

OTHER HALOGENATED POPs OF CONCERN

POLYCHLORINATED PYRENES (PCPYS) – A LESS STUDIED AND POSSIBLY TOXIC GROUP OF POPs

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Introduction

Polychlorinated pyrenes (PCPYs) are relatively little studied, but possible toxic members of persistent organic compounds contaminating the environment. A molecule of pyrene consists of four condensed benzene rings substituted or added with chlorine atoms (Fig. 1).

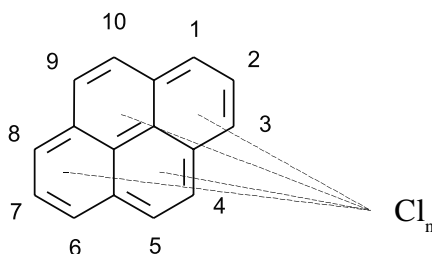


Figure 1. Structure and numbering system of PCPYs.

Due to a pattern of chlorine existing in the molecule, Nilson and Colmsjö^(15,16) have categorized chloropyrene congeners into two subgroups: chlorosubstituted (Cl-S PCPYs), and chloroadDED pyrenes (Cl-A PCPYs). Cl-A PCPYs are considered as definitively less stable than Cl-S PCPYs, and they are quickly degraded to chlorosubstituted derivatives by elimination of HCl^(1,15,16). Because of mentioned feature, chloroadDED congeners could be qualified as potentially not so much dangerous as chloropyrenes with substituted chlorine atoms. Additionally, Cl-S PCPYs, as far as all chlorosubstituted aromatic compounds, are more persistent than the parent molecule, because of the electron withdrawing effect of the chlorine atoms. The class of Cl-S pyrenes consists of 281 theoretically possible congeners containing from one to ten chlorine atoms per molecule. As it can be observed, there are some important variations in physico-chemical properties between each PCPY homologue group, but also similarity to some other members of POPs.

Knowledge on the composition, sources, and environmental concentrations of chloropyrenes is very limited. Mono- to tetra-CPYs have been detected in concentrations between 8.7 and 23 $\mu\text{g}/\text{m}^3$ in flue gas emitted from the coal-fired boilers, as well as the municipal solid waste incinerators (MWI)⁽²⁾. Gas effluents from domestic flame heating systems and MWI remain the only identified sources of environmental pollution with PCPYs, but many other remains to be possible. The city of Stockholm urban air concentration of 1-chloropyrene was around 10 pg/m^3 ⁽⁵⁾. Although 'thermal' sources seem to be the most significant contributors, there are another 'no-thermal' processes, where chloropyrenes may be synthesized, e.g. chlorination of tap water and pulp bleaching. PCPYs were identified in settling particulate matter (SPM) over Sweden, and in surface sediments in the Stockholm Archipelago, mainly

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near a pulp and paper mill. The total concentration of Cl-PAHs (included Cl-PCPYs) of SPM varied between 3.2 and 44 ng/gC, while of surface bottom sediment (Lake Mälaren, Sweden, Baltic sediments from the Swedish waters) varied between 17 and 44 ng/gC^(8,9).

There is very limited number of data on toxicity of chloropyrenes. 1-chloro-, 1,3-dichloro-, 1,6-dichloro-, and 1,8-dichloropyrene appeared to be strongly mutagenic in the *Salmonella typhimurium* test, while the parent (unsubstituted) molecules were not mutagenic⁽¹⁾.

The aim of this study was to generate and evaluate some physico-chemical descriptors of Cl-S PCPYs, and to explore the internal structure of this data matrix. It could help to understand similarities and differences in toxicity and features influencing environmental transport and distributions between each of the congeners.

Methods and Materials

Table 1. QSAR descriptors used in multivariate characterization of PCPYs.

Symbol	Descriptor	Unit	References
CI_0	Molecular connectivity index of zero order, $^0\chi$	-	6,11
CI_1	Molecular connectivity index of first order, $^1\chi$	-	6,11
CI_2	Molecular connectivity index of second order, $^2\chi$	-	6,11
DIPOLE	Total dipole moment of the molecule	D	17,18
DV_X	Dipole vector X	D	17,18
DV_Y	Dipole vector Y	D	17,18
DV_Z	Dipole vector Z	D	17,18
E_AFF	Electron affinity	eV	17,18
HOMO	Energy of HOMO	eV	17,18
LOGP	Logarithm of the n-octanol/water partition coefficient	-	7,12
LUMO	Energy of LUMO	eV	17,18
MOL_REF	Molecular refraction	Å ³	10
MASA	Molecular weight	g/mol	17,18
K_1	Kappa index of first order, $^1\kappa$	-	11
K_2	Kappa index of second order, $^2\kappa$	-	11
K_3	Kappa index of third order, $^3\kappa$	-	11
SAS	Solvent accessible surface area	Å ³	14
VCI_0	Valence molecular index of zero order, $^0\chi^v$	-	6,11
VCI_1	Valence molecular index of first order, $^1\chi^v$	-	6,11
VCI_2	Valence molecular index of second order, $^2\chi^v$	-	6,11
HF	Standard heat of formation	kJ/mol	17,18

In the first step, input files with internal coordinates were prepared for each of 281 possible congeners of Cl-S PCPYs. Initial bond lengths were set to C-C as 1.335 Å, to C-H as 1.089 Å, and to C-Cl as 1.750 Å while, all of the initial valence angles as 120° and torsion angles as 0° or 180°. An initial geometry was optimized on the level of semi-empirical Parametric Method 3 (PM3) using MOPAC2000 Fujitsu software^(17,18). Next, based on the optimized structures, 21 quantitative structure – activity relationships (QSAR) were computed. All physico-chemical and quantum-mechanical descriptors are listed and described in details in table 1.

