} Sc_w^{-0.67} \quad (u_* < 0.3) \\ u_* &= 10^{-2} U_{10} (6.1 + 0.63 U_{10})^{0.5} \end{aligned} \quad (1.21)$$

where U_{10} is wind velocity at 10m height, (m/s)

Sc_w and Sc_a are Schmidt molecular numbers for water and air.

The overall mass transfer coefficient of PCBs calculated by equations (1.20) for the Great Lakes using typical values of K_w and K_a (0.2 and 20 m/hour correspondingly) equals to 0.03-0.3 m/day [*Mackay*, 1986].

In the above described model, the rate of chemical transfer across the stagnant gas and liquid films at the air-water interface is assumed to be governed by molecular diffusion. The real mechanism of the chemical air-water exchange is more complex. Some processes, which can contribute to the POPs volatilization rate from water are briefly described below.

Formation of water drops and air bubbles in the water surface at high wind velocities.

This processes can lead to a significant increase of the water surface area, and, consequently, to more rapid vaporization of POPs [*Pivovarov*, 1987].

POPs concentration in the surface water layer.

Due to their hydrophobic nature, POPs are concentrated in the surface layer of water. According to *V.Savenko* [1990], concentration of hydrophobic chemicals in the upper few micrometres of the water surface can be thousand times as much as in the bulk water.

Water drops throwing out as a result of air bubbles collapse on the water surface.

Air bubbles collapse leads to water drops throwing out of the water surface [*Savenko*, 1990]. The drops vaporization leads to gaseous and particulate POPs release into the atmosphere.

The effect of the above processes on the POPs volatilization rate from water is uncertain because methods of their quantitative description are not developed.

Tables 1.2 shows POP characteristics determining “atmosphere - water” exchange at wind speed 5 m/s at 10m height.

Table 1.2: POP characteristics determining “atmosphere - water” exchange at wind speed 5 m/s at 10 m height.

POP	K_h	$D_a, \text{cm}^2/\text{s}$	$D_w, \text{cm}^2/\text{s}$	$K_T, \text{m/s}$
HCB	2.2e-2	0.044	5.1e-6	5.6e-5
PCB-153	6.24e-3	0.037	4.3e-6	1.6e-5
γ -HCH	1.6e-4	0.043	5.0e-6	6.3e-7

BaP	2.2e-5	0.048	5.5e-6	9.2e-8
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1.3 Wind resuspension

The POP resuspension from the soil surface is one of the sources of their emissions to the atmosphere. The bottom boundary condition for the atmospheric dispersion model for aerosol particles can be written as [Slinn, 1976]:

$$-F = v_g q_0 - P \quad (1.22)$$

where F is POP particulate flux, $\text{ng/s} \cdot \text{m}^2$

v_g is velocity of dry deposition of POPs containing aerosol particles, m/s;

q_0 is particles concentration in air at $z=0$, m^{-3} ;

P is upward vertical flux of POP due to resuspension from the soil, $\text{ng/s} \cdot \text{m}^2$;

z - vertical co-ordinate, m.

Three methods are usually used for parameterization of P. The first is an estimation of P through the resuspension rate, the second - through the resuspension factor and the third - using the concept of mass load [Henson, 1985]. Below we consider each of these methods and their possible application to estimating of POP flux to the atmosphere due to wind resuspension.

1.3.1 Resuspension rate approach

POP deposited on the particles of the soil surface re-enter the atmosphere under the action of wind (turbulent wind pulsations and convective jets formed on the soil surface [Nicholson, 1988]). The upwind vertical flux of pollutants to the atmosphere is found on the basis of data on the soil surface contamination density from the ratio [Sehmel, 1984; Nicholson, 1988]:

$$P = \alpha \cdot A \quad (1.23)$$

where A is soil surface contamination density;

α is resuspension rate (wind resuspension intensity).

It is assumed that the surface area is large enough to neglect the edge effect and the contamination is distributed uniformly.

For the determination of α , either gradient measurements of pollutant concentrations in the atmosphere [Garger et al., 1990; Naidenov and Lukoyanov, 1994] or fitting POP concentrations and deposition calculated by the dispersion model to measurement data are used [Makhonko, 1992; Vozhennikov, 1994; Gavrilov et al., 1996].

It has been derived in multiple laboratory and field studies of wind resuspension of tracers and radioactive dust from different surfaces [Makhonko 1992; Sehmel 1984; Nicholson, 1988; Hollander and Garger, 1996] that the resuspension rate is dependent basically on wind speed, condition and type of the underlying surface, particle size, time, and other factors. The increase in α with wind speed has been noted by several researchers [Sehmel, 1984]. The dependence of wind resuspension intensity on wind speed is usually written as an exponential function:

$$\alpha \propto U^a \quad (1.24)$$

The values of the exponent are in the range 1-6 [Sehmel, 1984] and most of the estimates give a ≥ 3 . V.Gavrilov et al. [1996] studied the dependence of resuspension rate on wind speed using the diffusion

model of α and field measurements. First, α was determined for different wind speeds by comparison of calculated and measured 3-hour concentrations of Cs^{-137} in the air and its precipitation in Novozybkov. Then an appropriate formula was found for the α function of wind speed U at the vane level. It has been estimated:

$$\alpha = 10^{-10} U^{1.2} \quad \text{for } U = 1 - 3 \text{ m/s} \quad (1.25)$$

$$\alpha = 0.3 \cdot 10^{-10} U^{2.9} \quad U = 4 - 6 \text{ m/s} \quad (1.26)$$

$$\alpha = 0.02 \cdot 10^{-10} U^5 \quad U = 8-10 \text{ m/s} \quad (1.27)$$

Result (1.27) for wind speed 8-10 m/s agrees with the relation [Henson, 1985]:

$$\alpha = 1.96 \cdot 10^{-13} U^{4.82} \quad (1.28)$$

K.Makhonko [1992] gives empirical formulae describing the dependence of α on roughness of the underlying surface Z_0 , grass height h_t and amount of phytomass on the underlying surface in the air-dried state m :

$$\alpha = 2.0 \cdot 10^{-10} / z_0^{1.4} \quad (1.29)$$

$$\alpha = 2.5 \cdot 10^{-9} / h_t^{1.4} \quad (1.30)$$

$$\alpha = 2.9 \cdot 10^{-8} / m^{1.4} \quad (1.31)$$

where z_0 and h_t are expressed in cm and m - in g/m^2 .

These functions have been derived based on results of wind resuspension of radioactive dust in forest steppe piedmont of the South Urals. Though the change in resuspension rate as a function of size of dust particles can be expected, as the force of aerodynamic lift increases with wind speed and particle surface area [Nicholson, 1988] and some experimental results exist confirming this dependence, there is still no database which would permit describing the dependence of α on particle size with a sufficient degree of accuracy [Sehmel, 1984]. It should be kept in mind that the above dependencies of α on a number of parameters provide justification for the assessment of α . By some data [Makhonko, 1992; Sehmel, 1984; Nicholson, 1988] the estimated resuspension rates, mostly for radioactive dust, range from 10^{-13} to 10^{-6} s^{-1} . The recent published estimates of α [Hollander and Garger, 1996] obtained for different areas contaminated after the Chernobyl accident lie in a more narrow range of 10^{-12} to 10^{-8} s^{-1} . Based on the results of field studies of wind resuspension of radioactive dust using measurement of vertical profiles of Cs-137 concentration in the lower 15 meter atmospheric layer above the Chernobyl- contaminated cultivated field in July-August 1992 in the area of Novozybkov, the three-day averaged rate of wind resuspension were in the range of $7 \cdot 10^{-11}$ to $8.6 \cdot 10^{-11} \text{ s}^{-1}$ [Naidenov and Lukoyanov, 1994].

In the calculations of the upward flux of POP to the atmosphere by equation (1.23) in some cases for rough estimation one can use the values $\alpha \approx (1.0 \div 7.7) \cdot 10^{-8} \text{ s}^{-1}$ obtained in the studies of wind resuspension of DDT in the forest with three day exposure time [Henson, 1985]. At present, practically no data are available for assessing, with a sufficient accuracy, α for any POP.

1.3.2 The resuspension factor approach

For assessment of an upward flux of POP above a dusting surface of limited size one can use the method described by *O.Vozhennikov* [1994]. It has been proposed to determine P from measurement of pollutant concentration at one height or by data on the resuspension factor and soil surface contamination density. The flux of POP can be calculated with the following formula:

$$P = k_1 U \cdot q_1 / \ln(\delta/z_1) = k_1 U \cdot K_{\alpha} A / \ln(\delta/z_1) \quad (1.32)$$

where $k_1 = k/Pr_t$; $Pr_t = 0.85$ is turbulent Prandtl number;

$k = 0.4$ is Karman constant

U is dynamic speed;

$K = q_1/A$ is resuspension factor (the wind resuspension coefficient) for height z_1 ;

q_1 is POP concentration at height z_1 ;

δ is characteristic height of the near surface atmospheric layer.

The generalized data on K_{α} [Makhonko, 1992; Sehmel, 1984; Nicholson, 1988] show that the values of resuspension factors, mostly for radioactive dust, are in the range 10^{-4} to 10^{-10} m^{-1} . The results of recent studies of wind resuspension [Hollander and Garger, 1996] indicate that K varies from 10^{-7} to $3 \cdot 10^{-10} \text{ m}^{-1}$. According to the data obtained above a cultivated field in the vicinity of Novozybkov in July-August 1992, the average value of the resuspension factor is $5 \cdot 10^{-9} \text{ m}^{-1}$ [Lukoyanov and Naidenov, 1992]. Unfortunately, data on POP resuspension factor are missing in the sources available to us.

1.3.3 Mass load approach

The upward vertical flux of POP can be determined by equation (1.32), given the POP concentration in air is known. For estimation of the latter, one can use the concept of mass load [Henson, 1985]. According to this concept q_1 is found as the product of POP concentration in soil and soil particle concentration in air:

$$q_1 = A_s C_d \quad (1.33)$$

where A_s is specific concentration of POP in the upper soil layer;

C_d is dust concentration in air.

So, if the dust content of the atmosphere and POP concentration in soil in a given area is known, the POP concentration in air can be approximately estimated, and hence, ultimately the upward vertical flux can be estimated with (1.32). According to the data obtained in UK in 1996 at the national air monitoring network, the average dust concentrations for urban stations lie in the range $33\text{-}254 \mu\text{g}/\text{m}^3$ and $9\text{-}79 \mu\text{g}/\text{m}^3$ for rural areas. By the data of N.Lukoyanov and A.Naidenov [1994] in July-August 1992 in the vicinity of Novozybkov the dust concentration was varying in the range from 30 to $170 \mu\text{g}/\text{m}^3$, the average value being $95 \mu\text{g}/\text{m}^3$. L.Anspaugh et al. [1975] conducted a verification of the mass load method. They measured concentrations of some radionuclides in air and compared them to those calculated by radionuclides concentrations in soil under the assumption of the air dust content of $100 \mu\text{g}/\text{m}^3$. Results of the comparison of calculated and measured concentrations point to the workability of the mass load method. N.Lukoyanov and A.Naidenov [1994] have compared experimental values of Cs-137 concentrations in air above the cultivated field at the height of 1.3 m during July-August 1992 with those calculated by measurements of counting dust concentration in the atmosphere and specific activity of soil fractions performed in the same period. It appeared that the average over the period value of experimental concentration was higher than the calculated concentrations of Cs⁻¹³⁷ in air only by a factor of 1.4.

Thus, using data of the national network of air dust content monitoring and soil contamination with POP, the concentration of POP in air can be assessed and then the upward flux of POP can be derived to be used in the model. True enough, when using data of the air monitoring network, some uncertainties can arise. For example, since air samples can contain particles of industrial origin POP

concentrations in air may be overestimated. Besides, if the POP concentration in the fraction containing fine particles and mostly involved in the wind resuspension differs significantly from that in the fractions of other sizes, it may be expected that the concentration in air will be underestimated, given the total POP concentration in soil is used.

1.3.4 POPs distribution with soil particles

When modelling wind resuspension it is important to have an idea on what soil particles POP are sorbed. As is said in section 3.2, the key characteristic of the soil solid phase influencing POP sorption is the organic carbon content. Table 1.3 shows data on the content of soil humus in fine granulometric fractions of some soil types of Russia.

It can be seen that the content of soil organic matter in fine soil fractions is much higher than in the soil in general and amounts to 5-16%. Hence, POP should be sorbed better on fine soil particles than on large ones.

L.Aleksandrova [1980] based on the analysis of a large array of experimental data proposed a hypothesis that in all soil fractions <1 μm in diameter the humus content is approximately the same and equals about 15%. It is notable that this is very close to the average content of organic carbon in the atmospheric aerosol particles [*Bidleman and Foreman*, 1987].

Table 1.3: Humus content in granulometric fractions of soils [Vozbutskaya, 1968]

Granulometric fraction in μm	Light grey forest soil	Leached chernozem
	humus in % of weight fraction	
10-5	1.10	1.60
5-1	5.14	8.16
< 1	10.49	16.11
soil in general	1.62	7.0

Recommendations

If data on the rate (α) and factor (K_α) for POP resuspension from the soil surface are not currently available, for calculation of the upward vertical flux of POP to the atmosphere formula (1.32) including the POP concentration in the lower atmospheric layer at the height Z_1 is recommended to be used. Estimation of q_1 can be made by the mass load method from (1.33) using data of the national network of dust content monitoring in the atmosphere and soil contamination with POP.

2 REMOVAL OF POPs FROM THE ATMOSPHERE

2.1 Dry deposition of POPs

The process of deposition is a complex phenomenon controlled by many factors such as atmospheric conditions, type of substance, its properties and surface state. The velocity of POP deposition on different surfaces can be estimated either based on experimental studies or using physico-mathematical deposition models accounting for POP transport from the atmosphere to the surface.

As a rule, modern models, for simplifying the mathematical description of transport processes, use a multi-layer model accounting for POP deposition by analogy with the Ohm's law through characteristics of resistance to transport.

$$V_d = 1/(r_a + r_b + r_c) \quad (2.1)$$

The problem is reduced to finding an analytical form of resistances with consideration of the above factors influencing the deposition velocity.

2.1.1 The empirical data on aerosols deposition.

Experimentally measured deposition velocities of different aerosols particles on different surfaces range from 10^{-3} to $180 \text{ cm}\cdot\text{s}^{-1}$ and can differ by one order of magnitude even in the same experiment [Sehmel, 1980]. Table 2.1 summarizes experimental data on deposition velocities of submicron sulphate particles on different surfaces under different atmosphere and surface conditions. Let's note that deposition velocities values are less than $1 \text{ cm}\cdot\text{s}^{-1}$ and depend on atmosphere stability.

J.Roed [1985] gives results of field study of deposition of the Be-7 and Cs-137 containing dust on walls of the break houses and walls covered with a plaster. Deposition velocities obtained for these isotopes ranged from 0.004 to $0.044 \text{ cm}\cdot\text{s}^{-1}$. These data show that deposition velocities for particles of submicron size in urban area are less than in rural, for example in the pine-tree forests in spite of approximately the same aerodynamic roughness length (z_0). It means that surface type is an important factor influencing aerosol particles deposition velocity.

Estimations of deposition velocities of some submicrone size heavy metals containing particles on different surfaces are given by *J.Muller* [1990]. For these particles he calculated the deposition velocities as a function of particles sizes using the following equation:

$$V_d = \frac{\sum_i V_{di} C_i}{\sum_i C_i} \quad (2.2)$$

where V_{di} is deposition velocity corresponding to the i -th particle size range;

\tilde{N}_i is mass concentration within the i -th size range.

Calculated deposition velocities for five heavy metals are presented in table 2.2.

Table 2.1: Experimental deposition velocities of submicron size sulphate particles on different surfaces.

