심포지엄 5) Analytical Methods for Indoor, Outdoor and Personal Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) and Its Application to a Survey in Shizuoka, Japan

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1. Introduction

Polycyclic aromatic hydrocarbons(PAHs), including benzo[*a*]pyrene, are well-knownmutagenes and/or carcinogens in the air [1]. PAHs are emitted from incomplete combustion processes such as fossil fuel combustion in plants, incinerators, automobiles and heating. Cooking, smoking and incense burning is also important emission sources. Thus they are widely distributed in the environment. Among PAHs, benzo[a]pyrene(BaP) is classified as human carcinogen by International Agency for Research on Cancer(IARC). Based on epidemiological data, a unit risk for BaP is estimated to be $8.7x10^{-5}(ng/m^3)^{-1}$. The corresponding concentration of BaP producing excess life time cancer risks of 10^{5} is $0.12ng/m^3$. Dibenz[*a,h*]anthracene, dibenzo[*a,l*]pyrene and cyclopenta[cd]pyrene are classified as probablehuman carcinogens, and some of other PAHs are classified as possible human carcinogens.

PAHs are distributed in both gaseous and particulate phase. Two- or three-ring PAHs are mainly distributed in gaseous phase, and 5- to 7- ring PAHs are mainly distributed in particulate phase. Four-ring PAHs are present in both gaseous and particulate phases. Since most of the mutagenic and/or carcinogenic PAHs are particulate PAHs, we have mainly discussed about particulate PAHs in this study.

Since fine particulates rather than coarse ones areeasy to enter the bronchial tube and lungs, and to cause respiratory diseases, then size distributions of particulate PAHs is also necessarily to determine.

2. Sampling of particulates

The requirements of the personal sampler are as follows: portable and silent it can work by battery at least one day; size-fractionated airborne particulates can be collected. Since the annual average of the personal exposure is used for risk assessment of the hazardous compounds, sampling period should be as long as possible.

To meet these requirements, $PM_{2.5}$ cascade impactor with noise reduction type mini pump(MP-150S, Shibata Sci. Technol., Tokyo) have been developedfor determination of personal exposure of particulate PAHs. The noise level of this pump is below 29dB, then we can use this sampler even in the bed room. Since this sampler can work with battery, we can bring it to everywhere. Flow rate is 1.5L/min. If the flow rate increases, battery cannot work for 24 hours. If the flow rate decreases, mass of the collected particulate are not enough to weight. For determination of indoor concentrations of PAHs, 3 stage cascade impactor($PM_{>10}$, $PM_{2.5\text{-}10}$, $PM_{2.5}$) is used for collecting particulates. Flow rate is 2.5L/min. If the flow rate decreases, mass of the collected $PM_{>10}$ and/or $PM_{2.5\text{-}10}$ are not enough to weight.

3. Pre-treatment and analysis of PAHs

Particulate PAHs were extracted by ultrasonication with dichloromethane for 10 min. After centrifugation (10min, 3000rpm), 30μL of dimethylsulfoxide was added to the solution. The solvent was removed under the gentle air stream of nitrogen, and the residue was dissolved by 970μL of acetnitrile. Then PAHs were separated and analyzed with HPLC/ spectrofluorometry. Wakosil-PAH (250mm×4.6mm i.d.for separation column and 30mm×4.6mm i.d. for pre-column Wako Pure Chemicals, Osaka) was used for HPLC column. Since PAHs can be concentrated on pre-column with a mobile phase of 50% methanol distilled water, a large volume sample(>300μL) can be injected. Gradient conditions were shown in Table 1. Excitation and emission wavelengths of each PAH changed automatically to detect PAHs selectively and sensitively. In our method, 23 PAHs can be determined simultaneously.

Table 1 Mobile phase of the HPLC analysis.

	Methanol : distilled water
0-5 min	50 : 50
5-15 min	65 : 35
15-30 min	65 : 35 - 90 : 10
30-37 min	90 : 10
37-51 min	90 : 10 - 100 : 0
51-64 min	100"F0

4. Survey of indoor, outdoor and personal concentrations of PAHs in Shizuoka

In our study, personal, indoor and outdoor PAH concentrations have been determined in Shizuoka, Japan. Participants of the survey were 45 persons from 35 residents, and there are 6 smokers out of 45 participants. The particulate samples were taken in each living room, kitchen, bedroom outdoor of the houses, and in workplace.

5. Results and Discussion

In this study, 23 PAHs were detected. Table 2 shows the geometrical concentrations of PAHs in each microenvironment. The levels of PAHs indoors were usually same levels as those of outdoors. These results suggest that there are a few indoor emission sources of PAHs in Shizuoka.

