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Size Distribution of Polycyclic Aromatic Hydrocarbons in Indoor Airborne Particulates

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Key Words
Polycyclic aromatic hydrocarbons · Size distribution · Indoor pollution · $PM_{2.5}$

Abstract
A survey of the particle-size distribution of 17 polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air was performed in 20 homes in several Japanese cities. Highest PAH concentrations were found in the fine-particle fraction (smaller than 2.5 μm in diameter). The proportion of indoor PAH concentrations in fine particles was found to be higher than that of outdoors. For 4-ring PAHs, indoor sources elevated the indoor PAH concentrations in the 2.5- to 10-μm and >10-μm fractions, whereas the indoor PAH concentrations in particles smaller than 2.5 μm were comparable with or lower than the outdoor concentrations. In contrast, for PAHs with more than 5 rings, the indoor concentrations were determined essentially by outdoor concentrations. The indoor/outdoor benzo[*a*]pyrene concentration ratio varied considerably in homes with smokers because the residents opened the windows of the room in which smoking took place.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are usually generated during incomplete combustion processes, such as fossil fuel combustion, or in natural processes [1], and many of these compounds are known to be mutagenic and/or carcinogenic [2]. Because most of us spend more than 80% of our time indoors [3], any evaluation of human exposure to air pollutants should include the monitoring of these compounds in the air in indoor environments such as homes.

A number of studies have been conducted to characterise the PAHs present in the air. Studies of the size distribution of particulate PAHs as well as the distribution between gaseous and particulate phases have shown that PAHs with 5–7 aromatic rings are associated primarily with the fine-particle fraction of airborne particulates [4–8].

The US Environmental Protection Agency has enacted the National Ambient Air Quality Standard and has promulgated an ambient air quality standard for particles smaller than 2.5 μm in diameter ($PM_{2.5}$) in addition to that for particles smaller than 10 μm in diameter (PM_{10}) [9]. However, there have been only a few field surveys

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undertaken to investigate the composition of indoor PAHs and the relationships between outdoor and indoor PAH concentrations [10–12].

We have developed a portable, simple low flow rate cascade impactor suitable for collecting size-fractioned indoor airborne particulates [13]. The cascade impactor was used in a survey of indoor and outdoor particulate concentrations in 20 homes in selected areas of Japan to evaluate the usefulness of the sampler and to obtain basic data on concentrations and size distributions of indoor and outdoor particulates [14]. The survey suggested that there were important indoor particulate sources, such as tobacco smoke. We have also developed an analytical method for the measurement of indoor PAH concentrations that combines a portable air sampler and a highly sensitive HPLC analytical system [15].

In this study, the concentrations of 17 size-fractionated particulate PAHs were determined in the air collected outdoors and in indoor rooms in the 20 homes studied previously; the particle-size distributions of PAHs indoors and outdoors were related to the number of aromatic rings present in the compounds.

Materials and Methods

Sampling Apparatus

Size-fractionated airborne particulates were collected using a sampler that combined a mini-pump (MP-603T; Shibata Sci. Technol. Ltd., Tokyo, Japan) with a three-stage cascade impactor (Tokyo Dylec Corp., Tokyo, Japan) [13]; flow rate for sampling was 3.0 litres·min^{-1}. Airborne particulates were size-fractionated based on particle diameters: smaller than 2.5 μm, 2.5–10 μm, and larger than 10 μm. Quartz fibre ring filters (outside diameter, 47 mm; inside diameter, 20 mm; 2500QAT-UP; Pallflex Products Corp., N.Mex., USA) were used for the collection of particulates with aerodynamic diameters larger than 10 μm and from 2.5 to 10 μm; quartz fibre round filters (47-mm diameter; 2500QAT-UP; Pallflex Products Corp.) were used for the collection of particles smaller than 2.5 μm. The sampling system has been described in detail in a previous report [14].

Sampling

Sampling was performed in 20 homes in the Japanese cities of Kawasaki, Yokohama, Hamamatsu, Mishima, Shimoda, and Shizuoka from August through November 1998. These cities are large or middle-sized cities located near Tokyo. The sampling was performed outdoors and in living rooms, kitchens, and bedrooms over a period of 24 h. The 20 homes consisted of 14 detached houses and 6 apartment houses; 10 of the homes included a resident smoker.

In this survey, households were asked to complete a questionnaire regarding house type, house age, location of the house, smoking, hours of open windows, doors or closets and use of the cooking oven.

PAH Extraction and Analysis

Particulate PAHs collected on the filters were placed in sonic bath and extracted with 10.0 ml dichloromethane fo After centrifugation of the extraction mixture (3,000 rp min), 8.0 ml of supernatant was transferred to another test the solvent was evaporated (30 μl dimethyl sulfoxide from Chem. Corp., Kumamoto, Japan, was added to prevent l during evaporation). The residues were then dissolved in 9 tonitrile (HPLC grade, Wako Pure Chem. Corp., Osaka, Ja the target PAHs were separated by high-performance liquid tography (HPLC). The HPLC apparatus consisted of ar series pump, an L-5090 degasser, an AS-2000 autosampl 1080 spectrofluorimeter (Hitachi Corp., Tokyo, Japan), (Hewlett-Packard Corp., Pa., USA), a C0630 column o a 6-way valve (GL Science Corp., Tokyo, Japan). The pr (4.6 mm i.d. × 30 mm) and the main column (4.6 mn 250 mm) were filled with Wakosil-II 5C-18 PAH (Wako Pur Corp., Osaka, Japan). PAHs were detected by two spectrofl ers connected in series, with detection wavelengths changing tically during analysis. PAH extraction and analysis ha described in detail in a previous report [14].

The concentrations of the following PAHs, selected be their mutagenic and carcinogenic properties, were determi rene (Py), triphenylene (Tri), fluoranthene (Fluor), chryse benzphenanthrene: Chry), benz[*a*]anthracene (BaA), peryl benz[*de,kl*]anthracene: Pery), picene (3,4-benzchrysene: Pi) [*e*]pyrene (BeP), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluor (BkF), benzo[*a*]pyrene (BaP), dibenz[*a,c*]anthracene (DBacA no[1,2,3-*cd*]pyrene (IP), benzo[*ghi*]perylene (BghiP), benzo sene (BbC), dibenzo[*a,e*]pyrene (DBaeP), and coronene (Cor

Stepwise Regression Analysis

Variables that affected indoor PAH concentrations wer mined using a stepwise regression method (linear mod included outdoor PAH concentrations and items on a questi given to residents:

$$y = k + \Sigma(b_i x_i)$$

where y is the logarithm of the indoor concentration, k is the sion intercept, b is the regression slope (partial correlation cient) and x is the questionnaire index variable or the logari the corresponding outdoor concentration. An investigation nearity was done before analysis. A forward selection of variab employed with a criterion of $F = 2.0$ for inclusion; the final included only variables for which $p < 0.05$.

