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TOP 2011

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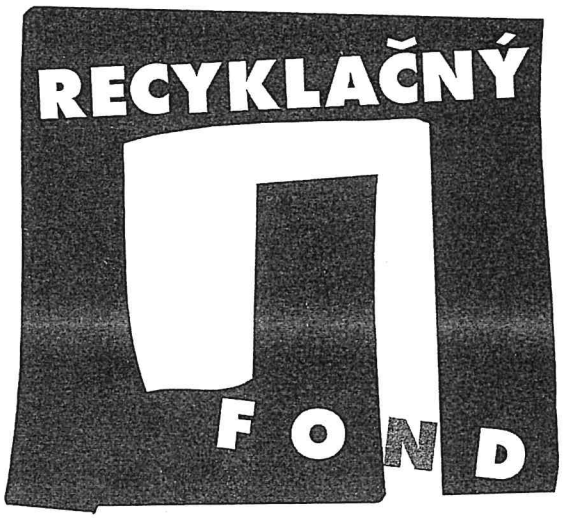

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MOLECULAR STRUCTURE MODEL FOR PREDICTING ATMOSPHERIC DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS

Okuka Marija*, Šenk Nevena *, Miloradov Vojinović Mirjana *, Radonić Jelena *, Sekulić Turk Maja *

ABSTRACT

Intensive industrial development in the 20th century has raised and changed living standards and at the same time, increased contamination and degradation of environmental resources. Contaminants that are distributed in all segments of the environment are a risk to ecosystems and human health and therefore, monitoring of harmful substances and especially waste management, which prevents release of toxic and hazardous substances, is crucial and important for environmental protection. Polycyclic aromatic hydrocarbons (PAHs) are especially studied organic molecules due to their continuous release from uncontrolled and incomplete combustion, resistance, long-range transport, ubiquity and global distribution and high toxicity of certain representatives of this group. The largest emissions of PAHs result from industrial processes, human activities and incomplete combustion of organic matter. Released gas molecules of PAHs in the atmosphere are mainly ad/absorbed onto particulate matter. Partitioning of PAHs between gaseous and particulate phase of ambient air and concentration levels are important for determining their fate in the environment. The partition of sixteen PAHs from EPA's priority pollutants list between gaseous and particulate phase, has been predicted using molecular structure model. Gas/particle partitioning coefficient has been calculated using an on-line calculator SPARC v4.5 (Molecular Structure Model) and then compared with experimentally gained values at 6 locations in Republic of Serbia, in two cities Novi Sad and Kragujevac [1]. Experimental values are obtained within APOPSBAL project [2].

Key Words: PAHs, gas/particle partitioning coefficient, molecular structure model

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1. INTRODUCTION

Environmental pollution is an undesirable change in physical, chemical and biological properties of three different physical states – gaseous, liquid and solid i.e. air, water and soil. These modifications have harmful effects on humans and biota, living conditions, industrial production, cultural and historical monuments and many natural resources. Polycyclic aromatic hydrocarbons (PAHs) with hazardous impact are detected in all environmental media: water, air, soil and living beings [3]. PAHs are a group of complex organic compounds where basic structure is made of hydrogens and carbons, organized in ring structures (number of rings is between two and eight). There are two groups of PAHs: non-substituted and substituted, mostly oxy-, nitro-, hydroxy-PAHs, polycyclic aromatic carboxyaldechides, carboxylic acids etc [3]. Transport and distribution of PAHs in the atmosphere are determined by physical and chemical properties of these compounds. PAHs are all semi volatile and extremely mobile in the environment, thus, deposition and re-evaporation of PAHs occur, as well as distribution and thermodynamically reversible partitioning between all environmental media [4][5][6]. The atmosphere is a dominant medium for transport of many substances in the environment, and therefore the presence of PAHs in the atmosphere is a universal problem. PAHs are products of industrial and human activities, and uncontrolled and incomplete combustion of organic matter. PAHs origins could be anthropogenic (from households, from mobile sources, industrial and agricultural sources) and natural (cosmic origin or natural atmospheric sources) [4]. Historically, PAHs are one of the first atmospheric pollutants which are identified as suspect and highly carcinogenic, toxic and mutagenic molecules (benzo(a)pyrene) [3]. Toxicity of PAH molecules depends on molecular structure and stereochemistry. Structure of four, five, or six aromatic rings is considered to be very carcinogenic. PAHs have been of environmental concern and are included in most environmental monitoring programs [4][5][6].

Human organism can be contaminated per cutem, by inhalation and ingestion, and different adverse effects can be manifested [3]. Study of partitioning processes in the atmosphere is highly significant because PAH molecules are partly ad/absorbed onto particulate matter and partly found free as gas molecules in gaseous phase [4][6]. The need for accurate and reliable prediction of organic compounds fate in the environment resulted in the development of SPARC on-line calculator [7][8]. Molecular structure model is based on this software calculation.