Fig. 1 shows the example of the relationships between personal exposure and indoor (a), and between personal exposure and outdoor (b) BaP concentrations.

In these case, personal concentration of BaP is significantly correlated ($p<0.01$) with thoseof living room, whereas no correlation was found between personal and outdoor concentrations. Same trends can be shown in the cases of other PAHs. The results suggest that personal exposure of PAHs can be estimated from their indoor concentrations. Smoking is not also significant PAH sources indoors in this study, perhaps because smokers used to open the windows when they smoke.

Table 2. Geometrical mean concentrations of PAHs(ng/m^3) and $PM_{2.5}$(μg/m^3).

	Personal	Living room	Kitchen	Bedroom	Outdoor	Workplace
$PM_{2.5}$(μg/m^3)	24.8	17.5	15.7	18.0	17.6	16.1
Fluoranthene	0.096	0.197	0.180	0.153	0.207	0.210
Pyrene	0.229	0.218	0.220	0.220	0.254	0.226
1-Methylpyrene	0.015	0.016	0.016	0.016	0.019	0.017
Benzo[b]fluorene	0.008	0.010	0.010	0.009	0.012	0.011
Benzo[a]fluorene	0.018	0.029	0.030	0.027	0.037	0.031
Chrysene	0.178	0.201	0.200	0.210	0.265	0.212
Triphenylene	0.119	0.101	0.100	0.093	0.126	0.111
Benz[a]anthracene	0.066	0.082	0.095	0.088	0.127	0.100
p-Terphenyl	0.034	0.039	0.041	0.040	0.052	0.038
Perylene	0.043	0.044	0.041	0.041	0.044	0.042
Benzo[a]pyrene	0.263	0.264	0.255	0.255	0.280	0.250
Benzo[e]pyrene	0.269	0.256	0.248	0.244	0.286	0.266
Benzo[b]fluoranthene	0.325	0.343	0.332	0.316	0.405	0.350
Benzo[j]fluoranthene	0.130	0.169	0.176	0.156	0.224	0.190
Benzo[k]fluoranthene	0.143	0.142	0.137	0.133	0.165	0.143
Indeno[1,2,3-cd]pyrene	0.391	0.292	0.296	0.345	0.347	0.300
Benzo[ghi]perylene	0.375	0.327	0.305	0.315	0.343	0.338
Benzo[b]chrysene	0.024	0.025	0.023	0.025	0.024	0.020
Dibenz[a,c]anthracene	0.033	0.029	0.027	0.030	0.028	0.023
Dibenz[a,h]anthracene	0.040	0.037	0.033	0.034	0.038	0.031
Picene	0.057	0.067	0.066	0.069	0.082	0.065
Coronene	0.135	0.113	0.114	0.137	0.149	0.163
Dibenzo[a,e]pyrene	0.062	0.057	0.057	0.061	0.062	0.056

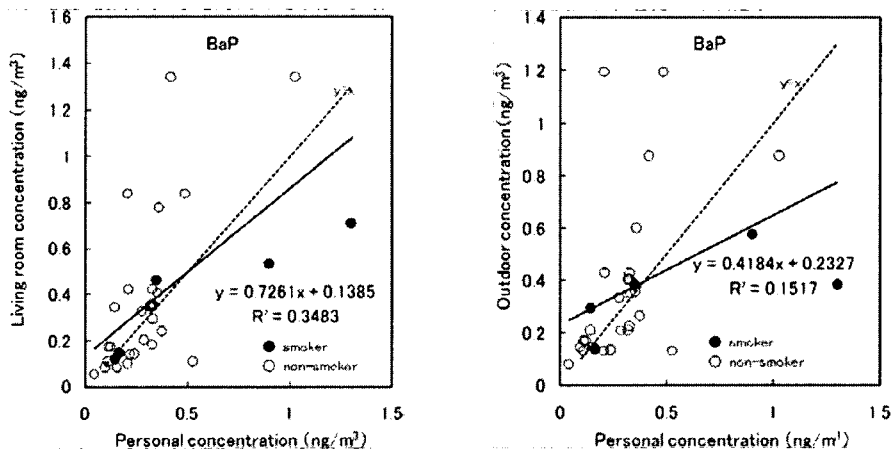

Fig. 1. (a) Relationships between personal exposure and living room concentrations of BaP. (b) Relationships between personal exposure and outdoor concentrations of BaP.

Acknowledgement

This research was partly supported by Strategic International Cooperative Program, Japan Science and TechnologyAgency (JST) and Smoking Research Foundation, Japan.

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