Results

PAH Concentrations in Indoor and Outdoor Ai

sults of the survey including the arithmetic means metric means, maximum and minimum concentra and ratios of maximum to minimum PAH concentra for each particle-size range were measured outdoor in the living room, kitchen, and bedroom. These r are summarised in tables 1–4. Mean concentrations calculated assuming that concentrations of the undet compounds were half of their detection limits.

Table 1. Size distribution of PAH concentrations: outdoor

		Arithmetic		Geometric		Max.	Min.	Max./Min.
		mean	SD	mean	SD			
Py	<2.5 μm	0.331	0.269	0.262	1.96	1.10	0.0730	15.1
	2.5–10 μm	0.0852	0.0453	0.0749	1.70	0.192	0.0247	7.79
	>10 μm	0.0645	0.0407	0.0565	1.63	0.200	0.0297	6.74
Tri	<2.5 μm	0.189	0.215	0.127	2.33	0.864	0.0296	29.2
	2.5–10 μm	0.0429	0.0548	0.0260	2.59	0.227	0.00780	29.1
	>10 μm	0.0492	0.0981	0.0219	3.10	0.437	<0.0075	>120
Fluor	<2.5 μm	0.332	0.311	0.241	2.22	1.14	0.0552	20.7
	2.5–10 μm	0.0987	0.0843	0.0712	2.27	0.292	0.0192	15.2
	>10 μm	0.0656	0.0668	0.0401	3.00	0.240	<0.0094	>51
Chry	<2.5 μm	0.443	0.528	0.279	2.52	1.97	0.0542	36.3
	2.5–10 μm	0.0612	0.0597	0.0428	2.27	0.202	0.0135	14.9
	>10 μm	0.0238	0.0209	0.0185	1.99	0.0930	0.00510	18.2
BaA	<2.5 μm	0.180	0.213	0.115	2.46	0.838	0.0235	35.6
	2.5–10 μm	0.0244	0.0288	0.0151	2.51	0.0926	<0.0037	>19
	>10 μm	0.0090	0.0098	0.0058	2.50	0.0364	<0.0037	>20
Pery	<2.5 μm	0.0516	0.0546	0.0345	2.44	0.221	0.00663	33.3
	2.5–10 μm	0.0061	0.0072	0.0039	2.41	0.0275	<0.0018	>17
	>10 μm	0.0026	0.0031	0.0017	2.21	0.0136	<0.0018	>15
Pi	<2.5 μm	0.144	0.143	0.0936	2.74	0.597	0.0102	58.7
	2.5–10 μm	0.0174	0.0209	0.0100	2.82	0.0787	<0.0051	>31
	>10 μm	0.0057	0.0060	0.0042	2.02	0.0267	<0.0051	>10
BeP	<2.5 μm	0.386	0.372	0.251	2.95	1.58	<0.018	>170
	2.5–10 μm	0.0470	0.0462	0.0314	2.52	0.176	<0.018	>19
	>10 μm	0.0168	0.0129	0.0136	1.87	0.0494	<0.018	>5.4
BbF	<2.5 μm	0.634	0.720	0.400	2.63	2.86	0.0572	50.0
	2.5–10 μm	0.0660	0.0724	0.0417	2.56	0.247	0.0133	18.5
	>10 μm	0.0165	0.0154	0.0124	2.07	0.0667	0.00431	15.5
BkF	<2.5 μm	0.239	0.264	0.152	2.61	0.978	0.0213	45.8
	2.5–10 μm	0.0260	0.0298	0.0160	2.61	0.110	0.00494	22.2
	>10 μm	0.00590	0.00627	0.00407	2.28	0.0241	0.00110	22.0
BaP	<2.5 μm	0.324	0.350	0.212	2.53	1.40	0.0356	39.3
	2.5–10 μm	0.0388	0.0485	0.0228	2.69	0.187	0.00623	30.0
	>10 μm	0.00975	0.0123	0.00503	3.53	0.0466	<0.00084	>110
DBacA	<2.5 μm	0.0378	0.0439	0.0220	3.18	0.157	<0.0017	>180
	2.5–10 μm	0.0044	0.0058	0.0025	2.70	0.0205	<0.0017	>24
	>10 μm	0.0015	0.0011	0.0013	1.76	0.00447	<0.0017	>5.1
IP	<2.5 μm	0.540	0.570	0.357	2.52	2.17	0.0593	36.7
	2.5–10 μm	0.0482	0.0579	0.0287	2.68	0.217	<0.017	>25
	>10 μm	0.0134	0.0113	0.0113	1.66	0.0569	<0.017	>6.6
BghiP	<2.5 μm	0.449	0.430	0.318	2.28	1.76	0.0791	22.3
	2.5–10 μm	0.0387	0.0430	0.0259	2.33	0.171	0.00855	20.0
	>10 μm	0.0202	0.0178	0.0116	3.75	0.0585	<0.0012	>100
BbC	<2.5 μm	0.0388	0.0437	0.0240	2.72	0.178	0.00337	52.8
	2.5–10 μm	0.0043	0.0055	0.0024	2.75	0.0207	<0.0014	>31
	>10 μm	0.0014	0.0017	0.0010	2.08	0.00730	<0.0014	>11
DBaeP	<2.5 μm	0.0928	0.0942	0.0604	2.67	0.374	0.00798	46.9
	2.5–10 μm	0.0116	0.0138	0.0072	2.55	0.0535	<0.0064	>22
	>10 μm	0.0056	0.0077	0.0040	1.88	0.0365	<0.0064	>15
Cor	<2.5 μm	0.0218	0.0193	0.0162	2.16	0.0837	0.00500	16.7
	2.5–10 μm	0.00146	0.00137	0.00105	2.21	0.00557	<0.00076	>17
	>10 μm	0.00122	0.00111	0.00082	2.48	0.00378	<0.00076	>9.9