Surface type	Surface condition	Atmospheric stability (class)	Deposition velocity $\tilde{m}\cdot s^{-1}$
Bare soil	dry	\hat{A}	0.01
Bare soil	wet	\hat{A}	0.38
Bare soil	wet	\hat{A}	0.25
Bare soil	frozen	$\hat{A}-\hat{A}$	-0.0008
Short grass	dry	\hat{A}	0.20
Short grass	wet	\hat{A}	0.09
Short grass	wet	D	0.04
Short grass	dry	\hat{A}	0.42
Short grass	dry	\hat{A}	0.38
Short grass	dry	\tilde{N}	0.35
Short grass	dry	D	0.02
Short grass	dry	\hat{A}	0.04
Short grass	dry	F	0.04
Long grass	dry	\hat{A}	0.35
Pasture	dry	\hat{A}	0.33
Pasture	dry	\hat{A}	0.07
Pasture	dry	D	0.27
Pasture	dry	\hat{A}	0.24
Pasture	dry	\hat{A}	0.20
Pasture	dry	E-F	0.17
Pasture	wet	\hat{A}	0.18
Barley	dry	D	0.21
Barley	wet	\hat{A}	0.04
Barley	wet	\hat{A}	0.04
Foliage forest		C,D,E	-0.08
Pine-tree forest		\tilde{N}	0.90
Pine-tree forest		D	0.48

Table 2.2: Heavy metal deposition velocities ($\text{m}\cdot\text{s}^{-1}$) on different surfaces.

Particle surface	Coniferous forests	Foliage forest	Grass	Water
Pb	5.9	1.9	0.1	0.04
Cd	5.5	1.8	0.1	0.03
Mn	21.0	7.3	0.2	0.10
Cu	19.6	6.6	0.2	0.10
Fe	27.8	9.7	0.2	0.10

2.1.2 Theoretical approaches to aerosols deposition description.

At present many mathematical models for aerosol particles dry deposition prediction are developed. The main problem of aerosol particles deposition modelling is finding of an analytical expression for resistance parameters in equation (2.1). Aerodynamic resistance (r_a) caused by turbulent diffusion can be described as:

$$r_a = (ku_*)^{-1} \left[\ln \frac{z-d}{z_0} - \theta \right] \quad (2.3)$$

where u_* is friction velocity;

k is Karman constant ($k = 0.4$);

θ is atmosphere stability factor.

P.Tilden et al., [1988] give the following equations for r_a as a function of atmosphere stability and of the wind speed (\bar{u}) and its standard deviation (σ_θ):

$$r_a \approx 4 (\bar{u} \sigma_\theta^2)^{-1} \quad (2.4)$$

for neutral and stable conditions;

$$r_a \approx 9 (\bar{u} \sigma_\theta^2)^{-1} \quad (2.5)$$

for unstable conditions;

$$r_a = \frac{\bar{u}}{u_*^2} \quad (2.6)$$

for neutral conditions.

D.Wratt [1987] gives equations for σ_θ as a function of convective (w_*) and dynamic (u_*) contributions to the turbulence of different atmosphere states.

In case of small particles the resistance of the quasi-laminar boundary layer (r_b) is a function of wind speed and surface properties and can be described as:

$$r_b = \left[\frac{1}{ku_*} \right] \left[\ln \left(\frac{z_0}{z_{0c}} \right) \right] \quad (2.7)$$

where z_{0c} is roughness length for a pollutant.

Since the roughness length z_{0c} is difficult to estimate, the quasi-laminar resistance is often expressed in terms of reciprocal Stanton number (\hat{A}):

$$ku_*r_b = kB^{-1} = \ln(z / z_{oc}) \quad (2.8)$$

Empirical data show that kB^{-1} can be estimated in terms of surface roughness, Reynolds number (Re) and Schmidt number (Sc). *J.Garland* [1977] proposes some expressions for B for different surfaces. So, for grass:

$$B^{-1} = 1.45Re^{0.24} Sc^{0.8} \quad (2.9)$$

And finally, resistance $r_{\tilde{n}}$ connected with processes on the surface can be determined as:

$$r_{\tilde{n}} = -\frac{C_0}{F} \quad (2.10)$$

where F is particle flux to the surface;

\tilde{N}_0 is concentration on the surface elements.

Since \tilde{N}_0 is difficult to measure, it is impossible to use expression (2.10) for $r_{\tilde{n}}$ estimation. At present, $r_{\tilde{n}}$ is calculated from experimentally measured V_d and calculated r_a and r_b values using equation (2.1).

C.Davidson and W.Yee-Lin Wu [1989] presented five frequently used mathematical models for the prediction of aerosols dry deposition velocities on several types of surfaces. These models pay attention to analytical description of mechanisms responsible for particles transport through quasi-laminar layer of different surfaces. Based on predictions obtained by these models and experimental results the calculation scheme for the deposition velocity on different surfaces was developed [*Giorgi*, 1986]. The critical step of the scheme is calculation of particles transport in a quasi-laminar layer (K_{IL}), which is expressed as:

$$K_{IL} = C_{D0}^{1/2} u_* G \quad (2.11)$$

where $C_{D0}^{1/2}$ is a coefficient for every type of surface.

For rough surface with Reynolds numbers from 2 to 1000 the expression for G is:

$$G = BC_{D0}^{-1/2} \quad (2.12)$$

where $B^{-1} = 7.3(z_0 u_* / \nu)^{0.25} \cdot Sc^{1/2}$, ν is kinematic air viscosity.

For vegetation:

$$G = \left(\frac{\eta}{C_d} \right)^{1/2} \quad (2.13)$$

where η - an average probability for a single vegetation element to capture the particle,
 $C_d = 0.2 \div 0.5$.

The η value is determined by sum of contributions of the capture mechanisms: Brown diffusion, inertial movement, crossing, capturing by small vegetation collectors like filaments:

$$\eta = \eta_{BD} + \eta_{int} + \eta_{imp} + \eta_{sm} \quad (2.14)$$

where $\eta_{BD} = C_V S_c^{-1.3}$ - contribution to η due to Brown diffusion;

$\eta_{int} = R^2 / 2$ - contribution to η due to mechanism of the crossing with vegetation elements; $R = \frac{r}{a}$; a - an average radius of the obstacle element; r - particle radius;

$$\eta_{\text{imp}} = \frac{\text{Sta}^{3.2}}{(\text{Sta} + 0.6)^{3.2}} - \text{contribution to } \eta \text{ due to mechanism of the inertial movement;}$$

$\eta_{\text{sm}} = A_{\text{sm}} R_{\text{sm}} \ln(1 + R_{\text{sm}})$ – contribution to η due to capturing by small vegetation collectors, for example by filaments;

$$R_{\text{sm}} = \frac{r}{a_{\text{sm}}}, \quad a_{\text{sm}} - \text{characteristic radius of collectors;}$$

A_{sm} - constant.

All capture mechanisms were determined taking into account the size of vegetation elements of different kind. *F.Giorgi* [1988] provides all necessary input parameters for different surfaces which allow to calculate dry deposition velocity as a function of particle size. Table 2.3 summarizes some values of these parameters for the type of surfaces concerned.

Table 2.3: Characteristics of the different surfaces used for deposition velocity calculations.

N	Type of the surface	$z_{0,s}$, m	C_d	a, mm	a_{sm} , μm	A_{sm}	C_v/C_d	$C_{DO}^{-1/2}$
1	field of wheat	6	0.3	1	10	10^{-4}	1/3	2.5
2	short grass	2	0.3	0.5	10	$5 \cdot 10^{-5}$	1/3	2.5
3	broad leaves forest	80	0.4	10	10	10^{-4}	1/4	3
4	high grass	10	0.3	0.5	10	$5 \cdot 10^{-5}$	1/3	2.5
5	foliage bushes	10	0.4	10	10	10^{-4}	1/4	2.5
6	swamp	3	0.3	0.5	10	$5 \cdot 10^{-5}$	1/3	2.5
7	tundra	4	0.3	0.5	10	$5 \cdot 10^{-5}$	1/3	2.5

Figure 2.1 presents the results of V_d calculations for different surfaces. The model sensitivity to some input parameters was investigated.

Figure 2.1 shows the results of dry deposition velocity estimation versus wind speed at 100 m height. It can be seen that deposition velocity increases with the wind speed increase, especially for particles of diameter less than 1 μm . Calculations showed that the deposition velocity in forest increases by one order of magnitude with the wind speed increase from 1 $\text{m}\cdot\text{s}^{-1}$ to 20 $\text{m}\cdot\text{s}^{-1}$ for 0.5 μm particles. The dependence on particle density is quite weak and can be significant only for particles bigger than 10 μm . Practically, the model is insensitive to the air temperature.

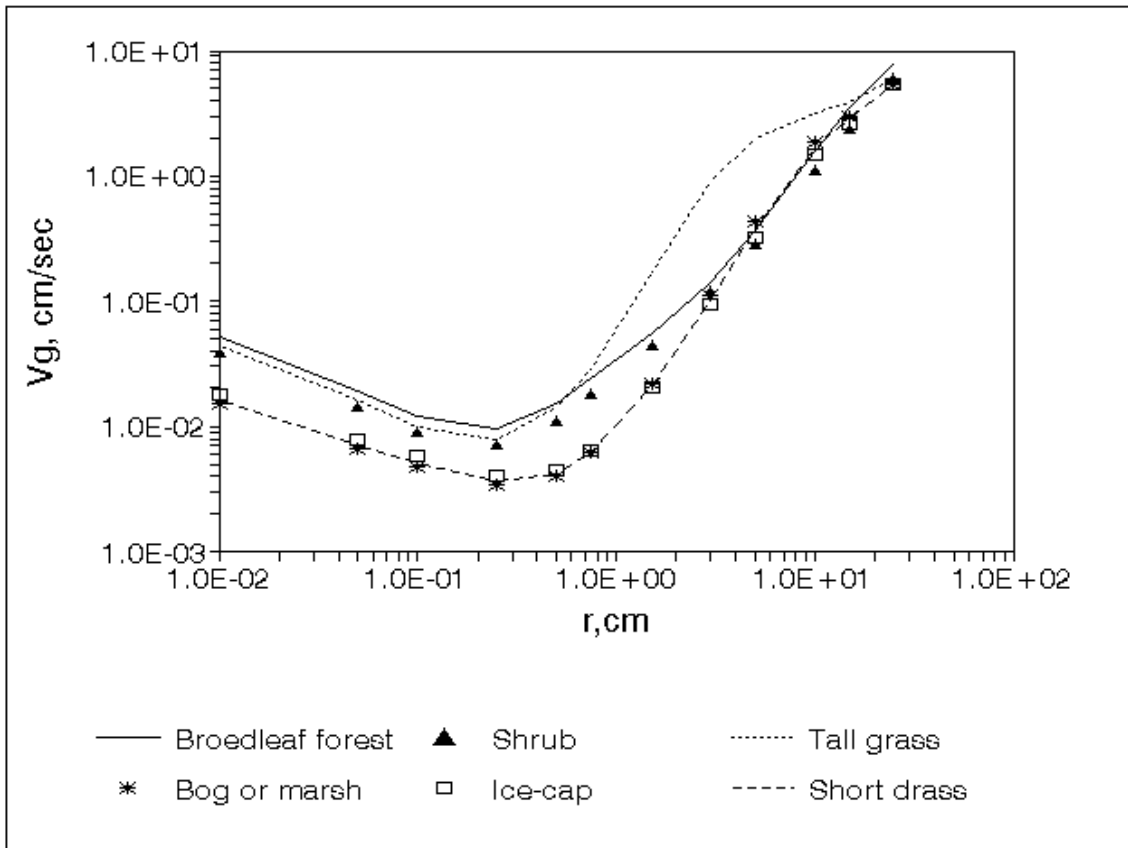


Figure 2.1: Deposition velocity on different surfaces as a function of particle size.

Recommendations

The literature analysis performed showed that at present there are practically no experimental results of the POPs depositions on different surfaces. For this reason the usage of V_d model [Giorgi, 1986] with input parameters described by *F.Giorgi* [1988] is preferable. To calculate V_d using this model it is necessary to know the surface type, roughness parameter (this parameter is tabulated by *F.Giorgi* [1988]), wind speed at 100 m height (or u_*), air temperature, particle density, size spectrum of particles containing POPs (or just mass average size of aerosol particles).

From the literature analysis it should be pointed out that V_d value is mostly affected by the following factors: the type of surface, particle size spectrum and stratification of the atmosphere. Also it should be noted that the surface state can vary accordingly to atmospheric conditions and this can result in mistakes of V_d estimation. *N.Lukoyanov et al.* [1992] has shown that the condition of the snow layer results in wide variation of deposition velocities of the solid dispersed aerosol under other equal conditions.

2.1.3 Dry deposition of gases

2.1.3.1 Peculiar specific features of gas deposition

The approach to calculation of the gas deposition rates on various surfaces remains the same as in the previous chapter. On the base of the experimental and theoretical investigations the expression for the quasi-laminar boundary layer resistance was obtained [Tilden and Dennis, 1988]:

$$r_b = (2 / k u_*) \cdot (D_i / D_{\delta})^{2/3} \quad (2.15)$$

where k is Karman constant;

D_i is heat transfer molecular coefficient in air;

D_a is gas molecular diffusion coefficient in air.

The resistance of vegetation (r_c) according to the diagram is calculated as:

$$\frac{1}{r_c} = \left[1 / (r_s + r_m) + 1 / r_{soil} + 1 / r_{cuticle} \right] \quad (2.16)$$

Where r_s is a stomato resistance;

R_m is a mesophyll resistance;

$R_{cuticle}$ is a cuticle resistance;

R_{soil} is a soil resistance.

Stomato resistance is function of photosynthesis active radiation, air temperature, leaf water potential and vapor pressure deficit. This resistance is usually small and does not exceed 20 s/m for water vapor diffusion to leaves with the area $< 1 \text{ dm}^2$ [Horsker and Linberg, 1982]. The resistance to gases capture by the mesophil cells is determined by the mesophil area and the gas solubility. It is usually in the range of 0.1-0.5 s/cm. The cuticle resistance is associated with the gas capture on the leaf surface. This resistance depends on chemical characteristics of gases, and is also determined by the leaf surfaces area, leaf fluff and leaf wax. The cuticle resistance of a dry leaf is usually very high and can exceed 200 s/m. In spite of the high value the cuticle resistance becomes especially important at night when stomato resistance is low [Hicks and Matt, 1988]. The soil capture resistance (r_{soil}) to the particular POP is a function of the soil type, soil moisture content and temperature. At present there are no published data on values of soil resistances for gases.

2.1.3.2 Theoretical approaches to the description of gas deposition

A leaf can accumulate a chemical through cuticle (water exchange) and stomato (air exchange). The model of stomato resistance for a gas deposition has been described in details by *D. Baldocchi et al.* [1987], which takes into account the main parameters of the capture. However this model requires a lot of input data, which are not always known. A more simple model of vegetative stomato resistance was developed by *C. Jds* [1988]. This model requires only four input parameters: the aerodynamic resistance of the cover, the leaf temperature of the upper cover, the deficit of the vapor pressure in air and the air temperature.

The chemical transport into the leaf is very important and can be described by the partition coefficient:

$$C_L = K_{L/A} C_{av} \quad (2.17)$$

where C_L is chemical concentration on the leaf;

C_{av} is air concentration near the leaf surface.

Partition coefficient in the leaf-air system $K_{L/A}$ can be assessed from the ratio:

$$K_{L/A} = V_A + V_W/K_{A/W} + V_C K_{C/A} + V_G K_{G/A} \quad (2.18)$$

where V_A , V_W , V_C , V_G are relative volumes of air, water, cuticle and glycerol lipid in a leaf, accordingly;

$K_{A/W}$ is partition coefficient in the air - water system;

$K_{C/A}$ is cuticle - air partition coefficient;

$K_{G/A}$ is glycerol lipid - air partition coefficient, which is assumed to be equal to octanol-water partition coefficient ($K_{O/W}$).

