#### -Research Letter -

# Evaluation of a Compact Sampler Designed for the Simultaneous Collection of Atmospheric Polycyclic Aromatic Hydrocarbons in Size-fractionated Particulate Matter and the Gaseous Phase

# Masao Kishida,<sup>\*, a, b, 1</sup> Takahide Okamoto,<sup>c</sup> Keiichi Fujimori,<sup>c</sup> Kiyoshi Imamura,<sup>a</sup> Yasuki Nishimura,<sup>d</sup> Yasuhiko Shibutani,<sup>c</sup> and Hiroshi Bandow<sup>e</sup>

<sup>a</sup>Research Institute of Environment, Agriculture and Fisheries, Osaka Prefectural Government, 1–3–62 Nakamichi, Higashinari-ku, Osaka 537–0025, Japan, <sup>b</sup>Environmental Management Division, Department of Environment, Agriculture, and Fisheries, Osaka Prefectural Government, 2–1–2 Otemae, Chuo-ku, Osaka 540–0008, Japan, <sup>c</sup>College of Engineering, Osaka Institute of Technology, 5–16–1 Ohmiya, Asahiku, Osaka 535–8585, Japan, <sup>d</sup>Customer Support of Osaka, GL Science, Inc., 4–1–48 Temma, Kita-ku, Osaka 530–0043, Japan and <sup>e</sup>Graduate School of Engineering, Osaka Prefecture University, 1–1 Gakuen-cho, Naka-ku, Sakai, Osaka 599–8531, Japan

(Received January 12, 2010; Accepted March 14, 2010; Published online March 17, 2010)

A compact sampler consisting of a three-stage cascade impactor and a holder for polyurethane form (PUF) plugs was designed for the simultaneous collection of atmospheric polycyclic aromatic hydrocarbons (PAHs) in fine particles and the gaseous phase. To evaluate its collection efficiency, air was passed through a quartz-fiber filter (QFF) spiked with 28 authentic PAHs and then through cleaned PUF plugs and backup filters for 24 hr in the dark at a constant room temperature (20 or 35°C). PAHs retained on the QFF and those trapped within PUF plugs and backup filters were separately determined. We observed no obvious difference in recoveries between 20 and 35°C except for benzo[a]anthracene (BaA) and triphenylene + chrysene. Most of the PAHs with low molecular weight (166-202) vaporised from the QFF and were trapped in the PUF plugs and backup filters at recoveries of 42-108%, while those with high molecular weight ( $\geq 252$ ) were largely retained on the OFF (recoveries of 75–114%). BaA and triphenylene + chrysene (molecular weight = 228) were largely retained on the QFF at 20°C (recoveries of  $\geq$  84%), but at 35°C the recovery values decreased to levels similar to those trapped with PUF plugs and backup filters (recoveries of 40-56%). The proposed sampler was applied in an investigation of ambient PAHs at a roadside site in a heavy-traffic area in Osaka, Japan, during August 2006 and February 2007.

**Key words** — polycyclic aromatic hydrocarbons, particulate matter, gaseous phase

# INTRODUCTION

Polycyclic aromatic hydrocarbon (PAH) pollution in the environment is of great concern because of PAH mutagenicity and carcinogenicity in human health.<sup>1)</sup> In particular, PAHs with high molecular weight [HMW, e.g., benzo[a]pyrene (BaP), dibenzo[a,h]pyrene and benz[a]anthracene (BaA)] are listed by the Agency for Toxic Substances and Disease Registry (ATSDR) as priority compounds in terms of health risk.<sup>2)</sup> HMW PAHs in the atmosphere occur mainly in particulate matter (PM), especially in fine particles with an aerodynamic diameter ( $d_{ae}$ ) less than approximately 2.5 µm (PM<sub>2.5</sub>), which can readily deeply penetrate into the respiratory system.<sup>3-7)</sup> Thus, HWM PAHs are potential contributors to human health risk. In contrast, low-molecular-weight (LMW) PAHs (e.g., phenanthrene and pyrene), which are considered to be less mutagenic and carcinogenic compared with 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.<sup>8-11</sup> Therefore, it is important to understand the gas-particle and particle-size distributions of atmospheric PAHs.