Table 2. Size distribution of PAH concentrations: living room

		Arithmetic		Geometric		Max.	Min.	
		mean	SD	mean	SD			
Py	<2.5 μm	0.268	0.166	0.226	1.82	0.708	0.0835	
	2.5–10 μm	0.0682	0.0220	0.0647	1.40	0.109	0.0350	
	>10 μm	0.0558	0.0332	0.0495	1.60	0.170	0.0232	
Tri	<2.5 μm	0.132	0.104	0.0980	2.22	0.360	0.0280	
	2.5–10 μm	0.0780	0.120	0.0397	2.85	0.441	0.0105	
	>10 μm	0.0736	0.124	0.0310	3.36	0.438	<0.0075	>
Fluor	<2.5 μm	0.258	0.201	0.197	2.15	0.828	0.0562	
	2.5–10 μm	0.0662	0.0450	0.0543	1.89	0.165	0.0227	
	>10 μm	0.0518	0.0363	0.0429	1.85	0.149	0.0161	
Chry	<2.5 μm	0.312	0.299	0.209	2.52	1.12	0.0355	
	2.5–10 μm	0.0375	0.0237	0.0312	1.90	0.0989	0.00550	
	>10 μm	0.0210	0.0149	0.0162	2.46	0.0711	<0.0014	>
BaA	<2.5 μm	0.139	0.131	0.0910	2.68	0.439	0.0110	
	2.5–10 μm	0.0121	0.0105	0.0095	1.97	0.0475	<0.0037	>
	>10 μm	0.0051	0.0037	0.0041	1.89	0.0169	<0.0037	>9
Pery	<2.5 μm	0.0606	0.0608	0.0379	2.80	0.238	0.00565	4
	2.5–10 μm	0.0032	0.0038	0.0022	2.30	0.0169	<0.0018	>1
	>10 μm	0.0010	0.0002	0.0009	1.16	0.0018	<0.0018	>2
Pi	<2.5 μm	0.149	0.134	0.0909	3.14	0.489	0.00995	4
	2.5–10 μm	0.0078	0.0082	0.0055	2.22	0.0363	<0.0051	>1
	>10 μm	ND		ND				
BeP	<2.5 μm	0.358	0.332	0.207	3.70	1.15	<0.018	>1
	2.5–10 μm	0.0303	0.0197	0.0254	1.87	0.0968	<0.018	>1
	>10 μm	0.0174	0.0249	0.0122	1.95	0.119	<0.018	>1
BbF	<2.5 μm	0.501	0.490	0.320	2.76	1.87	0.0406	4
	2.5–10 μm	0.0314	0.0258	0.0239	2.13	0.111	0.00503	2
	>10 μm	0.00890	0.00383	0.00822	1.50	0.0200	0.00450	4.
BkF	<2.5 μm	0.193	0.187	0.123	2.80	0.629	0.0155	4(
	2.5–10 μm	0.0122	0.0120	0.00849	2.38	0.0521	0.00126	4
	>10 μm	0.00276	0.00121	0.00251	1.57	0.00548	0.00128	4.
BaP	<2.5 μm	0.333	0.336	0.204	2.90	1.26	0.0249	5(
	2.5–10 μm	0.0180	0.0220	0.0103	3.21	0.0952	<0.00084	>23
	>10 μm	0.00226	0.00195	0.00153	2.63	0.00815	<0.00084	>19
DBacA	<2.5 μm	0.0429	0.0450	0.0194	5.01	0.161	<0.0017	>19
	2.5–10 μm	0.00231	0.00232	0.00165	2.19	0.0101	<0.0017	>12
	>10 μm	ND		ND				
IP	<2.5 μm	0.495	0.452	0.321	2.79	1.76	0.0424	41
	2.5–10 μm	0.0230	0.0235	0.0172	2.03	0.107	<0.017	>12
	>10 μm	ND		ND				
BghiP	<2.5 μm	0.423	0.354	0.295	2.51	1.36	0.0484	28
	2.5–10 μm	0.0185	0.0188	0.0115	3.31	0.0836	<0.0012	>14
	>10 μm	0.0045	0.0050	0.0021	3.87	0.0170	<0.0012	>29
BbC	<2.5 μm	0.0500	0.0509	0.0288	3.21	0.192	0.00344	55.
	2.5–10 μm	0.0022	0.0028	0.0015	2.33	0.0123	<0.0014	>21
	>10 μm	ND		ND				
DBaeP	<2.5 μm	0.0962	0.0882	0.0578	3.28	0.324	<0.0064	>11
	2.5–10 μm	0.0059	0.0054	0.0048	1.76	0.0264	<0.0064	>8.4
	>10 μm	ND		ND				
Cor	<2.5 μm	0.0188	0.0153	0.0139	2.25	0.0632	0.00330	19.
	2.5–10 μm	0.00072	0.00059	0.00060	1.77	0.00285	<0.00076	>7.5
	>10 μm	ND		ND				

ND = Not detected.