2. MATERIALS AND METHODS

Molecular structure model can be used for quantifying partition of any organic compound, which enables a wide range of use in environmental monitoring, and as a partitioning predictor model, when experimental data are not available. Using the molecular structure model, gas/particle partitioning coefficient (Kp) is calculated using the formula (1)[9][10]:

$$Kp = f_{wiom} \cdot K_{wiom} \quad (1)$$

Where K_{wiom} is the sorption coefficient, calculated with SPARC sofware, f_{wiom} is the mass fraction of water insoluble organic matter (WIOM) in dry aerosol. It is reccomended to use the value of 0.4 (40%),which proved to be the most adequate for atmospheric aerosols [3][4]. To calculate with SPARC software required input data (molecular surrogate for ambiental aerosol) must be determined. For determining a surrogate for hydrophobic, organic phase, it was necessary to find a compound that would in an appropriate way substitute a group of organic substances.The biggest ratio in organic matter of urban air have hydrophobic polymers of a secondary organic aerosol. The model was validated for three types of WIOM polymers shown in Fig. 1. [10]. The most adequate polymer for designing the molecular structure model was WIOM B. It has been used as a solvent in the calculation.

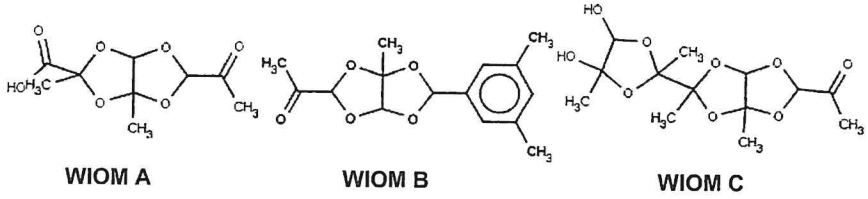

Figure 1. Secondary organic aerosol polymers used in calculations as organic matter surogat [10]

The comparison between experimental data and calculated data are rare. Due to natural variability of ambiental conditions (relative humidity and temeperature), properties of aerosols (f_{wiom}, pH, hydrophylicity) are going to change. Thus, for environmental fate models, specific analysis for all these parameters is recommended. Using the SPARC software, partitioning coefficient of sixteen PAHs, which are included in the U.S. EPA list of priority pollutants, have been quantified. Estimated values were compared with experimental values at six selected locations in Republic of Serbia, in two cities Novi Sad and Kragujevac. Experimental values are gained within APOPSBAL project [2].

3. RESULTS AND DISCUSSION

The main reason for developing a general mathematical model is the need for predicting data that cannot be directly measured. The use of model is accurate and appropriate to predict the fate of toxic compounds in the environment, which can have a significant impact on preserving the natural balance.

Chosen locations for determining gas/particle partitioning coefficient are: in Novi Sad-N1-NIS refinery, N2-Sangaj kindergarden, N3-City's Assembly; in Kragujevac: K1-Zastava factory-PGB, K2-Zastava factory-MPB, K3-Faculty of Science [3][4][5].

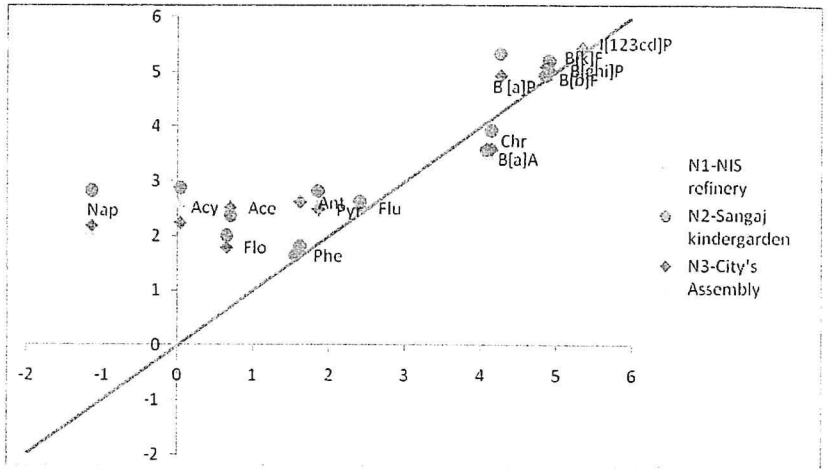

Figure 2. Comparison of experimental (y-axis) and SPARC values (x-axis) for Novi Sad [m^3/g]

For dibenz[a,h]anthracene, partitioning coefficient was unspecified in both Novi Sad and Kragujevac, because the molecule was sorbed dominantly onto particulate matter, so division would be by zero. Results for this PAH are not shown in Fig. 1 and Fig. 2.

