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POLYCYCLIC AROMATIC HYDROCARBONS IN HOUSE DUST FROM WARSAW

WIELOPIERŚCIENIOWE WĘGLOWODORY AROMATYCZNE W KURZU MIESZKAŃ WARSZAWSKICH

Abstract: The content of polycyclic aromatic hydrocarbons (PAHs) in the dust from Warsaw apartments were studied. Samples were collected from 48 flats, from a few places in each flat: living room (floor, shelves), bedroom (bed), kitchen, lavatory. At the same time a survey by questionnaire was carried out, in which outside and internal factors were described. PAHs concentration in samples were determined by reversed-phase high performance liquid chromatography (HPLC). The levels of PAHs concentration varied between 8 and 173 mg/kg. The content of PAHs in dust from most of Warsaw apartments was high (from 5 to 50 ppm), and in more than ten was extremely high (> 50 ppm). It could be one of the sources of health hazards in home environment. In the greater part of analyzed samples, very high levels of the following hydrocarbons have been found: benzo[b]fluoranthene, fluoranthene, pyrene, fluorene and phenanthrene. Among microenvironments, selected for the study, the sum of PAHs in kitchen and cellars has been two-three times higher as compared with that in other places. The results show a clear trend to an increased concentration of PAHs in apartment of tobacco smokers.

Keywords: house dust, Warsaw, polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are one of the most hazardous groups of xenobiotics that are polluting natural environment as a result of human activity [1–3]. They are present in commonly used raw materials, such as coal tar, coal-tar pitch, mineral oils, gas pitch, asphalts, soot, or cresol oil. Emission sources of these substances are various processes, [4, 5], for example:

– combustion of solid, liquid or gaseous fuels in cars, power stations, steelworks, and stoves;

– manufacturing of coke, aluminum, coal tar processing and other industrial processes;

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– food processing (barbecue or frying over open fire);
– smoking of cigarettes, cigars, or pipe tobacco;
– wearing of tires and abrasion of asphalt surfaces;
– naturally occurring processes such as forest or steppe fires or emission of volcanic gases and dust.

PAHs, formed in the aforementioned processes are emitted to the atmosphere, where they settle on the surface of aerosol particles. Hence, they could be transferred over long distances form their source. Depending on weather conditions, the pollutant could travel several thousands kilometers. They settle on roof surfaces, leaves, rocks, etc. from where they are washed down with rains and pollute soil and groundwaters. They can settle also in apartments as constituents of common dust where they become a direct hazard to the inhabitants [6]. The amount of PAHs in home dust depends on many factors such as the level of particulate contamination of surrounding air, as well as activity of inhabitants, methods of preparing food, presence of tobacco-smokers, frequency of ventilation, etc.

Numerous toxicological and epidemiologic studies indicate a strong correlation between exposure to those compounds and the increased risk of developing cancer [7]. Metabolites of those compounds (quinones, diols, phenols and epoxy derivatives) could add to DNA and RNA molecules, thus generating neoplastic transformations and genetic alterations. The compounds show systemic toxicity, causing damages of adrenal glands, the lymphatic, circulatory and respiratory systems [8, 9].

Considering the above information, it becomes obvious that monitoring of human environment for the level of PAHs in home dust is the essential part of environmental studies. Levels of PAHs are usually determined according to guidelines of US Environmental Protection Agency (US EPA) [10, 11] that recommends assaying 16 most representative PAHs: naphthalene (Nap), acenanaphthylene (Acy), acenaphtene (Ace), fluorene (Fle), phenanthrene (Ph), anthracene (An), fluorantene (Fla), pyrene (Py), benzo[a]anthracene (BaA), chryzene (Chr), benzo[b]fluorantene (BbF), benzo[k]fluorantene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP), and indeno[1,2,3-c,d]pyren (Ind) in environmental samples. World Health Organization (WHO) and International Agency for Research on Cancer (IARC) have considered the compounds, in particular benzo[a]pyrene as extremely hazardous due to their extreme carcinogenicity and mutagenicity.