Table 3. Size distribution of PAH concentrations: kitchen

		Arithmetic		Geometric		Max.	Min.	Max./Min.
		mean	SD	mean	SD			
Py	<2.5 μm	0.225	0.155	0.184	1.97	0.611	0.0578	10.6
	2.5–10 μm	0.0853	0.0380	0.0783	1.54	0.172	0.0377	4.57
	>10 μm	0.0573	0.0371	0.0445	2.27	0.135	0.00904	15.0
Tri	<2.5 μm	0.106	0.0656	0.0899	1.83	0.275	0.0372	7.39
	2.5–10 μm	0.0514	0.0631	0.0365	2.10	0.246	0.0155	15.9
	>10 μm	0.0503	0.0868	0.0291	2.39	0.324	0.00912	35.5
Fluor	<2.5 μm	0.236	0.172	0.184	2.15	0.661	0.0505	13.1
	2.5–10 μm	0.0756	0.0434	0.0656	1.74	0.173	0.0261	6.63
	>10 μm	0.0493	0.0178	0.0468	1.38	0.0882	0.0295	2.99
Chry	<2.5 μm	0.227	0.173	0.182	1.99	0.684	0.0620	11.0
	2.5–10 μm	0.0342	0.0169	0.0313	1.52	0.0793	0.0171	4.63
	>10 μm	0.0187	0.00914	0.0160	1.92	0.0378	0.00334	11.3
BaA	<2.5 μm	0.109	0.110	0.0763	2.33	0.384	0.0211	18.3
	2.5–10 μm	0.0117	0.0104	0.00947	1.81	0.0419	0.00521	8.04
	>10 μm	0.0052	0.0022	0.0048	1.58	0.0086	<0.0037	>3.8
Pery	<2.5 μm	0.0502	0.0498	0.0338	2.52	0.171	0.00712	23.9
	2.5–10 μm	0.0028	0.0031	0.0021	2.03	0.0121	<0.0018	>13
	>10 μm	0.0010	0.0003	0.0010	1.23	0.0018	<0.0018	>2.0
Pi	<2.5 μm	0.135	0.125	0.0845	3.10	0.419	0.00763	54.8
	2.5–10 μm	0.0074	0.0073	0.0055	2.12	0.0280	<0.0051	>11
	>10 μm	0.0025	0.0001	0.0025	1.03	0.0026	<0.0051	>1.1
BeP	<2.5 μm	0.282	0.252	0.210	2.18	0.933	0.0586	15.9
	2.5–10 μm	0.030	0.017	0.025	1.82	0.071	<0.018	>7.7
	>10 μm	0.014	0.009	0.012	1.69	0.032	<0.018	>3.4
BbF	<2.5 μm	0.377	0.344	0.266	2.44	1.27	0.0531	24.0
	2.5–10 μm	0.0301	0.0214	0.0247	1.89	0.0837	0.0106	7.91
	>10 μm	0.00986	0.00376	0.00926	1.44	0.0181	0.00553	3.27
BkF	<2.5 μm	0.154	0.160	0.101	2.61	0.565	0.0191	29.7
	2.5–10 μm	0.0117	0.0104	0.00901	2.03	0.0401	0.00414	9.70
	>10 μm	0.00330	0.00117	0.00311	1.44	0.00505	0.00196	2.57
BaP	<2.5 μm	0.257	0.274	0.169	2.54	0.909	0.0354	25.7
	2.5–10 μm	0.0162	0.0181	0.0109	2.42	0.0674	0.00270	24.9
	>10 μm	0.00312	0.00171	0.00258	2.08	0.00644	<0.00084	>15
DBacA	<2.5 μm	0.0361	0.0367	0.0208	3.63	0.125	<0.0017	>140
	2.5–10 μm	0.0024	0.0021	0.0018	2.24	0.0074	<0.0017	>8.6
	>10 μm	0.0011	0.0006	0.0010	1.44	0.0031	<0.0017	>3.6
IP	<2.5 μm	0.448	0.411	0.316	2.47	1.49	0.0538	27.7
	2.5–10 μm	0.022	0.021	0.016	2.02	0.079	<0.017	>9.2
	>10 μm	ND		ND				
BghiP	<2.5 μm	0.364	0.347	0.263	2.25	1.25	0.0665	18.8
	2.5–10 μm	0.0176	0.0137	0.0149	1.72	0.0566	0.00783	7.23
	>10 μm	0.0062	0.0025	0.0053	2.11	0.0097	<0.0012	>17
BbC	<2.5 μm	0.0437	0.0457	0.0258	3.06	0.141	0.00345	40.7
	2.5–10 μm	0.0021	0.0025	0.0014	2.19	0.0094	<0.0014	>14
	>10 μm	0.0007	0.0001	0.0007	1.13	0.0010	<0.0014	>1.5
DBaeP	<2.5 μm	0.0862	0.0794	0.0567	2.76	0.271	0.00906	29.9
	2.5–10 μm	0.0057	0.0045	0.0047	1.82	0.018	<0.0064	>8.4
	>10 μm	ND		ND				
Cor	<2.5 μm	0.0179	0.0141	0.0142	2.01	0.0529	0.00429	12.3
	2.5–10 μm	0.00074	0.00057	0.00062	1.78	0.00231	<0.00076	>6.1
	>10 μm	ND		ND				

ND = Not detected.

Table 4. Size distribution of PAH concentrations: bedroom

		Arithmetic		Geometric		Max.	Min.	M.
		mean	SD	mean	SD			
Py	<2.5 μm	0.248	0.138	0.223	1.57	0.625	0.131	4.7
	2.5–10 μm	0.0636	0.0344	0.0416	4.80	0.122	0.00027	44
	>10 μm	0.0573	0.0323	0.0508	1.63	0.128	0.0252	5.0
Tri	<2.5 μm	0.125	0.105	0.101	1.89	0.421	0.0485	8.6
	2.5–10 μm	0.0250	0.0185	0.0156	4.21	0.0682	<0.0075	>31
	>10 μm	0.0533	0.103	0.0267	2.76	0.392	<0.0075	>74
Fluor	<2.5 μm	0.248	0.148	0.219	1.63	0.644	0.118	5.4
	2.5–10 μm	0.0592	0.0318	0.0509	1.82	0.126	0.0177	7.1
	>10 μm	0.0441	0.0215	0.0381	1.85	0.0868	0.0119	7.2
Chry	<2.5 μm	0.312	0.341	0.225	2.11	1.29	0.113	11.
	2.5–10 μm	0.0286	0.0122	0.0262	1.54	0.0534	0.0127	4.2
	>10 μm	0.0127	0.0079	0.0087	3.21	0.0274	<0.0014	>41
BaA	<2.5 μm	0.133	0.127	0.101	2.00	0.486	0.0522	9.3
	2.5–10 μm	0.0099	0.0055	0.0085	1.79	0.0195	<0.0037	>5.9
	>10 μm	0.0034	0.0015	0.0031	1.56	0.0064	<0.0037	>3.5
Pery	<2.5 μm	0.0489	0.0441	0.0384	1.95	0.178	0.0169	10.5
	2.5–10 μm	0.0026	0.0016	0.0022	1.76	0.00568	<0.0018	>6.2
	>10 μm	ND		ND				
Pi	<2.5 μm	0.143	0.109	0.115	1.99	0.432	0.0418	10.3
	2.5–10 μm	0.0062	0.0039	0.0052	1.79	0.0154	<0.0051	>6.1
	>10 μm	ND		ND				
BeP	<2.5 μm	0.356	0.363	0.218	3.42	1.35	<0.018	>150
	2.5–10 μm	0.024	0.017	0.019	2.10	0.058	<0.018	>6.3
	>10 μm	0.013	0.012	0.011	1.64	0.054	<0.018	>5.9
BbF	<2.5 μm	0.549	0.572	0.395	2.18	2.18	0.163	13.4
	2.5–10 μm	0.0274	0.0173	0.0225	1.98	0.0689	0.00680	10.1
	>10 μm	0.00745	0.00225	0.00713	1.37	0.0114	0.00440	2.59
BkF	<2.5 μm	0.200	0.190	0.150	2.09	0.726	0.0638	11.4
	2.5–10 μm	0.0103	0.00639	0.00816	2.19	0.0227	0.00141	16.1
	>10 μm	0.00217	0.00077	0.00205	1.43	0.00345	0.00130	2.66
BaP	<2.5 μm	0.307	0.271	0.239	2.00	1.07	0.0903	11.8
	2.5–10 μm	0.0143	0.00967	0.0114	2.06	0.0336	0.00282	11.9
	>10 μm	0.00182	0.00114	0.00138	2.37	0.00337	<0.00084	>8.0
DBacA	<2.5 μm	0.0368	0.0374	0.0219	3.57	0.141	<0.0017	>160
	2.5–10 μm	0.0028	0.0034	0.0019	2.32	0.0135	<0.0017	>16
	>10 μm	0.0015	0.0023	0.0010	1.93	0.0093	<0.0017	>11
IP	<2.5 μm	0.494	0.384	0.396	1.96	1.55	0.143	10.8
	2.5–10 μm	0.020	0.011	0.018	1.66	0.044	<0.017	>5.1
	>10 μm	ND		ND				
BghiP	<2.5 μm	0.422	0.290	0.347	1.93	1.17	0.119	9.80
	2.5–10 μm	0.0152	0.00765	0.0135	1.66	0.0293	0.00589	4.97
	>10 μm	0.0025	0.0023	0.0015	2.94	0.0069	<0.0012	>12
BbC	<2.5 μm	0.0431	0.0347	0.0324	2.21	0.131	0.0108	12.1
	2.5–10 μm	0.0017	0.0012	0.0014	1.87	0.0044	<0.0014	>6.5
	>10 μm	ND		ND				
DBaeP	<2.5 μm	0.0923	0.0709	0.0739	1.97	0.284	0.0287	9.92
	2.5–10 μm	0.00473	0.00210	0.00439	1.46	0.00959	<0.0064	>3.6
	>10 μm	ND		ND				
Cor	<2.5 μm	0.0187	0.0117	0.0157	1.89	0.0462	0.00523	8.83
	2.5–10 μm	0.00057	0.00029	0.00052	1.58	0.00125	<0.00076	>4.6
	>10 μm	ND		ND				