For some locations, there were no results for several PAHs. At locations in Kragujevac, there are no results for benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene, because they were sorbed onto particulate matter, and division for calculating partitioning coefficient would be by zero.

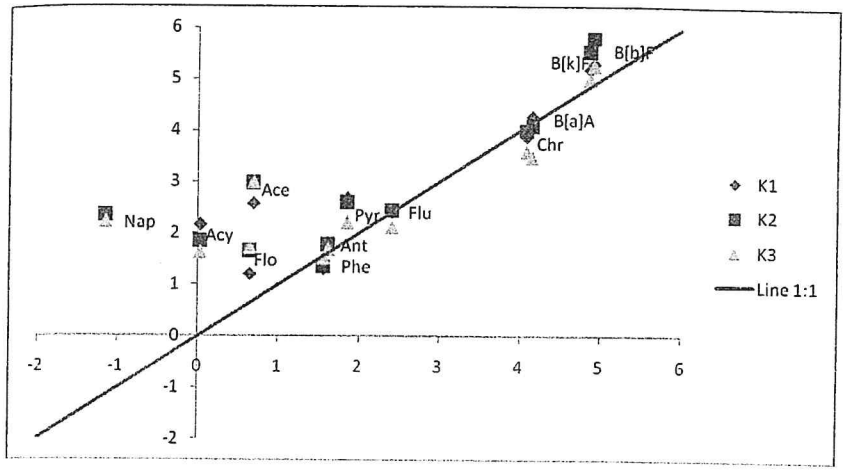

Figure 3. Comparison of experimental (y-axis) and SPARC values (x-axis) for Kragujevac [m^3/g]

The clustering of data near the 1:1 line for the WIOM B indicates that f_{WIOM} value of 0.4 was appropriate; otherwise, the data would be clustered systematically away from the 1:1 line. Measuring points with a completely accurate prediction of gas/particle partitioning coefficients are: N1 for phenanthrene, N2 for benzo(b)fluoranthene, N3 for phenanthrene and benzo(ghi)perylene, K1 for benzo(k)fluoranthene, K2 for anthracene and benzo(a)anthracene, K3 for benzo(k)fluoranthene and anthracene.

4. CONCLUSIONS

Deviation from line 1:1 is not negligible, but the reason of deviation could be explained and with further development and improvement of model, it could be reduced. Deviation from line 1:1 is noticeable for four molecules of PAHs: naphthalene, acenaphthylene, acenaphthene and fluorene in both Novi Sad and Kragujevac. The greatest deviation is for naphthalene, PAH with two condensed aromatic rings in structure, and mainly found as a free gas molecule in gaseous phase. Deviation from predicted values leads to a conclusion that this compound is sorbed to particulate phase, more than it was predicted by the model.

The most important conclusion is that predictions for PAHs with carcinogenic, mutagenic and teratogenic properties (chrysene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene) are close to 1:1 line, which means that this model can be used for predicting partitioning between particulate and gaseous phase

for these PAHs. Predictions for phenanthrene, anthracene, fluoranthene and pyrene are also satisfactory accurate. Our results confirm that molecular structure model could be used for predicting atmospheric distribution of PAHs.

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LISOVANIE SENA NA EXPERIMENTÁLNOM ZARIADENÍ PLG 2010

Ondruška Juraj*, Križan Peter; Šooš Ľubomír, Matúš Miloš, Biath Peter

ABSTRACT

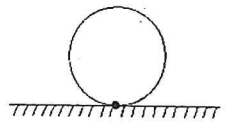
The goal of this contribution is to describe the experiment of hay waste compacting and to confirm the suitability for use of hay waste at energy recovery. Amounts of wood waste for energy recovery are rapidly decreasing. Therefore is needed to use the materials which have very similar energetic value. We have very high possibilities to use materials which are in common calls phytomass. In this contribution is describing the hay pelleting process. Authors are also describing the mechanical indicators (pellets density, pellets durability) of hay pellets quality testing.

ÚVOD

Pre potreby skúšania a testovania lisovateľnosti rôznych druhov materiálov, naše pracovisko disponuje laboratórnym peletovacím lisom (Obr. 3). Lis je určený na testovanie lisovania rôznych druhov materiálov. Bol navrhnutý a skonštruovaný na našom pracovisku, s uvažovaním všetkých základných princípov procesu zhutňovania. Príkon peletovacieho lisu je 4 kW a výkon sa pohybuje v rozmedzí od 45 do 70 kg/hod, v závislosti od zhutňovaného druhu materiálu. Experimentálne zariadenie PLG 2010 je novej nízkoenergetickej koncepcie

Obr. 1 Starodávny ručný mažiar

$$F_\sigma = k.\sigma^n$$



Obr. 2 Pôsobenie gule na rovinu, v pravo

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