Gas–particle concentrations of atmospheric polycyclic aromatic hydrocarbons at an urban and a residential site in Osaka, Japan: Effect of the formation of atmospherically stable layer on their temporal change

Masao Kishida [a,b,*], Ayako Nishikawa [c], Keiichi Fujimori [c], Yasuhiko Shibutani [c]

[a] Research Institute of Environment, Agriculture, and Fisheries, Osaka Prefectural Government, 1-3-62 Nakamichi, Higashinari-ku, Osaka 537-0025, Japan
[b] Commerce and Industry Promotion Office, Department of Commerce, Industry and Labor, Osaka Prefectural Government, Sakishima Building, 1-14-16 Nankohkita, Suminoe-ku, Osaka 559-8555, Japan
[c] College of Engineering, Osaka Institute of Technology, 5-16-1 Ohmiya, Asahi-ku, Osaka 535-8585, Japan

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ABSTRACT

A comparative study on atmospheric polycyclic aromatic hydrocarbons (PAHs) in particulate matter and the gaseous phase was performed at an urban and a residential site in Osaka, Japan, during 2005–2006. PAH concentrations at the urban site were found to be approximately twice higher than those at the residential site. At both sites, particulate PAH concentrations increased mainly in winter while the trends of temporal change in gaseous PAH concentrations were not clearly observed. The main sources of PAHs were estimated to be local traffic, e.g., diesel engines with catalytic converter. PAH concentrations did not significantly negatively correlate with ozone concentrations and meteorological parameters. Gas–particle partitioning coefficients of representative PAHs with low molecular weight (LMW) significantly negatively correlated with ambient temperature, showing that temporal change in the LMW PAH concentrations in PM could be attributable to the shift of their gas–particle distribution caused by the change in ambient temperature. For the first time, we studied the effect of the formation of atmospherically stable layer following an increase in PAH concentrations in Japan. At the urban site, PAHs showed a significant positive correlation with potential temperature gradients, indicating that temporal variability in PAH concentrations would be dominantly controlled by the formation of atmospherically stable layer in Osaka area.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been of great concern to human health because of their mutagenicity and/or carcinogenicity [1]. In particular, high-molecular-weight (HMW) PAHs with four to six aromatic rings, such as benzo[a]pyrene, are considered to be carcinogenic and/or mutagenic [2], and most of these PAHs occur in particulate matter (PM) in the atmosphere as they have low vapor pressure [3]. In contrast, low-molecular-weight (LMW) PAHs (e.g., phenanthrene and pyrene), which are considered to be less mutagenic and/or carcinogenic than HMW PAHs, occur mainly in the gaseous phase, where they react with other pollutants such as ozone and NO_x to form more toxic compounds [4]. Until now, many studies have focused not only on particulate PAHs [5–9], but also on gas–particle concentrations of PAHs [4,9–19].

In Japan, particulate PAHs in the atmosphere have been also studied at many cities, for example in Tokyo [20,21], Osaka [22], Sakai [7], Sapporo [21], Kitakyushu [21], Shizuoka [23], Nagasaki [24], Higashi-Hiroshima [25], among others. With respect to gas–particle PAHs, Yamasaki et al. [3] sampled at an urban site in Osaka, Japan, during 1978–1979 using a conventional sampling apparatus in order to understand their gas–particle partitioning using Langmuir adsorption concept. Then, Pankow et al. [26] studied the effect of relative humidity on the gas–particle partitioning of PAHs using Yamasaki et al. dataset [3]. However, Yamasaki et al. [3] and Pankow et al. [26] did not pay attention to the causes of temporal change in PAH concentrations in more detail (e.g., effect of meteorological parameters). Clearly, air quality in Japan has been drastically improved as a result of regulation of air pollutants by local governments, improvement of automobile engines, and other measures since the 1970s [27,28], but we cannot understand the trend of variability in atmospheric PAH concentrations for the last few decades at urban cities in Japan (e.g., Osaka) due to nonavailability of such data.

Osaka is the largest city in West Japan with a population of about 8,800,000 spread across approximately 1800 km². This
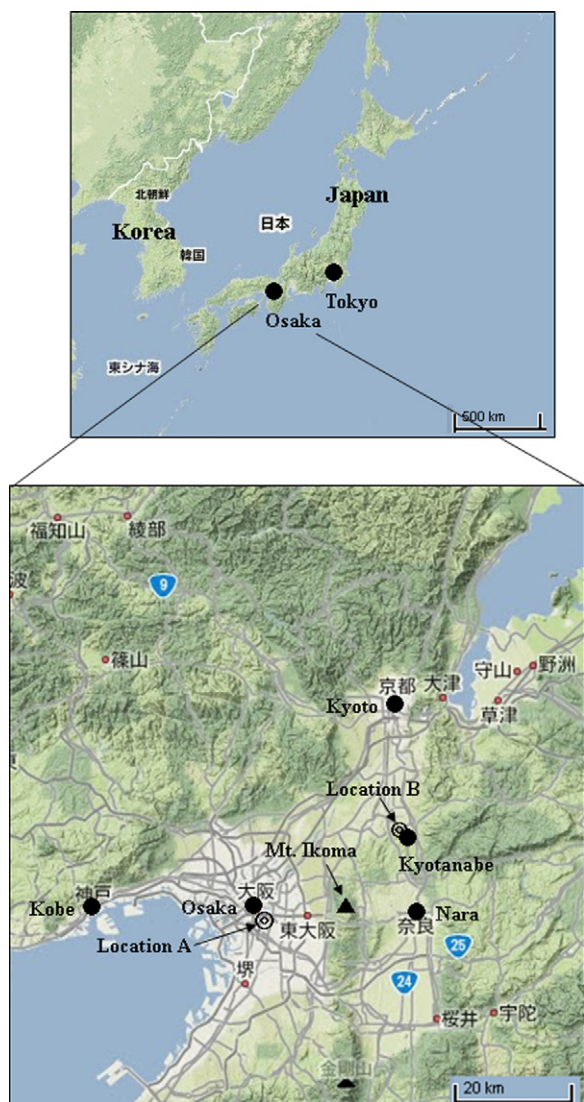

Fig. 1. A map of Osaka showing sampling locations, major cities and Mt. Ikoma Local Meteorological Observatory. Location A: an urban location. Location B: a residential site.

city is renowned for the soil and sedimentary pollution of polychlorinated dibenzo-*p*-dioxin (PCDDs) and polychlorinated dibenzofurans (PCDFs) caused by incinerators [29]. In terms of atmospheric PAHs, there are many possible sources e.g., automobiles, factories and incinerators in this city [28,30]. Further, Osaka urban area is surrounded in the north, east and west by mountains (Ikoma Mountains, etc.), causing the frequent formation of atmospherically stable layer mainly in the winter season [30] as in China [31–33] and Canada [34]. Formation of the layer often leads to increase in air pollutant concentrations [9]. Tao et al. [31] collected air samples at various heights between 8 and 320 m on a meteorological tower in order to understand vertical distribution of PAH concentrations in atmospheric boundary layer of Beijing, China. Similar studies were performed in the other cities in China (e.g., Tianjin [32] and Guangzhou [33]) and Toronto, Canada [34]. However, relationship between formation of atmospherically stable layer and the temporal change in PAH concentrations has not been also studied in Japan.

In our research, we made a comparative survey on particulate and gaseous PAHs in the air at an urban and a residential site in Osaka, Japan during September 2005 and August 2006. This study is aimed at understanding the seasonal variability in PAH concen-

trations, emission sources and effect of meteorological conditions. In particular, for the first time, we focused on the effect of the formation of atmospherically stable layer following an increase in PAH concentrations in Japan. In the present study, we collected air samples using a mini-pump at a low flow rate (5 L min^{-1}) in order to minimize artifact formations, which are often caused by a high-volume air sampling system [12,16].

2. Materials and methods

2.1. PAH compounds examined

Twenty-eight PAH compounds with molecular weights ≥ 178 were examined in this study. These compounds were classified into five categories depending on the number of aromatic rings in the molecule as follows: (1) 3 rings: fluorene (Fluo), phenanthrene (Ph), anthracene (Ant), 1-, 2-, 3-, 4-, 9-methylphenanthrene (1-, 2-, 3-, 4-, 9-MePh), and 2-, 9-methylanthracene (2-, 9-MeAnt); (2) 4 rings: 4*H*-cyclopenta[*def*]phenanthrene (4*H*-CdefP), pyrene (Py), fluoranthene (Flu), benz[*a*]anthracene (BaA), triphenylene (Tri), chrysene (Chr), and 7-methylbenz[*a*]anthracene (7-MeBaA); (3) 5 rings: benzo[*b*]fluoranthene (BbF), benzo[*j*]fluoranthene (BjF), benzo[*k*]fluoranthene (BkF), benzo[*e*]pyrene (BeP), benzo[*a*]pyrene (BaP), perylene, 7-methylbenzo[*a*]pyrene (7-MeBaP), and dibenz[*a,h*]anthracene (DiBahA); (4) 6 rings: indeno[1,2,3-*cd*]pyrene (INcdP) and benzo[*ghi*]perylene (BghiP); and (5) 7 rings: coronene (Cor).

