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Pollution level, phase distribution and source analysis of polycyclic aromatic hydrocarbons in residential air in Hangzhou, China

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ABSTRACT

A survey of polycyclic aromatic hydrocarbons (PAHs) in residential air in Hangzhou, China, was carried out. Air samples were collected from indoor and outdoor environments during both summer and winter and analyzed for the level of 16 PAHs. The results showed total PAH contents ranging from 0.425 to $36.2 \,\mu$ g/m³ with highest concentrations in the kitchen areas generally. Particulate PAHs were predominantly absorbed on PM_{2.5} with proportion of 59–97% to total particulate phase, followed by PM_{2.5-10} (3–24%) and PM_{>10} (0–17%). PAH concentrations in indoor air of smoking residences tended to be higher than those of non-smoking residences. Outdoor environment, Chinese conventional cooking practice, mothball emission and unknown source accounted for –10.5%, 32.8%, 71.5% and 6.2% of total PAHs in indoor air of nonsmoking residences, respectively. Outdoor environment was the fate for indoor PAHs in general, and consumed 10.5% of total PAHs. Finally, health risks associated with the inhalation of PAHs were assessed, and the results indicated that health-based guideline levels for lung cancer risk were exceeded. The largest contribution to total health risks in summer and winter was NA (72.9%) and BaP (45.2%), respectively.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of widespread environmental pollutants containing two or more fused benzene rings [1]. They are typically formed during incomplete combustion of organic materials such as coal, oil, gas, and wood and natural sources of PAHs include volcanic activity and forest fires [2–5]. Indoor emission sources of PAHs include smoking, cooking and heating [6,7]. PAHs are considered the most widely distributed class of potent carcinogens present in the human environment [5,8], and many of them are listed as proved or possible carcinogens by various international and national agencies. Consequently, PAHs are widely studied with focus on their health-related impacts [9].

The first survey of PAHs in ambient air was performed in London in the 1950s [10], and since then, routine monitoring have been carried out at several locations, locally as well as around the world [11–15]. Most of these studies have focused on determining PAH pollution in outdoor air. However, people nowadays spend most of their time in indoor environments, in which case indoor air quality has increasing impact on human health. In addition, several studies showed that PAH concentrations found in indoor air were typically higher than those found in outdoor air [16,17]. Researchers have found that indoor sources may contribute to pollution with PAHs of 2 or 3 rings, whereas larger PAH molecules predominantly originated from outdoor sources [18,19].

PAHs in air are partitioned in a vapor and a particulate phase. A few studies have been taken to discuss the PAH phase distribution and their distribution on particles of different sizes in ambient air [7,18,20,21]. The results indicated that particulate PAHs were more harmful to humans. This was due to the fact that PAHs of high molecular weights, which were more carcinogenic than those of low molecular weights, were mainly in particulate phase. However, limited information on PAH phase distribution in indoor air is available, particularly in terms of the size distribution of particles.

In China, the characteristics of indoor PAH pollution are significantly different from most other countries due to the peculiar Chinese culinary and living practices. Use of mothballs and cooking practice are common sources of indoor air pollution within Chinese homes. Little study has been conducted to quantify the emission sources of PAHs in residential air.

In the present study, PAH pollution in indoor and outdoor air was measured in Hangzhou residences. The objectives of the study were: (1) to assess the PAH concentrations in indoor and outdoor air in selected residences, and discuss results and trends in respect to room function; (2) to characterize the distribution of PAHs in vapor/particulate phases and their distribution on particles of dif-



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ferent sizes; (3) to qualify and quantify the emission sources of PAHs in residential air; (4) to evaluate health risks associated with inhalation PAHs in indoor environments.

2. Experimental

2.1. Sampling sites

A monitoring program was carried out in Hangzhou, China, during the summer (2–15 August, 2006) and the winter (10 January to 6 February, 2007). A total of 26 houses (6 houses in both seasons) were selected. In each house, samples were collected from living room, kitchen, bedroom and work room, and outdoor samples were taken from the balcony.

