# PERSISTENCY OF THE INDIVIDUAL CHLORONAPHTHALENE CONGENERS IN AIR, WATER AND SOIL

Puzyn T., Ziemecki P., Falandysz J.

*Department of Environmental Chemistry and Ecotoxicology, University of Gdańsk, Sobieskiego 18, Gdańsk 80-952, Poland, e-mail: puzi@pcb.chem.univ.gda.pl*

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## Introduction

Polychlorinated naphthalenes (chloronaphthalenes, PCNs, CNs) are widely dispread and toxic organic compounds, which are probably persistent in the environment and accumulate in food chains.[1-6] One of the most important physical-chemical parameter controlling environmental transport and fate of such compounds is persistency measured by half-life times ($t_{1/2}$) in the individual media: air, water and soil. According to the criteria defined in UN-ECE POP Protocol, chemical compounds for which $t_{1/2}$ in water > 2 months or $t_{1/2}$ in soil > 6 months should be classified as persistent, while if $t_{1/2}$ in air > 2 days and vapor pressure < 1000 Pa, the compound is potentially long-range transported in the atmosphere.[7] Because of the environmental half-lives have never been determined for all chloronaphthalene congeners and PCNs are 'candidate' compounds for including in the list of UN-ECE POP Protocol, these properties were estimated by means of Quantitative Structure – Property Relationship (QSPR) approach.

## Materials and Methods

In the investigations, three GA-PLS models describing relationships between molecular descriptors and half-life times in air, water and soil were identified, internally (LOO cross-validation) and externally validated and used in predictions for PCNs. In the GA-PLS approach, Partial Least Squares statistical technique is used for model computation, while a genetic algorithm is applied for selection of the most informative input variables (molecular descriptors).[8] Because there was any data for CN congeners available, relatively well studied POPs, such as polychlorinated dibenzo-*p*-dioxins, furanes, biphenyls and PAHs were included in the training and the validation sets. Applicability domains of the models were validated using Principal component ranges procedure. The training set in this study are wholly representative and can be used to make prediction for all congeners of PCNs. Predictive abilities of the model were expressed by root mean square errors of cross-validation (RMSECV) and external validation (RMSEP).[9-12] All models used molecular descriptors from quantum mechanical calculations at the level of Density Functional Theory (B3LYP functional) in 6-311++G** basis.[13] Experimental data for POPs were taken from published papers.[14-22]

## Results and Discussion

Statistical parameters of the final models are presented in table 1. As it could be observed, there were satisfactory agreements between experimental and estimated data.

| Model | n (training set) | n (validation set) | $R^2X$ | $R^2Y$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|
| Air | 32 | 18 | 99.99 | 91.82 | 0.171 | 0.157 |
| Water | 24 | 10 | 100 | 93.89 | - | 0.255 |
| Soil | 28 | 14 | 99.88 | 92.66 | 0.506 | 0.423 |

The descriptors such as: energy of the highest unoccupied molecular orbital (LUMO), total energy of the molecule (Et), solvent accessible surface in water (SASw), solvent accessible volume in water (SAVw), total electrostatic energy of solvation in water (TEESolw), solvent accessible volume in octanol (SAVo), cavitation

energy in octanol (CEo), total non-electrostatic energy of solvation in octanol (TNEo) were the most important for half-lives prediction in air. They are corresponding to the photochemical and radical degradation, partitioning to the air-born organic particles and, wet and dry deposition. Degradation of chloronaphthalenes in water was described by descriptors correlated with solubility in water, polarity and photolytic degradation, such as: dipole moment (D), polarized solute-solution interaction energy in water (PolSSw), LUMO, TEESolw, PolSSw and CEw. Descriptors: energy of the highest occupied molecular orbital (HOMO), LUMO, SAVw, PolSSw, SASo, SAVo and TNEo used in the model for soil probably correspond to microbial and photolytic degradation, partitioning between organic phase and water as much as vaporization.