Many previous studies have focused on the particle-size<sup>3-7, 12</sup>) and gas-particle<sup>8-11, 13-20</sup>) distributions of PAHs. Size-fractionated PM is gener-

<sup>&</sup>lt;sup>1</sup>Present address: Environmental Management Division, Department of Environment, Agriculture, and Fisheries, Osaka Prefectural Government, 2–1–2 Otemae, Chuo-ku, Osaka 540–0008, Japan.

<sup>\*</sup>To whom correspondence should be addressed: Research Institute of Environment, Agriculture and Fisheries, Osaka Prefectural Government, 1–3–62 Nakamichi, Higashinari-ku, Osaka 537–0025, Japan. Tel.: +81-6-6972-1321; Fax: +81-6-6972-5865; E-mail: kishida82477@iris.eonet.ne.jp

ally collected using a high- or low-volume cascade impactor.<sup>3-6)</sup> Ohura et al.<sup>7)</sup> used a compact threestage cascade sampler for the collection of sizefractionated particulate PAHs ( $d_{ae} > 10$ ; 10–2.5;  $< 2.5 \,\mu$ m). The authors used this compact sampling system to investigate PAHs at more than 40 households in Shizuoka, Japan. In the latter case, particulate PAHs are generally collected on a glass-fiber filter (GFF) or a quartz-fiber filter (OFF), and gaseous PAHs are collected with polyurethane form (PUF) plugs or XAD resin after the collection of particulate PAHs, using a high- or low-volume air sampler.<sup>14–20</sup> Recently, as an alternative to the classical PUF plug, Galarneau et al.<sup>21)</sup> tested a GFF impregnated with XAD resin. In addition, a high-volume air sampler equipped with an XAD-4 resin column has been developed for the collection of PAHs and their nitro compounds in the atmosphere.<sup>22)</sup> Elsewhere, a compact sampler for particulate and gaseous PAHs has been applied to the collection of gas-particle PAHs,<sup>8-10)</sup> including studies of atmospheric PAHs in Hanoi, Vietnam<sup>8,9)</sup> and Kathmandu, Nepal,<sup>10)</sup> where such investigations had not been previously performed. However, no studies would have employed a compact system for the simultaneous sampling of PAHs in fine particles and the gaseous phase.

Here, for the first time, we designed a new compact sampler, consisting of a multi-nozzle cascade impact (MCI) sampler with a three-stage cascade<sup>23</sup>) and a holder for PUF plugs, for the simultaneous collection of atmospheric PAHs in size-fractionated particulate matter ( $d_{ae} > 10; 10-2.5; < 2.5 \,\mu\text{m}$ ) and the gaseous phase, and evaluated the collection efficiency of atmospheric PAHs using the sampler. To minimize photolytic degradation of PAHs, sampling was conducted for 24 hr in the dark in a temperature-controlled room. Air was sampled using a mini-pump at a low flow rate (5 l/min) to reduce the amount of oxidants (e.g., ozone) passing through the OFF and PUF plugs<sup>24)</sup> and artifact formation, e.g., blow-off.<sup>25)</sup> The proposed sampler was applied in an investigation of atmospheric PAHs at a roadside site in a heavy-traffic area in Osaka, the second-largest city in Japan. Previously, higher concentrations of hazardous chemicals, e.g., polychlorinated dibenzo-p-dioxin and dibenzofurans,<sup>26)</sup> polychlorinated biphenyls<sup>26,27)</sup> and perfluorinated compounds,<sup>28)</sup> were found in river waters and/or sediment samples from this city. A few studies have also investigated the atmospheric PAHs associated with airborne particles from Osaka.<sup>18, 29, 30)</sup> However, measurements of gas-particle PAHs have not been performed since the  $1970 \, \text{s}^{(18)}$  and their size distributions have yet to be measured in the Osaka area.