2.2. Air sampling

Vapor PAHs were adsorbed using XAD-2 tubes (2.5 g, Supelco, USA), which prior to sampling was cleaned with dichloromethane and methanol. Particulate PAHs were collected and size-fractionated using a Personal Cascade Impact (PCI) sampler (2.5 L-SPM10, Sibata Scientific Technology Ltd., Tokyo, Japan) equipped with teflon fibre filters (Pallflex Products Corp., USA). The filters were preheated at 400 °C for 6 h to remove organic compounds before sampling. Airborne particle size fractionation were based on aerodynamic particle diameters <2.5 μ m (PM_{2.5}), 2.5–10 μ m (PM_{2.5-10}) and >10 μ m (PM_{>10}). Both XAD-2 tubes and the PCI sampler were connected with a mini-pump (DDY-1.5, Xingyu, China) for air sampling. The sampling flow rates for vapor and particulate PAHs were 1.0 and 2.5 L/min, respectively.

Two separate samples were collected at each sampling site and the result used was the mean of these two samples. The sampling took place during a 12 h period (8:00 a.m. to 8:00 p.m.). The flow rates were measured before and after the sampling programs and all deviations of the rates were less than 2%.

2.3. Analysis of PAH samples

After air sampling, the XAD-2 were poured into a 25 mL glass stoppered tube containing 20 mL mixture of dichloromethane and acetonitrile (v/v = 3/2). The teflon fibre filters were cut into pieces, placed in a 25 mL glass stoppered tube containing 10 mL dichloromethane. The samples were sonicated for 30 min while the water in the ultrasonic bath was replaced frequently in order to prevent overheating. Subsequently, 10 mL extracts of XAD-2 and 5 mL extracts of teflon fibre filters were transferred into new glass stoppered tubes. Extracts with 30 μ L dimethyl sulfoxide (DMSO) were evaporated under a gentle flow of nitrogen gas at room temperature and then added 970 μ L acetonitrile.

The samples were analyzed for the following 16 PAHs: naphthalene (NA), acenaphthylene (ACY), acenaphthene (AC), fluorene (FLUOR), phenanthrene (PHEN), anthracene (AN), fluoranthene (FLUR), pyrene (PY), benzo[a]anthracene (BaA), chrysene (CHRY), benzo[b]fluoranthrene (BbF), benzo[k]fluoranthrene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DA), benzo[ghi]perylene (BP), indeno[1,2,3-cd]pyrene (IN). The PAHs were determined by HPLC (1200 series, Agilent Technologies, USA) containing a column (Lichrospher PAH, 250 mm × 4.6 mm, Agilent Technologies, USA), a fluorescence detector and an ultraviolet detector (determine ACY only).

2.4. Quality control

Before sampling program, PAHs recovery studies were undertaken to demonstrate the availability of the method. We produced

Table 1

The recoveries and detection limits of 16 PAHs

	Vapor recoveries (%)	Particulate recoveries (%)	Detection limits (ng/m ³)
NA	77.0 ± 2.7	78.8 ± 5.4	1.15
ACY	86.4 ± 2.6	87.4 ± 5.0	4.65
AC	85.7 ± 4.2	87.2 ± 3.7	0.27
FLOUR	88.0 ± 6.2	85.3 ± 4.9	0.11
PHEN	98.4 ± 4.2	96.5 ± 5.0	0.73
AN	89.9 ± 3.0	91.2 ± 3.4	0.05
FLUR	94.5 ± 4.0	94.2 ± 4.7	0.28
PY	87.9 ± 1.6	91.1 ± 4.9	0.13
BaA	91.5 ± 3.2	92.6 ± 4.6	0.72
CHRY	92.6 ± 3.3	88.7 ± 7.5	0.14
BbF	93.8 ± 3.5	90.4 ± 5.5	0.22
BkF	94.8 ± 2.5	94.6 ± 2.7	0.04
BaP	95.7 ± 3.4	96.2 ± 2.6	0.12
DA	93.5 ± 4.6	93.1 ± 4.4	0.21
BP	98.7 ± 3.8	94.9 ± 3.2	0.46
IN	96.2 ± 4.3	90.9 ± 2.2	0.56

cleaned XAD-2 and teflon fibre filters doped with PAHs to correspond to concentrations in air of, for example, $100-800 \text{ ng/m}^3$ in vapor phase and $2-10 \text{ ng/m}^3$ in particulate phase for PHEN, respectively. The recoveries (n = 5) and detection limits of 16 PAHs are presented in Table 1. The recoveries for vapor and particulate phase ranged from $85.3 \pm 4.9\%$ to $98.7 \pm 3.8\%$ except for NA (its recoveries were $77.0 \pm 2.7\%$ and $78.8 \pm 5.4\%$ for vapor and particulate phase, respectively). The detection limits of 16 PAHs were $0.04-4.65 \text{ ng/m}^3$.