The value of the total mass transfer coefficient in a vegetation layer is defined by the ratio:

$$\beta_V = A_f C_{t_f} \quad (2.19)$$

where A_f is leaves surface area per a volume unit, which is connected with the leaf index [LAI] by the ratio:

$$LAI = \frac{1}{2} \int_0^{h_0} A_f(z) dz \quad (2.20)$$

where Z is the vertical co-ordinate;

H_0 is average height of vegetation;

$$C_{t_f} = a_L \cdot Re^{-m} Sc^{-n} \quad (2.21)$$

where $A_L \approx 0.28$ is the constant;

$Re = \frac{u_{*c} L_f}{\nu}$ is Reynolds number near to a leaf surface;

L_f is leaf characteristic size;

ν is kinematic air viscosity;

Sc is molecular Schmidt number.

The m and n values are in the rather narrow range $1/5 < m < 1/2$; $1/2 < n < 2/3$.

The value of the local wind velocity u_{*c} is defined through the solution of the appropriate hydrodynamic problem for a vegetation layer [Dubov *et al*, 1978].

Calculation of the chemical accumulation on vegetation requires, as was shown earlier, the definition of a number of parameters, which for POPs of interest are frequently unknown (hexachlorobenzene is an exception, for which the parameters can be find in [Riederer, 1990]).

In this connection *M.Riederer* [1990] gave a simplified scheme of the deposition rate calculation on the basis of known parameters of the model substance is offered. The leaf conductivity (g_L), equalled to reciprocal r_c was estimated as the sum of stomato ($g_s = 1/r_s$) and cuticle ($g_{cuticle} = 1/r_{cuticle}$) conductivities:

$$g_L = g_{cuticle} + \alpha g_s \quad (2.22)$$

And $\alpha = 0$, when stomato are closed,

$\alpha = 0.5$, when stomato are open.

The total conductivity (g_T), including conductivity of the boundary layer (g_B), can be expressed as:

$$\frac{1}{g_T} = \frac{1}{g_L} + \frac{1}{g_B} \quad (2.23)$$

Water vapor is used as the model substance, assuming the value of the open stomato conductivity equals 1×10^{-3} m/s, and the boundary layer conductivity equals 1×10^{-2} m/s. The conductivity of the chemical of interest (g) was estimated by the model substance conductivity and the molecular weight ratio:

$$g \approx g^W \left(\frac{M_m^W}{M_m} \right)^{0.5} \quad (2.24)$$

where M_m^W is molecular weight of water;

M_m is molecular weight of a chemical;

g^W is water vapor conductivity.

The cuticle conductivity is usually determined experimentally and, as a rule, for an isolated leaf. In [Riederer, 1990] values of cuticle, stomato and total conductivity for a number of organic substances are listed. For example, the total conductivity for leaves at open stomato varied from 1.37×10^{-4} (2.4D) to 2.50×10^{-3} (4-NP) m/s^{-1} . It is easy to see that the deposition rates are insignificant and did not exceed the tenth of a centimetre in a second. Estimated conductivity values for HCB, lindane and PCB-153 are shown in table 3.1. The data on leaf absorption were taken from [Riederer, 1990]. For other POPs the assessment of the foliage absorption were calculated with the use of ratios (3.5 - 3.7)

Analysis of the tab. 2.4. shows, that the values of deposition rates for considered POPs, as a rule, do not exceed $\sim 0.04 \text{ cm}\cdot\text{h}^{-1}$ for open stomato. It is necessary to note, that dry deposition rates for POPs are insignificant and in consistency with the experimental data for known inorganic substances [Sehmel, 1980]; for example, for SO_2 the dry deposition rate was in the range of values from 0.04 to $7.5 \text{ cm}\cdot\text{h}^{-1}$, I_2 - from 0.02 to $26 \text{ cm}\cdot\text{h}^{-1}$, H_2S - from 0.015 to $0.38 \text{ cm}\cdot\text{h}^{-1}$.

Table 2.4: POPs conductivity values

Substance	$\times 10^{-5} \text{ m}\cdot\text{c}^{-1}$				$\log K_{J/W}$	$\log K_{A/W}$
	g_{cuticle}	g_s	g_T^{open}	g_T^{close}		
HCB	29.8	25.1	36.3	26.7	5.47	-2.54
Lindane	22.2	24.8	30.4	20.4	3.4	-3.85
PCB -153	4.27	22.3	14.4	4.2	7.0	-2.25

Conclusions

At present, a chemical compound accumulation on the leaf surface can be calculated by the known technique. However it requires a number of empirical input data, which for considered POPs are frequently unknown. In this connection a simple calculation scheme based on the data for a model substance is offered.

2.2 Wet deposition of POPs

The total extend of organic pollutant (OP) scavenging by precipitation may be given as [Ligorcki et al., 1995a]:

$$W_T = W_v(1-\phi) + W_p\phi \quad (2.25)$$

where W_T , W_v and W_p are the total, gas-phase and aerosol washout ratios equal to ratios of the corresponding fraction concentration in the precipitation to that in air;

ϕ is a fraction of the total atmospheric concentration occurring in the particle phase.

Gases and aerosol particles can be captured by the fallen raindrops under the cloud (sub-cloud washout) or directly in the cloud (in-cloud washout). Gases transfer from air to drops as a result of dissolution. The velocity of this process is quite high and equilibrium concentrations of the gaseous OP in the drop-air system are achieved in several seconds [Slinn *et al.*, 1978]. Equilibrium of a gas dissolution in liquid is described by Henry's law constant and W_v value for both in-cloud and sub-cloud washout is calculated as follow:

$$W_v = RT/H = 1/K_H \quad (2.26)$$

where R - universal gas constant, Pa.m³/mol.°K;

T - temperature, °K;

H- Henry's law constant, Pa.m³/mol;

K_H - unit less Henry's law constant.

Validity of equation (2.26) for different classes of nonpolar POPs, including PAH and organochlorine compounds was experimentally proved by *M.Ligorcki et al.* [1995a] The measured W_v values were not more than two times different from the corresponding $1/K_H$ values at the same temperature [Bidleman and Foreman, 1987]. However, some examples of significant deviation from Henry's law are described in literature [Leuenberger *et al.*, 1985; Glotfelty *et al.*, 1987; Schomburg *et al.*, 1991].

Concentrations of some pesticides in fog drops were tens and even thousands times higher than calculated with equation (2.2) [Glotfelty *et al.*, 1987; Schomburg *et al.*, 1991]. This fact can be explained by possible formation of colloids or fine suspension in fog's drops and(or) POPs adsorption on the drops surface.

Chlorinated phenols concentrations in the rain water were somewhat lower those calculated using equation (2.2) [Leuenberger *et al.*, 1985]. Authors explained this observation with possible mistakes of the analytical procedure and exhaust of the washed out substances in the air.

At present there are no methods of parameterization of the aerosol particles washout by means of their physico-chemical properties and precipitation characteristics. *Y.Izrael et al.* [1983] analysed the mechanisms of the processes responsible for aerosol particles capture by rain drops and arrived at the conclusion that quantitative description of the aerosol particles washout from atmosphere is impossible so far because of the lack of the experimental data. No significant progress in the area during the last 15 years was achieved and expert judgements are used in the modern models to estimate W_p values [Cotham and Bidleman, 1991; Mackay and Paterson, 1991; Eisenreich *et al.*, 1992; Mackay and Wania, 1995; Wania and Mackay, 1995].

Most effective particles scavenging from atmosphere takes place when they serve as condensation nuclei for cloud water. According to Scott's estimation, in-cloud scavenging can produce W_p values of about 10^6 [Scott, 1981]. This estimation is in a good agreement with the experimental data. W_p values measured for watersoluble particles (dyes and inorganic salts) are in the range from 6.8×10^5 to 1.6×10^6 , for aerosol particles containing radionuclides - from 0.6×10^5 to 9.1×10^5 [Peterson, 1983]. Washout ratio for hydrophobic particles are expected to be significantly less [Bidleman, 1988].

Separate estimation of the sub-cloud and in-cloud particle washout ratios is difficult because published W_p values are calculated as a rule from the data on POPs concentrations in the precipitation and in the

near-ground air layer, while vertical particles distribution and cloud layer height are unknown. However, some estimations can be done.

F.Rovinskiy et al. [1988] report benzo(a)pyrene monthly average concentrations in the precipitation and near-ground air layer in the background regions of the European part of the former USSR. The ratios of these concentrations were an order of magnitude higher at summer time ($10^4 - 10^5$) than at winter time ($10^3 - 10^4$). They can be used as a W_p value estimation because washout of the gase phase fraction gives a negligible contribution into the benzo(a)pyrene total washout ratio ($W_v(1-\phi) \approx 10^1 - 10^2$). At summer time, when the influx from remote urban territories is probably the main source of benzo(a)pyrene in air, it can be supposed that its vertical distribution in the atmosphere is quite uniform. According its vertical to *W.Slinn et al.* [1978] the sub-cloud washout effectivity is significantly less than that for in-cloud washout. Therefore it is reasonable to assume that W_p values determined in background regions at summer time characterize mainly in-cloud washout of benzo(a)pyrene. These values are somewhat underestimated because of the rain averaged benzo(a)pyrene concentration was used for their calculation. Experimentally measured PAH concentration in the rain water has a tendency to decrease with time, so in some cases at the end of the rain it can be one-two orders of magnitude less than at the beginning [*Van Noort and Wondergem*; 1985, *Andrukov et al.* 1982]. Taking into account W_p values determined for PAH by *B.McVeety and R.Hites* [1988] - $1.4 \times 10^5 - 2.5 \times 10^5$, and *D.Poster and J.Baker* [1996a] - $10^5 - 10^6$ for particles larger than $0.5 \mu\text{m}$ and $10^4 - 10^5$ for smaller particles, the $W_p = 2 \times 10^5$ can be recommended as in-cloud washout ratio for benzo(a)pyrene.

W.Slinn et al. [1978] estimated sub-cloud W_p value for the aerosol particles of the size from 0.1 to $1 \mu\text{m}$ as $10^3 - 10^5$. This estimation is in a good agreement with benzo(a)pyrene washout ratios calculated from data of *F.Rovinskiy et al.* [1988] for winter time, early spring and late fall ($10^3 - 10^4$), and measured by *R.Herrman* [1987] in December 1984 in Germany (4.6×10^3). At this period of time benzo(a)pyrene is emitted into the atmosphere mostly from local overground sources and it can be expected that its concentration in the sub-cloud layer is much higher than in cloud. However the contribution from cloud washout can be significant in this case as well. Therefore the range $10^3 - 10^4$ is just the upper estimate of W_p values for benzo(a)pyrene sub-cloud washout. This is confirmed by W_p values ($10^2 - 10^3$) measured for benzo(a)pyrene in February-April 1984 in Portland, Oregon State by *M.Ligorcki et al.* [1985b]. Taking into account benzo(a)pyrene tendency to associate with hydrophobic fraction of the atmosphere aerosol, for example with soot particles, it is reasonable to use the lowest limit of the range recommended by *W.Slinn et al.* [1978], i.e. $W_p = 10^3$ as an estimation of its sub-cloud washout ratio.

According to equation (2.26) W_v doesn't depend on the rain intensity and duration. For nonpolar organic substances it is confirmed by *M.Ligorcki et al.* [1985a]. Standard deviations of W_v values averaged over seven different rains did not exceed 30% for the most of studied POP.

Assuming constant rain intensity and uniform vertical distribution of the gaseous fraction of POP concentration in the cloud and subcloud layers its decrease with time can be described by the following equation:

$$\chi_v(t) = \chi_v^0 \exp(-W_v h^{-1} I t) \quad (2.27)$$

where $\chi_v(t)$ è χ_v^0 - gaseous fraction concentration at time t and before the beginning of the rain, (ng/m^3);

h - cloud and sub-cloud layers total thickness (m);

I - rain intensity (m/s);

t - time passed after the rain (s).

With precipitation intensity dependent on time the amount of precipitation (m^{-1}) fallen at moment t must be included in equation (2.27) instead of its product.

Assuming that the order of magnitude of h is 10^3 m and W_v for POP doesn't exceed 10^4 , we obtain that essential decreasing of $\chi_v(t)$ can happen only if the amount of precipitation is about 10 mm or more. At lower rain intensity noticeable change of the gas-phase POP concentration can take place only at its ununiform vertical distribution with the atmosphere.

W_p in contrary to W_v , depends on precipitations intensity. The main reason for this is supposed to be the different drop sizes in rains of different intensity [Makhon'ko, 1967]. The concentration of the aerosol particles in the rain water is inversely proportional to the drop radius [Makhon'ko, 1967], which is, in turn, directly proportional to rain intensity powered by 0.25 [Slinn, 1977]. Therefore, rain intensity changing in hundred times leads to only three times change of washout ratio. W_p values dependence on rain characteristics and particles properties is much stronger. Washout ratio for particles larger than $0.5 \mu m$ was an order of magnitude higher than for smaller particles [Poster and Baker, 1996a], standard deviations of W_p values for PAH averaged over several different rains was about 100% [Poster and Baker, 1996a]. Quantitative description of the aerosol particle washout dependence on rain characteristics and particles properties is impossible because of lack of experimental data and theoretical approaches. Thus it is not reasonable to account for relatively a dependence of W_p on rain intensity. This conclusion is supported by the fact that experiments often don't show significant correlation between W_p and I [Peterson, 1983].

Decrease of POP concentration in rain drops occurs due to dilution of in-cloud drops by ambient water vapor condensation and as a result of sub-cloud concentration depletion [Makhon'ko, 1967; Avramenko and Makhon'ko, 1970]. Both these processes can be described by equation (2.27) with W_v and h replaced by W_p and corresponding layer thickness. However there are some significant differences between vapor and particles washout.

The first, particles can be assumed to be irreversibly captured by falling raindrops and concentration of the particulate fraction of POP can be calculated as follows:

$$\tilde{N}_p = W_p(c)\chi_p(c) + W_p(sc)\chi_p(sc) \quad (2.28)$$

where $W_p(c)$ and $W_p(sc)$ are in-cloud and sub-cloud washout ratios;

$\chi_p(\tilde{n})$ and $\chi_p(sc)$ - average concentrations of particulate fraction of POP in cloud and sub-cloud layers (ng/m^3);

C_p - concentrations of particulate fraction in rain water near the ground (ng/m^3).

The second, concentration of particulate fraction in rain water can very rapidly decrease with time [Van Noort and Wondergem, 1985; Andriukov et al., 1982].

Only few data are available on POP scavenging by snow. J.T.Hoff et al. [1996] show that the main mechanism governing transfer of gaseous POPs from air to snow is adsorption on the ice crystals surface. They proposed the following equation for the calculation of ice-air distribution coefficient, defined as a ratio of the equilibrium POP concentration in air (ng/m^3) to its concentration on the ice crystal surface (ng/m^2):

$$\log k_{ia} = -0.769 \log S_L + \log(RT/H_{293}) + (\Delta H_a/2.303R)(T^{-1} - 293^{-1}) \quad (2.29)$$

where k_{ia} - ice-air distribution coefficient, m;

S_L - solubility of supercooled liquid at $293\hat{E}$, mol/m^3 ;

H_{293} - Henry's law constant at $293\hat{E}$, $Pa \cdot m^3/mol$;

ΔH_a - enthalpy of adsorption, kJ/mol , for nonpolar POP $\Delta H_a = 0.879\Delta H_b$,

where $\Delta H_{\bar{n}}$ - enthalpy of supercooled liquid sublimation, kJ/mol.

The ice-air distribution coefficient permits the calculation of the gaseous OP washout ratio:

$$W_v = k_{ia} a_s \quad (2.30)$$

where a_s is a specific surface area of snowflakes, m^2/g .

An order of magnitude of a_s for fresh snow was estimated as $1 m^2/g$ [Hoff *et al.*, 1995]. Individual snowflakes obviously have a larger specific surface area, but it has not been measured experimentally.