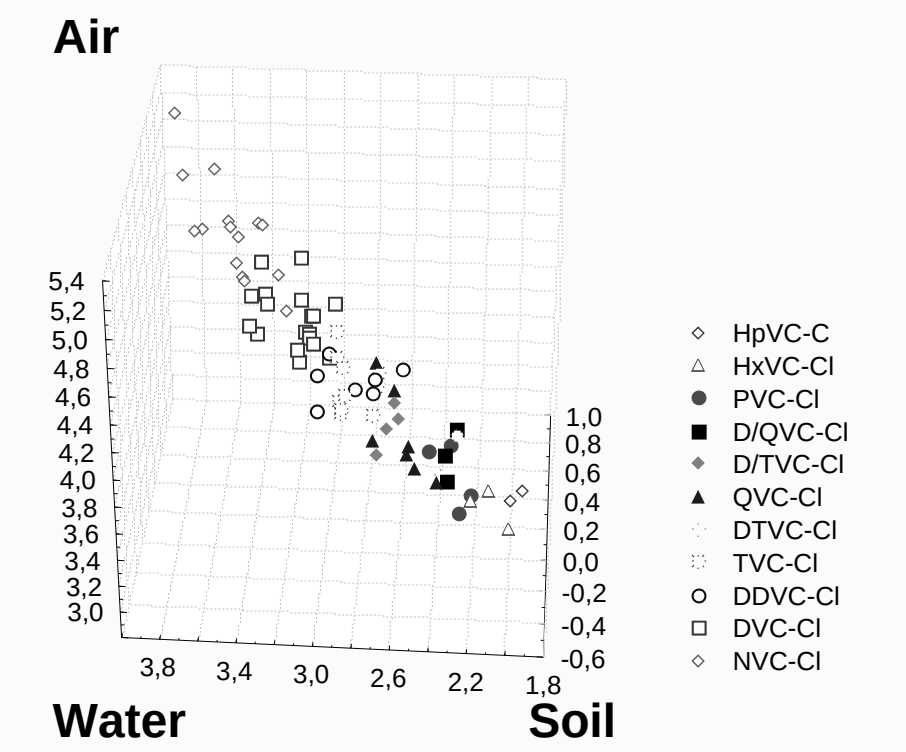


Figure 1.

Polychlorinated naphthalenes were characterized by the estimated log $t_{1/2}$ values in air in range of 2.96 to 5.18. The estimated log $t_{1/2}$ values in water for individual CN congeners ranged between 2.05 and 3.83, while its estimated persistence in soil was very low (between –0.46 and -0.9 logarithmic units). All values were given in hours [h].

As it could be observed at figure 1, persistency of the individual congeners depended not only on the number of attached chlorine atoms but also on their structure (substitution pattern). The most persistent congeners in all media were those have no vicinal hydrogen atoms unsubstituted by chlorine atoms (NVC-Cl). Persistency decreases in the following sequence: NVC-Cl (congeners with no vicinal carbon atoms unsubstituted with chlorine or vicinal hydrogen atoms) > DVC-Cl (congeners which have two vicinal carbon atoms unsubstituted with chlorine/two vicinal hydrogen atoms) > DDVC-Cl (congeners which have two pairs of vicinal carbon atoms unsubstituted with chlorine/two pairs of vicinal hydrogen atoms) > TVC-Cl (having three vicinal carbon atoms unsubstituted with chlorine/three vicinal hydrogen atoms) > DTVC-Cl (congeners which have two and three vicinal carbon atoms unsubstituted with chlorine/two and three vicinal hydrogen atoms) > QVC-Cl (congeners which have four vicinal carbon atoms unsubstituted with chlorine/four vicinal hydrogen atoms) > D/TVC-Cl (congeners which have two and three vicinal carbon atoms unsubstituted with chlorine/two and three vicinal hydrogen atoms) > D/QVC-Cl (congeners which have two and four vicinal carbon atoms unsubstituted

with chlorine/two and four vicinal hydrogen atoms) > PVC-Cl (congeners which have five vicinal carbon atoms unsubstituted with chlorine/five vicinal hydrogen atoms) > HxVC-Cl (congeners which have six vicinal carbon atoms unsubstituted with chlorine/six vicinal hydrogen atoms) > and HpVC-Cl (congeners which have seven vicinal carbon atoms unsubstituted with chlorine/seven vicinal hydrogen atoms). It is possible that NVC-Cl and DVC-Cl congeners were the most persistent because of their more stabilized mesomeric structures, formed in a degradation process. These congeners were deducted earlier as the most environmentally persistent members amongst CNs.[5,23] It is worthy to note, that they are also characterized by the greatest values of bioaccumulation and biomagnification factors.

Based on the estimated parameters $t_{1/2}$ it could be finally stated, that PCNs meet the UN-ECE POP Protocol criteria in air (all congeners), but in water only the NVC-Cl and DVC-Cl PCNs. Its persistence in soil is to low.

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