ESTIMATION OF SELECTED PARAMETERS OF PCDD/Fs MIGRATION IN THE ENVIRONMENT

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Introduction

Modeling of POP migration is primarily aimed at prediction of their dispersion in the environment and effects on humans. Transport of POPs mostly takes place in the atmosphere and their transfer to humans basically occurs through inhalation and ingestion pathways. As a result, most of the existing models account for atmospheric transport and migration of POPs by food chains [1-4]. Many parameters of hazardous POPs, among them PCDD/Fs, required for prediction, however, remain unknown. For example, the dependence of the PCDD/Fs partitioning coefficient in the air-aerosol particles system on vapor pressure is available only for coastal areas[5] and application of this dependence to continental areas may lead to significant errors due to differences in the composition of atmospheric aerosols. Another example of important but unavailable characteristics of PCDD/Fs are kinetic and equilibrium parameters of their accumulation by plants from the atmospheric air. Estimation of these parameters from the physico-chemical properties of POPs is actually the subject matter of the present paper.

Distribution of PCDD/Fs in the air-aerosol particle system

The dependence of the PCD/FS partitioning coefficient in the system aerosol particles-air on the congener vapor pressure was derived by us[6] as $LogK_p=m_rLog(p_L)+b_r$, where K_p is the partitioning coefficient, $m^3/\mu g$, p_L is the pressure of overcooled liquid vapor, Pa, m_r and b_r are the constants for a class of compounds. The values of K_p for several PCDD/Fs in the temperature range from 0 to 20 °C were estimated using the data obtained in Germany at a distance of 500 km from the sea shore and described in Hippelein et al., (1996)[7]. For each value of K_p the vapor pressure of congener overcooled liquid was calculated. The temperature dependencies of the vapor pressure for 2,3,7,8-substituted congeners of PCDD/Fs were estimated as $Log(p_L)=A/T+B$, where T is the temperature; K, A and B are the constants for individual compounds (see Table 1). For this purpose estimates of thermodynamic properties of PCDD/Fs and formula reported by Rordorf[8] were used. Then using the estimated 36 $LogK_p$-$Log\ p_L$ pairs the least square method was applied to derive the following regression equation:

$$LogK_p = -1.24Log(p_L) - 6.70 \qquad R=0.97 \qquad (1)$$

As can be seen from Fig. 1 formula (1) describes quite well the experimental dependence of K_p on p_L. For obtaining the temperature dependence $LogK_p$ for a specific congener it is enough to substitute a corresponding dependence of vapor pressure from Table 1 in formula (1).

Table 1. Estimates of PCDD/Fs migration parameters

Position of Cl atoms	Parameters			
	Log(p_L, Pa)	Log(K_{OA})	Log(D, m^2/s)	Log(k_{SR}, m/s)
PCDD				
2,3,7,8	-4392/T + 11.42	8,92	-18,37	-11,55
1,2,3,7,8	-4778/T + 11.90	9,64	-18,54	-11,73
1,2,3,4,7,8	-4840/T + 11.75	9,90	-18,70	-11,89
1,2,3,6,7,8	-4803/T + 12.41	10,12	-18,70	-11,89
1,2,3,7,8,9*	-4957/T + 12.01	10,03	-18,70	-11,89
1,2,3,4,6,7,8	-5017/T+ 11.91	10,24	-18,85	-12,05
1,2,3,4,6,7,8,9	-4676/T+ 11.20	9,71	-18,99	-12,20
PCDF				
2,3,7,8	-4344/T + 11.46	8,90	-18,31	-11,48
1,2,3,7,8	-4504/T + 11.54	9,26	-18,48	-11,67
2,3,4,7,8	-4607/T + 11.70	9,45	-18,48	-11,67
1,2,3,4,7,8	-4655/T + 11.54	9,67	-18,65	-11,84
1,2,3,6,7,8	-4645/T + 11.49	9,69	-12,15	-11,84
1,2,3,7,8,9*	-4643/T + 11.51	9,66	-12,15	-11,84
2,3,4,6,7,8	-4629/T + 11.49	9,63	-12,15	-11,84
1,2,3,4,6,7,8	-4735/T + 11.49	9,89	-18,80	-12,00
1,2,3,4,7,8,9	-4777/T+ 11.43	10,09	-18,80	-12,00
1,2,3,4,6,7,8,9	-4805/T + 11.24	10,28	-18,95	-12,15