3. Results and discussion

3.1. PAH concentrations in residential air

Boxplots of PAH concentrations in indoor air of selected residences are shown in Fig. 1. Total concentrations of 16 PAHs (\sum PAHs) ranged from 0.425 to 36.2 µg/m³, with an average and median of 6.04 and 3.48 µg/m³, respectively. The results showed significantly higher PAH level than found in a similar study of indoor air pollution in 10 American residences, where the median concentration of \sum PAHs was 0.207 µg/m³ [1].

NA was in this study found to be the most abundant of the 16 PAHs studied. The NA concentration varied from 0.258 to



Fig. 1. Concentrations of individual PAHs in residential air (The box represented 25–75th percentiles, the whiskers were 10th and 90th percentiles, the lowest and highest circles were the minimum and maximum, and line inside the box showed the median. The figure was acquired by averaging the data from all residences with 4 sampling sites, living room, bedroom, work room and kitchen).



Fig. 2. PAH concentrations in air of different areas in residences (The box represented 25–75th percentiles, the whiskers were 10th and 90th percentiles, the lowest and highest circles were the minimum and maximum, and line inside the box showed the median).

 $35.4 \,\mu g/m^3$ with an average of $5.35 \,\mu g/m^3$ and accounted for 60.6-97.9% of \sum PAHs. Previous studies found that NA emissions in indoors environments were highly correlated with the use of mothballs [7], hence this was also believed to be the case in this study.

PHEN and AC were found in concentrations ranging from 21.1 to 2103 ng/m³ and 10.8 to 1472 ng/m³, respectively. Moreover, BaP concentrations detected was ranging from 0.109 to 12.4 ng/m³. All PAHs with molecular weight (MW) between 128 and 202 had average and median concentrations higher than 9.0 ng/m³, whereas PAHs with MW 252–276 was found in much lower concentrations. The low contents of heavy PAHs relative to light PAHs have been reported in several previous studies [19,22].

PAH concentrations detected in 4 different rooms are given in Fig. 2. The average concentrations of \sum PAHs in living room, bedroom, work room and kitchen were 5.59, 6.98, 6.15, and 7.69 μ g/m³, respectively. Correspondingly, the medians were 4.07, 4.82, 3.48, 5.31 μ g/m³, respectively. The results indicated that PAH pollution in kitchen was the most serious. However, in our previous study [7], the concentrations of PAHs in bedroom were relatively higher than those in the other areas. This may be attributed by the following two reasons. Firstly, air purification and exchange between indoor and outdoor by air conditioners were more commonly observed during the sampling periods of this study. Secondly, the amounts of mothballs used to protect clothes were somewhat decreased in recent years in China. Concentrations of 3-4-ring PAHs in kitchen accounted for 12.2–23.7% of \sum PAHs with the average of 15.9%, which was higher than that in the other places (12.4%). Cooking processes such as frying, boiling and steaming would originate PAHs, and 3-ring PAHs was abundant in cooking fume [23,24]. Though each kitchen we sampled had ventilating fans, PAHs could not be diluted sufficiently during cooking. As mothballs were used commonly in the bedrooms, concentrations of 2-ring PAHs (NA) in there accounted for 85.0–97.9% of \sum PAHs with the average of 89.5%, which was higher than that in the other places (87.3%). PAHs were here presented the second highest concentrations. There was smoking activity in some of the sampling houses, which increased PAH concentrations in indoor air.

3.2. Seasonal variations of indoor/outdoor PAH concentrations

Results of PAH measurements carried out during summer and winter season, respectively, are given in Table 2. In general, vapor Table 2

Seasonal variations of average PAH concentrations (ng/m³)

PAHs	Summer	Winter
NA	1.01 E4	1.78 E3
ACY	69.9	40.8
AC	247	37.8
FLOUR	229	48.9
PHEN	464	124
AN	12.9	6.74
FLUR	17.0	12.2
PY	36.1	16.4
BaA	34.4	11.7
CHRY	7.20	6.10
BbF	1.38	5.63
BkF	0.678	2.41
BaP	0.611	4.48
DA	0.310	0.696
BP	1.19	4.34
IN	0.652	4.89
\sum PAHs	1.12 E4	2.11 E3

The table was acquired by averaging the data from all residences with 4 sampling sites, living room, bedroom, work room and kitchen.