The purpose of this study was to determine according to EPA guidelines the content of PAHs in samples of home dust drawn from Warsaw apartments.

Materials and methods

Methods of sample collection

Samples of house dust were collected to cellulose bags from 48 flats (45 of them were situated within the town, 3 outside of the town) using Kärcher vacuum cleaner, in autumn 2003 and spring 2004. Samples were taken from a few places in the house: the living room (floor, shelves), bedroom (beds), kitchen, lavatory. At the same time a survey by questionnaire was carried out, in which some parameters referring to house such as the traffic density, age of the building, surrounding greenery, and to homeowner behaviour as smoking, frequency of housework and air filtration, presence of animals etc. were rated on a gradual scale.

Analytical methods

The aforementioned aromatic hydrocarbons have been assayed by reversed-phase high performance liquid chromatography (HPLC).

The samples were kept at 4 °C in glass containers protected against light. Before the analysis, the samples were sifted to obtain a fraction of particle size < 150 μm. The samples were then extracted by sonication [12] in dichloromethane that has proved to be the most effective among three solvents that had been tried in the study: petroleum ether, hexane and dichloromethane. The extracts were filtered through Nylon filters 25 mm of pore size 0.45 μm, and then evaporated *in vacuo* under nitrogen. The dry extracts were dissolved in acetonitrile and again filtered through PTFE syringe filters 4 mm of pore size 0.2 μm directly before the analysis.

Concentrations of PAHs have been determined using a Dionex liquid chromatograph provided with a UV/VIS diode array detector at the wavelength λ = 254 nm. The chromatographic system was controlled by Dionex's Chromeleon computer software. A highly selective chromatographic column Bakebound PAH 16-PLUS was used to separate PAHs. The water and acetonitrile in a gradient system has been used to elute PAHs from the column. Test conditions have been set up using EPA-610 reference standard that contains all 16 PAHs listed above and the certified reference material ERM-CC013, having similar matrix composition that has been used in quantitative analysis as the external standard. The studies on assaying PAHs in samples of home dust [13] have been used to optimize test conditions.

Results and discussion

The levels of PAHs found in samples of home dust vary between 8 and 173 mg/kg (Fig.1). According to the standard SBM-2003 [14], the content of PAHs in home dust (Table 1) found in our study is high (in 77 % of the samples very high, in 23 % of samples – extremely high) and it could be one of the sources of health hazards in home environment. The highest level of PAHs has been found in an outpatient clinic just after completed refurbishing. Literature references inform about similar, very high PAHs levels in home dust (up to 500 mg/kg) in Columbus, Ohio at the time of repairing an asphalt road 500 m from the sampling site [15, 16], or in New York City (200–300 mg/kg) after collapse of World Trade Centre [17].

Table 1

Ranges of PAHs concentration in house dust according to the standard SBM-2003 [14]

	Normal	High	Very high	Extremely high
PAHs concentration in house dust ($mg \cdot kg^{-1}$)	< 0.5	0.5–5	5–50	> 50