2.2. Sampling sites

Atmospheric PAHs were collected at the Research Institute of Environment, Agriculture, and Fisheries (RIoEAF), Osaka Prefectural Government (location A: 34°40′46″N, 135°32′08″E) and a residential building (location B: 34°49′39″N, 135°45′25″E). Location A is situated in an urban area in Osaka. This place is located within 200 m south of Hanshin Highway and Central Great Motorway, which are busy motorways linking central and eastern Osaka. In contrast, location B is a suburban area in Kyotanabe, located approximately 30 km north-east of location A and outside Ikoma Mountains. Kyotanabe city has a population of approximately 63,000 inhabitants in an area of 43 km^2. Concentrations of air pollutants (e.g., nitrogen oxides [NO$_x$], carbon monoxide [CO], ozone, PM with a diameter <10 μm [PM$_{10}$], and/or PM with a diameter <2.5 μm [PM$_{2.5}$]) were monitored at location A [35] and Tanabe Monitoring Station (TMS) [36]. TMS is located approximately 1 km east of location B. The meteorological data were obtained from the website of Japan Meteorological Agency (JMA), Government of Japan [37]. Meteorological data used were monitored at Osaka District Meteorological Observatory (ODMO: 34°40′54″N, 135°31′06″E) and Kyotanabe Regional Meteorological Observatory (KRMO: 34°49′48″N, 135°45′36″E), both part of JMA. ODMO is located approximately 2 km west of location A, while KRMO is located several hundred meters east of location B. In addition, in order to understand the formation of atmospherically stable layer at Osaka urban area, we used temperature data monitored at Mt. Ikoma Local Meteorological Observatory (MILMO: 34°40′30″N, 135°40′36″E), another JMA located on top of Mt. Ikoma. Locations of PAH sampling, major cities and Mt. Ikoma are shown in Fig. 1.

2.3. Sampling methods

PAHs in PM and the gaseous phase were collected monthly from locations A and B during September 2005 and August 2006 similar to previous studies [9,10]. Air was first passed through a quartz-fiber filter (QFF) (Supelco, USA; diameter, 32 mm) to collect particulate PAHs and then through two layers of polyurethane foam

Table 1
Concentrations of PAHs ($ng\,m^{-3}$) in PM and the gaseous phase in Osaka, Japan.

	Location A				Location B			
	Particulate PAHs		Gaseous PAHs		Particulate PAHs		Gaseous PAHs	
	Concn.[a]	Range	Concn.[a]	Range	Concn.[a]	Range	Concn.[a]	Range
Fluo	0.05 ± 0.04	0.01–0.10	9.96 ± 3.41	6.22–16.38	0.03 ± 0.02	0.00–0.06	6.28 ± 2.91	3.01–10.75
Ph	0.49 ± 0.41	0.01–1.21	17.92 ± 7.70	9.46–33.46	0.30 ± 0.30	0.00–1.08	8.92 ± 3.19	4.65–13.81
1-MePh	0.05 ± 0.05	0.00–0.14	0.98 ± 0.43	0.37–1.89	0.03 ± 0.02	0.00–0.06	0.52 ± 0.28	0.06–1.01
2-MePh	0.08 ± 0.07	0.00–0.20	1.76 ± 0.86	0.86–3.82	0.04 ± 0.04	0.00–0.13	0.83 ± 0.40	0.05–1.44
3-MePh	0.06 ± 0.06	0.00–0.18	1.58 ± 0.70	0.56–2.68	0.03 ± 0.04	0.00–0.11	0.89 ± 0.36	0.22–1.34
4-+9-MePh	0.03 ± 0.02	0.00–0.06	0.49 ± 0.26	0.18–0.98	0.01 ± 0.02	0.00–0.04	0.32 ± 0.25	0.00–0.69
Ant	0.12 ± 0.14	0.00–0.49	1.44 ± 0.98	0.00–3.19	0.08 ± 0.07	0.00–0.18	0.80 ± 0.86	0.00–2.65
2-MeAnt	0.03 ± 0.03	0.00–0.08	0.27 ± 0.41	0.00–1.18	0.02 ± 0.02	0.00–0.04	0.28 ± 0.47	0.00–1.52
9-MeAnt	0.21 ± 0.55	0.00–1.89	0.46 ± 0.89	0.00–2.31	0.02 ± 0.07	0.00–0.25	0.54 ± 1.14	0.00–3.04
Σ3rings	1.10 ± 0.88	0.14–3.01	34.85 ± 11.70	18.84–52.81	0.56 ± 0.45	0.07–1.65	19.38 ± 6.28	8.45–28.49
4H-CdefPh	0.07 ± 0.07	0.00–0.21	1.00 ± 0.48	0.38–1.96	0.03 ± 0.03	0.00–0.09	0.66 ± 0.62	0.00–2.03
Flu	1.31 ± 1.15	0.09–3.34	5.87 ± 2.88	2.10–10.96	0.68 ± 0.66	0.00–2.37	2.26 ± 0.84	0.86–4.04
Py	1.62 ± 1.44	0.06–4.98	6.09 ± 6.36	0.99–21.14	0.92 ± 0.93	0.07–2.88	3.61 ± 4.85	0.00–16.49
BaA	0.53 ± 0.50	0.05–1.60	0.06 ± 0.09	0.00–0.29	0.17 ± 0.12	0.03–0.38	0.02 ± 0.03	0.00–0.12
Tri + Chr	0.41 ± 0.32	0.10–1.03	0.13 ± 0.15	0.00–0.50	0.20 ± 0.14	0.04–0.53	0.05 ± 0.05	0.00–0.15
7-MeBaA	0.23 ± 0.17	0.03–0.53	0.01 ± 0.01	0.00–0.04	0.10 ± 0.14	0.00–0.49	0.03 ± 0.03	0.00–0.06
Σ4rings	4.45 ± 3.57	0.47–10.29	13.50 ± 7.68	4.35–30.06	2.21 ± 1.88	0.20–6.39	6.84 ± 5.82	1.03–20.91
BbF + BjF	0.69 ± 0.62	0.13–1.98	0.01 ± 0.03	0.00–0.12	0.33 ± 0.21	0.10–0.74	0.01 ± 0.01	0.00–0.03
BkF	0.55 ± 0.51	0.09–1.58	0.01 ± 0.04	0.00–0.15	0.23 ± 0.14	0.06–0.46	0.00 ± 0.01	0.00–0.03
BeP	0.50 ± 0.41	0.09–1.27	0.00 ± 0.00	0.00–0.01	0.24 ± 0.16	0.06–0.51	0.00 ± 0.00	0.00–0.01
BaP	0.74 ± 0.61	0.11–1.99	0.00 ± 0.00	0.00–0.01	0.34 ± 0.27	0.09–0.98	0.00 ± 0.00	0.00–0.01
perylene	0.11 ± 0.09	0.01–0.28	0.00 ± 0.00	0.00–0.00	0.05 ± 0.05	0.00–0.16	0.00 ± 0.00	0.00–0.00
7-MeBaP	0.05 ± 0.03	0.01–0.12	0.00 ± 0.00	0.00–0.00	0.03 ± 0.03	0.00–0.08	0.00 ± 0.00	0.00–0.00
DiBahAnt	0.07 ± 0.08	0.00–0.27	0.00 ± 0.01	0.00–0.02	0.02 ± 0.01	0.00–0.04	0.00 ± 0.00	0.00–0.00
Σ5rings	2.70 ± 2.33	0.47–7.41	0.03 ± 0.09	0.00–0.31	1.24 ± 0.83	0.34–2.94	0.01 ± 0.02	0.00–0.08
INcdP	1.35 ± 1.23	0.20–4.36	0.00 ± 0.00	0.00–0.00	0.60 ± 0.29	0.25–1.13	0.00 ± 0.00	0.00–0.00
BghiP	1.25 ± 0.99	0.25–3.23	0.00 ± 0.00	0.00–0.01	0.57 ± 0.30	0.24–1.33	0.00 ± 0.00	0.00–0.00
Σ6rings	2.85 ± 2.30	0.50–7.93	0.00 ± 0.00	0.00–0.01	1.41 ± 0.96	0.52–3.98	0.00 ± 0.00	0.00–0.00
Cor	0.37 ± 0.24	0.12–0.86	0.00 ± 0.00	0.00–0.01	0.22 ± 0.15	0.08–0.56	0.00 ± 0.00	0.00–0.01
Σ28PAHs	11.49 ± 8.75	1.79–26.94	48.39 ± 16.45	23.18–70.93	5.64 ± 3.83	1.64–15.52	26.23 ± 9.38	9.67–41.00

[a] Mean ± S.D.