PCDD/Fs partitioning coefficient in the octanol-air system

The partitioning coefficient in the octanol-air system K_{OA} is an important parameter accounting for the equilibrium distribution of organic compounds in the system «cuticle of plant leaf-air»[1,3,4]. This coefficient was measured, unfortunately, for several compounds only, primarily PCBs[9-11]. For other POPs the value of this parameter can be estimated by the formula $K_{OA}=K_{OW}RT/H$, where K_{OW} is the partitioning coefficient octanol-water; H is the Henry constant, Pa×m^3/mole, the universal gas constant R=8.314 J/(K×mole).
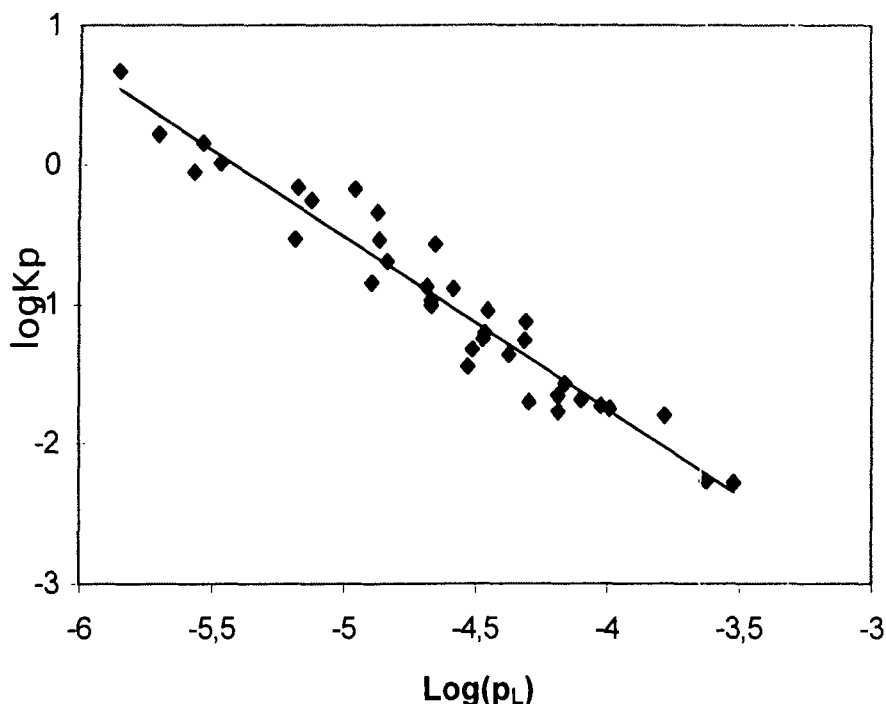
Fig. 1. Dependence of $LogK_p$ on $Log(p_L)$ for PCDD/F.

The derived estimates have both systematic and unbiased error. More precise estimation of K_{OA} seems possible using the following formula:

$$K_{OA} = \frac{RTS_s^o}{p_s} = \frac{RTS_L^o}{p_L} \tag{2}$$

where S_s^O and S_L^O are the solubility of the substance in octanol in the solid state and in the overcooled liquid state, respectively, mole/m^3; p_s is the solid substance vapor pressure, Pa.

It was shown[12] that formula (2) gives satisfactory estimates of K_{OA} for PCBs even in the case when the octanol solubility is calculated by the method OCTASOL[13] rather than measured. Using the same method we calculated the solubility in octanol of 3,4,7,8-substitited PCDD/Fs congeners in the state of overcooled liquid and using the temperature dependencies of Table 1 corresponding vapor pressure at 25°C. Then the values of K_{OA} were calculated using formula (2) (see Table 1.)

Kinetic parameters of PCDD/Fs accumulation by plant leafs

Qualitative description of the kinetics of pollutant transfer from air to plant leafs is normally based on using several parameters. Comparison of characteristic values of K_{OA} and H for POPs shows that these compounds occur in cuticle in equilibrium with the surrounding air in the amounts several orders of magnitude higher than in the aquatic part of the leaf. Thus cuticle is the main

reservoir and diffusion to its volume is the main mechanism of POPs transfer to plants leafs. The optimum parameters for modeling this process is the diffusion coefficient in cuticle D (m^2/s) and the coefficient of mass transfer from cuticle surface to its volume[3,4], k_{SR} (m/s). Experimental data making possible calculation of these parameters are available only for limited sets of organic substances [3,4,14]. For other compounds it was proposed to use the dependence of these parameters on molar volume V_m(cm^3/mole) which is corollary of hydrodynamic concepts of diffusion of low-molecular compounds in polymer media[15]. The coefficients of this dependence for D and k_{SR} were estimated[15] by the least square method:

$$Log(D, m^2/s) = -5.17 - 5.41 \times LogV_m \qquad\qquad R = 0.75 \text{ (3)}$$

$$Log(k_{SR}, m/s) = 2.19 - 5.63 \times LogV_m \qquad\qquad R = 0.90 \text{ (4)}$$

In deriving formula (3) we used data on penetration of 4-nitrophenol, 2,4-D, 2,3,4-T, pentachlorophenol, hexachlorobenzene, atrazine and perylene through the cuticle of *Citrus aurantium*[14]. Formula (4) was derived based on experimental data on accumulation of hexachlorobenzene, α-hexachlorohexane, γ-hexachlorohexane, PCB-28, PCB-52, PCB-101, phenanthrene, anthracene, 1-chloroanthracene, 1,2,3,4-tetrachloronaphthalene in leafs of *Lolium multiflorium*[3,4]. The molar volume of compounds was estimated by the structural formula of the compounds using the LeBas technique. This method gives equal molar volumes for congeners with equal number of chlorine atoms. Therefore, they, as can be seen from Table, have also the same values of parameters D and k_{SR} calculated by formula (3) and (4).

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