W_p values measured for washout by snow of elementary carbon - 0.8×10^5 [Noone and Clarke, 1988] and PAH - $(0.5-0.7) \times 10^5$ [McVeety and Hites, 1988] are very close to that of rain scavenging. The value $W_p = 0.7 \times 10^5$ can be recommended as an estimation of the washout ratio for POPs particulate fraction by snow.

Recommendations

W_p values estimated above for benzo(a)pyrene (2×10^5 for in-cloud and 10^3 for sub-cloud washout) can be also used for any other nonpolar POP because it makes a sense to suppose that their distributions with aerosol particles are not significantly different. This assumption is supported by the fact that washout ratio for PCBs are quite close to that of PAHs [Capel *et al.* 1991].

For washout of POPs by snow $W_p = 0.7 \times 10^5$ is recommended.

W_v values for POPs scavenging by rain and snow can be calculated using equations (2) and (6) correspondingly.

3 DISTRIBUTION OF POPs BETWEEN SOLID, WATER AND GAS PHASES

3.1 Solubility

Solubility in water is one of the most important POP characteristics influencing its migration in the environment including penetration into vegetation and water organisms, vaporization from surfaces of soils and water bodies, and washout rate from the atmosphere by precipitation.

Problems of nonpolar and weakly polar organic compound solubilities estimation are connected both with difficulties of their experimental measurement and with the lack of physically based estimation methods. Solubility of the same compound published in different studies shows variation in the range of one order of magnitude [Mackay and Shiu, 1984; Sabljic, 1989]. On the other hand all solubility calculation methods are partly or totally based on correlation analysis and therefore their precision directly depends upon the quality of experimental data used for the determination of the empirical coefficients. Therefore 2-3 times difference of the assessed solubility from the measured value is believed to be quite satisfactory [Lyman, 1986].

The following methods are usually used for the solubility estimation: UNIFAC method [Gmehling, 1978], correlation equation $S = F(K_{ow})$, where K_{ow} is the partition coefficient of POP in the octanol-water system, and the correlation of the POP solubility with the molecular connectivity indices of different orders [Samiullah, 1990]. As has been shown by the precision analysis of these methods the most reliably the POP solubility can be assessed by the UNIFAC method [Andrien and Doccette, 1987].

It is necessary to take into account when using experimental or calculated solubility values for modelling of POPs behaviour in the environment that these data are usually provided for distilled water. Solubility of organic compounds in natural waters can differ considerably from its solubility in distilled water. The most important characteristics of natural waters influencing POPs solubility are:

Content of dissolved organic matter

Solubility of a POP in natural water containing dissolved organic matter (DOM) may be tens times as much as that in distilled water. The extent of this effect depends on the chemical nature of DOM and POP [Boehm and Quinn, 1973]. For example solubility of PCBs increases from 5 to 7 times as humic acid concentration increases from 0 to 100 mg/L. At the same time the increase of fulvic acid concentration in the same range does not have such pronounced effect on PCB solubility. Lindane and 1,2,3-trichlorobenzene solubility for these conditions remained practically constant and was not affected by nature and concentration of DOM [Choiu et al., 1986].

Salinity Concentration of dissolved salts in water also influence POP solubility. For example solubility of almost all PAHs in sea water is 1.5-2 times lower than in distilled water and the effect increases at decreased temperatures [Whitehouse, 1984]. At the same time solubility of 1,2-benzanthracene is higher in sea water (approximately 6 times at 3.7 °C).

pH. Solubility of organic compounds capable to form ions in solution, depends considerably on the pH value of natural waters. For example the solubility of pentachlorophenol is controlled by pH. Influence of pH on solubility of nonpolar organic compounds is not so pronounced.

Temperature. Solubility of compounds in water is also temperature dependent. Most organic compounds is better dissolved in water at high temperature, but there are a lot of exceptions from this rule [Lyman, 1982]. UNIFAC method, as was mentioned earlier, allows to assess solubility at any temperature, but the uncertainty of the assessment for temperatures other than at 25°C may be significant.

Recommendations

For modelling of POP behaviour in the environment the use of the empirical correlations of solubility with temperature seems to be the most reasonable approach. As the temperature range of interest is relatively narrow (0-50°C), the empirical equations may provide reasonably good precision. It is desirable to use two different equations - one for fresh and one for sea waters.

The effect of DOM on POPs solubility can be significant, especially for soil solutions and surface fresh waters. This effect, however, can not be quantitatively described because of the lack of systematized experimental data on DOM chemical nature role in solubilizing of POPs.

3.2 Sorption in soils and sediments

Hydrophobic interactions with soil and sediment organic matter is the main mechanism of sorption of nonpolar and weakly polar organic compounds in soils and sediments. Therefore sorption capacity of soils and sediments for these compounds usually quantitatively described with only one parameter: organic carbon content. The value of POP partition coefficient normalized to the weight fraction of organic carbon (\hat{E}_{in}) usually is not changed more than 2 times for different soils, although for some compounds standard deviation from average value is more than 100% [Lyman, 1982; Von Oepen, 1991]. Partition coefficient normalized to the organic matter content in soils K_{om} is also used along with \hat{E}_{in} . The equation $\hat{E}_{in} = 1.724 K_{om}$ is common way of relating these coefficients.

In addition to soil organic matter content the following characteristics of the soil-water system influence sorption of nonionic POPs.

Nature of soil organic matter. Partition coefficient of nonionic POP on the organic matter of different origin may vary within one order of magnitude. Most important characteristics of natural humic acids influencing their sorption capacity are the fraction of aromatic fragments in the molecular structure, the size of the molecules and their polarity [Enfield, 1989].

Temperature. Adsorption is an exothermic process and partition coefficient decreases with temperature increase. For most POP the \hat{E}_{in} value decreases by approximately 30% as temperature changes from 5 to 30°C [Lyman, 1982].

Salinity. Adsorption of nonpolar and weakly polar organic POP is not considerably affected by salt concentration in water. S.Karickhoff et al. [1979] has shown that the change of \hat{E}_{in} value in sea water would be not more than 10-20% in comparison with fresh water.

Acidity of the water phase. Change in pH of the water phase influences sorption of a compound capable to form ions in solution. For example the partition coefficient of pentachlorophenol in the same soil suspension decreases 20-30 times as pH of water phase is changed from 3 to 7 [Lee et al., 1990].

DOM Content. Presence of dissolved organic matter in natural waters may influence sorption of nonpolar compounds very much. For example the value of γ -hexachlorocyclohexane partition coefficient is increased approximately in 2 times as the concentration of dissolved organic matter is increased from 8 to 24 mg/L [Enfield et al., 1989]. This effect can be pronounced considering that the maximum DOM concentration in natural waters may reach 100 mg/L.

POP sorption by soils and sediments is a function of both sorbent characteristics and POP properties. Octanol-water partition coefficient and molecular connectivity indices are used in conventional methods of \hat{E}_{in} assessment as a sorption characteristic of POP. The value of organic carbon partition coefficient for nonpolar POP can be calculated by these methods with sufficient accuracy.

In addition to the equilibrium sorption parameters (partition coefficients) sorption kinetic and reversibility may play considerable part in the transport processes of POPs in the environment. Most of the existing models of POPs sorption by natural sorbents (soil and sediment solids, suspended particles in natural waters, atmospheric aerosol particles) consider sorption as instantaneous and completely reversible. But there are a lot of experimental evidences of irreversible sorption of organic pollutants by soils [Horzempa and DiToro, 1983], sediments [Karickhoff, 1986] and atmospheric aerosol [Bidleman and Foreman, 1987]. Irreversible sorption of POPs may considerably affect the rate of their sorption and degradation in the environment and one of the main directions of improvements of transport models in the environment is accounting for sorption kinetics.

Recommendations

For modelling of POPs behaviour in the environment it looks reasonable to assume that POPs distribution in soil-water system depends only on K_{oc} value of chemical and soil organic carbon content.

3.3 Vapor pressure

The vapor pressure of a POP determines its maximum concentration in the air, the volatilization rate to the atmosphere from the water bodies and soils, and distribution between the gas and aerosol fractions in the atmosphere. Dozens of equations were proposed for vapor pressure estimation [Lyman, 1982].

Most of them were derived by integration of the Clausius-Clapeyron equation. Antoine equation is one of the simplest and sufficiently accurate equation for the vapor pressure calculations:

$$\ln P_v = A - B/(T + C) \quad (3.1)$$

where P_v is vapor pressure, Pa;

T is temperature, $^{\circ}\text{K}$;

A,B,C are constants.

Constants A, B and C can be calculated by semi-empirical relations. As a rule the accuracy of the vapor pressure assessment in the range from 10 to 1500 torr by Antoine equation is not more than 10% [Lyman, 1982]. Even more accurate assessment of the vapor pressure for this interval can be achieved by using coefficients A, B and C derived by regression analysis of the experimental data [Reed *et al.*, 1982].

For vapor pressures below 10 torr Watson correlation in Grain modification gives more accurate assessments [Lyman, 1986]. D.Mackay *et al.* [1982] derived another equation for aromatic and chloroaromatic compounds. Both equations give satisfactory results for compounds with the vapor pressure more than 10^{-5} atm [Lyman, 1986]. Recently for less volatile compounds the correlation relationships of the vapor pressure and temperature in the form $\ln P_{vp} = A - B/T$ has been used [Wania *et al.*, 1994]. Such relationships provide enough accuracy, considering rather narrow temperature range of interest.

Recommendations

For modelling of POPs behaviour in the environment the use of empirical correlations of vapor pressures and temperature seems to be the most reasonable approach.

3.4 Partitioning between water and gas phases

Equilibrium of POPs exchange between water and gas phases is characterized by the Henry's law constant (H).

Henry's law constant is defined as the ratio of the POP equilibrium concentration in the gas phase to that in the solution. As well as saturated vapor pressure and solubility, the H value is a function of water phase composition and temperature.

In literature one can find a lot of Henry constant values for POPs calculated as the relation of their saturated vapor pressures to their solubilities. Over the last several years experimental values of H for POPs were published, and often as a function of temperature [Kucklik *et al.*, 1991; ten Hulscher *et al.*, 1992]. Several methods of theoretical evaluation of Henry constants were also developed [Lyman, 1986]. But these methods can not assess H values for compounds with low solubilities and vapor pressures with satisfactory precision. Therefore it is advisable to use empirical relationships for routing prognosis. Dependence of a Henry's law constant on temperature is usually presented in the form $\log H = A/T(K) + B$, where A and B are coefficients.

Recommendations

For modelling of POP behaviour in the environment the use of empirical correlations of Henry's law constant and temperature seems to be the most reasonable approach. As the temperature range of interest is relatively narrow, it seems that the empirical equations may provide reasonably good precision. It is desirable to use two different equations - one for fresh and one for sea waters.

3.5 Partitioning between aerosol and gas phases in atmosphere

3.5.1 Relationship of atmospheric characteristics emission source and sampling site location

POPs partitioning in atmosphere between the gas and the aerosol fractions depends on physical-chemical properties of an organic compound and aerosol characteristics. Atmospheric aerosol can be classified as urban, suburban and rural (background).

Rural aerosol comprises global aerosol, soil particles, and sea aerosol when sampling site located near the sea. In terrestrial rural regions more than half of the tropospheric aerosol originated from soil [Van Malderen *et al.*, 1996].

In towns additional sources of aerosol particle emission to the atmosphere include car exhaust, fuel combustion, and industrial emissions.

The particle size spectrum ranges from 0,005 to 20 μm in diameter. The life time of the finest and the largest particles are limited by the rapid coagulation of smaller particles and by the gravitational settling of the large ones. Therefore almost all atmospheric aerosol comprises particles from the fraction of μm to several μm in diameter [Bidleman, 1988].

Particulate organic and elemental carbon constitutes approximately 10% and 5% in urban aerosol, respectively, and is very important for POP sorption. In aerosol fraction with aerodynamic diameter less than 2.5 μm the carbon content is 1.5-2 times higher than average [Bidleman and Foreman, 1987].

3.5.2 POPs distribution with atmospheric aerosol sizes

POPs fate in the atmosphere greatly depends on the particle size distribution they are adsorbed on. In urban aerosol the main mass of the organic aerosol is associated with particles less than 2 μm in diameter. It was experimentally found for PAHs [Schneller *et al.*, 1995, Poster *et al.*, 1995, Back *et al.*, 1991], polychlorinated dibenzodioxins and dibenzofurans [Kaupp *et al.*, 1994], aliphatic hydrocarbons [Van Vaeck *et al.*, 1978]. The main fraction of PAH collected in London was associated with particles from 0.4 to 1 μm in diameter [Back *et al.*, 1991], and in road tunnels more than 85% PAH was bound on particles with diameter less than 0.12 μm [Venkataraman and Friedlander, 1994].

Reported data on POPs associated with different size fractions of the urban aerosol allow to make some conclusions about the size distribution of POPs containing particles in emissions to the atmosphere, because the main sources of the atmosphere pollution, if do not take into account agricultural chemicals, are situated in urban areas. Absence of essential quantity of the organic POPs on the coarse fraction of the urban (collected near the emission source) aerosol particles indicates that the main part of the POPs in emissions is associated with the gas phase or fine particles and, therefore, is able to long-range atmospheric transport.

In rural areas organic POPs are distributed more evenly with different size-fractions of the atmospheric aerosol [Allen *et al.*, 1997]. It may be due to particles transformation and the POP transfer between particles of different sizes in the process of their transport, and the result of predominantly soil origin of the rural aerosol. As was mentioned in chapter 1.2.2, organic POP distribution with soil granulometric fractions can be regarded as uniform.

3.5.3 Influence of the environmental characteristics and particle properties on the POP vapor/particles partitioning

3.5.3.1 Temperature dependence of POPs vapor/particles partitioning

Taking into account that adsorption is always an exothermic process, the equilibrium gas-phase fraction of a compound increases as temperature increases. Assuming that the enthalpy of adsorption does not depend on temperature, the particles-air distribution coefficient, defined as the ratio of POP concentration in particles (ng/μg) to that in air (ng/m³), can be given as:

$$K_p = P/G(\text{TSP}) = A \exp(B/T) \quad (3.2)$$

where K_p is particles-air distribution coefficient, m³/μg;

P and G are particle-associated and gaseous concentrations, ng/m³;

TSP is total suspended particulate matter concentration, μg/m³;

A and B are compound- and particle-dependent coefficients;

T (K) is temperature.

H. Yamasaki et al. [1982] found that the equation 3.2 suited well to the experimental data of PAH partitioning in the atmosphere; afterwards many authors used it in different modifications for a description of experimentally derived POPs K_p values [*Bidleman and Foreman*, 1987; *Pankow*, 1991; *Back et al.*, 1991; *Lane*, 1992; *Hoff et al.*, 1992; *Poissant and Koprivniak*, 1996].

3.5.3.2 POPs vapor/particles partitioning as a function of air humidity

Mechanism of water vapor effect in the atmosphere on the POP adsorption on aerosol particles depends on relative humidity (RH). At low RH water molecules compete with POP molecules for the adsorption sites on the particles surfaces. The effect of RH on POPs adsorption depends on the relative affinity of water and POP to the particle matrix. On mineral surfaces water is sorbed much better, and RH increase results in sharp decrease of the partition coefficient value [*Valsaraj and Thibodeaux*, 1992]. On the contrary, on the surfaces of a hydrophobic soot particles or an organic soil, POPs are sorbed much stronger than water. RH change does not considerably influence POPs sorption by these particles [*Keener and Zhou*, 1990].

After humidity has reached some value, a monomolecular layer of adsorbed water molecules is formed over the particle surface. At this and higher RH POPs are sorbed not on the particle surface itself, but on the surface of the water film.

On mineral surfaces the water monolayer forms at RH ≈ 20% [*Valsaraj and Thibodeaux*, 1992]. Therefore, mechanism of POPs competitive sorption for such particles may be important only in soils, as typical RH range in atmosphere is from 30 to 95%. On the surfaces of the hydrophobic particles the film of water molecules is formed at much higher RH. Therefore even at ordinary values of RH competitive adsorption of POP and water molecules takes place. However, taking into account the low affinity of water molecules to hydrophobic sorbents the effect of RH on POPs sorption can be regarded as negligible.