(PUF) plugs (Supelco; diameter, 22 mm; height, 76 mm) to obtain gaseous PAHs using a mini-pump (MP-Σ500; Shibata, Japan) at a flow rate of 5 L min^{-1} for 24 h. Prior to sampling, the QFFs were combusted at 600 °C for 4 h, while the PUF plugs were washed with warm water, rinsed with acetone, and Soxhlet extracted with acetone for 8 h and then with dichloromethane (DCM) for 16 h. After sampling, the QFF and PUF plugs respectively were sealed in plastic cases and a glass container and stored at 4 °C. In this study, par-

Table 2
Temporal changes in air pollutant concentrations and meteorological parameters at locations A and B.

Location	Sampling date (dd/mm/yy)	Air pollutant concn.					Meteorological conditions			
		NO_x (ppbv)[a]	CO (ppmv)	O_3 (ppbv)	PM_{10} ($\mu g\,m^{-3}$)	$PM_{2.5}$ ($\mu g\,m^{-3}$)	Temp. (°C)	RH (%)	WS (m s^{-1})	Total SH (h)
A	15–16/09/2005	25.7	2.7	19.9	18.0	8.8	23.6	59.8	2.7	8.1
	13–14/10/2005	26.2	3.7	28.5	20.3	14.9	23.3	60.6	2.2	6.7
	16–17/11/2005	41.3	4.2	11.5	13.4	8.4	9.5	64.9	1.9	6.1
	19–20/12/2005	59.3	5.8	11.6	15.8	13.1	3.9	62.1	2.3	5.0
	25–26/01/2006	58.5	7.7	13.7	27.8	21.3	4.8	60.3	2.0	2.8
	22–23/02/2006	46.2	6.0	19.5	43.2	25.0	10.2	70.9	2.7	2.1
	27–28/03/2006	61.5	7.4	25.2	64.6	36.9	14.3	44.9	1.7	7.4
	19–20/04/2006	27.3	4.2	33.7	29.6	15.0	16.3	54.8	4.1	5.4
	15–16/05/2006	78.8	9.2	18.3	67.9	42.8	18.5	51.2	1.7	0.0
	29–30/06/2006	41.0	4.4	13.9	39.4	19.2	27.5	69.5	2.7	5.1
	26–27/07/2006	32.1	3.2	15.3	64.3	20.8	30.0	70.2	3.1	9.3
	28–29/08/2006	34.8	3.8	14.6	30.0	NM	29.1	68.2	1.9	8.2
B	18–19/09/2005	31.1	NM	19.9	54.0	NM	25.3	NM	1.1	5.9
	16–17/10/2005	28.8	NM	7.9	23.9	NM	18.0	NM	1.2	0.6
	27–28/11/2005	51.9	NM	18.0	40.5	NM	10.4	NM	1.3	7.4
	14–15/12/2005	43.6	NM	16.3	9.7	NM	2.6	NM	1.7	8.1
	25–26/01/2006	57.4	NM	15.2	37.0	NM	1.8	NM	1.3	6.0
	25–26/02/2006	15.8	NM	32.6	15.2	NM	8.1	NM	1.8	9.9
	28–29/03/2006	12.7	NM	38.7	24.3	NM	5.3	NM	2.4	5.8
	08–09/04/2006	8.0	NM	43.7	101.1	NM	10.6	NM	2.0	9.0
	20–21/05/2006	12.4	NM	37.2	17.9	NM	18.0	NM	1.3	10.8
	03–04/06/2006	9.5	NM	39.7	51.8	NM	22.5	NM	1.6	4.4
	22–23/07/2006	22.7	NM	30.8	38.9	NM	26.9	NM	1.0	4.5
	28–29/08/2006	19.2	NM	20.9	25.5	NM	27.1	NM	1.2	4.6

NM, not measured; Temp., temperature; RH, relative humidity; WS, wind speed; SH, sunshine hours.
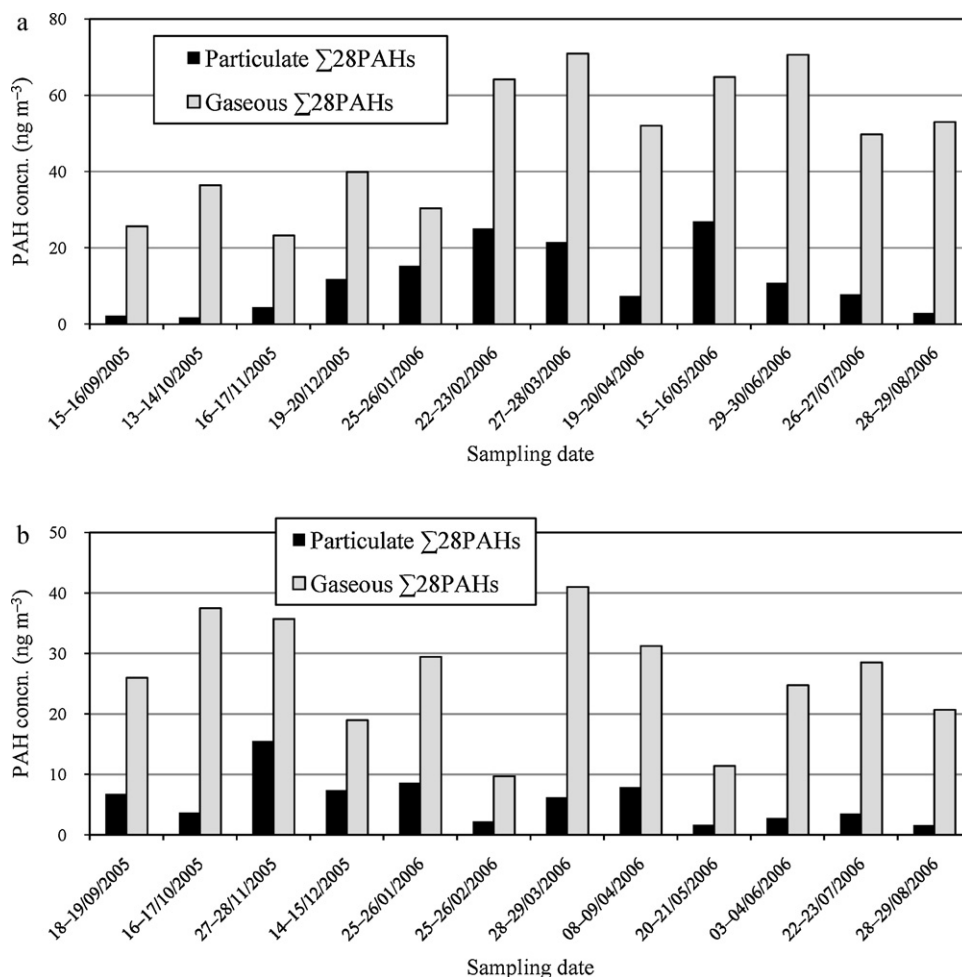
[a] NO plus NO_2.

Fig. 2. Temporal changes in the $\sum$28PAH concentrations in PM and the gaseous phase at locations (a) A and (b) B.

ticulate PAHs are defined as those collected on the QFFs, whereas gaseous PAHs are defined as those collected on the two layers of PUF plugs.

2.4. Analyses of samples

Prior to extraction, five deuterated PAH compounds (Ph-d_{10}, Chr-d_{10}, BaP-d_{12}, BghiP-d_{12}, and Cor-d_{12}) used as internal standards were spiked in both the QFF and PUF plugs. The QFF and PUF plugs were separately extracted with DCM using ultrasonic extraction for 10 min (repeated three times) and Soxhlet apparatus for 24 h, respectively. After the solvent was changed to hexane, each concentrate was purified with silica (deactivated by 5% distilled water) by gel column chromatography, and then concentrated under a gentle stream of pure nitrogen gas after spiking two injection internal standards (Flu-d_{12} and perylene-d_{12}). All samples were analyzed using a high-resolution gas chromatograph (GC)/high-resolution mass spectrometer (MS) (HP5890; Agilent, USA; JMS700D; JEOL, Japan) equipped with an HP-1MS capillary column (15 mm × 0.25 mm i.d. × 0.25 μm film thickness; J&W, USA). The presence of individual PAHs in the blank sample were at low levels and in most cases even below the level of detection. Therefore, limits of detection (LODs) for individual PAHs were derived from the 3σ (standard deviation) values of replicate analyses of a standard solution [19]. The LODs of PAHs ranged between 4 and 64 pg m^{-3}. Details of analytical procedures are described in the literature [9,10].