## MATERIALS AND METHODS

**PAHs** Investigated —— Twenty-eight PAH compounds were examined, classified into five categories based on the number of aromatic rings in the molecule: 3 rings: fluorene, phenanthrene (Ph), anthracene (Ant), 1-, 2-, 3-, 4-, 9-methylphenanthrene (1-, 2-, 3-, 4-, 9-MePh) and 2-, 9-methylanthracene (2-, 9-MeAnt); 4 4H-cyclopenta[def]phenanthrene (4Hrings: CdefP), pyrene (Py), fluoranthene (Flu), BaA, triphenylene (Trip), chrysene (Chr) and 7methylbenz[a]anthracene (7-MeBaA); 5 rings: benzo[b]fluoranthene (BbF), benzo[i]fluoranthene (BjF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), BaP, perylene, 7-methylbenzo[a]pyrene (7-MeBaP) and dibenzo[ah]anthracene (DiBahAnt); 6 rings: indeno[1,2,3-cd]pyrene (INcdP) and benzo[ghi]perylene (BghiP); 7 rings: coronene These native and deuterated compounds (Cor). were purchased from Supelco (Bellefonte, PA, U.S.A.), Chiron AS (Trondheim, Norway), Wako Pure Chemical Industries Ltd. (Osaka, Japan), AccuStandard Inc. (Shelton, CT, U.S.A.), Aldrich Chemical Co., Inc. (Milwaukee, WI, U.S.A.), Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan) and Nakarai Chemicals Ltd. (Kyoto, Japan).<sup>8,9)</sup>

Sampling Apparatus —— Figure 1 shows a schematic diagram of the proposed compact sampler. The sampler combines a MCI sampler with a three-stage cascade impactor (Tokyo Dylec Co., Tokyo, Japan)<sup>23)</sup> and holders for PUF plugs and a filter (Special order, GL Science Inc., Tokyo, Japan). PM was aerodynamically separated into three size fractions on QFFs according to the following equivalent cutoff diameters at 50% efficiency: first stage (S1):  $d_{ae} > 10 \,\mu\text{m}$  (PM<sub>>10</sub>), second stage (S2):  $2.5-10\,\mu m$  (PM<sub>2.5-10</sub>), and final stage (S3):  $< 2.5 \,\mu m$  (PM<sub>2.5</sub>). OFF with a hole space (47 mm o.d. and 20 mm i.d.; Model 2500 OAT-UP, Tokyo Dylec Co.) was used for the collection of  $PM_{>10}$  and  $PM_{25-10}$ , while QFF without a hole space (diameter 47 mm; Model 2500 QAT-UP, Tokyo Dylec Co.) was used for PM<sub>2.5</sub>. Two PUF plugs (diameter 50 mm, length 50 mm; Special order, GL Science Inc.) and two



Fig. 1. Schematic Diagram of a Compact Sampler Newly Designed for the Simultaneous Collection of Atmospheric PAHs in Sizefractionated Particulate Matter and the Gaseous Phase

MCI sampler: multi-nozzle cascade impact sampler, S1: first stage (PM<sub>>10</sub>), S2: second stage (PM<sub>2.5-10</sub>), S3: final stage (PM<sub>2.5</sub>), A: holder for PUF plugs, B: holder for backup filters, P: mini-pump [size: 109 mm (w)  $\times$  67.5 mm (d)  $\times$  138 mm (h), voltage of electricity source (AC adapter or seven AA dry batteries): 7.2 V].

