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ASSESSMENT OF ATMOSPHERIC DISTRIBUTION OF POPs USING PP-LFER MODEL

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Abstract: *The objective of the study was to assess the consistency between the gas-particle partitioning coefficient of selected PCBs and PAHs predicted by the PP-LFER model and the experimental results gained within the field measurements. A total number of 20 air samples was obtained from six urban, residential and industrial monitoring stations in two towns of Vojvodina region. Conventional high volume sampling method was applied, with quartz filters for collecting the atmospheric particles (GFF) and polyurethane foam filters (PUF) for retaining the free gas molecules of PCBs and PAHs.*

Key Words: ***PCBs, PAHs, gas-particle partition, PP-LFER model***

1. INTRODUCTION

Air pollution has become a global problem since numerous air pollutants are transported over long ranges with atmospheric and ocean currents. Thus, even if a country reduces its major emissions, air pollution can continue to increase. Polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are organic compounds distributed in the environment with moderate vapor pressure, low solubility and low reactivity. PCBs are a well-known class of ubiquitous pollutants characterized by extreme toxicity and high resistance to environmental degradation processes. They were commercially produced for almost 50 years (from the early 1930s to the mid-1980s) and they were widely used in a variety of equipment and consumer products, such as electrical transformers and capacitors, hydraulic and heat transfer systems, paints, plastics, sealants and adhesives. Although banned for over 20 years, PCBs are still detected in all environmental compartments including surface water, soils, ambient air and they remain a topic of intense research interest [1]. PAHs are a class of potentially carcinogenic and ubiquitous global pollutants that can be emitted to the environment as a result of natural combustion processes (e.g., forest fires and volcanoes), human activities are believed to dominate global PAH emissions, because high atmospheric concentrations of PAHs are usually observed in urban and industrial areas where vehicle traffic, aluminum smelting, residential heating, and other activities emit PAHs into the atmosphere.

Because of their physical and chemical stability, PCBs and PAHs are distributed throughout the globe and are detected in remote regions where they never have been used. The atmosphere is the dominant transport pathway for PCBs and PAHs. A key process determining the fate of chemicals in the atmosphere is their partitioning between gas and particle phase. This process has a decisive influence on the fate of PCBs and PAHs in the atmosphere [2]. The extent of gas-aerosol particle partitioning of semi-volatile organic compounds (SOCs) such as PCBs and PAHs in the atmosphere affects the rates of wet and dry deposition as well as air-water exchange. Therefore, the partitioning of PCBs and PAHs in the atmosphere is an important factor in their transformation and transport. Models of gas-particle partitioning are a crucial part of multimedia chemical fate and transport models which seek to describe the long-term fate of SOCs in the environment.

Destruction of the industrial and military targets accompanied by complete or incomplete combustion during the air strikes in the spring of 1999 caused emission of the persistent organic pollutants /PAHs, PCBs, dioxins and furans/ into the atmosphere, ground and underground water, sediment and soil. As the result of the air sampling campaign, the concentration levels of PCBs and PAHs in air samples in gaseous and particulate phase at the 6 selected locations from the city of Novi Sad and Pancevo, Serbia, was determined using active sampling method. This type of air analysis on presence of selected POPs was performed for the first time in Serbia [3]. In addition, we analyzed gas and particle partitioning of sixteen priority PAHs and seven PCB congeners.

Being semi-volatile organic compounds, PCBs and PAHs in atmosphere simultaneously present in gas and particle phase [4]. The partitioning in heterogeneous system could be quantified using partitioning coefficient, K_P, or particle-bound fraction, ϕ. The gas/particle partition coefficient, regardless of the mechanisms, can be expressed as:

$$K_P = \frac{(F/TSP)}{A} \qquad (1)$$

where Kp has the unit of $m^3\ mg^{-1}$, F and A ($ng\ m^{-3}$) are the particle-associated and gaseous concentrations, respectively, and TSP is the total suspended particulate matter ($\mu g\ m^{-3}$). Fraction ϕ is defined as a ratio of compound concentration associated with the particle phase (F, $ng\ m^{-3}$) over the sum of gas (A, $ng\ m^{-3}$) and particle concentrations:

$$\phi = \frac{F}{A+F} \qquad (2)$$

The gas/particle partitioning highly affects long-range atmospheric transport, chemical reactions, and fate of PCBs and PAHs. Therefore, sufficient data on Kp of PCBs and PAHs are indispensable to better interpret these processes by mathematical models. Besides, Kp values are also quite useful for their environmental risk assessment. The objective of the study was to assess the consistency between the gas-particle partition coefficient of selected PCBs and PAHs predicted by the *PP-LFER model* and the experimental results gained within the field measurements.

2. MATERIAL AND METHOD

2.1. Eksperimental

A total number of 20 air samples was obtained from 6 urban and industrial monitoring stations in two towns of Vojvodina region, Serbia. Conventional high volume sampling method, Hi-Vol was applied, with quartz filters for collecting the atmospheric particles and polyurethane foam filters (PUF) for retaining the free gas molecules of PCBs and PAHs. Duration of sampling was 24 hours. All filters were cleaned before the campaign. PUF filters were extracted with acetone and dichloromethane in a Soxhlet extractor, quartz filters were heated to 450°C. The samples were analyzed using GC-ECD (HP 5890) supplied with a Quadrex fused silica column 5% Ph for PCBs, while 16 US EPA polycyclic aromatic hydrocarbons were determined in samples using a GC-MS instrument (HP 6890 - HP 5972) supplied with a J&W Scientific fused silica column DB-5MS. All analytical procedures were done in the laboratories of the Research Centre for Environmental Chemistry and Ecotoxicology (RECETOX), Masaryk University, Brno, CR.

2.2. PP-LFER model

There are many assumptions when it comes to deciding which is the dominating sorption mechanism in the gas/particle partitioning process. Many studies show that Poly-parameter linear free energy relationships (PP-LFERs) that describe absorptive partitioning are an appropriate way to model partitioning of PCBs and PAHs into the organic matter component [5].

The overall free energy of phase transfer is the sum of free energy of the specific and nonspecific interactions, and as free energies are directly proportional to log K values (i.e. ΔG = - log K / 2.303RT + constant), equation can be written as:

$$\log K_{i\ sorb/air} = \sum \log K^{n\text{-}spec.}_{i\ sorb/air} + \sum \log K^{spec.}_{i\ sorb/air} + 2{,}303 \cdot RT \cdot const \qquad (3)$$

Ki sorbent/air data sets at 50%RH for individual aerosol samples were fitted to the following PP-LFER:

$$\log K_{isorbent/air} = sS_i + aA_i + bB_i + lL_i + vV_i + c \qquad (4)$$

where *Si*, *Ai*, *Bi*, *Li* and V*i* are the compound-specific Abraham descriptors for the polarizability /dipolarizability, electron acceptor (H-bond donor) capability, electron donor (H-bondacceptor) capability, logarithm of the hexadecane/air partition coefficient, and McGowan volume, respectively. Corresponding to the Abraham descriptors are the sorbent (i.e., particle)-specific descriptors *s*, *a*, *b*, *l*, and *v*, along with the fitting constant, *c*. Sorbent-specific descriptors can be calculated by performing a multiple-linear regression using experimental log Kp values as the dependent variables and Abraham descriptors as the independent variables.

Arp et al. [6][7] used a set of experimental data of over 500 partitioning coefficient values gained at 9 different locations, at 50% relative humidity (RH). The results were used to calculate sorbent-specific descriptors, for the use of PP-LFERs as a mathematical model. It has been concluded that descriptors are very similar for all sample data, which leads to the conclusion that sorption of organic compounds in water insoluble organic matter phase is negligibly dependent on the aerosol origins.

It is recommended that for the assessment of partitioning properties of polar, apolar and ionizable organic compounds in the atmosphere, descriptors gained for two sample locations – Berlin Winter and Duebendorf Fall [6][7] should be used. These two new fitted equations of equation (4) are great models for sorption properties of terrestrial aerosols.