3. Results and discussion

3.1. PAH concentrations in PM and the gaseous phase in Osaka

Table 1 shows the PAH concentrations at locations A and B. The concentrations of all 28 PAH ($\sum$28PAH) compounds in PM ranged between 1.79 and 26.94 ng m^{-3} (mean ± SD: 11.49 ± 8.75 ng m^{-3}) at location A and between 1.64 and 15.52 ng m^{-3} (mean ± SD: 5.64 ± 3.83 ng m^{-3}) at location B. In the case of gaseous compounds, $\sum$28PAH concentrations ranged between 23.18 and 70.93 ng m^{-3} (mean ± SD: 48.39 ± 16.45 ng m^{-3}) at location A and between 9.67 and 41.00 ng m^{-3} (mean ± SD: 26.23 ± 9.38 ng m^{-3}) at location B. The $\sum$28PAH concentrations at the urban site thus were approximately twice as high compared to those at the residential site. Compared to previous studies, the $\sum$28PAH concentrations at the urban site are the same level as those in Texas, USA [4], Cardiff, UK [11], and Heraklion, Greece [19], but lower than those in Kathmandu, Nepal [9], Hanoi, Vietnam [10], Manchester and London, UK [11], Chicago, USA. [12] and Beijing, China [13]. Further, the $\sum$28PAH concentrations obtained in the present study were much lower than $\sum$16PAH concentrations in PM and the gaseous phase collected at location A during the 1970s (mean ± SD of particulate and gaseous $\sum$16PAHs: 52.1 ± 32.3 and 221.7 ± 95.3 ng m^{-3}, respectively) [3].

The temporal changes in $\sum$28PAH concentrations in PM and the gaseous phase at locations A and B are shown in Fig. 2. The $\sum$28PAH concentrations in PM at location A were lower in summer, and then increased from fall to reach higher values in winter and spring. The

Table 3
Pearson product-moment correlation coefficients between concentrations of representative PAHs and other parameters (air pollutant concentrations or meteorological parameters).

Location	PAHs	Air pollutants					Meteorological parameters				
		NO_x[c]	CO	O_3	PM_{10}	$PM_{2.5}$	Temp.	RH	WS	SH	G
A	Fluo[a]	0.49	0.51	−0.07	0.67**	0.90***	0.25	−0.08	−0.43	−0.07	0.55*
	Ph[a]	0.15	0.11	−0.23	0.52	0.44	0.44	0.44	0.01	0.14	0.42
	Flu[a]	0.34	0.32	−0.16	0.78***	0.68**	0.43	0.15	−0.02	0.23	0.51
	Py[a]	0.12	0.26	0.68**	0.39	0.41	−0.10	−0.68**	0.23	0.38	0.54*
	BaA[a]	0.54*	0.57*	−0.10	0.63**	0.71**	0.03	0.02	−0.20	−0.34	0.44
	Trip + Chr[a]	0.50	0.44	−0.23	0.61**	0.66**	0.16	0.08	−0.25	−0.30	0.42
	Σ28PAHs[a]	0.34	0.40	0.23	0.70**	0.74***	0.25	−0.18	−0.01	−0.28	0.72**
	Fluo[b]	0.46	0.70**	0.37	0.31	0.56*	−0.52	−0.41	−0.08	−0.33	0.32
	Ph[b]	0.65**	0.72***	−0.16	0.21	0.41	−0.78***	−0.16	−0.21	−0.57*	0.31
	Flu[b]	0.71**	0.82***	0.00	0.45	0.67**	−0.62**	−0.31	−0.24	−0.47	0.54*
	Py[b]	0.62**	0.73***	0.29	0.56*	0.73***	−0.47	−0.61*	−0.11	−0.11	0.73***
	BaA[b]	0.64**	0.72**	0.03	0.51	0.68**	−0.49	−0.23	−0.20	−0.37	0.71**
	Trip + Chr[b]	0.75***	0.80***	−0.13	0.60*	0.78***	−0.39	−0.15	−0.27	−0.47	0.64**
	BeP[b]	0.71**	0.80***	−0.02	0.70**	0.85***	−0.24	−0.21	−0.24	−0.37	0.64**
	BaP[b]	0.75***	0.78***	−0.13	0.70**	0.83***	−0.24	−0.14	−0.26	−0.40	0.64**
	BkF[b]	0.71**	0.80***	−0.11	0.61*	0.78***	−0.27	−0.13	−0.25	−0.48	0.50
	INcdP[b]	0.81***	0.86***	−0.03	0.77***	0.94***	−0.16	−0.37	−0.34	−0.33	0.65**
	BghiP[b]	0.76***	0.80***	0.02	0.77***	0.91***	−0.21	−0.32	−0.28	−0.29	0.77***
	Cor[b]	0.91***	0.94***	−0.04	0.61*	0.88***	−0.47	−0.45	−0.40	−0.52	0.65**
	Σ28PAHs[b]	0.81***	0.89***	0.01	0.65**	0.87***	−0.41	−0.37	−0.29	−0.75***	0.69**
B	Fluo[a]	0.53	NM	−0.57*	0.13	NM	0.39	NM	−0.70**	−0.52	NM
	Ph[a]	0.64**	NM	−0.75***	−0.14	NM	0.24	NM	−0.66**	−0.70**	NM
	Flu[a]	0.53*	NM	−0.41	0.24	NM	−0.09	NM	−0.14	−0.52	NM
	Py[a]	−0.41	NM	0.55*	0.28	NM	−0.26	NM	0.73***	−0.06	NM
	BaA[a]	0.28	NM	−0.69**	−0.24	NM	0.10	NM	−0.43	−0.71**	NM
	Trip + Chr[a]	0.22	NM	−0.45	−0.05	NM	0.20	NM	−0.38	−0.64**	NM
	Σ28PAHs[a]	0.22	NM	−0.19	0.35	NM	−0.10	NM	0.15	−0.58*	NM
	Fluo[b]	0.21	NM	−0.08	0.49	NM	−0.55*	NM	0.38	−0.11	NM
	Ph[b]	0.65**	NM	−0.44	0.14	NM	−0.46	NM	0.01	0.05	NM
	Flu[b]	0.58*	NM	−0.22	0.29	NM	−0.55*	NM	0.18	0.20	NM
	Py[b]	0.05	NM	0.30	0.60*	NM	−0.54*	NM	0.59*	0.29	NM
	BaA[b]	0.81***	NM	−0.45	0.17	NM	−0.52	NM	−0.01	0.05	NM
	Trip + Chr[b]	0.85***	NM	−0.48	0.15	NM	−0.36	NM	−0.23	0.02	NM
	BeP[b]	0.75***	NM	−0.45	0.29	NM	−0.24	NM	−0.26	−0.12	NM
	BaP[b]	0.84***	NM	−0.52	0.13	NM	−0.25	NM	−0.31	−0.01	NM
	BkF[b]	0.76***	NM	−0.44	0.33	NM	−0.26	NM	−0.25	−0.09	NM
	INcdP[b]	0.77***	NM	−0.37	0.27	NM	−0.32	NM	−0.19	−0.10	NM
	BghiP[b]	0.77***	NM	−0.44	0.23	NM	−0.38	NM	−0.12	−0.11	NM
	Cor[b]	0.81***	NM	−0.61*	0.09	NM	−0.33	NM	−0.21	−0.07	NM
	Σ28PAHs[b]	0.67**	NM	−0.28	0.36	NM	−0.53	NM	0.11	0.10	NM

NM, not measured; Temp., temperature; RH, relative humidity; WS, wind speed; SH, sunshine hours; G, potential temperature gradient.

[a] PAH compound in gaseous phase.
[b] PAH compound in particulate phase.
[c] NO plus NO_2.
* $p < 0.10$.
** $p < 0.05$.
*** $p < 0.01$.

seasonal characteristic of particulate PAHs at location B (residential site) was similar to location A (urban site), except for a low concentration in February. In case of gaseous PAHs, higher concentrations were observed during spring and summer at location A, while at location B, PAH concentrations increased in fall and spring. The trends of temporal variability in gaseous PAH concentrations were not clearly observed.

The ratios of average $\sum$28PAH concentrations in PM relative to those in PM + gaseous phase were 18% at location A and 16% at location B. At both the locations, atmospheric PAHs mainly occur in the gaseous phase. These observations were in agreement with previous studies [4,19].