PAHs, typically containing 2–3 rings, were abundant in the summer season compared to in winter. However, the concentrations of 4ring PAHs were comparable in both the summer and winter season. In contrast, particulate PAH (mainly existed in 5–6 rings) concentrations found were significantly higher in winter than in summer. This effect was reported to relate to fossil fuel consumption for heating, photodegradation to related compounds in summer, and reductions in combustion temperature [12,15,25,26]. The seasonal variations in this study were similar to findings of a Japanese study [18].

The I/O ratios of PAH concentrations measured in this study are presented in Fig. 3. Ratios greater than 1 indicated that indoor sources made a significant contribution to PAH concentrations in indoor air, whereas in the absence of strong indoor sources, the ratios were expected to be close to or lower than 1. In general, the I/O ratios were higher for PAHs of low MW in both summer and winter, which was consistent with the data reported in other studies [19,27].

In summer, all median I/O ratios were greater than 1, suggesting that PAHs in indoor air were dominated by indoor sources. The median I/O ratio for NA was 2.0, and its value reached 2.6 in bedroom, which was related to the use of mothballs. In winter, most median ratios of 2–4-ring PAHs were greater than 1, whereas all median ratios of 5–6-ring PAHs were lower than 1, indicating indoor concentrations controlled by outdoor sources.

Indoor versus outdoor concentrations for 16 individual PAHs were evaluated for 26 houses. For 2–4-ring PAHs, the coefficient R^2 ranged from 0.03 to 0.53, showing no or weak correlation between indoor and outdoor levels. By comparison, R^2 for 5–6-ring PAHs was ranging from 0.68 to 0.93 except for DA. The stronger correlation indicated that high ring PAHs in indoor air probably originated from outdoor sources. It has been reported that high ring PAHs were usually originated at higher temperatures, such as those in the gasoline combustion engines, than those involved in most indoor combustion processes such as cooking and smoking [28].

3.3. Phase distribution of PAHs and their distribution on particles of different sizes

PAHs exist in both vapor and particulate phase, and the distribution depends on the volatility of the compounds and physical conditions such as temperature and humidity. One researcher reported that the concentrations of vapor PAHs correlated well with the subcooled liquid vapor pressure [29]. The phase distribution of



Fig. 3. Ratios of indoor/outdoor PAH concentrations in summer and winter (The box represented 25–75th percentiles, the whiskers were 10th and 90th percentiles, the lowest and highest circles were the minimum and maximum, and line inside the box showed the median. The indoor PAH concentrations were acquired by averaging the data from all residences with 4 sampling sites, living room, bedroom, work room and kitchen).



Fig. 4. Distribution of PAHs between vapor and particulate phase in residential air (The figure was acquired by averaging the data from all residences with 4 sampling sites, living room, bedroom, work room and kitchen).



Fig. 5. Particle size distribution of PAHs in residential air (The figure was acquired by averaging the data from all residences with 4 sampling sites, living room, bedroom, work room and kitchen).

PAHs in this study is given in Fig. 4, and significant positive correlation was found between the proportion of particulate phase and MW of PAHs (r = 0.966, p < 0.01).

Fine particles with diameter less than 2.5 μ m (PM_{2.5}) are of the greatest health concern, because they can be deposited deeply in the lungs when breathing [30]. Particle size distribution of individual PAHs in indoor air is presented in Fig. 5. Particulate PAHs mainly existed on PM_{2.5}, accounting for 59–97% of the total particulate phase, followed by PM_{2.5-10} (3–24%) and PM_{>10} (0–17%). In general, proportion of the PM_{2.5} fraction increased with the increase of MW for individual PAHs. Significant positive correlation was found between the proportion of PM_{2.5} fraction and MW of PAHs (*r*=0.658, *p*<0.01).