In the paper, experimentally gained values of partitioning coefficient have been compared with PP-LFER model predicted values, where descriptors for *Berlin Winter* and *Duebendorf Fall* have been used. Berlin Winter descriptors are used for the so-called "upper level" and Duebendorf Fall descriptors are used for "lower level".

3. RESULTS

Comparison of predicted log K_P values at 15°C and 50% relative humidity using PP-LFERs for the Berlin Winter and Duebendorf Fall samples with experimental values at six locations in Novi Sad and Pančevo for polychlorinated biphenyls and polycyclic aromatic hydrocarbons are presented in Fig. 1 and Fig. 2, respectively. Locations labeled with a letter "N" represent monitoring stations in Novi Sad, and locations with a letter "P" monitoring stations in Pančevo. Locations N1, P1 and P2 are industrial sites, locations N3 and P3 are urban sites, and location N2 is a suburban site.

Predicted log Kp values shown in Fig. 1 and Fig. 2 are results of modelling with upper and lower level descriptors gained in the research by Arp et al. [6][7]. These predicted values are presented in units of $m^3\ g^{-1}$, which is a bit different than the usual $m^3\ \mu g^{-1}$.

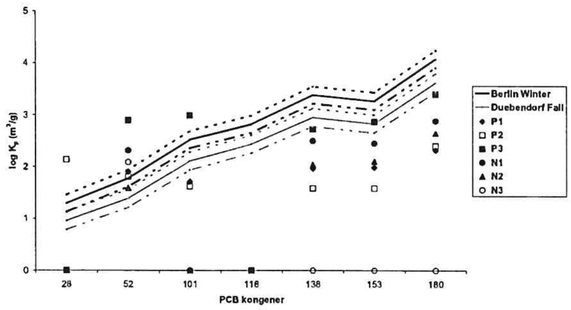

Fig. 1. Illustration of results obtained for PCBs.

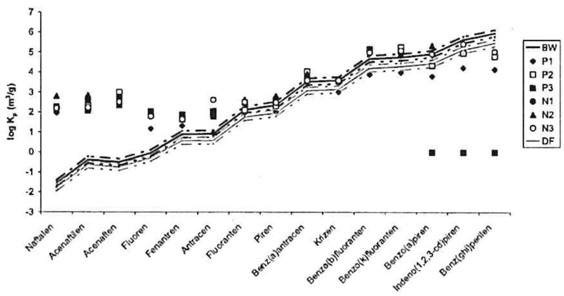

Fig. 2. Illustration of results obtained for PAHs.

Dashed lines indicate the range covered by the root-mean-square error of the predictions.

As it is shown in Fig. 1 and Fig 2., there are a lot of PCBs and PAHs in different locations that are detected beyond the root-mean-square error of the predictions. Also, after analysing the results, it can be concluded that there are more compounds outside of the prediction range. Depending on which compound is analyzed, different conclusions could be made.

4. CONCLUSIONS

The deviation between predicted and measured log Kp values was significant for the most of selected PCB congeners. Good correlations were gained just in 9.5% of the analyzed samples. In the earlier research by Arp et al. [7], results of modelling using PP-LFERs for PCBs had better agreement with experimental and literature results.

The results of modelling the atmospheric distribution of PAHs using the PP-LFER model showed small deviation between the measured and predicted values for fluoranthene, pyrene, benzo(a)anthracene and chrysene (molecules with 4 rings). Very good agreement was confirmed in 62.5% of these analyzed samples. Previously mentioned research by Arp et al. [6][7] had similar results for these PAHs.

More significant differences between measured and modelled values were obtained for the other PAHs, molecules that exist dominantly in gaseous phase. This is also similar to conclusions of Arp et al. [6][7] research. The general conclusion for using the PP-LFER model for PAHs that exist dominantly in gaseous phase is negative, because the predicted values are significantly different than literature and experimentally gained values.

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