Dominant PAH compounds in the gaseous phase are three- and four-ring PAHs with LMW (e.g., Ph and Fluo, each with three aromatic rings, Flu and Py, each with four rings) at locations A and B. In contrast, dominant compounds of particulate PAHs are four- to seven-ring PAHs with HMW, characterized by a bi-modal peak with four- and six-ring PAHs (Flu and Py, each with four rings, BghiP and INcdP, each with six rings) at both locations. The content of the four-ring PAHs in PM from both locations

was relatively higher, compared to other countries [4,10,19]. This observation may be attributable to emission from diesel engines [7].

Concentrations of the dominant gaseous PAH compounds varied without an observable seasonal trend as in the case of $\sum$28PAHs. In terms of the dominant particulate compounds, their trend was similar to that of the $\sum$28PAHs. Notably, concentrations of the dominant particulate PAHs with four rings exceeded those with six rings mainly in winter (during November and April). This may be due to adsorption of the 4-ring PAHs in the gaseous phase onto the surface of PM with decreasing ambient temperature [3].

3.2. Estimation of emission sources of PAHs using diagnostic molecular ratios

In order to estimate the sources of PAH emissions, many surveys used the diagnostic molecular ratios of PAHs. In the current study, we used five ratios with different MWs. The average ratios of total MePh isomers ($\sum$MePh) relative to Ph in

PM plus the gaseous phase were 0.29 ± 0.10 at location A and 0.30 ± 0.15 at location B, while those for $BaA/(BaA + Trip + Chr)$ were 0.48 ± 0.11 at the A and 0.41 ± 0.10 at the B. Both of the diagnostic molecular ratios corresponded to PAHs of pyrogenic origins [38,39].

Next, we used two ratios (INcdP/BghiP and BghiP/BeP) in order to understand the origin of combustion sources. The average ratios of INcdP/BghiP at locations A and B were 1.00 ± 0.27 and 1.07 ± 0.18, respectively, while the values for BghiP/BeP were 2.66 ± 0.55 and 2.66 ± 0.69, respectively. The former ratios corresponded clearly to diesel engines, while the latter ratios suggest that PAHs are attributable to both gasoline and diesel engines [7]. As mentioned above, profiles of particulate PAHs characterized by the higher content of four-ring compounds might be attributable to diesel engines. Therefore, the contribution of diesel engines is likely to be larger at both sites. Further, the average $Cor/(Cor + BghiP)$ values were 0.26 ± 0.08 at location A and 0.27 ± 0.06 at location B, corresponding to engines with catalytic converters [8–10,22,40]. Above all, the main sources of atmospheric PAHs are estimated to be diesel engines with catalytic converters at both locations A and B.

RIoEAF [35] reported on its website that the number of automobiles monitored at many roadside sites in Osaka did not largely change during the sampling period. Further, in urban and residential areas of Japan, electric air conditioners, kerosene stoves and/or gas heaters are predominantly used for heating, and coal and/or wood stoves are hardly used [41]. These facts indicate that the additional emission sources of PAHs would not appear when PAH concentrations increased. Other factors, e.g., meteorological parameters, may affect the temporal change in PAH concentrations.

The ratio BaP/BeP was used to examine the stability of PAHs in the environment [7,9,12,42]. BaP is well known to be an easily reactive compound because of its short photochemical half-life, whereas BeP, with a longer half-life, is more stable. The average BaP/BeP ratios were 1.55 ± 0.50 at location A and 1.41 ± 0.44 at location B. These values were higher than those at roadside sites in Hanoi, Vietnam [10] and residential sites in Ho Chi Minh City, Vietnam [7]. Obviously, the degradation of BaP is accelerated under strong solar radiation [43,44]; however, sunlight in Osaka could be weaker than that in Vietnam. Cotham and Bidleman [12] suggested that reactive PAHs (e.g., BaP) would be depleted during the period of longer transportation because irradiated time would become longer. Therefore, higher BaP/BeP ratios at both locations A and B show the effect of PAHs emitted from local sources being stronger than that of PAHs transported from the outskirts.

3.3. Relationship between the PAH concentrations and air pollutant concentrations or meteorological parameters in Osaka

Temporal changes in air pollutant concentrations and meteorological parameters are shown in Table 2. NO_x ($NO + NO_2$) concentrations were higher at location A than at location B, while ozone concentration was higher at location B than at location A, and PM_{10} concentration at location A was similar to that at location B. Meteorological data at both locations show a typical moderate monsoon climate in all the four seasons: spring (March–May), summer (June–August), fall (September–November) and winter (December–February). Ambient temperature increased from spring and attained the maximum value in summer, while it decreased from fall and reached the minimum value in winter. During the winter season, relative humidity and duration of sunshine were lower.

Pearson product-moment correlation coefficients between PAH concentrations and air pollutant concentrations or meteorological parameters are shown in Table 3. Most of the representative PAH members in both PM and the gaseous phase positively correlated with NO_x, CO, PM_{10} and/or $PM_{2.5}$ at both locations. NO_x, CO and/or

Table 4
Relationship between K_p value of representative PAH compound and ambient temperature.

Location	PAHs	r value
A	Fluo	−0.63[**]
	Ph	−0.85[***]
	Flu	−0.90[***]
	Py	−0.85[***]
	BaA	−0.69[**]
	Trip + Chr	−0.58[*]
	BeP	NC
	BaP	NC
	BkF	NC
	INcdP	NC
	BghiP	NC
	Cor	NC
	Σ28PAHs	−0.66[**]
B	Fluo	−0.67[**]
	Ph	−0.67[**]
	Flu	−0.63[**]
	Py	−0.49
	BaA	−0.55[*]
	Trip + Chr	−0.45
	BeP	NC
	BaP	NC
	BkF	NC
	INcdP	NC
	BghiP	NC
	Cor	NC
	Σ28PAHs	−0.59[*]

NC, not calculated.
[*] $p < 0.10$.
[**] $p < 0.05$.
[***] $p < 0.01$.

PM could be related to exhaust gas from vehicles [19], suggesting that the simultaneous changes in PAHs, NO_x, CO and/or PM were controlled by common factors (e.g., meteorological parameters). However, most of PAH compounds in PM and the gaseous phase showed weak correlations with PM_{10} at location B. As is well known, atmospheric PAHs generally originated from combustion sources that produced fine particles; consequently, in most cases, PAHs mainly occurred in the gaseous phase and fine particles after PM is emitted into the air [7,45,46]. Although $PM_{2.5}$ concentrations are not monitored at TMS, we estimate that the concentrations of fine particles (e.g., $PM_{2.5}$) could be higher at location A than at the B because traffic is much busier in Osaka urban area [47]. However, PM_{10} concentrations monitored at location A (mean $\pm$ SD: $36.2 \pm 19.8 \, \mu g \, m^{-3}$) were similar to those at TMS (mean $\pm$ SD: $36.7 \pm 25.6 \, \mu g \, m^{-3}$), suggesting that concentrations of PM with diameter 2.5–10 μm ($PM_{2.5-10}$), which are mainly attributable to natural sources [30], might be higher at location B than at location A. Thus, high content of coarse particles (e.g., $PM_{2.5-10}$) where less PAHs are adsorbed and/or absorbed [46,48,49] may cause a weak correlation between PAHs and PM_{10} at location B. Surely, there are many possible sources of coarse particles such as mountains, rice fields, and firms around location B [50].