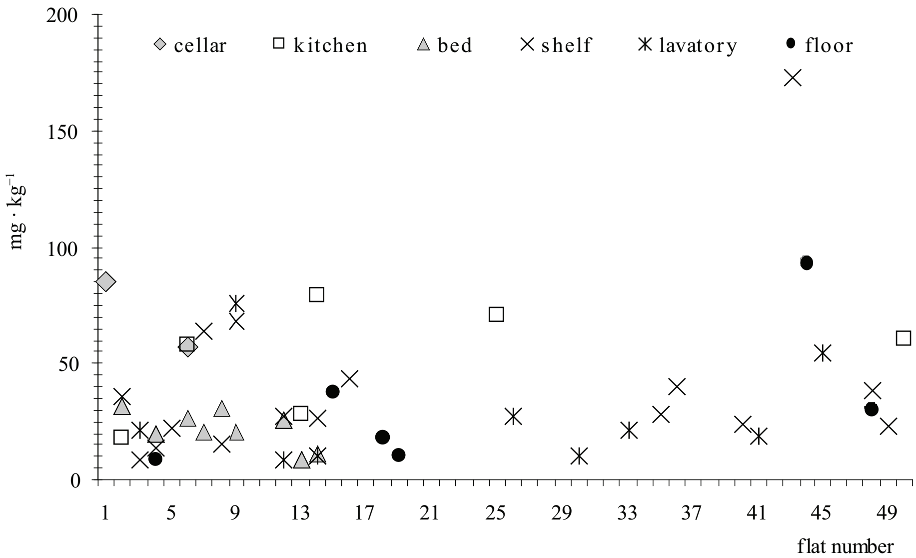

Fig. 1. Concentration of PAHs (the sum of the sixteen PAHs) in house dust from Warsaw

In majority of analyzed samples, extremely high levels of the following hydrocarbons have been found: benzo[b]fluoranthene (BbF), fluoranthene (Fla), pyrene (Py), fluorene (Fle) and phenanthrene (Ph) (Table 2). They constituted about 80 % of the

Table 2

Descriptive statistics referring to PAHs concentration in house dust from Warsaw

PAH	N	Sum	Mean	SD	Median	Max	Min
Nap	48	62.11	1.29	1.77	0.73	7.96	0.06
Acy	48	54.41	1.73	4.68	0.47	31.91	0.01
Ace	48	20.05	0.42	0.40	0.35	2.28	0.01
Fle	48	101.53	2.12	1.29	2.19	5.81	0.05
Ph	48	292.51	6.09	4.27	4.82	18.66	0.80
An	48	39.38	0.82	0.56	0.71	2.12	0.11
Fla	48	324.46	6.76	11.90	2.46	71.75	0.16
Py	48	184.23	3.84	6.98	2.17	38.99	0.13
BaA	48	68.37	1.42	1.94	0.54	8.05	0.02
Chr	48	13.39	0.28	0.36	0.16	1.64	0.00
BbF	48	420.45	8.76	10.27	5.28	49.07	1.51
BkF	48	36.46	0.76	1.74	0.17	10.65	0.01
BaP	48	33.67	0.70	1.78	0.18	11.29	0.01
DahA	48	24.73	0.52	1.00	0.14	4.86	0.01
BghiP	48	20.37	0.42	0.90	0.16	5.66	0.01
Ind	48	18.51	0.39	0.64	0.18	3.98	0.03

16 assayed PAHs (Fig. 2). The results confirm data obtained by other authors, and presented by Maertens [6], where it has been stated that the presence of these hydrocarbons could be a result of burning variety of fuels. A relatively high content of BbF in an urban agglomeration is not surprising as the main sources of this hydrocarbon as well as of Fla and Py are exhaust gases from gasoline and Diesel engines. According to Mukerjee [18], Ph, Fla, and Py hydrocarbons are being emitted from barbecuing and frying processes while Ph and Py are associated with the tobacco burning process. Pyrene and fluoranthene have been suggested as potential source markers for incineration, wood burning and oil combustion [19], with the ratio of fluoranthene to pyrene providing information about a PAH source. If the fluoranthene/pyrene ratio is greater than 1, the PAHs are considered to have been generated by pyrolytic processes, whereas if the ratio is less than 1, they are considered to be petrogenic in origin [20]. In our study, in 62 % of tested samples the ratio is greater than 1, which proves that the hydrocarbons come predominantly from combustion processes.

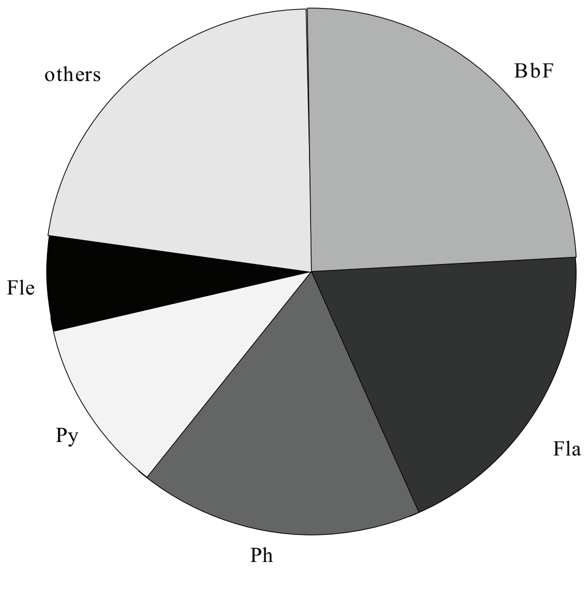

Fig. 2. Proportions [in %] of five PAHs (BbF, Fla, Ph, Py, Fle) in house dust from Warsaw