ND = Not detected.

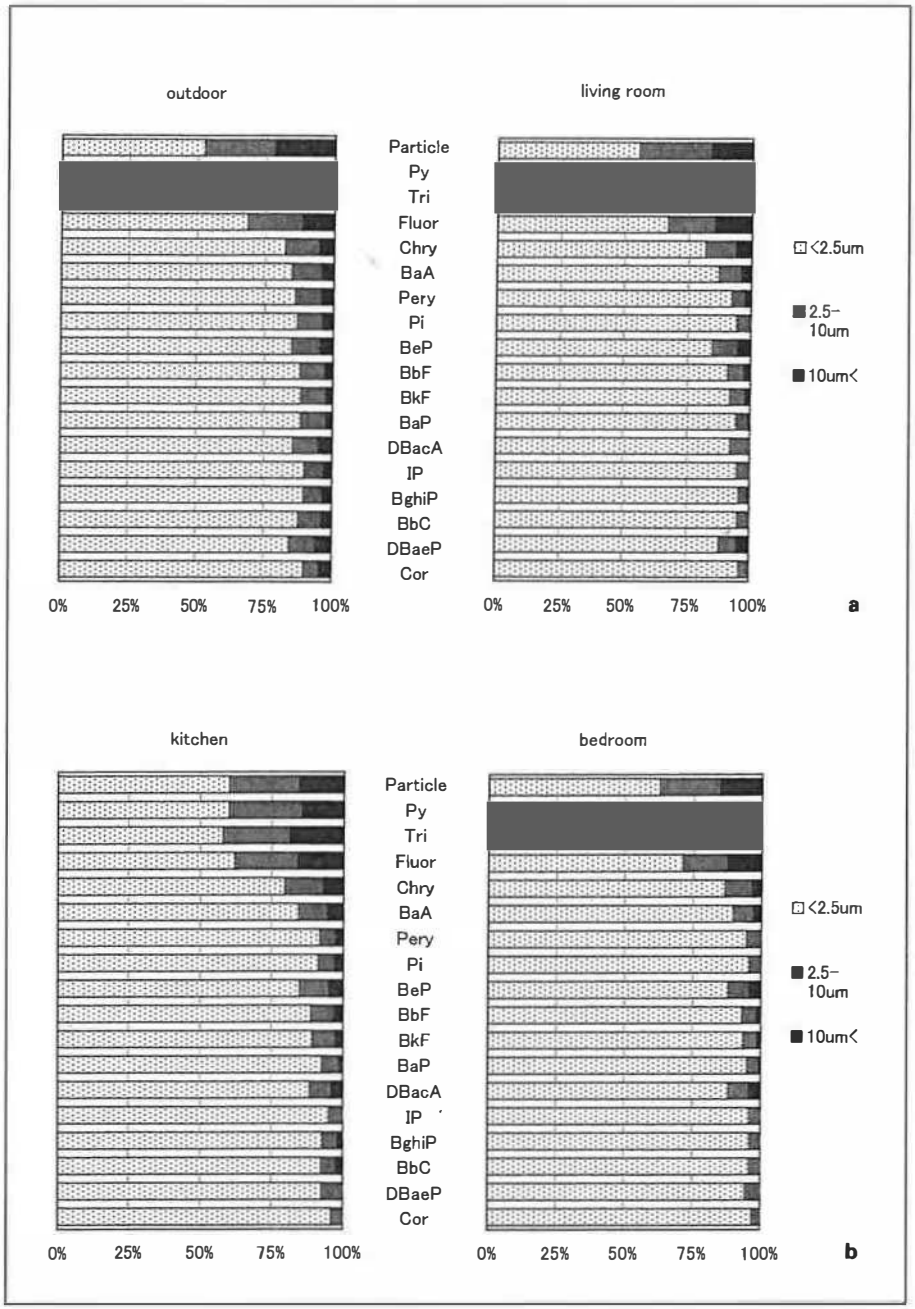

Fig. 1. Comparison of the size distribution of PAH concentrations in outdoor and indoor air. **a** Samples were taken from outdoor air and living rooms. **b** Samples were taken from kitchens and bedrooms.

Particle Size and Distribution of PAHs. The size distributions of various PAHs measured outdoors and in the living room, kitchen, and bedroom are shown in figure 1a, b (size distribution of airborne particles is given at the top of the figures); 50–60% of all particles were found in the fraction smaller than 2.5 μm in diameter, whereas 25–30% of particles were present in each of the other fractions (2.5–10 μm and >10 μm in diameter).

Indoor-to-Outdoor PAH Concentration Ratios. The ratio of indoor (living room) to outdoor PAH concentration for particles smaller than 2.5 μm is shown in table 5.

Correlations of PAH Concentration between Sampling Sites in Homes. Figure 2 gives results for Py in particles in each size range at the various sampling sites, table 6 and figure 3 give the results for BaP. Results for other higher molecular weight PAHs showed they behaved similarly.