An obvious relationship was not obtained between most PAH compounds in PM and the gaseous phase and ozone concentrations at location A, while most PAHs showed negative correlation with ozone at location B; however, the correlation was not significant, except for Cor in PM and Fluo, Ph, Py and BaA, each in the gaseous phase. In the atmosphere, NO easily reacts with oxygen to form NO_2 when NO is emitted into the air from vehicles; consequently, NO_2 is dissociated into NO and ozone by sunlight. In general, increased ozone concentration is likely to cause the degradation of PAHs in the air. However, Sadanaga et al. [51] suggested that ozone in the air in Osaka was depleted due to its reaction with NO to form NO_2. In fact, as mentioned above, average ozone concentrations monitored at location A ($18.8 \pm 7.0 \, ppb$) were lower than those at TMS
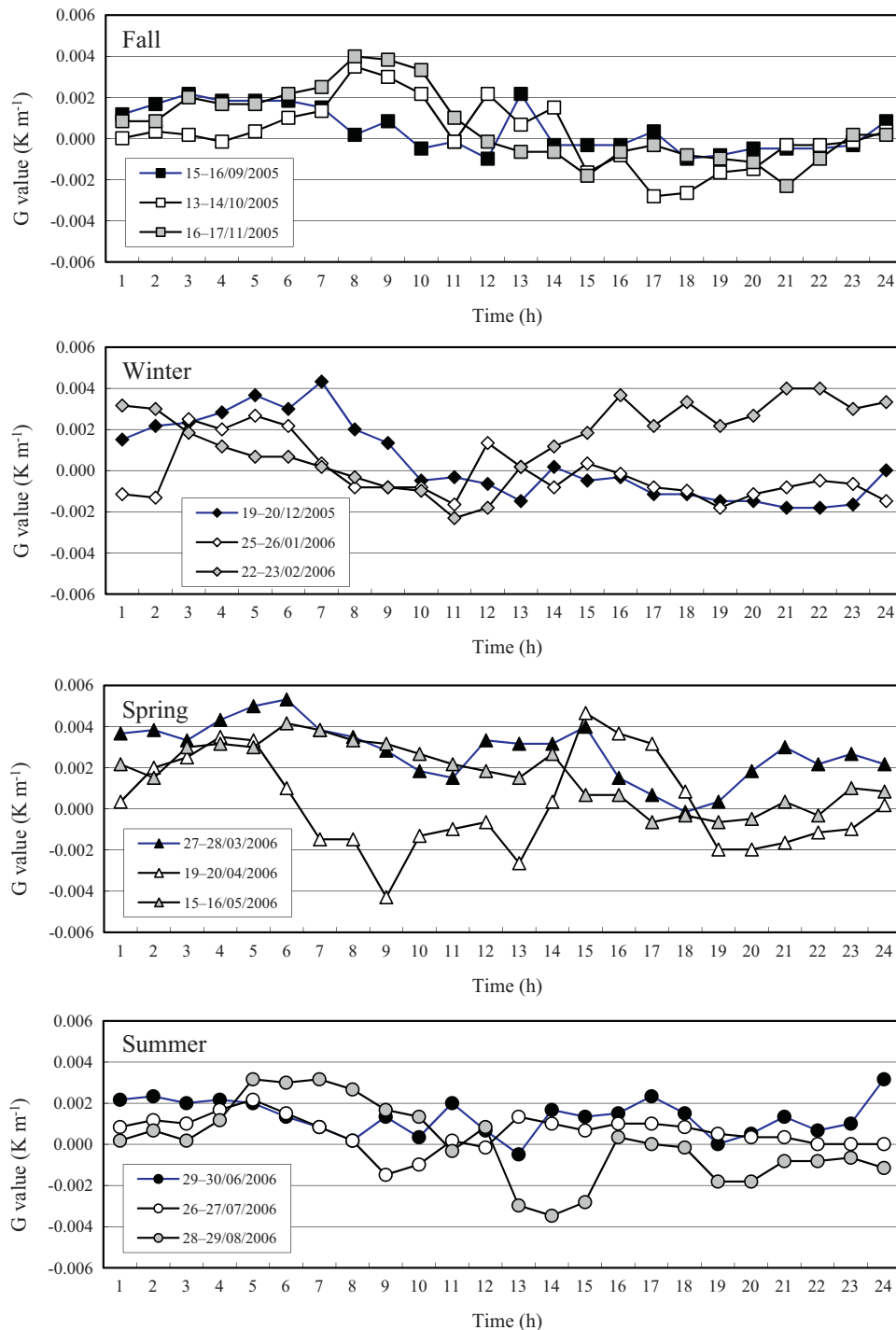
Fig. 3. Hourly changes in *G* values during 24 h sampling procedures from September 2005 to August 2006.

$(26.7 \pm 12.2 \, \text{ppb})$. Thus, a decrease in ozone concentrations by NO might depress the degradation of PAHs, especially at location A.

At both locations A and B, most of representative PAH compounds in PM and the gaseous phase had negative correlations with ambient temperature, relative humidity, wind speed and sunshine hours; however, in most cases, the correlations were not significant. This shows that the effect of each meteorological parameter might not be the main cause of the temporal variability in PAH concentrations.

In order to understand the effect of ambient temperature on the temporal change in PAH concentrations, the gas–particle partitioning coefficient K_p $(\text{m}^3 \, \mu\text{g}^{-1})$ was approximately calculated for each

compound using PM_{10} concentration instead of total suspended particle concentration as follows:

$$K_p = \frac{C_p/C_{PM10}}{C_g} \tag{1}$$

where C_{PM10} is the concentration of PM_{10} $(\mu\text{g m}^{-3})$, and C_p and C_g are the PAH concentrations in PM and the gaseous phase, respectively. Relationships between K_p and ambient temperature at locations A and B are shown in Table 4. At both locations, K_p values of LMW PAHs (e.g., Flu and Py) showed significantly negatively correlated with ambient temperature. This indicates that the temporal change in the LMW PAH concentrations in PM could be
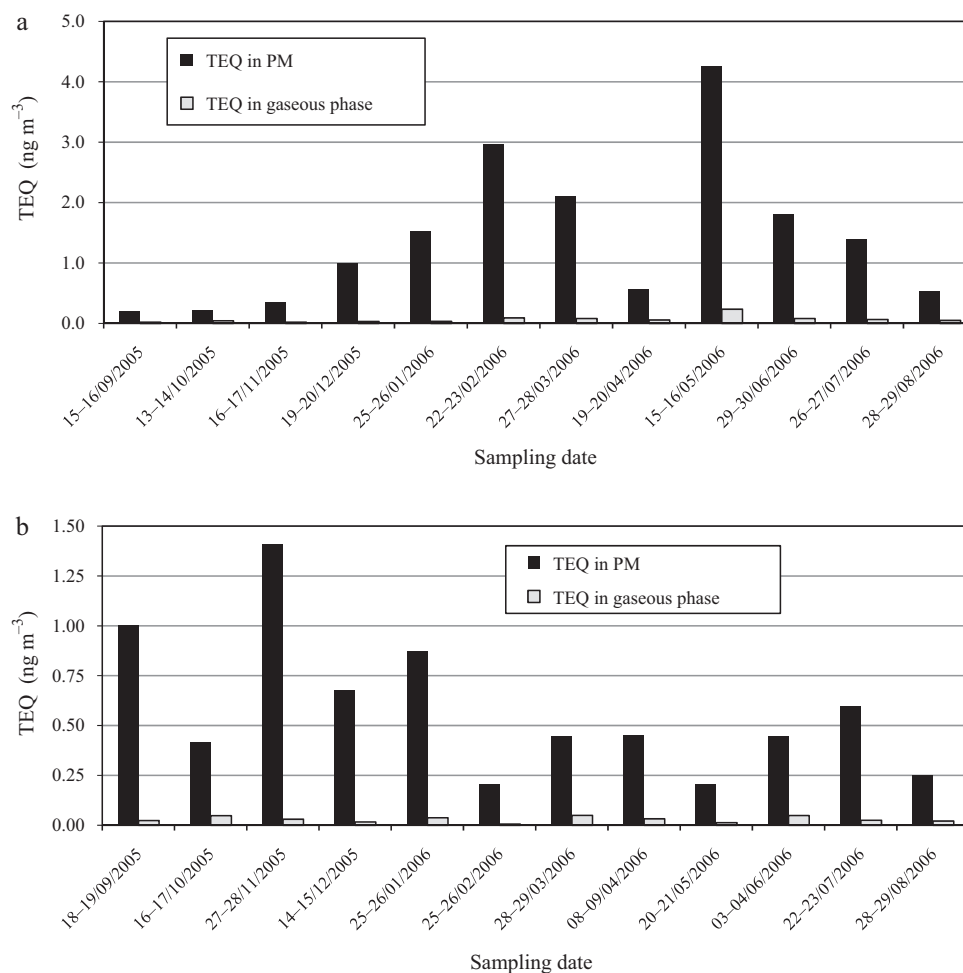
Fig. 4. Temporal changes in the TEQ values in PM and the gaseous phase at locations (a) A and (b) B.

attributable to the shift of their gas–particle partitioning caused by the seasonal change in ambient temperature. In contrast, K_p values of HMW PAHs (e.g., BaP) could not be obtained because they occur mainly in the particulate phase at any atmospheric temperature due to their low vapor pressures [3]. Our results obtained are similar to previous studies [3,19].

3.4. Effect of the formation of atmospherically stable layer on the increase in PAH concentrations in Osaka

Kondo et al. [52] estimated the formation of atmospherically stable layer using the potential temperature gradient. The potential temperature gradient G $(K\,m^{-1})$ was roughly determined by

$$G = \frac{d\theta}{dz} = \frac{\theta_1 - \theta_2}{z_1 - z_2} \tag{2}$$

where θ and z represent potential temperature and altitude (subscripts 1 and 2 represent the values at higher and lower altitudes). The value θ at dry adiabatic condition was expressed as

$$\theta = T + 0.0098z \tag{3}$$

where T is ambient temperature at altitude z. In Eq. (2), positive G values show the formation of an atmospherically stable layer, while negative values show an unstable condition. In Fig. 3, we present the hourly changes in G values on 12 sampling days at location A. Positive G values were observed in winter and spring (especially in January, March and May) when PAH concentrations were higher. Further, most of representative PAHs in both PM and the gaseous

phase positively correlated with G values. In particular, most of the particulate PAHs, and Fluo and Py in the gaseous phase showed significant correlations with the G values. These facts indicate that the formation of atmospherically stable layer plays an important role in the temporal variability in PAH concentrations at Osaka urban area.