Among microenvironments, selected for the study, the sum of PAHs in kitchen and cellars has been from two- to three-fold higher as compared with that in other places (beds, shelves, bathrooms, and floors) (Fig. 3). The differences, assessed by the Mann-Whitney test were statistically significant at the level $p < 0.05$. The high content of PAHs in kitchens confirms the suggestion of Mukerjee [18] that gas cooking is significantly increasing the level of PAHs. On the other hand, the high level of PAHs in cellars is most likely associated with a long lasting sedimentation of dust due to infrequent cleaning.

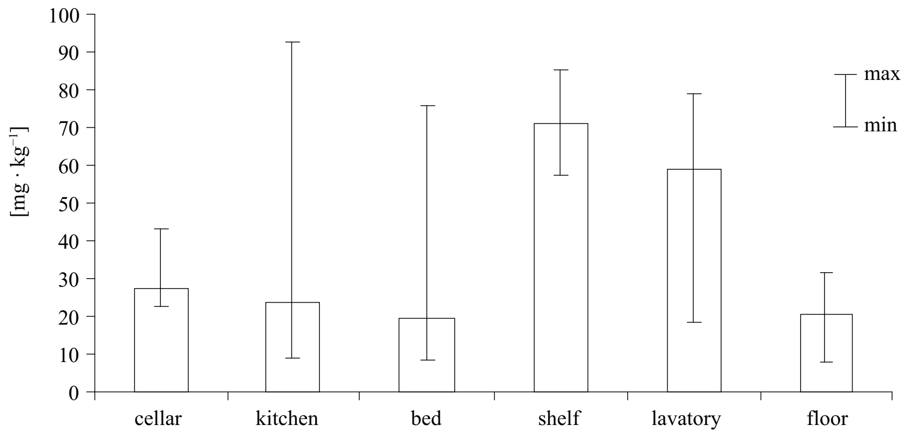

Fig. 3. Median values of PAHs concentration (the sum of the sixteen PAHs) in dust from different mikroenvironments

The high level of PAHs in dust samples is presumably related to numerous factors that have impact on concentration of these substances. In our studies, we have analyzed data from questionnaires concerning tobacco smoking, frequency of cooking, mobility of inhabitants and ventilation and their impact on the content of PAHs in dust samples. The results show a clear trend to an increased concentration of PAHs in apartment of tobacco smokers (Fig.4). A similar trend has also been found by Lewis [21] and Mukerjee [18].

A comparison of variability coefficients for the hydrocarbons that constitute about 80 % of all analyzed PAHs (BaP, Fla, BbF, BaA, Ph and Py) have proven that inter-

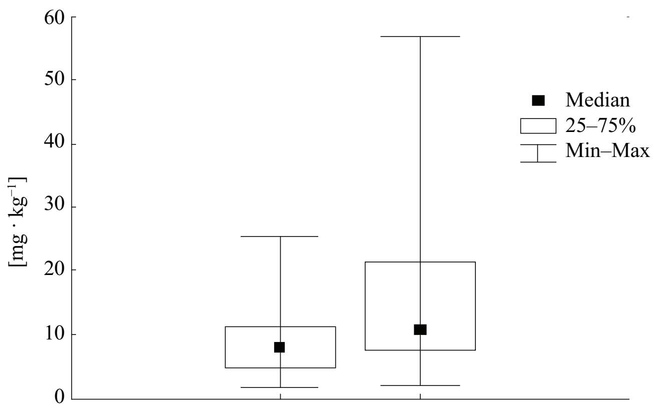

Fig. 4. Comparision of concentration of four PAHs (Ph, BaP, Chr and Fla) in house dust from nonsmokers (1) and smokers (2) apartments

