PREDICTION OF LOG K_{OA}, T_C AND LOG P_L - THE KEY PARAMETERS IN ENVIRONMENTAL TRANSPORT AND FATE OF CHLOROSUBSTITUTED PYRENES (CL-S PCPYS)

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Introduction

Polychlorinated pyrenes (PCPYs) are possible toxic group of persistent organic pollutants (POPs)[1]. They had been identified in many antropogenic sources, like domestic flame heating systems, municipal solid waste incineratoration, chlorination of tap water or pulp bleaching. The most persistent congeners, known as chlorosubstituted pyrenes (Cl-S PCPYs), are synthetizied in chlorosubstitution reactions[2,3,6,7,13,14]. There are 281 theoretically possible congeners of Cl-S PCPYs. Some of them probably can be transported for long range distances, similarly to "classic" POPs, *e. g.* polychlorinated dibenzo-*p*-dioxins or polychlorinated biphenyls etc.[17].

In this study, three parameters ($\log K_{OA}$ - logarithm of *n*-octanol/air partition coefficient, T_C - temperature of cold condensation, and $\log P_L$ – logarithm of vapor pressure of the subcooled liquid) were predicted for all 281 Cl-S PCPYs. A significance of mentioned three parameters in predictions of environmental transport and fate of the POPs were explained and described in detail by Wania and Mackay[18].

Materials and Methods

All predictions were done based on the Principal Component Regression Method[8]. At the beginning, the structural data matrix for the 281 possible Cl-S PCPYs congeners together with 23 another 'reference' POPs was computed. Structural descriptors used in the study were: molecular connectivity indices of the zero, first, and the second order; total dipole moment (PM3 semi-empirical method); dipole vectors: X, Y, and Z; electron affinity; energy of HOMO and LUMO (PM3); molecular weight and refraction; solvent accessible surface area; logarithm of the *n*-octanol/water partition coefficient; valence molecular indices of the zero, first, and the second order; kappa indices of the first, second, and the third order; standard heat of formation (PM3)[4,5,9,10,12,15,16].

Including 'reference' compounds with known values of $\log K_{OA}$, T_C, and $\log P_L$, it was possible to identify the models describing these parameters, as linear functions of structural descriptors. The models were validated using cross-validation method[11].

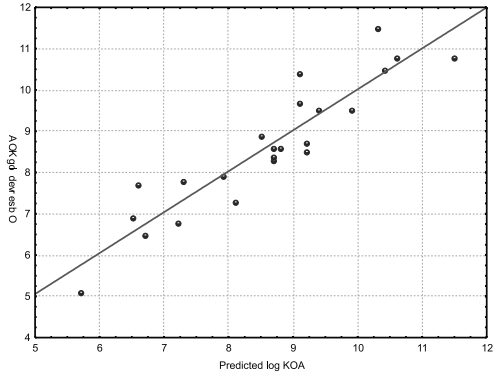
Results and discussion

Three model equations together with corresponding descriptive characteristics and plots of correlation between observed and predicted values of $\log K_{OA}$, T_C, and $\log P_L$ are presented in Figures 1-3. Values of the key parameters, which are predicted using these models for chlorosubstituted pyrenes are listed in Table 1.

It should be noted that, monochlorosubstituted pyrenes are characterized by the properties similar to that of di- to tetrachlorodibenzo-*p*-dioxins and furans as well as of octa- to nonachlorobiphenyles.

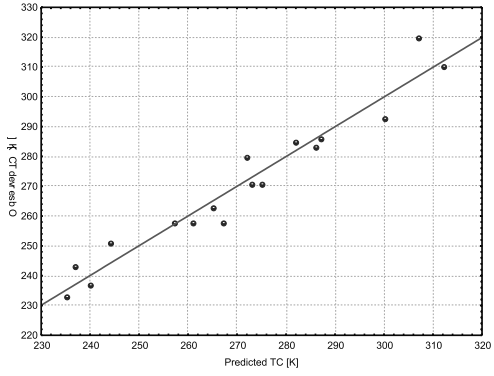
ENVIRONMENTAL TRANSPORT AND FATE

All of these POPs were classified as compounds, which are relatively low mobile under an environmental conditions, while another members of each particular homologue group are definitely low mobility compounds.