At medium and high RH values it influences POPs adsorption by changing particles surface area. The main fraction of particles surface area is associated with pores of different diameter. Pores with diameter less than some critical RH-dependent value are filled with water as the result of capillary condensation and their surface is unavailable to the POP sorption. At RH close to 100% atmospheric aerosol can be considered as a three-phase system, comprising solid particles, water phase and air.

Interphase POP partitioning is determined by their dissolution in water and adsorption from the water solution.

Experimental data showed that for urban aerosol the air humidity did not considerably influence POP partitioning. *W.Coatham and T.Bidleman* [1995] showed that relative humidity in the 30-95% range had little effect on the organochlorine pesticides adsorption by urban aerosol particles. Partition coefficient of PAH measured experimentally for urban aerosol depends on RH, but much weaker than on temperature [*Pankow, 1993; Lee et al., 1994*].

On the other hand increasing of RH from 30 to 70% under laboratory conditions leads to a decrease of PAH adsorption on quartz by a factor of 10 [*Storey et al., 1995*]. Considering this contradiction between the laboratory and field measurements the authors concluded that in urban aerosol nonpolar organic molecules are adsorbed mainly on hydrophobic aerosol components. This conclusion is supported by much lower PAH adsorption by unit of quartz surface in comparison with urban aerosol particles.

Modern models of atmospheric transport do not usually take into account the effect of humidity on the POPs vapor/particles partitioning, that is quite reasonable for the urban aerosol. Influence of humidity on POPs adsorption can be significant in rural regions, where the fraction of the hydrophobic particles is much less than in the urban aerosol. Unfortunately, experimental data on the POPs vapor/particles partitioning dependence on humidity for rural regions are unavailable.

3.5.3.3 Theoretical models of POP sorption on the atmospheric aerosol particles

Currently several models of POPs adsorption on aerosol particles in atmosphere are available in literature. *C.Junge*, [1977] proposed, that concentration of a POP adsorbed on aerosol is directly proportional to its partial pressure in the atmosphere divided by the saturated vapor pressure at a given temperature and got the following equation:

$$C_p = C/(K_J C_{sa} + 1) \quad (3.3)$$

where $K_J = 1/N_s a_{TSP}$;

a_{TSP} is specific surface area of the aerosol, m^2/g ;

$C_{sa} = 4.2 \times 10^{-4} p_v$, $mol/m^3 atm$;

p_v is saturated vapor pressure, Pa;

\tilde{N} is total concentration of POP in air, ng/m^3 ;

C_p is concentration of POP on particles, mol/m^3 ;

N_s is density of adsorption sites on the particles surface (mol/m^2).

For modelling of the organic compound adsorption with enthalpy of desorption close to the enthalpy of vaporization of subcooled liquid the following equation was proposed [*Pankow, 1987*]:

$$\hat{E}_\delta = \hat{A}/p_{OL} \quad (3.4)$$

where \hat{A} is aerosol particles, POP and temperature-dependent parameter.

p_{OL} is saturated vapor pressure of subcooled liquid, Pa.

Later the author modified this equation for compounds with the adsorption enthalpy much higher than the enthalpy of vaporization and included the term describing partitioning into an organic matter phase [*Pankow et al., 1994*]:

$$K = \frac{1}{\rho_L^0} \left[\frac{N_s a_{tsp} T e^{(Q_i - Q_v)/RT}}{1600} - \frac{f_{om} 760RT}{MW_{om} \zeta 10^6} \right] \quad (3.5)$$

where: Q_i is enthalpy of desorption, kJ/mol;

Q_v is enthalpy of vaporization of subcooled liquid, kJ/mol;

f_{om} is weight fraction of organic matter;

MW_{om} - molecular weight of the organic matter (g/mol);

ζ is activity coefficient of an organic compound in organic matter phase.

Equations (3.3)-(3.5) describe adsorption of organic compounds on the aerosol particle itself and do not take into account the influence of the atmospheric humidity. They seem to be relevant with some level of accuracy for the urban aerosol, where vapor/particles partitioning of POPs does not depend considerably on RH. The detailed analysis of equations (3.3)-(3.5) are given by *J.Pankow* [1987] and *J.Pankow et al.*, [1994].

As was mentioned above, the atmospheric humidity in rural aerosol can be much more important than in urban sites because of a larger fraction of mineral particles. Therefore for rural areas semi-empirical equation for adsorption of organic compounds on mineral surfaces as a function of RH and temperature seems to be more useful [*Goss*, 1994a]:

$$\ln K_d = A^* - \frac{\Delta H_s}{R} (1/T - 1/323.15) - C(100 - RH) \quad (3.6)$$

where A^* and \tilde{N} are constants;

ΔH_a is enthalpy of adsorption.

Constants A^* and \tilde{N} and the enthalpy of adsorption can be calculated from the quantity characteristics of substance and aerosol using regression relationships [*Goss*, 1994a].

In practice equations (3.3)-(3.6) can be used only if there are data about quantity characteristics of organic compounds adsorption on aerosols particles of different chemical nature, aerosol composition and specific surface area of different kinds of particles. Usually these data are unavailable. In addition these equations based on the assumption that adsorption is completely reversible, but in real aerosol a considerable part of organic compound can be sorbed irreversibly. Therefore it seems better to use for modelling of POPs vapor/particles partitioning the empirical correlations of the partition coefficient value with temperature and RH.

3.5.3.4 Empirical equations for POPs partition coefficients as a function temperature and relative humidity

Accuracy of the used experimental data is very important for coefficient calculations of the empirical relationships. Sampling train consists of a filter retaining aerosol particles and adsorbent cartridge absorbing organic compound in the vapor phase. During sampling POPs can be blown down from the aerosol particles and can be sorbed by the filter material from the vapor phase. As a consequence the ratio of the filter-retained and absorbed compound can be different from the ratio of the gas and particle fractions in the real aerosol. It is believed now, that this difference does not exceed 1.5-2 times [*Pankow et al.*, 1994]. For this reason the experimentally measured partition coefficient is defined not as in equation (3.2), but as the ratio of concentration of a compound retained by the filter (F , ng/m³) and retained by the absorber (A , ng/m³):

$$K_p = F/A(TSP) \quad (3.7)$$

Dependence of K_p on temperature is usually described by log form of the equation 3.2:

$$\log K_p = m_p/T + b_p \quad (3.8)$$

where m_p and b_p are constants.

The equation connecting the partition coefficient and the vapor pressure of subcooled liquid is also used:

$$\log K_p = m_r \log p_{OL} + b_r \quad (3.9)$$

where m_r and b_r are constants for a class of substances.

These equations coincide in form, if dependence of $\log p_{OL}$ on temperature is presented in the form $\log p_{OL} = A/T + B$, where A and B are constants.

For dependence of K_p on relative humidity the following equation was developed [Pankow, 1991]

$$\log K_p = m_p/T + b_p + \tilde{n}_p RH + d_p, \quad (3.10)$$

where \tilde{n}_p and d_p are constants.

Methods were developed for the assessment of substance-specific values of equations (3.8-3.10) constants [Pankow, 1991]. However, when empirical dependencies of K_p on temperature and humidity are available, it is better to use them.

Recommendations

For modelling temperature dependence of POPs distribution with gaseous and particle fractions the use of empirical correlations seems to be the most reasonable approach. Recommended relationships of \hat{E}_δ value and temperature for selected POPs are given in table 3.1.

Table 3.1. Recommended relationships of \hat{E}_δ value and temperature.

POP	p_L° (Pa) (25°C)	A_L	B_L	m_r	b_r	K_p (25°C) $m^3/\mu g$	m_p	b_p	K_p (25°C) $m^3/\mu g$
HCB	$1.25 \cdot 10^{-1}$	$11.11^{[1]}$	$-3582^{[1]}$				$3328^{[4]}$	$-16.117^{[4]}$	$1.11 \cdot 10^{-5[4]}$
Lindane	$6.42 \cdot 10^{-2[1]}$	$11.15^{[1]}$	$-3680^{[1]}$						
PCB-153	$1.58 \cdot 10^{-3[2]}$			$-0.726^{[3]}$	$-5.18^{[3]}$	$4.7 \cdot 10^{-3[3]}$			
BAP	$7.19 \cdot 10^{-6[1]}$	$11.59^{[1]}$	$-4989^{[1]}$				$5301^{[5]}$	$-18.48^{[5]}$	$0.20^{[5]}$

References:

[1] - *D.Hincley et al.* [1990]; [2], *R.L.Falconer et al.* [1995]; [3] - *W.Coatham and T.Bidleman* [1995]; [4] - *T.Bidleman and W.Foreman* [1987]; [5] - *J.Pankow* [1991].

\hat{E}_δ dependence on humidity can be modelled using equation (3.10) with the constant calculated as proposed by *J.Pankow* [1991].

For estimation of POPs vapor/particles partitioning equation (3.6) can be useful.

3.5.3.5 POPs sorption by water aerosols

In sections presented above POPs adsorption on solid aerosol particles was discussed. However important part in removal of POPs from the atmosphere can play water-droplets aerosols (fog). As was mentioned in chapter 2.2, concentration of some pesticides in fog droplets can be tens and thousands times higher than estimated from Henry's law [*Glotfelty et al.*, 1987; *Schomburg et al.*, 1991]. Two mechanisms were proposed for explanation of this fact: organic POPs adsorption on suspended in the

droplets microparticles [Glotfelty *et al.*, 1987; Schomburg *et al.*, 1991; Poster and Baker, 1996a; Poster and Baker, 1996b] and adsorption on the water surface of the droplet [Valsaraj, 1994; Goss, 1994b].

Absorption of organic compounds by fog droplets can be described by two partition coefficients:

$$K_{\text{pair}} = C_s/C_{\text{air}}; K_{\text{pwater}} = C_s/C_w \quad (3.11)$$

where K_{pair} is water surface-air partition coefficient, m.

K_{pwater} is water surface- water volume partition coefficient, m.

C_s is POP concentration on the air-water surface, ng/m²;

C_{air} is POP concentration in air, ng/m³.

C_w is POP concentration in water, ng/m³.

Valsaraj related octanol-water partition coefficient with surface partition coefficient [Valsaraj, 1994], and Goss proposed to relate K_{pair} values with saturated vapor pressure and POP hydrogen bond parameter [Goss, 1994b].

It was calculated that for fog droplets with diameter 8 μm the enrichment factor (excess of calculated by Henry's law concentration in water) for benz(a)pyrene equals 88, and for 2,2'-3,4,5'-pentachlorobiphenil equals 208.

Recommendations

The effect of fogs in the atmospheric transport of POPs can be significant, especially in territories with high probability of fog formation. This effect should be evaluated and, if necessary, taken into consideration in future modifications of the atmospheric transport models.

4 DEGRADATION PROCESSES OF POPs IN THE ENVIRONMENT

As a rule POPs is present in the environment at very low concentrations and therefore their degradation can be described by the first order kinetic equations with the effective rate constant which is equal to the sum of all degradation processes rate constants:

$$k_e = \sum k_i \quad (4.1)$$

where k_e is effective degradation rate constant;

k_i is degradation rate constant by i mechanism.

The main mechanisms of POPs degradation in the environment are presented below.

4.1 Biodegradation

Degradation of POPs as the result of microbiological activity is one the main process of their degradation in soils and natural surface waters. Kinetics of POPs biodegradation can be described by the equation of zero, first, and second order. Zero order kinetic equation is a simplified Mono equation at high POPs concentrations. It assumes the constant rate of POPs degradation:

$$dP/dt = -k^0 \quad (4.2)$$

where P is POP concentration in soil, mg/kg and in water (mg/L);

t is time, days;

k^0 is zero order rate constant, mg kg⁻¹ day⁻¹ or mg kg⁻¹ day⁻¹.

First order kinetic equation can be derived from the Mono equation assuming low POP concentrations:

$$dP/dt = -k^1P \quad (4.3)$$

where k^1 is the first order rate constant, day^{-1} .

Equation (4.3) can be also presented in the following form:

$$dP/dt = -k^bBP \quad (4.4)$$

where k^b is the second order rate constant, $\text{kg (mg of biomass)}^{-1} \text{ day}^{-1}$ or $\text{L (mg of biomass)}^{-1} \text{ day}^{-1}$;

B is specific biomass of the microorganisms, μkg^{-1} or mg L^{-1} .

There are no reliable methods of estimation of POPs biodegradation rate constants based on their properties and media characteristics. Therefore it is necessary to use published experimental data for a compound providing that the conditions of the rate constant measurement is as close as possible to the model one. The bulk of the experimental biodegradation data for POPs in soils are available for agricultural chemicals. Disappearance rate constants from soil for 150 pesticides were presented by *V.Kononiuk* [1985]. Bearing in mind that in addition to biodegradation, hydrolysis and volatilization also decrease POPs concentration in soils, these rate constants are equal to the biodegradation rate constants only for hydrolysis of stable and nonvolatile substances and can be regarded as top estimation for others. According to *V.Kononiuk* [1985], polychlorinated aromatic and aliphatic hydrocarbons are the most stable compounds with k^1 range from 0.001 to 0.01 day^{-1} .

POPs biodegradation rate constants in natural waters can be found only for a few compounds and it is difficult to assess the values of these constants for a given water body or a stream with good precision. As a rule POPs biodegradation in water is faster than in soil. The main reason for this phenomenon is that large proportion of a POP is in the sorbed pool and unavailable for degradation.

Choice of the kinetic equation for biodegradation modelling depends on the POP concentration in water or in soil. For the most POPs the critical concentrations in natural waters are in the range from 0.1 to 10 mg L^{-1} or 10^{-6} - 10^{-4} mol L^{-1} [*Battersby*, 1990]. If a POP concentration is higher than that range, for example at accidental petroleum spills, the biodegradation follows zero order kinetics. At lower concentrations equation (4.2) should be used.

Attempts to normalize biodegradation rate constant to the microorganisms number in soil or water give contradictory results. Constant k^b found in some references did not depend on the sampling site location, but in others the k^b values for the same POP can be three orders of magnitude higher [*Battersby*, 1990].

Recommendations

At present there are no reliable methods for the evaluation of biodegradation rate constants using POP properties and environmental characteristics. Therefore expert estimates are recommended to be used. Expert judgements are the only way for biodegradation rate constants estimation.

4.2 Hydrolysis

Hydrolysis, or reaction with water, is an important mechanism of an organic compound degradation in natural waters and soils. Hydrolysis rate constant can be presented in the following form:

$$k_w = k_a [H] + k_n + k_{OH} [OH] \quad (4.5)$$

where k_a , k_n , k_{OH} are rate constants for acid, neutral and base hydrolysis, respectively;

[H] and [OH] are H⁺ cation and OH⁻ anion concentrations, respectively.

Therefore POP hydrolysis rate depends on pH of natural waters. In addition it is a function of temperature:

$$k_i = A_i \exp(-E_{Ai}/RT) \quad (4.6)$$

where k_i and A_i are rate constant and activation energy of acid, neutral and base hydrolysis, respectively;

A_i is a constant.

The most easily hydrolyzed compounds are esters and amides of carbonic and other acids [Lyman, 1982]. Polychlorinated aliphatic and aromatic compounds can be hydrolyzed with essential rate only at high temperatures and pH. For example at 45 °C and $\delta I = 7.8$ lindane half-life is 150 days [Kucklick *et al.*, 1991], and at 25 °C and $\delta I = 7$ is more than 2000 days (calculation by Ellington equation [Ellington *et al.*, 1987]).

Recommendations

Contribution of hydrolysis to POPs degradation is significant only in some specific soils and natural water and can be neglected.