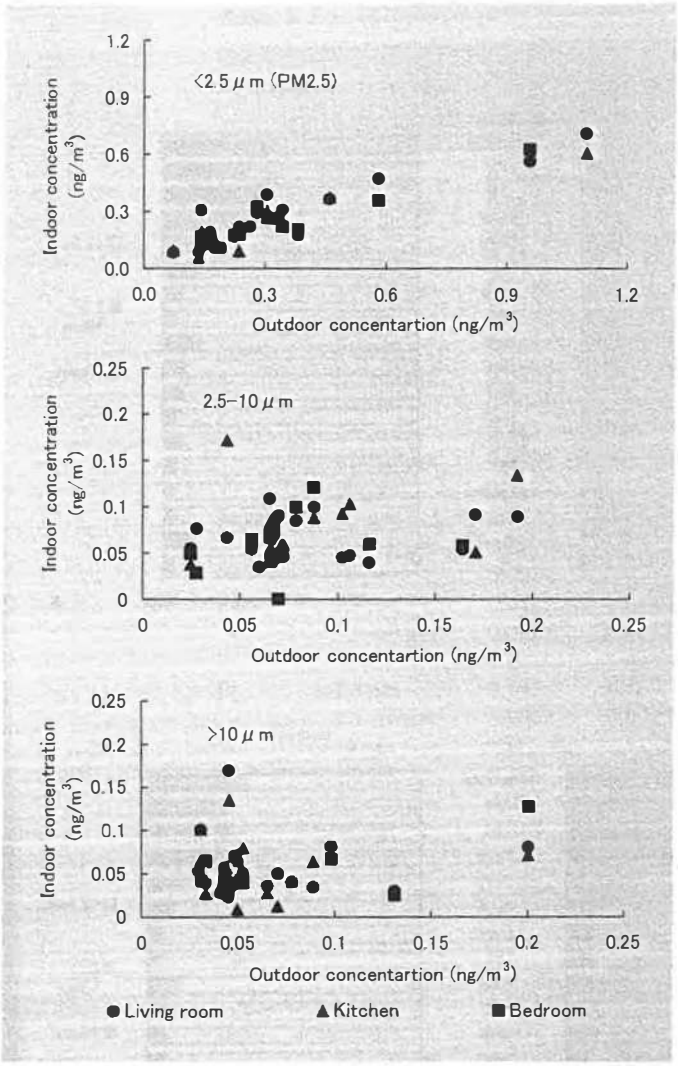

Fig. 2. Relationship between outdoor and indoor PAH concentrations (pyrene).

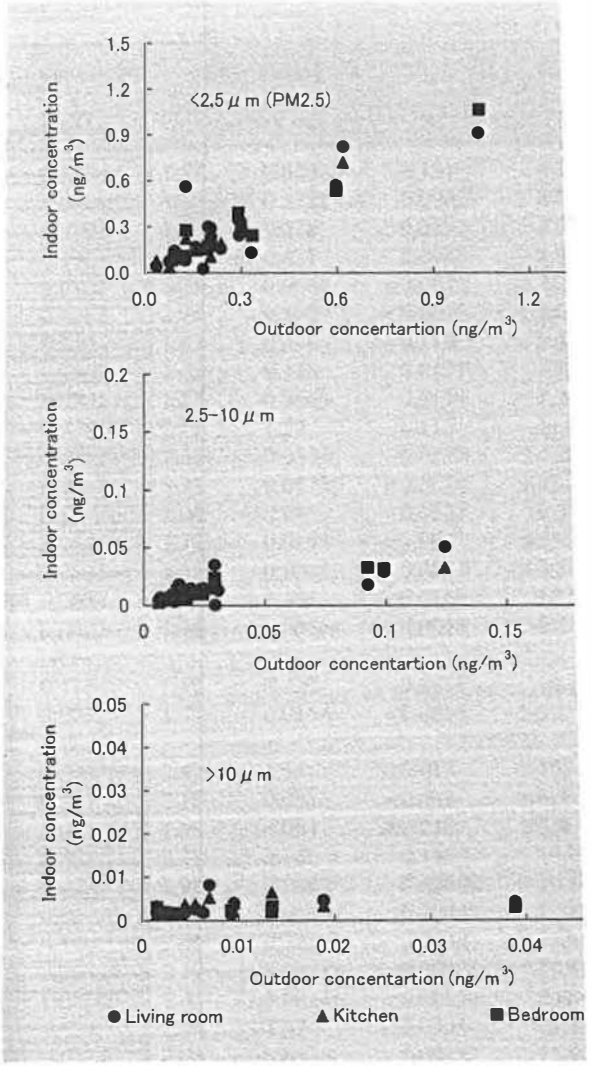

Fig. 3. Relationship between outdoor and indoor PAH co tions (benzo[*a*]pyrene).

In particles smaller than 2.5 μm ($PM_{2.5}$), correlations between PAH concentrations at each sampling site were significant ($p < 0.01$), with few exceptions. Figures 2 and 3 show the indoor PAH concentrations in fine particles ($PM_{2.5}$).

Factors Affecting Indoor PAH Sources. The results of a stepwise regression analysis of the variables affecting indoor PAH concentrations are given in table 7. In summary these suggest that indoor PAH concentrations were affected predominantly by outdoor PAH concentrations but also by other variables such as the length of time that windows were open and use of the cooking stove.

Effect of Smoking on Indoor PAH Concentratio ratio of indoor to outdoor PAH concentration and t ference between indoor and outdoor PAH concen were calculated to estimate the effect of smoki indoor PAH concentrations; indoor to outdoor were 1.4 (s.d. 1.1) for rooms in which smoking oc and 0.91 (s.d. 2.8) for 'non-smoking' rooms (samp was 10 in each case). The results for BaP in this part study are shown in figure 4. Statistical analysis show significant differences between the BaP indoor to ou concentration ratio or indoor minus outdoor BaP co trations in the rooms with and without smoking. Si results were obtained for other PAHs.