3.4. Sources analysis of PAHs in residential air

Smoking, cooking, and heating are the sources of PAHs in indoor air, with smoking being the major source [7,31]. In this study, there were only 3 houses smoked in summer and no house smoked in winter. So, there were not enough data to analyze statistically the influence of smoking on indoor PAH concentrations. Nevertheless, the differences of PAH concentrations were still found between the smoking and nonsmoking residences. The average of \sum PAHs was

Table 3

The rotated component matrix of indoor PAH concentrations

	Component			
	Factor 1	Factor 2	Factor 3	Factor 4
NA	-0.104	0.326	0.754	0.060
ACY	0.043	0.578	-0.162	-0.124
AC	-0.293	0.741	0.044	0.196
FLOUR	-0.355	0.748	0.172	0.223
PHEN	-0.267	0.852	0.273	0.174
AN	-0.151	0.793	0.179	0.320
FLUR	0.140	0.601	0.135	0.288
PY	-0.112	0.625	0.150	0.604
BaA	-0.142	0.189	0.139	0.914
CHRY	0.280	0.094	0.103	0.912
BbF	0.936	0.175	-0.108	0.226
BkF	0.942	0.140	-0.059	0.262
BaP	0.945	0.196	-0.113	-0.022
DA	0.794	0.232	0.052	-0.023
BP	0.959	-0.159	-0.079	0.067
IN	0.885	-0.211	-0.117	0.073

Extraction method: principal component analysis. Rotation method: varimax with kaiser normalization. The original data used to analyze statistically were from all residences with 4 sampling sites, living room, bedroom, work room and kitchen.

Table 4	
TEF-adjusted concentrations of PAHs in residential air (ng/m ³)	

PAHs	TEF	Summer			Winter				
		Living room	Bedroom	Work room	Kitchen	Living room	Bedroom	Work room	Kitchen
NA	0.001	8.3	25	9.6	22	1.6	1.7	1.8	2.0
ACY	0.001	0.060	0.068	0.077	0.074	0.039	0.041	0.035	0.048
AC	0.001	0.21	0.27	0.23	0.28	0.036	0.040	0.038	0.038
FLOUR	0.001	0.18	0.29	0.21	0.25	0.046	0.049	0.048	0.053
PHEN	0.001	0.41	0.56	0.38	0.51	0.12	0.13	0.12	0.14
AN	0.01	0.11	0.14	0.11	0.16	0.068	0.066	0.061	0.074
FLUR	0.001	0.016	0.019	0.013	0.020	0.012	0.012	0.011	0.013
PY	0.001	0.031	0.041	0.025	0.046	0.016	0.017	0.014	0.019
BaA	0.1	2.4	4.7	1.8	4.8	1.1	1.1	1.1	1.3
CHRY	0.01	0.058	0.087	0.049	0.094	0.060	0.060	0.058	0.066
BbF	0.1	0.13	0.14	0.093	0.19	0.57	0.53	0.54	0.62
BkF	0.1	0.060	0.078	0.046	0.087	0.24	0.23	0.23	0.27
BaP	1	0.79	0.54	0.48	0.63	4.5	4.2	4.3	4.8
DA	1	0.43	0.25	0.22	0.34	0.70	0.60	0.57	0.92
BP	0.01	0.014	0.012	0.0089	0.013	0.043	0.041	0.041	0.048
IN	0.1	0.072	0.058	0.069	0.062	0.45	0.51	0.43	0.57
\sum PAHs		13	32	13	29	9.6	9.4	9.4	11

19.7 μ g/m³ (6.08–36.2 μ g/m³) in smoking residences in summer. In contrast, the average of \sum PAHs was 8.71 μ g/m³ (5.24–18.0 μ g/m³) in nonsmoking residences in summer. PAH concentrations in indoor air of smoking residences tended to be higher than those of nonsmoking residences.

Factor analysis and multiple regression analysis were conducted to qualify and quantify the emission sources of PAHs in indoor air of nonsmoking residences. The rotated component matrix of indoor PAH concentrations is presented in Table 3. 4 factors were selected, and the variances were 41.2%, 24.1%, 10.0% and 8.9% for Factor 1–4.

Factor 1 was highly loaded on 5–6-ring PAHs. Former study indicated that high ring PAHs were usually emitted from outdoor sources, such as those in the gasoline combustion engines, rather than from most indoor combustion processes such as cooking and smoking [28]. Therefore, factor 1 was selected to represent outdoor environment.