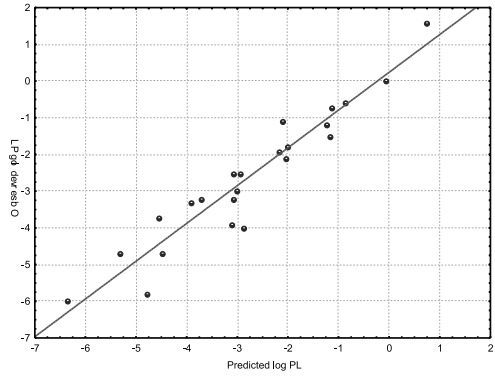
$\log K_{OA}$ = 11.66 (±0.38) + 1.28 (±0.14) PC1+
+0.11 (±0.06) PC2 - 0.30 (±0.07) PC3
s = 0.66
D = 84.8%
F = 35.34
N = 23
Q_{CV}^2 = 0.76

Figure 1. Correlation between observed and predicted values of K_{OA} of Cl-S PCPYs.



T_C = 331.29 (±5.20) + 27.06 (±2.14) PC1 +
+ 0.88 (±0.60) PC2 – 5.95 (±0.79) PC3
s = 6.41
D = 94.32%
F = 71.95
N = 17
Q_{CV}^2 = 0.88

Figure 2. Correlation between observed and predicted values of T_C of Cl-S PCPYs.



$\log P_L$ = -6.11 (±0.32) – 1.60 (±0.12) PC1 –
- 0.04 (±0.05) PC2 + 0.33 (±0.06) PC3
s = 0.56
D = 92,0%
F = 72.74
N = 23
Q_{cv}^2 = 0.89

Figure 3. Correlation between observed and predicted values of log P_L of Cl-S PCPYs.

Table 1. Principal component (PC) scores and predicted values of $logK_{OA}$, T_C and $logP_L$ of each Cl-S PCPYs homologue group.

Homologue	PC scores			Predicted parameters		
group	PC1	PC2	PC3	Log K_{OA}	T_C [K]	og P_L
Mono-	-2.37 ÷ -1.84	1.46 ÷ 1.75	-0.03 ÷ 0.25	9.4÷9.5	267÷283	-3.08 ÷ -2.17
Di-	-1.37 ÷ -1.30	0.73 ÷ 17.25	-0.24 ÷ 0.18	9.9÷10.2	294÷298	-4.01 ÷ -3.82
Tri-	-0.86 ÷ -0.78	0.45 ÷ 1.03	-0.42 ÷ 0.33	10.6÷10.9	308÷313	-4.90 ÷ -4.72
Tetra-	-0.38 ÷ -0.28	0.16 ÷ 0.81	-0.61 ÷ 0.30	11.2÷11.5	321÷326	-5.72 ÷ -5.48
Penta-	0.13 ÷ 0.23	-0.25 ÷ 0.42	-0.53 ÷ 0.26	11.8÷12.1	335÷339	-6.54 ÷ -6.36
Heksa-	0.63 ÷ 0.73	-0.59 ÷ 0.09	-0.57 ÷ 0.33	12.4÷12.7	347÷352	-7.34 ÷ -7.12
Hepta-	1.10 ÷ 1.18	-0.70 ÷ -0.23	-0.48 ÷ 0.05	13.0÷13.2	362÷365	-8.83 ÷ -7.95
Octa-	1.60 ÷ 1.66	-0.88 ÷ -0.61	-0.41 ÷ -0.05	13.3÷13.7	375÷377	-8.87 ÷ -9.60
Nona-	2.09 ÷ 2.10	-1.08 ÷ -0.95	-0.21 ÷ -0.30	14.3	388÷389	-9.60 ÷ -9.57
Deca-	2.55	-1.35	-0.99	14.8	400	-10.31

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