Table 5. Indoor (living room)-to-outdoor ratio of PAH concentrations

	Average ± SD	Max.	Min.
Particle	1.11±0.54	2.39	0.21
Py	0.92±0.37	2.18	0.46
Tri	0.87±0.44	2.06	0.28
Fluor	0.90±0.46	2.56	0.33
Chry	0.88±0.53	2.42	0.14
BaA	0.91±0.51	2.51	0.14
Pery	1.32±0.99	5.12	0.20
Pi	1.17±0.72	3.24	0.11
BeP	0.99±0.48	2.24	0.04
BbF	0.92±0.43	2.05	0.10
BkF	0.92±0.45	2.32	0.11
BaP	1.16±0.85	4.43	0.14
DBacA	1.35±1.20	4.24	0.05
IP	1.06±0.61	2.93	0.14
BghiP	1.06±0.56	2.78	0.18
BbC	1.55±1.31	5.32	0.22
DBaeP	1.22±0.81	3.46	0.06
Cor	0.93±0.35	1.85	0.21

Table 6. Correlation between outdoor and indoor PAH concentrations (benzo[*a*]pyrene)

	Outdoor	Living room	Kitchen	Bedroom
<2.5 μm				
Outdoor	–			
Living room	0.9195**	–		
Kitchen	0.9409**	0.9429**	–	
Bedroom	0.9702**	0.8966**	0.6715	–
2.5–10 μm				
Outdoor	–			
Living room	0.8969**	–		
Kitchen	0.9752**	0.9672**	–	
Bedroom	0.9147**	0.6756*	0.9785**	–
>10 μm				
Outdoor	–			
Living room	0.3290	–		
Kitchen	0.5703	0.7220*	–	
Bedroom	0.6664	0.8805*	–0.2780	–

* $p < 0.05$, ** $p < 0.01$.

Discussion

This survey of the concentrations of 17 PAHs measured in size-fractionated particles in indoor and outdoor air in 20 homes has shown that almost all of the selected group of PAHs were detected in all of the particle-size ranges of the indoor and outdoor samples. However, it can be seen from the results in tables 1–4 that while most of the 17 target PAHs were detected in outdoor samples, several PAHs from the group could not be detected in particles with aerodynamic diameters larger than 10 μm in any samples from the living room, kitchen, or bedroom. Overall contributions to particulate PAH concentrations were highest in particles smaller than 2.5 μm in aerodynamic diameter; particulates with middle-range particle diameters (2.5–10 μm) were less abundant, and the lowest contributions were in particles larger than 10 μm in diameter. Outdoor PAH concentrations in small particles were higher than concentrations in larger particles, similar to results reported previously [4–8], although mean concentrations of indoor PAHs measured in this study were lower than the literature values [10–12]. Also, the proportion of the concentrations of the PAHs in the indoor fine particle fraction were higher than the same proportion of the outdoor fine particle fraction.

As noted the highest concentrations of each PAH were found in fine particles (smaller than 2.5 μm). This trend was more apparent for the 5- to 7-ring PAHs than for the 4-ring PAHs. These differences might be due to the sources of PAHs or to phase distributions in the air. A significant portion of 4-ring PAHs is known to be present in the gaseous phase as well as in the particulate phase [8, 16, 17]. Gaseous 4-ring PAHs can precipitate on fine and coarse particulates, and particulate 4-ring PAHs can desorb into the gas phase, thus making redistribution among the different fractions possible. For 4-ring PAHs, indoor sources or redistribution elevated the indoor particulate PAH concentrations in the 2.5- to 10-μm and the >10-μm fractions. In contrast, in 5- to 7-ring PAHs, the indoor concentrations were determined essentially by outdoor concentrations. Consequently, 5- to 7-ring PAHs, which are associated mainly with fine particles, are considered to be tracers of particles originating from outdoors and penetrating into the indoor air.

Comparisons of the size distributions of PAHs in outdoor and indoor samples indicated that the proportion of 5- to 7-ring PAHs in indoor fine particles was higher than in outdoor fine particles. For example, BaP content in particles smaller than 2.5 μm was 88% for outdoor samples and was 94.5, 92.6, and 94.9% in living room, kitchen, and bedroom samples, respectively. In contrast, BaP

Table 7. Variables affecting indoor PAH concentrations

Compounds	Variable	b	SE	F	
Particle	Outdoor concentration	0.436	0.535	7.9	
	While the room was in use	0.521	0.417	4.8	
Py	Outdoor concentration	0.573	0.930	125	
Tri	Outdoor concentration	0.383	0.792	53.8	
	Use of cooking stove	−0.101	−0.298	8.0	
	Time of ventilation fan	0.005	0.252	5.3	
Fluor	Outdoor concentration	0.675	1.041	177	
	Opening of window	−0.098	−0.250	7.4	
	Use of cooking stove	−0.160	−0.244	10.0	
Chry	Outdoor concentration	0.486	0.859	122	
	Use of cooking stove	−0.261	−0.268	12.6	
	Time of ventilation fan	0.012	0.223	8.1	
BaA	Outdoor concentration	0.559	0.908	135	
	While the room was in use	0.002	0.164	5.0	
	Use of cooking stove	−0.107	−0.251	11.5	
	Time of ventilation fan	0.005	0.181	5.9	
Pery	Outdoor concentration	0.984	0.884	97.1	
	Opening of window	−0.025	−0.211	5.9	
Pi	Outdoor concentration	0.899	0.960	141	
	While the room was in use	0.002	0.196	5.9	
	Use of cooking stove	−0.094	−0.218	7.1	
	Use of instantaneous water heater	0.193	0.324	16.0	
BeP	Outdoor concentration	0.792	0.887	66.7	
BbF	Outdoor concentration	0.680	1.000	245	
	Opening of window	−0.217	−0.227	9.3	
	Use of air conditioner	−0.162	−0.166	5.9	
	Use of cooking stove	−0.389	−0.245	14.1	
	Time of ventilation fan	0.014	0.152	6.5	
BkF	Outdoor concentration	0.701	0.989	222	
	Opening of window	−0.075	−0.208	7.1	
	Use of air conditioner	−0.063	−0.170	5.5	
	Use of cooking stove	−0.137	−0.226	10.4	
	Time of ventilation fan	0.005	0.139	4.7	
BaP	Outdoor concentration	0.871	0.907	111	
DBacA	Outdoor concentration	0.948	0.925	47.5	
	Opening of window	−0.039	−0.453	8.6	
	Use of cooking stove	−0.045	−0.312	5.0	
IP	Outdoor concentration	0.810	1.020	156	
	Opening of window	−0.326	−0.370	15.2	
	Use of air conditioner	−0.241	−0.268	8.4	
	Use of cooking stove	−0.407	−0.276	10.6	
BghiP	Outdoor concentration	0.824	1.000	158	
	Opening of window	−0.186	−0.271	8.4	
	Use of air conditioner	−0.139	−0.197	4.8	
	Use of cooking stove	−0.270	−0.235	7.9	
BbC	Outdoor concentration	1.030	0.886	77.8	<
	Use of instantaneous water heater	0.070	0.307	7.6	
DbaeP	Outdoor concentration	0.849	0.908	74.8	<
	Use of instantaneous water heater	0.102	0.258	5.0	
Cor	Outdoor concentration	0.788	0.996	204	<
	Opening of window	−0.007	−0.233	6.3	
	Use of cooking stove	−0.010	−0.205	7.5	

b = Slope relating logarithm of observed concentration to the questionnaire index va or the logarithm of the corresponding outdoor concentration; SE = standard error of the F = F-value for slope estimate; p = probability that the slope is 0.