4.3 Direct photolysis

Direct photolysis is a reaction caused by the molecule absorption of a light quantum. Direct photolysis rate constant at a compound irradiation with wave length of λ can be described by the following equation [Skurlatov, 1996]:

$$k_{p\lambda} = 2.3 I_{0\lambda} \varepsilon_{\lambda} l \varphi \quad (4.7)$$

where $I_{0\lambda}$ is light intensity;

ε_{λ} is extinction coefficient;

l is light pass length;

φ is photolysis quantum yield.

As a rule direct photolysis is the main degradation mechanism of substances capable to absorb sun light. For example dissolved in water benzo(a)pyrene completely degrades on sun light in several hours [Lembrick, 1979]. If absorption spectrum and quantum yield of photodegradation of a compound is known, the direct photolysis rate can be calculated using the sun radiation data. Tables of the sun radiation intensity as a function of the wave length and the season can be found in literature [see, for example, Choudhry and Webster, 1985].

Recommendations

Direct photolysis is the main mechanism of benzo(a)pyrene degradation both in natural waters and in the vapor phase. For chlorinated benzenes, biphenyls and aliphatic hydrocarbons, it can be neglected.

4.4 Oxidation

Pollutants in the environment may be oxidized by oxygen and metals in oxidized state. However only specific POPs can react by this mechanism. Reactions with free radicals and other active reactants are more universal. The most important oxidants in the atmosphere are hydroxyl radical (OH^\bullet), ozone and

nitrate-radical, in natural waters - hydroxyl radical, singled oxygen, superoxed-radical (\hat{I}_2^{\bullet}), alcoxyl and hydroperoxide organic radicals.

Concentration of hydroxyl radicals in atmosphere and natural waters are low: the average concentration in the atmosphere is 10^6 molecules/cm³, in terrestrial waters - (10^{-17} - 10^{-15}) mol L⁻¹ [Skurlatov *et al.*, 1996], in sea water - (10^{-19} - 10^{-17}) mol L⁻¹ [Shtamm *et al.*, 1991]. However hydroxyl-radicals are the main POPs oxidants in the atmosphere and natural waters due to its very high reactivity [Finlayson-Pitts and Pitts, 1986]. The values of rate constants of the hydroxyl-radical interactions with almost all organic compounds are in the range of 10^8 - 10^{10} L mol⁻¹ [Pikaev and Kabakchi, 1982]. The gas-phase rate constants of organic compounds with hydroxyl radicals are typically in the range of 10^{-14} - 10^{-10} cm³molecule⁻¹s⁻¹ [Atkinson, 1994].

Experimental determinations of oxidants in natural waters were started only recently and systematic data of their concentration versus the time of day, season and natural waters characteristics are absent in the literature. Taking into account that one of the main mechanisms of radicals formation is photochemical generation [Skurlatov *et al.*, 1996], it can be expected that their concentration in summer would be higher than in winter. However experimental data do not agree with this assumption. For example, in a freshwater lake hydroxyl-radical concentration remained practically constant over the year [Ernestova and Semenova, 1995a].

Due to the lack of experimental data only annual average concentrations of hydroxyl radicals in natural waters can be estimated. Precision of the estimation for sea water seems to be not better than an order of magnitude because there are only few data on free radicals concentrations in seas and oceans [Shtamm *et al.*, 1991]. Annual average concentrations of hydroxyl radicals in natural waters are presented in table 4.1.

Table 4.1: Annual average concentrations of hydroxyl-radicals recommended for the assessment of POPs degradation rate constants in surface natural waters

Type of surface natural water	\hat{I}^{\bullet} concentration, mol L ⁻¹	References
freshwater rivers and lakes	2×10^{-16}	<i>Ernestova and Semenova 1995a</i> <i>Ernestova and Semenova 1995b</i> <i>Skurlatov et al. 1996</i> <i>Shtamm et al. 1991</i>
coastal sea water	10^{-17}	<i>Mooper et al. 1990</i>
ocean	5×10^{-19}	<i>Mooper et al. 1990</i> <i>Shtamm et al. 1991</i>

Rate constant values of POPs reaction with hydroxyl radical are presented in table 4.2. Rate constants for benzo(a)pyrene and PCB-153 were assumed to be of the same order of magnitude as for other polycyclic and halogenated aromatics [Pikaev and Kabakchi, 1982; Semenova, 1997].

Table 4.2: Recommended rate constant values of POPs interactions with hydroxyl-radicals

Compound	$k_{OH^{\bullet}}$, L/mol s	Notes
γ -HCH	3×10^{10}	<i>Semenova, 1997</i>
HCB	2.5×10^{10}	<i>Semenova, 1997</i>
Benzo(a)pyrene	10^{10}	assessment
PCB-153	10^{10}	assessment

Using data given in tables (4.1) and (4.2) it is easy to calculate the first order rate constant values for POPs interactions with hydroxyl radicals and the corresponding degradation half-lives in natural waters (see table 4.3).

Table 4.3: POPs degradation half-lives due to reaction with hydroxyl-radicals in natural waters

Compound	Half-lives, days		
	freshwater rivers and lakes	coastal sea waters	open ocean
γ -HCH	1.3	27	530
HCB	1.6	32	640
Benzo(a)pyrene	4.0	80	1600
PCB-153	4.0	80	1600

Superoxide radical may play an important role in POPs degradation, especially in sea water. Its maximum concentration in sea water is estimated as 10^{-8} - 10^{-7} mol L⁻¹ [Millero, 1987; Petasne and Zika, 1987]. Considering that the rate constants of the aromatic compounds reactions with superoxide radical are about 10⁶ L mol⁻¹ s⁻¹ [Mill, 1989], at such high concentrations of $\hat{I}_2^{\bullet-}$ in water POPs life time can not exceed several minutes. However these assessments should be carefully used, since there are no available experimental data.

At present several models are available which allows to calculate the hydroxyl radical concentration in the atmosphere [Tompson, 1995]. Yu Lu and M.Khall [1991] gave the table of calculated \hat{I}^{\bullet} concentrations as a function of geographical latitude, season, and time of the day. On 45⁰ N the average daily \hat{I}^{\bullet} concentration in the overground air layer of 2 km height is 2×10^6 molecules cm⁻³ in summer, 0.8×10^6 molecules cm⁻³ in fall and in spring, and 0.09×10^6 molecules cm⁻³ in winter. Rate constants of POPs interaction with hydroxyl radical in the atmosphere are 3×10^{-13} cm³ molecule⁻¹ s⁻¹ for PCB-153 [Kwok and Atkinson, 1995], 10^{-12} cm³ molecule⁻¹ s⁻¹ (our estimation) for γ -HCH, 10^{-13} cm³ molecule⁻¹ s⁻¹ (our estimation) for HCB, 10^{-10} cm³ molecule⁻¹ s⁻¹ (our estimation) for benzo(a)pyrene. Rate constants for benzo(a)pyrene and γ -HCH were assumed to be of the same order of magnitude as for polycyclic aromatic hydrocarbons, polychlorinated alyphatic hydrocarbons, and polychlorinated aromatics respectively [Atkinson, 1994; Kwok and Atkinson, 1995].

Above values of \hat{I}^{\bullet} concentrations and rate constants used for calculation of POPs degradation half-lives due to the reaction with hydroxyl radicals in the atmosphere are given in table 4.4.

Table 4.4: Degradation half-lives of POPs due to reaction with hydroxyl radical in atmosphere

Compound	Half-lives, days		
	summer	spring/fall	winter
γ -HCH	4.0	10	90
HCB	40	100	900
Benzo(a)pyrene	0.040	0.1	0.9
PCB-153	13	34	300

Hydroxyl radical is the main oxidizer of organic POPs in the atmosphere [Finlayson-Pitts and Pitts, 1986], however ozone and nitrate radical may also play an important role in their degradation, especially in the contaminated atmosphere.

Recommendations

Reactions with oxidants (primarily with hydroxyl radical) is the main pathway of degradation of the most POPs in the atmosphere and natural waters. It looks reasonable to include a submodel for hydroxyl radical concentration calculation in the model of POP long-range transport.

5 MIGRATION AND TRANSFORMATION PARAMETERS OF SELECTED POPs IN THE ENVIRONMENT

5.1 Benzo(a)pyrene

5.1.1 Melting and boiling temperature

$T_m = 176.5^\circ\text{N}$ [Schwarztzbach et al, 1993], $\dot{O}_b = 495^\circ\text{N}$ [Pearlman et al., 1984]

5.1.2 Solubility

5.1.2.1 Solubility at 25°C

Benzo(a)pyrene solubility data at 25°C found in literature are listed below.

Reference	S, mol/L	S, mg/L
<i>Mackay and Shiu, 1977</i>	1.5×10^{-8}	3.8×10^{-3}
<i>Smith et al., 1978</i>	0.48×10^{-8}	1.2×10^{-3}
<i>Yalkowsky et al., 1983*</i>	2.1×10^{-8}	5.3×10^{-3}
<i>Pearlman et al., 1984</i>	1.6×10^{-8}	4.0×10^{-3}
<i>Whitehouse, 1984</i>	0.61×10^{-8}	1.5×10^{-3}
<i>Baker et al., 1987</i>	1.6×10^{-8}	4.0×10^{-3}
<i>Schwarztzbach et al., 1993</i>	0.60×10^{-8}	1.5×10^{-3}
<i>Cohen and Clay, 1994**</i>	1.5×10^{-8}	3.8×10^{-3}

*Calculated as an average of 12 independent literature S values.

**Selected value

Recommended value is 1.5×10^{-8} mol/L.

5.1.2.2 Solubility dependence on temperature

Solubility of benzo(a)pyrene at four different temperatures in the range from 8 to 25°C was determined by *B.G.Whitehouse* [1984]. Equation of benzo(a)pyrene solubility as a function of temperature can be derived from these data by the least square method in the form $\log S = \frac{A}{T} + B$. Using A coefficient, calculated by the least square methods by *B.G.Whitehouse* [1984] data for distilled water and having $S(25^\circ\text{C}) = 1.5 \times 10^{-8}$ mol/L for fresh water we get:

$$\log S (\text{mol/m}^3) = -1790/T(\text{K}) + 1.18$$

Using coefficient A for sea water calculated in the same way and making an estimate of solubility in sea water at 25°C. Using K_s (see paragraph 5.1.2.3.) for sea water we have:

$$\log S (\text{mol/m}^3) = -2355/T(\text{K}) + 2.94$$

5.1.2.3 Solubility dependence on salinity

POP solubility dependence on salt content dissolved in water may be described by the equation analogous to one proposed by *Eganhouse and Calder* [*Eganhouse and Calder*, 1976]:

$$\log (S/S^s) = K_s C_s$$

where S^s is solubility in salt water, mol/l;

C_s is salt concentration, g/L;

K_s is proportionality coefficient, L/g.

K_s values calculated by *B.G.Whitehouse* [1984] data equal to 8.9×10^{-3} L/g at 8°C and 4.2×10^{-3} L/g at 25°C. It means that benzo(a)pyrene solubility in sea water ($C_s \approx 35$ g/L) was approximately 2 times less than its solubility in distilled water at low temperatures; at the same time the solubility difference at 25°C does not exceed 25-30%.

5.1.2.4 Solubility dependence on organic matter content in the water

Influence of DOM on the benzo(a)pyrene solubility was investigated by *B.G.Whitehouse* [1985]. Chemical nature of DOM was proved to be very important, and in some cases benzo(a)pyrene solubility in natural water containing DOM was several times (up to 5) higher than in water from which DOM was preliminary extracted.

5.1.3 Saturated vapor pressure

Benzo(a)pyrene saturated vapor pressure data found in literature are listed below.

References	t, °C	P _v , atm
<i>Bidleman and Foreman</i> , 1987***	20	3.2×10^{-12}
<i>Banerjee et al.</i> , 1990*	25	7.2×10^{-12}
<i>Hincley et al.</i> , 1990**	25	7.2×10^{-11}
<i>Mackay et al.</i> , 1992**	25	2.1×10^{-10}
<i>Cohen and Clay</i> , 1994***	25	7.4×10^{-12}

*Average value of literature data

**Data for subcooled liquid.

***Assessment based on literature data.

Recommended value is 7.3×10^{-12} atm or 7.3×10^{-7} Pa.

Dependence of saturated vapor pressure for subcooled liquid on temperature [*Hincley et al.*, 1990]:

$$\log P_L^O (\text{Pa}) = -4989/T(\text{K}) + 11.59$$

Dependence of saturated vapor pressure for solid substance on temperature (it was assumed that Å coefficient is the same as for subcooled liquid [Hincley *et al.*, 1990] and at 25⁰Ñ P_{OS} = 7.3×10⁻¹² atm):

$$\log P_{OS}(\text{Pa}) = -6319/T(\text{K}) + 15.07$$

5.1.4 Henry`s law constant

H = 0.05 Pa m³/mol at 25⁰Ñ [Mackay *et al.*, 1992, selected value]

Temperature dependence of Henry`s law constant was calculated by the formula $\log H = \log P_{OS} - \log S$ (see. sections 5.1.2 è 5.1.3).

For fresh water :

$$\log H (\text{Pa m}^3/\text{mol}) = -4529/T(\text{K}) + 13.89$$

For sea water:

$$\log H (\text{Pa m}^3/\text{mol}) = -3964/T(\text{K}) + 12.13$$

5.1.5 Sorption by soil, sediments and suspended particles

$\log K_{ow} = 6.13$ [Cohen and Clay, 1994, selected value], $\log K_{ow} = 6.2$ [Bayona *et al.*, 1991]. Recommended value is $\log K_{ow} = 6.2$.

$K_{oc} = 5.75$ is calculated by equation $K_{oc} = K_{ow} - 0.45$ [Karickhoff *et al.*, 1979]

5.1.6 Degradation rate in soil

Benzo(a)pyrene degradation rates in soils found in literature are listed below:

825 days is the selected value of the biodegradation half-life used by *D.Mackay and S.Paterson* [1991];

650 days is the biodegradation half-life in soils calculated by *Kolbow et al.* [1986] based on *P.Y.Lu et al.* [1977] data.

530 days is the literature assessment of the degradation half-life [Cohen and Clay, 1994].

60 days is the benzo(a)pyrene half-life in sod-podsolic soil after surface application of benzo(a)pyrene containing particles of soil dust [Shilina *et al.*, 1980].

20-50 days is the benzo(a)pyrene half-life in soils [Tonkopyi *et al.*, 1979].

10-20 days is the benzo(a)pyrene half-life in sod-podsolic soil after surface application as a powder or acetone solution [Shilina *et al.*, 1980].

5 days is the benzo(a)pyrene half-life on the territory of petroleum refinery plant [Shabad, 1980].

The data on microbiological benzo(a)pyrene degradation in soils are contradictory. It can be a result of the rate constant dependence on soil properties, however this reason can not explain two orders of magnitude differences. It is more likely that benzo(a)pyrene degradation is a function of its concentration in soils. At high concentrations in soils benzo(a)pyrene is degraded rapidly, but as its concentration is decreased its degradation rate is also decreased [Poglazova *et al.*, 1971]. Moreover, there is a possibility of benzo(a)pyrene microbiological synthesis in the soil [Shabad, 1980]. Therefore for modelling of benzo(a)pyrene degradation in soils it is, probably, necessary to use at least two different degradation half-lives: two years for background areas with soil concentrations from 1 to 10 µg/kg and two months for soils concentrations about 100 µg/kg.

5.1.7 Degradation rate in water

Found in literature benzo(a)pyrene degradation rates in water are listed below:

1.1 hour is the literature assessment of the degradation half-life [*Cohen and Clay*, 1994].

1 hour is the half-life of the dissolved benzo(a)pyrene photochemical degradation in the river surface layer (at summer noon) calculated with Lembrick data [*Lembrick*, 1979].

1.1, 0.69, 0.49 and 0.84 hour are the calculated degradation half-lives of dissolved benzo(a)pyrene due to direct photolysis in the surface water layer at 40°N at noon in winter, spring, summer and fall [*Mill et al.*, 1981].