In assumption, these variables quantitatively describe molecular structures of the congeners – theirs topology, shape, energy, polarity, and lipophilicity.

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The most significant part of this work was exploration of the structural data matrix using Principal Component Analysis (PCA) method⁽¹³⁾. The resulting score plot is a planar (or 3D) projection of the future space showing relationships between objects (here congeners). Compounds located close each other on the plot are characterized by similar structural and, in consequence, physicochemical properties. The corresponding plot of loadings illustrates, which descriptors are correlated, and how they influence to the individual PCs.

Results and discussion

Principal Component Analysis resulting a third-dimensional model explained 89.5 % (75.8 % + 7.7 % + 6.0 %) of the total variance in data. The first three significant principal components were chosen applying Kaiser's criterion and the screen plot criterion.

As it could be seen (Figure 2), the first PC is influenced mainly by descriptors connected with molecular shape and size. There are negatively correlated connectivity indices χ together with χ^v , of the zero, first, and second order, Kier indices κ of the first, second, and third order, molecular weight, molecular refraction, and logarithm of the *n*-octanol/water partition coefficient. It is interesting that, the positively correlated variables are energy of LUMO and standard heat of formation. PC2 is strongly depended on the polarity of the molecule expressed, as a value of the total dipole moment. Dipole vector Y and energy of HOMO are also characterized by relatively high values of loading (about 0.6). The third principal component is impacted by dipole vector X.

When analyzing the score plot, it could be noted, that the first PC distinguishes the different homologue groups. Each point represents one congener of PCPYs, which is described by the corresponding number. Compounds forming homologue groups are characterized by similar values of indices χ , χ^v , and κ , molecular weight, refraction, $\log K_{ow}$, such as solvent accessible molecular surface, standard heat of formation, and energy of LUMO. The second principal component separates homologue compounds owning to values of mainly the total dipole moment, but also energy of HOMO and dipole vector Y. PC3 (not shown) groups congeners with very similar values of dipole vector X.

Concluding, the most interesting features of polychlorinated pyrenes set are polarity (represented by total dipole moment and dipole vectors) and energy of the highest occupied molecular orbital (which decides about ionization potential of the molecule). These properties are probably responsible for diverse environmental and body transport, fate, and toxicity of each PCPY.

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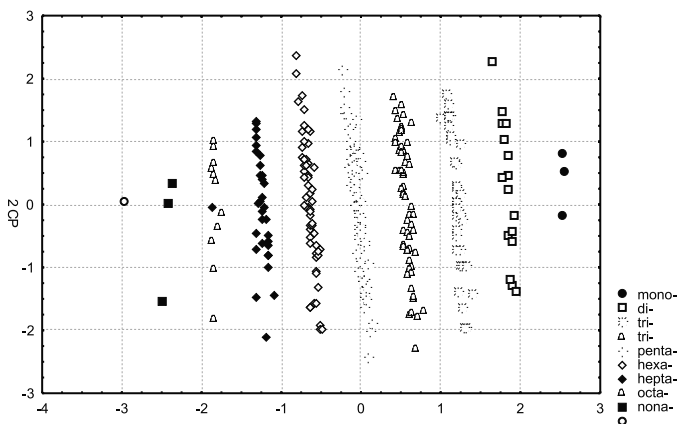


Figure 2. The loading plot of the second principal component (PC2) vs. the first principal component (PC1).

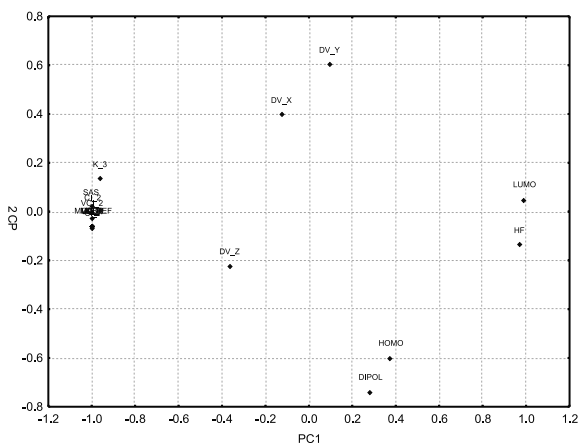


Figure 3. The score plot of the second principal component (PC2) vs. the first principal component (PC1).

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