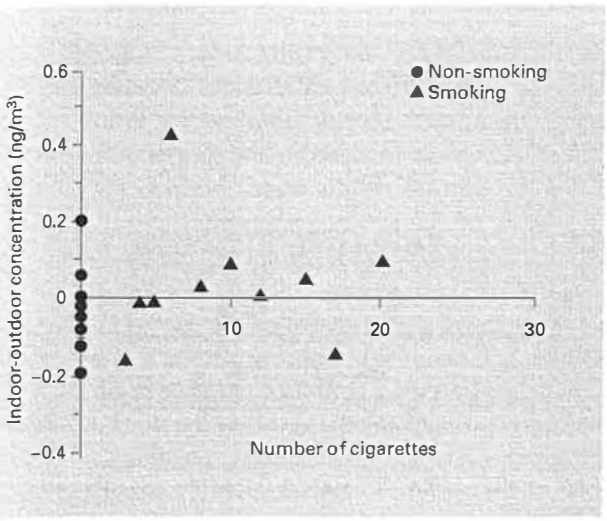

Fig. 4. Effect of smoking on outdoor – indoor BaP concentrations.

content in particles larger than 10 μm was 2.1% in outdoor samples and 0.7, 1.4, and 0.5% in living room, kitchen, and bedroom samples, respectively. Similar trends were found for other 5- to 7-ring PAHs, whereas the proportion of 4-ring PAHs in indoor fine particles was not always higher than in outdoor fine particles.

Correlations between Concentrations of 17 PAHs Measured Outdoors and in the Living Room, Kitchen, and Bedroom

Correlations between the concentrations of 17 PAHs were examined in various particle sizes in outdoor, living room, kitchen, and bedroom samples. Significant correlations ($p < 0.01$) were observed between airborne PAH concentrations in particles smaller than 2.5 μm in outdoor, living room, kitchen, and bedroom samples. For 2.5- to 10-μm particles, no significant correlations were found among concentrations of 5- to 7-ring PAHs and some 4-ring PAHs, although correlations between all 5- to 7-ring PAH concentrations were significant ($p < 0.01$). For example, Tri in outdoors samples, Py, Tri, and Fluor in living room samples, Py, Tri, and Fluor in kitchen samples, and Py and Fluor in bedroom samples were not correlated with 5- to 7-ring PAHs at the corresponding sites. The lack of significant correlation was due to different emission sources or to redistribution between gas-particle phases. For PAHs in particles larger than 10 μm, significant correlations were found between 5- to 7-ring PAH concentrations in outdoor air, although no significant correlations were found in indoor air.

Indoor-to-Outdoor PAH Concentration Ratios

Table 5 shows the ratio of indoor (living room) to outdoor PAH concentration for particles smaller than 2.5 μm. For most PAHs, the mean values of the ratio were around 1 (table 5), but the ratios varied considerably. Similar results were obtained for the kitchen-to-outdoor and bedroom-to-outdoor ratios. These results suggest that indoor PAH concentration was largely determined by outdoor PAH sources in most houses. Maximum indoor-to-outdoor ratios, however, were as large as 2–5, indicating that indoor PAH sources such as tobacco smoke and cooking cannot be neglected in some houses.

Correlations of PAH Concentration between Sampling Sites in Homes

Correlations of PAH concentration between outdoor and living room, kitchen, and bedroom samples were examined. Figure 2 gives results for Py in particles in each size range, table 6 and figure 3 give results for BaP. Higher molecular weight PAHs behaved similarly. In particles smaller than 2.5 μm ($PM_{2.5}$), correlations between PAH concentrations at each sampling site were significant ($p < 0.01$), with few exceptions. Figures 2 and 3 show that indoor PAH concentrations in fine particles ($PM_{2.5}$) were almost the same as those outdoors; indoor PAH in these particles originated predominantly from outdoors. In contrast, no relationship between outdoor-indoor Py concentrations at the 4 sampling sites for particles larger than 2.5 μm was observed, suggesting either that there are some indoor sources of Py in particles larger than 2.5 μm or that gaseous Py was precipitated on the coarse particles. Indoor concentrations of BaP in particulates larger than 2.5 μm were lower than outdoor concentrations. Note that outdoor-indoor correlations for BaP in 2.5- to 10-μm particles were still good, whereas indoor particulate BaP levels distributed in particles larger than 10 μm were negligibly low compared with outdoor air. This suggests that coarse particles that originate outdoors penetrate into houses with difficulty and that indoor 5- to 7-ring PAHs are tracers of particles originating outdoors. It can be estimated using the result shown in figure 3 that most particles smaller than 2.5 μm can move from outdoors to indoors, while about 40% of particles 2.5–10 μm but no particles larger than 10 μm can be transferred indoors. Indoor coarse particles may be emitted mainly from indoor sources.

Factors Affecting Indoor PAH Sources

A stepwise regression of variables affecting indoor PAH concentrations (table 7) suggests that indoor PAH

concentrations were affected predominantly by outdoor PAH concentrations; other variables affecting indoor PAH concentrations were length of time that windows were open and use of the cooking stove. The positive slope (*b*) of the regression equation with outdoor concentration as the index variable indicates that high indoor PAH concentrations were associated with high outdoor concentrations. In contrast, the negative slope obtained with the variables of open windows and use of the cooking stove shows that indoor PAH concentration decreased when windows were opened or when the cooking stove was used (the ventilation fan was on when the cooking stove was used, resulting in decreased indoor PAH concentrations). House type, house age, location of the house, smoking, hours of open doors or closets, and use of the cooking oven did not affect indoor PAH concentrations in this analysis.

Effect of Smoking on Indoor PAH Concentrations

The ratio of indoor to outdoor PAH concentration and the difference between indoor and outdoor PAH concentration were calculated to estimate the effect of smoking on indoor PAH concentrations. Statistical analysis showed no significant differences between the BaP indoor-to-outdoor concentration ratio or indoor minus outdoor BaP concentrations in the rooms with and without smoking. Similar results were obtained for other PAHs. This lack of significance was due to wide variations in PAH concentrations in rooms where there was smoking; in some smoking rooms, residents opened the windows so that much of the tobacco smoke flowed outside. Thus, although indoor PAH concentrations can be elevated by indoor sources such as smoking, the impact of this can be reduced through ventilation of which the commonest type in the domestic situation is open windows.

Acknowledgements

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