3 days is the microbiological degradation half-life of dissolved in river water benzo(a)pyrene calculated with Lembrick data [*Lembrick*, 1979].

4, 80, 1600 days are the mean annual degradation half-lives due to reaction with HO• in freshwater, terrestrial sea water and open ocean, respectively (our estimation, see Chapter 4).

As can be seen from the above data, direct photolysis is the main mechanism of the dissolved in water benzo(a)pyrene degradation. Degradation half-life in surface layer of water at 40°N at noon in winter, spring, summer and fall is 1, 0.7, 0.5 and 0.8 hours, respectively. These estimations were made for dissolved in water fraction of benzo(a)pyrene. In order to calculate the degradation half-life of the total (dissolved and sorbed by suspended matter and bottom sediments) benzo(a)pyrene it is necessary to divide them by the fraction of the substance dissolved in water.

5.1.8 Degradation rate in the atmosphere

Literature data and our estimations of benzo(a)pyrene degradation rate in the atmosphere are listed below:

8 days is the selected value of the degradation half-life of the aerosol fraction of benzo(a)pyrene in the atmosphere used by *Y.Cohen and R.E.Clay* [1994].

1.1 hour is the selected value of the degradation half-life of the gas-phase benzo(a)pyrene used by *Y.Cohen and R.E.Clay* [1994].

15 hours is the degradation half-life of benzo(a)pyrene sorbed on fly ash in direct sun light [*Korfmacher et al.*, 1980].

10 hours is the estimation of the degradation half-life of benzo(a)pyrene adsorbed on the silicagel, calculated for central Europe with experimentally measured quantum yield suggesting that absorption spectrum of the adsorbed compound is the same as its spectrum in n-hexane [*Blau and Gusten*, 1981].

1.5-10 hours is the experimentally measured half-lives of photochemical degradation of adsorbed on the quartz fiber filter benzo(a)pyrene at the different times of day in June-February in Italy [*Cimberle et al.*, 1983].

5 hours is the degradation half-life calculated with daily average intensity of sun radiation adsorption by benzo(a)pyrene in summer in central Europe [*Blau and Güster*, 1981] and quantum yield of the direct photolysis of benzo(a)pyrene in n-octane [*Shevchuk and Chekulaev*, 1982].

1 hour, 2.4 hours, 0.9 day are the estimations of the degradation half-life due to reaction with HO• in summer, spring/fall and winter, respectively.

It can be seen from the data above that the main benzo(a)pyrene degradation process in the vapor phase is the direct photolysis and the reaction with hydroxyl radical. Taking into account seasonal changes of the daily average sun radiation intensity in central Europe the following daily average

benzo(a)pyrene degradation half-lives in the atmosphere can be recommended: 1 hour in summer, 2 hours in spring/fall, 2.5 hours in winter. Estimation of the degradation half-lives of the total (gas-phase and sorbed) benzo(a)pyrene in the atmosphere due to gas-phase reactions can be made by division of that values in the gas-phase fraction of the substance. For example, if the benzo(a)pyrene gas-phase fraction is 10%, the total benzo(a)pyrene degradation half-lives are 10 hours in summer, and 25 hours in winter. Approximately the same half-lives was experimentally measured when exposing sorbed on the aerosol particles and neutral sorbents benzo(a)pyrene on the sun light. This indicates that reactions in the solid phase do not affect significantly the effective degradation rate of benzo(a)pyrene in the atmosphere. Therefore it seems reasonable for the assessment of the benzo(a)pyrene degradation half-lives in the atmosphere to use the gas-phase constants divided by the gas-phase fraction.

It also seems necessary to make correction for irreversible sorption. However irreversibly sorbed on aerosol particles fraction of benzo(a)pyrene can not be estimated due to lack of experimental data.

5.1.9 Ratio of aerosol and gas fractions in the atmosphere

M.Afanasiev et al. [1982] have measured the benzo(a)pyrene vapor/particles distribution in rural areas of the European part of the USSR and in CSSR in 1982. The gas fraction varied from 2.3 to 18.2%. Similar results (6-20% of the vapor fraction) were obtained in suburbs of large cities in Belgium and Netherlands [*Broddin et al.*, 1980].

5.2 Lindane (γ -hexachlorohexane, γ -HCH)

5.2.1 Melting and boiling temperature

$t_m = 113^\circ\text{C}$, $t_b = 288^\circ\text{C}$ [*CRC - Handbook*, 1972]

5.2.2 Solubility

5.2.2.1 Solubility at 25°C

Lindane solubility data at 25°C found in literature are listed below.

Reference	S, mol/L	S, mg/L
<i>Jury et al.</i> , 1976*	2.6×10^{-5}	7.5
<i>Irmann</i> , 1965	3.4×10^{-5}	10
<i>Schwarztnbach et al.</i> , 1993*	2.6×10^{-5}	7.6

*Selected value.

Recommended value is 2.6×10^{-5} mol/L.

5.2.2.2 Dependence of the solubility on temperature

The following equation is calculated by the least square method using literature data cited by *J.R.Kucklik et al.* [1991] for $t = 15-45^\circ\text{C}$:

$$\log S (\text{mol/m}^3) = -(1918 \pm 656)/T(\text{K}) + (4.75 \pm 2.16)$$

The following equation is calculated by *F.Wania and D.Mackay* [1995] as a product of the Henry's law constant in sea water for $t = 0.5 - 23^\circ\text{C}$ [*Kucklik et al.*, 1991] and vapor pressure [*Wania et al.*, 1994]:

$$\log S (\text{mol/m}^3) = -2787/T(\text{K}) + 8.03$$

The following equation is calculated as product of Henry's law constant for deionized water $t = 0.5-45^{\circ}\text{N}$ [Kucklik *et al.*, 1991] and vapor pressure [Wania *et al.*, 1994]:

$$\log S (\text{mol/m}^3) = -3108/T(\text{K}) + 9.18$$

5.2.2.3 Solubility dependence on organic matter content in water

Lindane solubility remained practically constant when concentration of humic and fulvic acids were increased from 0 to 100 mg/L and does not depend on the nature and concentration of the DOM [Choiu *et al.*, 1986].

5.2.3 Saturated vapor pressure

The following equation is calculated by the least square method using literature data cited by J.R. Kucklik *et al.* [1991] for $t = 15-45^{\circ}\text{C}$:

$$\log P_{\text{OS}} (\text{Pa}) = -(5290 \pm 222)/T(\text{K}) + (15.65 \pm 0.74)$$

Wania *et al.* correlation for $t = -30-30^{\circ}\text{C}$ [Wania *et al.*, 1994]:

$$\log P_{\text{OS}} (\text{Pa}) = -5490/T(\text{K}) + 16.72$$

Vapor pressure temperature dependence for subcooled liquid [Hinkley *et al.*, 1990]:

$$\log P_{\text{OL}} (\text{Pa}) = -3680/T(\text{K}) + 11.15$$

5.2.4 Henry's law constant

Recommended temperature dependencies:

For deionized water in the range from 0.5 to 45°N [Kucklik *et al.*, 1991]:

$$\log H (\text{Pa}\cdot\text{m}^3/\text{mol}) = -(2382 \pm 160)/T + (7.54 \pm 0.54)$$

For sea water in the range from 0.5 to 23°N [Kucklik *et al.*, 1991]:

$$\log H (\text{Pa}\cdot\text{m}^3/\text{mol}) = -(2703 \pm 276)/T + (8.68 \pm 0.96)$$

5.2.5 Sorption by soil, sediments and suspended particles

$\log K_{\text{oc}} = 2.99$ [Kushi *et al.*, 1990], $\log K_{\text{oc}} = 2.96$ [Kenaga and Goring, 1980], $\log K_{\text{oc}} = 3.03$ [Lyman, 1982]. Recommended value of $\log K_{\text{oc}} = 3.0$

$\log K_{\text{ow}} = 2.96$ [Kenaga and Goring, 1980], $\log K_{\text{ow}} = 3.30-3.89$ with average value 3.60 [Isnard and Lambert, 1988]. Recommended value is $\log K_{\text{ow}} = 3.4$.

5.2.6 Degradation rate in soil

Lindane degradation half-lives in soils measured in field experiments after the surface application varied in the range of 150-350 days [Éononiuk, 1986; Lyman, 1982; Tzukerman 1985]. However, under field conditions the main degradation mechanism of lindane is its volatilization to the atmosphere. Therefore the degradation rate constant for this pesticide can be determined only under the laboratory conditions, where volatilization is suppressed or controlled.

Based on the laboratory experiments data Laskovski *et al.* assesses the lindane half-life in soil as 600 days [Laskovski *et al.*, 1984].

Tzukerman investigated lindane degradation under laboratory conditions at different temperatures and moisture content and found that at 5°N no degradation takes place in the all investigated soils [Tzukerman, 1985]. In the temperature range from 15 to 35°N and moisture content from 20 to 75% of

field capacity the degradation rate constant k_b can be calculated by the following equations [Tzukerman, 1985]:

$$\text{Chernozem: } k_b (\text{day}^{-1}) = -(176 + 9.6t + 4.7w) \times 10^{-5}$$

$$\text{Serossem: } k_b (\text{day}^{-1}) = -(1185 + 40.8t + 15.9w) \times 10^{-5}$$

$$\text{Dark brown: } k_b (\text{day}^{-1}) = -(620 + 31.9t + 6.5w) \times 10^{-5}$$

where t is the temperature in $^{\circ}\text{N}$;

w is the moisture content in % from field capacity.

Recommended biodegradation half-life in soils is 600 days.

5.2.7 Degradation rate in water

Literature data and our estimations on γ -HCH degradation rate constant in water are listed below:

At $\delta\text{I}=7$ and 25°N the hydrolysis half-life is 6 years [Ellington *et al.*, 1987].

Estimated values of the degradation half-lives in water due to reaction with hydroxyl radical are 1.3, 27, 530 days for fresh water, coastal sea water and open ocean, respectively.

Recommended values are 1.3, 25, and 500 days for fresh waters, coastal sea waters and open ocean, respectively. These estimations were made for dissolved in water γ -HCH fraction. To calculation the degradation half-lives of the total (dissolved and sorbed by suspended matter and bottom sediments) γ -HCH it is necessary to divide them by the dissolved fraction of the compound.

5.2.8 Degradation rate in the atmosphere

The main mechanism of γ -HCH degradation in the atmosphere is reaction with hydroxyl radical. Recommended degradation half-lives are 4 days in summer, 10 days in spring/fall, 90 days in winter.

5.3 PCB

5.3.1 Melting and boiling temperature

$$\dot{O}_m = 103^{\circ}\text{C} [\text{Yalkowsky } et. al., 1983]$$

5.3.2. Solubility

5.3.2.1 Solubility at 25°C

PCB-153 solubility data at 25°N found in literature are listed below

Reference	S, mol/L	S, mg/L
<i>Pal et al.</i> , 1980	24×10^{-9}	8.8×10^{-3}
<i>Shiu and Mackay</i> 1986*	2.8×10^{-9}	1×10^{-3}
<i>Haque and Schmedding</i> 1975	2.6×10^{-9}	0.95×10^{-3}
<i>Chiou et al.</i> , 1977	2.6×10^{-9}	0.95×10^{-3}
<i>Yalkowsky et. al.</i> , 1983**	3.6×10^{-9}	1.3×10^{-3}
<i>Opperhulzen et al.</i> , 1988	3.3×10^{-9}	1.15×10^{-3}
<i>Dunnivant and Elzrmann</i> , 1988	2.4×10^{-9}	1.3×10^{-3}

* Selected value; ** Calculated as average of 8 independent literature values.

Recommended value is 3×10^{-9} mol/L.

5.3.2.2 Dependence of solubility on temperature

The following equation is calculated using dissolution enthalpy data [Doucette and Andren, 1988] and solubility at 25°C (3×10⁻⁹ mol/L):

$$\log S \text{ (mol/m}^3\text{)} = -2435/T + 2.65$$

5.3.2.3 Dependence of solubility on salinity

Atlas et al. showed that the average ratio of Henry's law constants of tetra- and penta-chlorobiphenyl in sea and fresh water is 5 [Atlas et al., 1982]. Consequently PCB-153 in sea water can be assessed as 20% of its solubility in distilled water.

5.3.2.4 Solubility dependence on organic matter content in water

Solubility of the chlorinated biphenyls increases 5-7 times as concentration of the humic acid increases from 0 to 100 mg/L, while the increase of fulvic acid concentration in the same range does not considerably affect PCB solubility [Choiu et al., 1986].

5.3.3 Saturated vapor pressure at 25(20)°C

PCB-153 saturated vapor pressure at 25(20)°C found in literature are listed below $P_{OS} = 3.2 \times 10^{-10}$ atm [Dunnivant and Elzermann, 1988]; $P_{OS} = 4.2 \times 10^{-10}$ atm (20°C) [Murphy et al., 1987]; $P_{OS} = 2.6 \times 10^{-10}$ atm [Harner et al., 1995].

Recommended value is 3×10^{-10} atm = 3×10^{-5} Pa.

Temperature dependence (slope $\log P_{OS} = a/T + b$ assumed to be equal to the sum of the slopes of temperature dependencies of $\log S$ and $\log H$, parameter b is calculated assuming that at 25°C $P_{OS} = 3 \times 10^{-5}$ Pa):

$$\log P_{OS} \text{ (Pa)} = -5851/T(\text{K}) + 15.10$$

Dependence of Henry's law constant for overcooled liquid was calculated using the following equation $\log P_{OL} = \log P_{OS} + \Delta S_m/2.303R(T_m/T-1)$, where dissolution entropy $\Delta S_m = 53.6$ J/K·mol [Harner et al., 1995], gas constant $R = 8.314$ J/K·mol, melting temperature $T_m = 376$ K:

$$\log P_{OL} \text{ (Pa)} = -4798/T(\text{K}) + 12.30$$

5.3.4 Henry's law constant

Henry's law constant values at 25°C for PCB-153 found in literature are listed below

References	t, °C	H, atm·m ³ /mol
Oliver, 1985	25	0.6×10^{-4}
Burkhard et al., 1985	25	1.77×10^{-4}
Murphy et al., 1987	20	0.99×10^{-4}
Dunnivant and Elzerman, 1988	25	1.32×10^{-4}
Harner et al., 1995*	25	2.0×10^{-4}

* Assessment by literature data

Recommended value is 1.4×10^{-4} atm·m³/mol = 14 Pa·m³/mol.

Dependence of H on temperature (slope of $\log H = a/T + b$ is taken from S.Tateya et al. [1988], parameter b is calculated from H value at 25°C):

$$\log H \text{ (Pa·m}^3\text{/mol)} = -3416/T(\text{K}) + 12.61$$

Henry's law constant dependence on salinity.

Atlas et al. [1988] showed than average ratio of Henry's law constant of tetra- and penta-chlorobepheyls in sea and fresh water is 5.

5.3.5 Sorption by soil, sediments and suspended particles

$\log K_{oc} = 6.07$ [*Karickhoff et al.*, 1979], $\log K_{oc} = 4.78-6.87$ with average value equals 5.70 [*Horzempa and DiTirro*, 1983]. Recommended value is $\log K_{oc} = 5.9$.

$\log K_{ow} = 7.00$ [*Shiu and Mackay*, 1986], $\log K_{ow} = 7.55$ [*Miller et al.*, 1984], $\log K_{ow} = 6.9$ [*Bayona et al.*, 1991], $\log K_{ow} = 6.9$ [*Risby et al.*, 1990]. Recommended value is 7.0.

5.3.6 Degradation rates in soils

PCB-153 degradation rate constant measurements are difficult due to its stability to the action of the soil microorganisms. It is reasonable for purposes of the short-term modelling to consider PCB-153 as undegradable substance; for long-term modelling its degradation half-life can be assumed, as for DDT, to equal 10 years.

5.3.7 Degradation rate in water

The main mechanism of PCB-153 degradation in natural waters is reaction with hydroxyl radical.