apartment variability of the levels of these hydrocarbons is larger than that observed for various microenvironments within the same apartment. However, high PAHs variability coefficients observed within the apartments (although slightly lower than those inter-apartment ones), show an impact of environmental factors within an apartment on the level of PAHs. This observation confirms the above discussed trends associated with tobacco smoking or gas cooking. Inflow of hydrocarbons into the apartments along with the air aerosols that contain the compounds originating in industrial burning processes, asphalt abrasion and exhaust gases from combustion engines is the key issue. In this aspect, the impact of weather conditions that favor formation of smog and accumulation of pollutants, or strong winds that would counteract these conditions and disperse the pollutants accumulated in the air aerosol around wide area. The authors of all studies on PAHs emphasize that small impact of tobacco smoking, location, frequency of ventilation and other factors suggests that the content of PAHs in dust depends much on the sum of all environmental factors.

No significant differences have been found in the content of PAHs in samples drawn in Warsaw and in those drawn in Dziekanów Leśny near Warsaw and in Famułki Królewskie, a village approximately 50 km from Warsaw, in the middle of Kampinos Forest (*Puszcza Kampinosk*a), away from any industry, where one could expect a lower pollution level. The most probable explanation of this observation is that the sample has been drawn in a forester's lodge, where large amount of wood is burned, in particular pinewood. Pinewood contains large amounts of resin that emits large amounts of PAHs upon combustion.

One should emphasize that in the natural environment aromatic hydrocarbons could undergo decomposition caused by such factors as sunlight, oxygen, ozone, increased temperature. The impact of these factors in home environment is smaller, and on the other hand, home environment favors accumulation of the hydrocarbons and their absorption by deposited dust. It is confirmed by high levels of PAHs found in cellars. Considering the above facts, and because more and more time is being spent indoor these days, one should avoid accumulation of dust in his/her nearest environment. It is particularly important for little children that by putting their hands and dusty objects in their mouth can swallow from 50 to 100 mg PAHs per day [6]. This route of entry for dust and the noxious substances accumulated on it could be a reason of increased incidence of diseases (allergies and similar diseases) in preschool children.

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WIELOPIERŚCIENIOWE WĘGLOWODORY AROMATYCZNE W KURZU MIESZKAŃ WARSZAWSKICH

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Abstrakt: Badano poziom zanieczyszczenia wielopierścieniowymi węglowodorami aromatycznymi (WWA[PAHs]) kurzu z mieszkań warszawskich. Próbki pobrano z 48 mieszkań, z kilku miejsc w każdym mieszkaniu: pokój dzienny (podłoga, półki), sypialnia (łóżko), kuchnia, łazienka. Równocześnie przeprowadzano ankietę, w której w kilku stopniowej skali oceniano różne czynniki zewnętrzne i wewnętrzne. Stężenie WWA w próbkach oznaczono metodą chromatografii cieczowej (HPLC). Uzyskane zakresy stężeń dla sumy szesnastu WWA, wahają się od 8 do 173 mg/kg. Wartości stężeń sumy WWA w większości próbek były duże, w granicach od 5 do 50 ppm, co może stanowić duże zagrożenie dla zdrowia. W kilkunastu próbkach stężenia WWA osiągały wartości bardzo duże. W większości próbek stwierdzono wyjątkowo duże stężenia takich węglowodorów, jak: benzo[b]fluoranten, fluoranten, piren, fluoren i fenantren. W wytypowanych do badań mikro-środowiskach stwierdzono dwu-trzykrotnie większe stężenie sumy szesnastu WWA w kuchniach i piwnicach niż w pozostałych miejscach. Porównanie zawartości węglowodorów w kurzu ze zwaloryzowanymi danymi z ankiety wskazuje na wyraźną tendencję większego stężenia WWA w mieszkaniach osób palących.

Słowa kluczowe: kurz domowy, Warszawa, węglowodory aromatyczne