For location B, ambient temperature was not monitored at the top of mountains surrounding the location. Thus, we cannot understand the formation of atmospherically stable layer in this area. Considering that this area is just like a bottom of valley surrounded in the east, west and south by mountains, the frequent formation of stable layer may affect the increasing air pollutant concentrations as in Osaka urban area.

3.5. Harmful effect of atmospheric PAHs on human health in Osaka

In order to understand the carcinogenicity of PAHs on human health, toxic equivalent quantity (TEQ) was often used as in the case of PCDD, PCDF, and dioxin-like polychlorinated biphenyls (DL-PCBs) [29,41]. TEQ value was obtained from PAH concentrations using toxic equivalency factors (TEF) proposed by Nisbet and LaGoy [53], which is the canrinogenic potency of each PAH relative to that of BaP. The average TEQ in PM plus the gaseous phase was $1.48 \pm 1.29\,ng\,m^{-3}$ at location A and $0.61 \pm 0.36\,ng\,m^{-3}$ at location B. The TEQ values at location A were more than twice as high as those at the B. Compared to previous studies, the TEQ values at both sites were similar to those in Sakai [7], Tokyo [21], Kitakyushu [21]

and Sapporo [21], Japan, Athens [15] and Heraklion [19], Greece, and Hanoi [10] and Ho Chi Minh City [7], Vietnam, but a magnitude lower than those in Kathmandu, Nepal [9], Beijing, China [13] and a truck and bus terminal in Hanoi, Vietnam [10]. Further, both the TEQ values at both locations exceeded the environmental standards of United Kingdom (annual average value for BaP in PM_{10}: $0.25 \, \text{ng m}^{-3}$) and the Netherlands (annual average value for BaP: $0.5 \, \text{ng m}^{-3}$).

At both locations, TEQ values in PM were ca. twenty times as high as those in the gaseous phase. The main contributors to TEQ values in PM are HMW PAHs with four to six aromatic rings, with the order of BaP > DiBahAnt > INcdP > BbF + BjF ≈ BkF ≈ BaA. The HMW PAH compounds accounted for 98% of TEQ value at both locations, showing that they play an important role on the harmful effect to human health. Lastly, we show the temporal changes in TEQ values at locations A and B in Fig. 4. Their trend was similar to that of PAH concentrations. TEQ values attained a maximum value of $5.50 \, \text{ng m}^{-3}$ at location A in May and $1.44 \, \text{ng m}^{-3}$ at location B in November, when PAH concentrations increased. The TEQ values significantly positively correlated with G values with an r value of 0.67 ($p < 0.05$). These facts indicate that the formation of atmospherically stable layer could lead to a high risk of PAHs, thereby affecting human health.

4. Conclusion

Atmospheric PAHs in PM and the gaseous phase were sampled at an urban and a residential location in Japan. PAH concentrations in PM plus gaseous phase were approximately twice higher at the urban location compared to the residential location. However, obvious differences were not clearly observed between the two locations in terms of emission sources and the causes of temporal change in PAH concentrations. PAHs were found to be mainly emitted from local sources, e.g., diesel engines equipped with catalytic converters. Temporal change in PAH concentrations was not strongly related to ozone concentrations and meteorological parameters. For the first time, we found that the formation of atmospherically stable layer could affect the rise of PAH concentrations in the urban area of Japan. To date, there are insufficient data with regard to atmospheric PAHs associated with PM and the gaseous phase in Japan. The conclusions of this study await confirmation by more detailed surveys.

References

[1] R.E. Waller, The benzpyrene content of town air, Br. J. Cancer 6 (1952) 8–21.
[2] Toxicological profile for polycyclic aromatic hydrocarbons, Agency for Toxic Substances and Disease Registry (ATSDR), Atlanta, GE, 1995.
[3] H. Yamasaki, K. Kuwata, H. Miyamoto, Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons, Environ. Sci. Technol. 16 (1982) 189–194.
[4] J.S. Park, T.L. Wade, S. Sweet, Atmospheric distribution of polycyclic aromatic hydrocarbons and deposition to Galveston Bay, Texas, USA, Atmos. Environ. 35 (2001) 3241–3249.
[5] G.-C. Fang, Y.-S. Wu, C.-N. Chang, T.-T. Ho, A study of polycyclic aromatic hydrocarbons concentrations and source identifications by methods of diagnostic ratio and principal component analysis at Taichung chemical Harbor near Taiwan Strait, Chemosphere 64 (2006) 1233–1242.
[6] H. Guo, S.C. Lee, K.F. Ho, X.M. Wang, S.C. Zou, Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong, Atmos. Environ. 37 (2003) 5307–5317.
[7] T.T. Hien, P.P. Nam, Y. Sadanaga, T. Kameda, N. Takenaka, H. Bandow, Comparison of particulate-phase polycyclic aromatic hydrocarbons and their variability causes in the ambient air at Ho Chi Minh City, Vietnam and in Osaka, Japan, during 2005–2006, Sci. Total Environ. 382 (2007) 70–81.
[8] M. Kishida, C. Mio, K. Fujimori, K. Imamura, N. Takenaka, Y. Maeda, T.T.N. Lan, Y. Shibutani, H. Bandow, Seasonal change in the atmospheric concentration of particulate polycyclic aromatic hydrocarbons in Ho Chi Minh City, Vietnam, Bull. Environ. Contam. Toxicol. 83 (2009) 747–751.
[9] M. Kishida, C. Mio, K. Imamura, A. Kondo, A. Kaga, M.L. Shrestha, N. Takenaka, Y. Maeda, B. Sapkota, K. Fujimori, Y. Shibutani, H. Bandow, Temporal variation of atmospheric polycyclic aromatic hydrocarbon concentrations in PM10 from Kathmandu Valley and their gas–particle concentrations in winter, Int. J. Environ. Anal. Chem. 89 (2009) 67–82.
[10] M. Kishida, K. Imamura, N. Takenaka, Y. Maeda, P.H. Viet, H. Bandow, Concentrations of atmospheric polycyclic aromatic hydrocarbons in particulate matter and the gaseous phase at roadside sites in Hanoi, Vietnam, Bull. Environ. Contam. Toxicol. 81 (2008) 174–179.
[11] C.J. Halsall, P.J. Coleman, B.J. Davis, V. Burnett, K.S. Waterhouse, P. Harding-Jones, K.C. Jones, Polycyclic aromatic hydrocarbons in U.K. urban air, Environ. Sci. Technol. 28 (1994) 2380–2386.
[12] W.E. Cotham, T.F. Bidleman, Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in air at an urban and a rural site near Lake Michigan, Environ. Sci. Technol. 29 (1995) 2782–2789.
[13] S. Liu, S. Tao, W. Liu, Y. Liu, H. Dou, J. Zhao, L. Wang, J. Wang, Z. Tian, Y. Gao, Atmospheric polycyclic aromatic hydrocarbons in North China: a winter-time study, Environ. Sci. Technol. 41 (2007) 8256–8261.
[14] M. Lodovici, M. Venturini, E. Marini, D. Grechi, P. Dolara, Polycyclic aromatic hydrocarbons air levels in Florence, Italy, and their correlation with other air pollutants, Chemosphere 50 (2003) 377–382.
[15] M. Mandalakis, M. Tsapakis, M. Tsoga, E.G. Stephanou, Gas–particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece), Atmos. Environ. 36 (2002) 4023–4035.
[16] R. Lohmann, T. Harner, G.O. Thomas, K.C. Jones, A comparative study of the gas–particle partitioning of PCDD/Fs, PCBs, and PAHs, Environ. Sci. Technol. 34 (2000) 4943–4951.
[17] M. Odabasi, E. Cetin, A. Sofuoglu, Determination of octanol–air partition coefficients and supercooled liquid vapor pressures of PAHs as a function of temperature: application to gas/particle partitioning in an urban atmosphere, Atmos. Environ. 40 (2006) 6615–6625.
[18] M. Tsapakis, E.G. Stephanou, Collection of gas and particle semi-volatile organic compounds: use of an oxidant denuder to minimize polycyclic aromatic hydrocarbons degradation during high-volume air sampling, Atmos. Environ. 37 (2003) 4935–4944.
[19] M. Tsapakis, E.G. Stephanou, Occurrence of gaseous and particulate polycyclic aromatic hydrocarbons in an urban atmosphere: study of sources and ambient temperature effect on the gas/particle concentration and distribution, Environ. Pollut. 133 (2005) 147–156.
[20] Y. Kojima, K. Inazu, Y. Hisamatsu, H. Okochi, T. Baba, T. Nagoya, Changes in concentration levels of polycyclic aromatic compounds associated with airborne particulate matter in downtown Tokyo after introducing government diesel vehicle controls, Asian J. Atmos. Environ. 4 (2010) 1–8.
[21] H. Kakimoto, Y. Matsumoto, S. Sakai, F. Kanoh, K. Arashidani, N. Tang, K. Akutsu, A. Nakajima, Y. Awata, A. Toriba, R. Kizu, K. Hayakawa, Comparison of atmospheric polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in an industrialized city (Kitakyushu) and two commercial cities (Sapporo and Tokyo), J. Health Sci. 48 (2002) 370–375.
[22] M. Kishida, C. Mio, K. Fujimori, K. Imamura, Y. Shibutani, H. Bandow, Temporal change in atmospheric polycyclic aromatic hydrocarbons in particulate matter from an urban location of Osaka, Japan: estimation of causes of a significant increase in their concentrations in the winter season, J. Environ. Chem. 19 (2009) 543–553.
[23] T. Ohura, T. Amagai, T. Sugiyama, M. Fusaya, H. Matsushita, Characteristics of particle matter and associated polycyclic aromatic hydrocarbons in indoor and outdoor air in two cities in Shizuoka, Japan, Atmos. Environ. 38 (2004) 2045–2054.
[24] M. Wada, H. Kido, N. Kishikawa, T. Tou, M. Tanaka, J. Tsubokura, M. Shironita, M. Matsui, N. Kuroda, K. Nakashima, Assessment of air pollution in Nagasaki City: determination of polycyclic aromatic hydrocarbons and their nitrated derivatives, and some metals, Environ. Pollut. 115 (2001) 139–147.
[25] Y.W.F. Tham, K. Takeda, H. Sakugawa, Polycyclic aromatic hydrocarbons (PAHs) associated with atmospheric particles in Higashi Hiroshima, Japan: influence of meteorological conditions and seasonal variations, Atmos. Res. 88 (2008) 224–233.
[26] J.F. Pankow, J.M.E. Storey, H. Yamasaki, Effects of relative humidity on gas/particle partitioning of semivolatile organic compounds to urban particulate matter, Environ. Sci. Technol. 27 (1993) 2220–2226.
[27] Ministry of the Environment (MOE), Government of Japan, Annual Report on the Environment in Japan, Tokyo, Japan, 2009.
[28] Osaka Prefectural Government, Annual Report on the Environment in Osaka, Osaka, Japan, 2009.
[29] M. Kishida, K. Imamura, N. Takenaka, Y. Maeda, P.H. Viet, A. Kondo, H. Bandow, Characteristics of the abundance of polychlorinated dibenzo-p-dioxin and dibenzofurans, and dioxin-like polychlorinated biphenyls in sediment samples from selected Asian regions in Can Gio, Southern Vietnam and Osaka, Japan, Chemosphere 78 (2010) 127–133.
[30] Osaka Prefectural Government, Report on the pollution of fine particles in the atmosphere in Osaka, Osaka, Japan, 2008.
[31] S. Tao, Y. Wang, S. Wu, S. Liu, H. Dou, Y. Liu, L. Chang, F. Hu, B. Xing, Vertical distribution of polycyclic aromatic hydrocarbons in atmospheric boundary layer of Beijing in winter, Atmos. Environ. 41 (2007) 9594–9602.
[32] S.P. Wu, S. Tao, W.X. Liw, Particle size distributions of polycyclic aromatic hydrocarbons in rural and urban atmosphere of Tianjin, China, Chemosphere 62 (2006) 357–367.
[33] C.L. Li, J.M. Fu, G.Y. Sheng, X.H. Bi, Y.M. Hai, X.M. Wang, B.X. Mai, Vertical distribution of PAHs in the indoor and outdoor PM2.5 in Guangzhou, South China, Build. Environ. 40 (2005) 327–339.