Recommended values are 4, 80 and 1600 days for fresh waters, coastal sea water and open ocean, respectively. These estimations were made for dissolved in water PCB-153 fraction. To calculate the degradation half-lives of the total (dissolved and sorbed by suspended matter and bottom sediments) PCB-153 it is necessary to divide them by the dissolved fraction of the compound.

5.3.8 Degradation rate in the atmosphere

Assessment of the degradation half-life in the overground atmospheric layer due to reaction with the OH radical is: 13 days in summer, 34 days in spring/autumn, 300 days in winter.

Recommended values in summer are 10 days, 30 days in the spring/fall, 300 days in winter. These estimations were made for gaseous PCB-153 fraction. For the calculation of the degradation half-lives of the total (gaseous and sorbed on particles) PCB-153 it is necessary to divide them by the vapor fraction of the compound.

5.4 Hexachlorobenzene(HCB)

5.4.1 Melting and boiling temperature

$T_{melt} = 228.5^{\circ}\text{N}$, $\dot{O}_{boil} = 321^{\circ}\text{N}$ [*Dannenfelsler and Paric*, 1991]

5.4.2 Solubility

5.4.2.1 Solubility at 25(20)⁰C

HCB solubility data at 25⁰N found in the literature are listed below.

Reference	S, mol/L	S, mg/L
<i>Dannenfelsler and Paric</i> , 1991*	2.0×10^{-8}	5.7×10^{-3}
<i>Schwarzmbach et al.</i> , 1993*	2.0×10^{-8}	5.7×10^{-3}

*Averaged published values.

Recommended value is 2.0×10^{-8} mol/L.

5.4.2.2 Dependence of solubility on temperature

The following equation was calculated by dividing of vapor pressure [*Wania et al.*, 1994] by Henry's law constant for fresh water [*ten Hulscher et al.*, 1992]:

$$\log S \text{ (mol/m}^3\text{)} = -1381/T(\text{K}) + 0.18$$

The following equation was calculated by *F.Wania and D.Mackay* [1995] by dividing the vapor pressure [*Wania et al.*, 1994] by Henry's law constant for sea water [*ten Hulscher et al.*, 1992]:

$$\log S \text{ (mol/m}^3\text{)} = -1314/T(\text{K}) + 0.254$$

5.4.3 Saturated vapor pressure

$P_{OS} = 1.35 \times 10^{-8}$ atm (20 $^{\circ}$ N) [*Dannenfelser and Paric*, 1991], $P_{OS} = 2.37 \times 10^{-8}$ atm (25 $^{\circ}$ N) [*Banerjee et al.*, 1990], $P_{OS} = 1.72 \times 10^{-8}$ atm (25 $^{\circ}$ N) [*Wania et al.*, 1994]

Recommended value is $P_{OS} = 2 \times 10^{-8}$ atm = 2×10^{-3} Pa

Vapor pressure dependence on temperature:

Correlation of *Wania et al.* (-30-+30 $^{\circ}$ C) [*Wania et al.*, 1994]:

$$\log P_{OS} \text{ (Pa)} = -3874/T(\text{K}) + 10.23$$

Vapor pressure of subcooled liquid [*Hinkley et al.*, 1990]:

$$\log P_{OL} \text{ (Pa)} = -3582/T(\text{K}) + 11.11$$

5.4.4 Henry's law constant

Temperature dependence for fresh water [*ten Hulscher et al.*, 1992]:

$$\log H \text{ (Pa.m}^3\text{/mol)} = -2493/T(\text{K}) + 10.05$$

Temperature dependence for sea water [*ten Hulscher et al.*, 1992]:

$$\log H \text{ (Pa.m}^3\text{/mol)} = -2560/T(\text{K}) + 9.88$$

5.4.5 Sorption by soils, sediments and suspended particles

$\log K_{oc} = 3.9$ [*Dannenfelser and Paric*, 1991] (Recommended value).

$\log K_{ow} = 5.5$ [*Bayona et al.*, 1991]

$\log K_{ow} = 5.4$ (20-30 $^{\circ}$ N) [*Dannenfelser and Paric*, 1991]

Recommended value $\log K_{ow} = 5.4$.

5.4.6 Degradation rate in soil

Information about HCB degradation rates in soils found in literature are listed below:

After two seasons from soil were extracted approximately $\approx 100\%$ of the applied HCB [*Scheunert and Korte*, 1986];

1500 days is the selected value for HCB degradation half-life in soil used by *D.Mackay and S.Paterson* [1991];

6.3 years is the selected value for HCB degradation half-life in subtropical and temperate soils used by *F.Wania and D.Mackay* [1995].

Measurement of HCB degradation rate constant in soils is a difficult task due to its stability to microbiological degradation. Therefore there are few data about its degradation half-lives in soils. It is reasonable for purposes of the short-term modelling to consider HCB as undegradable substance; for long-term modelling its degradation half-life can be assumed, as for DDT, to equal 10 years.

5.4.7 Degradation rate in water

HCB degradation rates in water found in literature are given below:

Estimated degradation rate constant in water is 0 [*Mackay and Paterson*, 1991] 6.3 years is the estimated degradation half-life in subtropical and temperate waters [*Wania and Mackay*, 1995].

Estimated degradation half-lives due to reaction with hydroxyl-radical are 1.6, 32 and 640 days in freshwaters, coastal sea water and open ocean, respectively.

Recommended values are 1.6, 30 and 600 days for freshwaters, coastal sea water and open ocean, respectively. These estimations were made for dissolved in water HCB fraction. To calculate the degradation half-lives of the total (dissolved and sorbed by suspended matter and bottom sediments) HCB it is necessary to divide them by the dissolved fraction of the compound.

5.4.8 Degradation rate in the atmosphere

2 days is the assessment of the degradation half-lives in the atmosphere [*Mackay and Paterson*, 1991]

700 days is the assessment of the half-life in the atmosphere in temperate and boreal air [*Wania and Mackay*, 1995].

Assessment of the half-lives in the surface layers of the atmosphere due to the reaction with hydroxyl radical: 40 days in summer, 100 days in spring/autumn, 900 days in winter.

Recommended value is 40 days in summer, 100 days in spring/fall, 900 days in winter. These estimations were made for gaseous HCB fraction. To calculate the degradation half-lives of the total (gaseous and sorbed on particles) HCB it is necessary to divide them by the vapor fraction of the compound.

ABBREVIATIONS

α - resuspension rate (wind resuspension intensity), s^{-1} ;

φ - photolysis quantum yield;

μ - additive first order POPs degradation constant in soil;

ϕ - fraction of the total atmospheric concentration occurring in the particle phase;

ρ - soil bulk density, $kg\ m^{-3}$;

ρ - air density, $kg\ m^{-3}$;

ϕ - universal function of the Monin-Obukhov similarity theory;

θ - volumetric soil moisture content, $m^3\ m^{-3}$;

δ - thickness of the layer occupied by the admixture, being function of the distance from downwind edge of the polluted area, m;

δ - characteristic height of the near surface atmospheric layer, m;

- η - average probability for single vegetation element to capture the particle;
 λ - constant describing the volatilization rate, day⁻¹;
 ν - kinematic air viscosity, m² s⁻¹;
 ζ - activity coefficient of an organic compound in organic matter phase;
 ε_λ - extinction coefficient, m² mol⁻¹;
 β_a - mass transfer coefficient in the atmosphere, m;
 ΔH_a - enthalpy of adsorption, kJ mol⁻¹;
 $\Delta H_{\bar{n}}$ - enthalpy of supercooled liquid sublimation, kJ mol⁻¹;
 H_1 - entalpy of desorption, kJ/mol;
 H_V - enthalpy of vaporization of subcooled liquid, kJ/mol;
 $\chi_p(\text{sc})$ - average concentrations of particulate fraction of POP in sub-cloud layer, ng m⁻³;
 $\chi_p(\bar{n})$ - average concentrations of particulate fraction of POP in cloud layer, ng m⁻³;
 $\chi_v(t)$ - gaseous fraction concentration at time t of the rain, ng m⁻³;
 χ_v^0 - gaseous fraction concentration before beginning of the rain, ng m⁻³;
 $[H]$ - H⁺ cation concentration, mol L⁻¹;
 $[OH]$ - OH⁻ anion concentration, mol L⁻¹;
 A - soil surface contamination density, g m⁻²;
 A_s - specific concentration of POP in the upper soil layer, g m⁻²;
 A_f - leaves surface area per a volume unit, m² m⁻³;
 a_s - specific surface area of snowflakes, m² g⁻¹;
 a_{sp} - specific surface area of the aerosol, m² g⁻¹;
 B - specific biomass of the microorganisms, μg^{-1} or mg L⁻¹;
 C_d - dust concentration in air, $\mu\text{g m}^{-3}$.
 C - total concentration of a POP in air, ng m⁻³;
 C_{air} - POP concentration in air, ng m⁻³;
 C_a - vapor phase chemical concentrations in the bulk air, mol m⁻³;
 C_a - concentration in vapor phase, ng m⁻³;
 C^a - concentration in the air near the soil-atmosphere interface, ng m⁻³;
 C_{aV} - air concentration near the leaf surface, ng m⁻³;
 C_{d0} - oversurface layer resistance coefficient;
 C_{DO} - coefficient for every type of surface;
 C_L - chemical concentration on the leaf, mg/m²;
 $C_0(t)$ - pesticide concentration in soil at the moment of time t, kg m⁻³;
 C_{00} - initial chemical concentration in soil, kg m⁻³;
 C_p - concentrations of particulate fraction in rain water near the ground, ng m⁻³;
 C_p - concentration of POP on particles, mol m⁻³;
 C_s - concentration in sorbed phase, mg m⁻³;

- C_s - POP concentration on the air-water surface, ng m^{-2} ;
 C_w - concentration in liquid phase, mol m^{-3} ;
 C_w - dissolved chemical concentrations in bulk water, mol m^{-3} ;
 C_{wi} - dissolved chemical concentrations at the air-water interface, mol m^{-3} ;
 C_{wr} - POP concentration in water, ng m^{-3} ;
 D_a - gas molecular diffusion coefficient in air, $\text{m}^2 \text{s}^{-1}$;
 Da_0 - oversurface Dalton number;
 D_e - effective diffusion coefficient, $\text{m}^2 \text{s}^{-1}$;
 D_i - heat transfer molecular coefficient in air, $\text{m}^2 \text{s}^{-1}$;
 D_w - POP diffusion coefficient in the soil solution, $\text{m}^2 \text{s}^{-1}$;
 F - particle flux to the surface, $\mu\text{g s}^{-1} \text{m}^{-2}$;
 F - particulate POP flux, $\text{ng s}^{-1} \text{m}^{-2}$;
 f_{om} - weight fraction of organic matter;
 G - gaseous concentrations, ng m^{-3} ;
 g - soil porosity, $\text{m}^3 \text{m}^{-3}$;
 g^W - water vapor conductivity, m s^{-1} ;
 h - cloud and sub-cloud layers total thickness, m ;
 H - Henry's law constant, $\text{Pa m}^3 \text{mol}^{-1}$;
 H_{293} - Henry's law constant at 293 K, $\text{Pa m}^3 \text{mol}^{-1}$;
 H_0 - average height of vegetation, m ;
 I - rain intensity, m s^{-1} ;
 $I_{0\lambda}$ - light intensity;
 J_T - total POP flux, $\text{ng s}^{-1} \text{m}^{-2}$;
 K - q_1/A - resuspension factor (the wind resuspension coefficient) for height z_1 , m^{-1} ;
 k - Karman constant;
 k^0 - biodegradation zero order rate constant, $\text{mg kg}^{-1} \text{day}^{-1}$;
 k^1 - biodegradation first order rate constant, day^{-1} ;
 K_a - gas mass transfer coefficients, m day^{-1} ;
 k_a - rate constants for acid hydrolysis, day^{-1} ;
 $K_{A/W}$ - partition coefficient in the air-water system;
 k^b - biodegradation second order rate constant, $\text{kg (mg of biomass)}^{-1} \text{day}^{-1}$;
 $K_{C/A}$ - cuticle - air partition coefficient;
 k_e - effective degradation rate constant, day^{-1} ;
 $K_{G/A}$ - glycerol lipid-air partition coefficient, which assumes to equal the octanol-water partition coefficient ($K_{O/W}$);
 $K_{O/W}$ - octanol-water partition coefficient;
 K_H - unitless Henry's law constant;

k_{ia} - ice-air distribution coefficient, m;
 k_n - rate constants for neutral hydrolysis, day^{-1} ;
 k_{OH} - rate constants for base hydrolysis, day^{-1} ;
 K_p - partition coefficient, $\text{m}^3 \text{kg}^{-1}$;
 K_p - particles-air distribution coefficient, $\text{m}^3/\mu\text{g}$;
 K_{pair} - water surface-air partition coefficient, m;
 K_{pwater} - water surface-water volume partition coefficient, m;
 K_w - liquid mass transfer coefficients, m day^{-1} ;
 l - light pass length, m;
 L - $(\text{mg of biomass})^{-1} \text{day}^{-1}$;
 L_f - leaf characteristic size, m;
 M_m - chemical molecular weight, g mol^{-1} ;
 M_m^W - molecular weight of water, g mol^{-1} ;
 MW_{om} - molecular weight of the organic matter, g mol^{-1} ;
 N_s - density of adsorption sites on the particles surface, mol m^{-2} ;
 P - POP concentration in soil, mg kg^{-1} ;
 P - particle-associated concentration, ng m^{-3} ;
 P - upward vertical flux of POP due to resuspension from the soil, $\text{ng s}^{-1} \text{m}^{-2}$;
 p_{OL} - saturated vapor pressure of subcooled liquid, Pa;
 p_v - saturated vapor pressure, Pa;
 P_v - vapor pressure, Pa;
 q_0 - particles concentration in air at $z=0$, m^{-3} ;
 q_1 - POP concentration at height z_1 ;
 R - universal gas constant, $\text{Pa m}^3 \text{mol}^{-1} \text{K}^{-1}$;
 R_{cuticle} - cuticle resistance, s m^{-1} ;
 Re - Reynolds number, s m^{-1} ;
 R_m - mesophyll resistance, s m^{-1} ;
 r_s - stomata resistance, s m^{-1} ;
 R_{soil} - soil resistance, s m^{-1} ;
 R_w - retardation factor;
 S_c - molecular Schmidt number;
 Sc_a - Schmidt molecular numbers for air;
 Sc_w - Schmidt molecular numbers for water;
 OS_L - solubility of supercooled liquid at 293K , mol/m^3 ;
 t - time, days;
 \dot{O} - temperature, $^{\circ}\text{K}$;
 TSP - total suspended particulate matter concentration, $\mu\text{g m}^{-3}$;

- U - dynamic speed, m s^{-1} ;
- u_* - friction velocity, m s^{-1} ;
- U_{10} - wind velocity at 10 m height, m s^{-1} ;
- v_g - velocity of dry deposition of POPs containing aerosol particles, m s^{-1} ;
- V_A , - relative volume of air in a leaf;
- V_C , - relative volume of cuticle in a leaf;
- V_{di} - deposition velocity corresponded to i-th particle size range;
- V_e - effective transport rate of a dissolved substance;
- V_G - relative volume of glycerol lipid in a leaf;
- V_w - Darcy flux of soil solution;
- V_w , - relative volume of water in a leaf;
- w - moisture content in % from field capacity, %;
- W_p - aerosol washout ratio equaled to the ratio of the corresponding fraction concentration in the precipitation to that in air;
- $W_p(c)$ - in-cloud washout ratio;
- $W_p(sc)$ - sub-cloud washout ratio;
- W_T , - total washout ratio equaled to the ratio of the corresponding fraction concentration in the precipitation to that in air;
- W_v - gas-phase washout ratio equaled to the ratio of the corresponding fraction concentration in the precipitation to that in air;
- z - vertical coordinate, m;
- z_0 - roughness parameter, m;
- z_{0c} - roughness length for a pollutant, m.

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