Factor 2 was highly loaded on 3-ring PAHs such as AC, FLOUR, PHEN and AN. the fingerprint of oil-fume from Chinese conventional cooking method was the abundance of 3-ring PAHs [24]. Factor 2 was selected to represent cooking practice.

Factor 3 had high loading on NA. Mothballs were commonly used in selected residences. As we mentioned above, NA were largely emitted from mothballs. Factor 3 was assigned to represent mothball emission.

Factor 4 had high loading on BaA and CHRY. There was no other emission source we found during sampling period in the residences. It maybe represent the environmental background concentrations of PAHs, however, further study should be conducted to clarify this factor. In this study, factor 4 was assigned to represent unknown source.

Multiple regression analysis was conducted to calculate the contribution of sources to \sum PAHs. The relationship between \sum PAHs and 4 factors was:

$$\sum PAHs = -0.11[Factor 1] + 0.345[Factor 2] + 0.753[Factor 3] + 0.065[Factor 4]$$

The results of multiple regression analysis indicated outdoor environment, Chinese conventional cooking practice, mothball emission and unknown source accounted for -10.5%, 32.8%, 71.5%, 6.2% of total PAHs, respectively, and outdoor environment consumed 10.5% of total PAHs in indoor air of nonsmoking residences. We believed low ring PAHs which were the predominant proportion of total PAHs in residential air were originated from indoor sources and outdoor environment was their fate.

3.5. Risks assessment of PAHs pollution in residential air

As the toxicity of the individual PAHs are much different, toxicity assessment of PAHs is complex [3,32]. Several approaches have been developed for evaluating the potencies of various PAHs in respect to inhalation cancer risks to humans [33,34]. A toxicity equivalency factor (TEF) based on BaP was usually used to assess the complicated toxicity potencies [33]. In this study, TEF-adjusted concentrations of PAHs in indoor air are shown in Table 4. In summer, the highest health risks were found in the bedroom, where the average TEF-adjusted PAH concentration (\sum TEF-PAHs) was 32 ng/m³, dominated by NA (72.9%), BaA (15.7%) and BaP (2.8%). In winter, however, the highest health risk was found in the kitchen with average \sum TEF-PAHs of 11 ng/m³, contributed mainly from BaP (45.2%), NA (18.0%) and BaA (11.7%).

Furthermore, values of \sum TEF-PAHs in summer and winter were used to estimate the corresponding lifetime lung cancer for exposure. The World Health Organization suggested the unit risk of $8.7 \times 10^{-5} (\text{ng/m}^3)^{-1}$ for lifetime (70 years) PAH exposure [18]. Thus, the lifetime lung cancer risks for PAH exposure in indoor air were 1.9×10^{-3} and 0.9×10^{-3} in summer and winter, respectively. The values exceeded a health-based guideline level significantly (10^{-5}) [35].

4. Conclusions

Total concentrations of 16 PAHs ranged from 0.425 to 36.2 μ g/m³ in sampling residences in Hangzhou. NA was the most abundant one owing to its large emission from mothballs. PAH pollution in kitchen was the most serious with an average total concentration of 7.69 μ g/m³. The concentrations of 2–3-ring PAHs in summer were much higher than in winter, whereas the opposite was the case for 5–6-ring PAHs. The phase distribution of PAHs strongly correlated with MW of the individual PAH compound, and significant positive correlation was found between the proportion of particulate phase and MW (r = 0.966, p < 0.01). Furthermore, significant positive correlation was found between the proportion of PM_{2.5} fraction and MW (r = 0.658, p < 0.01).

PAH concentrations in indoor air of smoking residences were observed to be higher than those of nonsmoking residences, although there were not enough data to statistical analyze the influence of smoking on indoor PAH concentrations. In nonsmoking residences, outdoor environment, Chinese conventional cooking practice, mothball emission and unknown source accounted for -10.5%, 32.8%, 71.5% and 6.2% of total PAHs in indoor air, respectively. Outdoor environment was the fate for indoor PAHs, and consumed 10.5% of total PAHs as a whole. NA and BaP made the largest contribution to total health risks in summer and winter, respectively. Compared to the health-based guideline level, remarkable high health risks associated with PAHs were found in sampled residences.

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