[34] N.J. Farrar, T. Harner, M. Shoeib, A. Sweetman, K.C. Jones, Field deployment of thin film passive air samplers for persistent organic pollutants: a study in the urban atmospheric boundary layer, Environ. Sci. Technol. 39 (2005) 28–42.

[35] Research Institute of Environment, Agriculture and Fisheries (RIoEAF), Osaka Prefectural Government, Ecogaralley, Osaka, Japan, 2010. <http://www.epcc.pref.osaka.jp/reaf/>.

[36] Environmental Management Division, Department of Culture and the Environment, Kyoto Prefectural Government, Monitoring of Air Pollutants, Kyoto, Japan, 2010. <http://www.taiki.pref.kyoto.jp/>.

[37] Japan Meteorological Agency (JMA), Government of Japan, Kisho Tokei Joho, Tokyo, Japan, 2010. <http://www.jma.go.jp/jma/>.

[38] M.B. Yunker, R.W. Macdonald, R. Vingarzan, R.H. Mitchell, D. Goyette, S. Sylvestre, PAHs in the Fraster river basin: a critical appraisal of PAHs ratios as indicators of PAH source and composition, Org. Geochem. 33 (2002) 489–515.

[39] M.P. Zakaria, H. Takada, S. Tsutsumi, K. Ohno, J. Yamada, E. Kouno, H. Kumata, Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in Malaysia – a widespread input of petragenic PAHs, Environ. Sci. Technol. 36 (2002) 1907–1918.

[40] W.F. Rogge, L.M. Hildemann, M.A. Mazurek, G.R. Cass, B.R.T. Simoneit, Sources of fine organic aerosol 2: noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks, Environ. Sci. Technol. 27 (1993) 636–651.

[41] S. Kadowaki, H. Naitoh, Gas–particle partitioning of PCDD/Fs in Nagoya urban air, Japan, Chemosphere 59 (2005) 1439–1453.

[42] B.C. Panther, M.A. Hooper, N.J. Tappe, A comparison of air particulate matter and associated polycyclic aromatic hydrocarbons in some tropical and temperate urban environments, Atmos. Environ. 33 (1999) 4087–4099.

[43] R.M. Kamens, Z. Guo, J.N. Fulcher, D.A. Bell, Influence of humidity, sunlight, and temperature on the daytime decay of polyaromatic hydrocarbons on atmospheric soot particles, Environ. Sci. Technol. 22 (1998) 103–108.

[44] G.N. Lu, Z. Dang, X.Q. Tao, C. Yang, X.Y. Yi, Modeling and prediction of photolysis half-lives of polycyclic aromatic hydrocarbons in aerosols by quantum chemical descriptors, Sci. Total Environ. 373 (2007) 289–296.

[45] S.P. Wu, S. Tao, W.X. Liu, Particle size distributions of polycyclic aromatic hydrocarbons in rural and urban atmosphere of Tianjin, China, Chemosphere 62 (2006) 357–367.

[46] B. Zielinska, J. Sagebiel, W.P. Arnott, C.F. Rogers, K.E. Kelly, D.A. Wagner, J.S. Lighty, A.F. Sarofim, G. Palmer, Phase and size distribution of polycyclic aromatic hydrocarbons in diesel and gasoline vehicle emissions, Environ. Sci. Technol. 38 (2004) 2557–2567.

[47] Department of Urban and Public Works, Osaka Prefectural Government, Traffic Census, Osaka, Japan, 2005.

[48] Y. Kawanaka, E. Matsumoto, K. Sakamoto, N. Wang, S. Yun, Size distributions of mutagenic compounds and mutagenicity in atmospheric particulate matter collected with a low-pressure cascade impactor, Atmos. Environ. 38 (2004) 2125–2132.

[49] T.T. Hien, L.T. Thanh, T. Kameda, N. Takenaka, H. Bandow, Distribution characteristics of polycyclic aromatic hydrocarbons with particle size in urban aerosols at the roadside in Ho Chi Minh City, Vietnam, Atmos. Environ. 41 (2005) 1575–1586.

[50] Kyotanabe City Hall, Website of Kyotanabe City Hall, Kyoto, Japan, 2011. <http://www.kyotanabe.jp/>.

[51] Y. Sadanaga, S. Shibata, M. Hamana, N. Takenaka, H. Bandow, Weekday/weekend difference of ozone and its precursors in urban areas of Japan, focusing on nitrogen oxides and hydrocarbons, Atmos. Environ. 42 (2008) 4708–4723.

[52] A. Kondo, A. Kaga, K. Imamura, Y. Inoue, M. Sugiyama, M.L. Shrestha, B. Sapkota, Investigation of air pollution concentration in Kathmandu valley during winter season, J. Environ. Sci. 17 (2005) 1008–1013.

[53] I.C.T. Nisbet, P.K. LaGoy, Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs), Regul. Toxicol. Pharmacol. 16 (1992) 290–300.