backup active carbon-fiber filters (ACFFs; diameter 47 mm; TOYOBO KF Paper P-175, Toyobo Co. Ltd., Osaka, Japan) were installed in holders A and B, respectively, for the collection of gaseous PAHs. Sampling Procedure —— As preparation for evaluating the collection efficiency of the sampler in terms of PAH compounds, 25 ng of each of 28 authentic compounds dissolved in hexane was uniformly deposited on a OFF as follows: 50 µl of the stock solution  $(0.5 \text{ ng/}\mu\text{l})$  was dribbled onto the QFF using a microsyringe, and the solvent was readily evaporated at room temperature. Next, the prepared QFF was set at S3, two cleaned PUF plugs were placed in holder A, and two cleaned backup filters were placed in holder B. A cleaned QFF and two cleaned ACFFs were placed at S2 to prevent contamination. In this case, two cut-off stages were not set within the sampler. Once the preparation was complete, air was passed through the sampler using a mini-pump (MP-Σ500; Shibata Scientific Technology Ltd., Osaka, Japan) at a flow rate of 5 l/min for 24 hr. Air sampling was performed in the dark at a temperature-controlled room (Hirayama, Ltd., Tokyo, Japan). The experiments were performed twice: at room temperatures of 20 and 35°C. Three replicate samples and a laboratory blank (QFF, PUF plugs and ACFFs) were analysed for each experiment.

The proposed sampling method was applied to the investigation of atmospheric PAHs under various meteorological conditions. Sampling was performed monthly between August 2006 and February 2007 at the Examination Center for Environmental Pollution and Health, Higashi-Osaka City (34°40′5″N, 135°35′51″E), east Osaka, at a roadside location in a heavy-traffic area with daily vehicle traffic of approximately 106000 vehicles.<sup>31)</sup> In this case study, a QFF with a hole space was placed at each of S1 and S2, a QFF without a hole space was placed at S3, two PUF plugs were placed in holder A, and two backup filters were placed in holder B. PAHs in the atmosphere were collected using the mini-pump at a flow rate of 5 l/min for 24 hr on a fine day. Meteorological data for the sampling days were obtained from the Web site of the Japan Meteorological Agency.<sup>32)</sup> The meteorological conditions in Osaka are typical of a temperate climate.

Prior to sampling, the QFF was combusted at 600°C for 4 hr, and then wrapped in aluminum foil and sealed in a plastic bag until use. The PUF plug and ACFF were washed with warm water, rinsed with acetone, and Soxhlet extracted with acetone for 8 hr and then with dichloromethane (DCM) for 16 hr. They were then left to dry in a vacuum dessicator for more than 24 hr and stored in a solvent-rinsed glass jar. After sampling, the QFF and PUF plug with ACFF were stored in separate containers at 4°C. In this study, particulate PAHs are defined as those collected on the QFF, whereas gaseous PAHs are defined as those collected on the PUF plugs and backup filters.

Analysis of PAH Compounds — QFFs and PUF plugs with backup filters, as used in both the recovery test and monitoring, were treated using the same procedure, as follows. After 24 hr of sampling, 25 ng of each of five deuterated surrogate standards (Ph- $d_{10}$ , Chr- $d_{10}$ , BaP- $d_{12}$ , BghiP- $d_{12}$  and

 $Cor-d_{12}$ ) was separately spiked on QFF(s) and the PUF plugs prior to extraction in order to correct for the recoveries of the different PAHs throughout the extraction and clean-up procedures. For the pretreatment of QFFs, we employed a simplified version of the method described by Kishida et al.<sup>8-10)</sup> PAHs were extracted from QFFs using sonication with DCM for 10 min, repeated three times. The extract was concentrated into 1 ml using a rotary evaporator with the water bath kept at approximately 30°C, using a hexane solvent. The concentrate was filtrated using a syringe filter (Millex<sup>®</sup>-LG; Millipore Co., Billerica, MA, U.S.A.), and then concentrated to 0.5 ml under a gentle stream of pure nitrogen gas after the addition of 25 ng of two deuterated injection internal standards (Flu- $d_{12}$  and perylene $d_{12}$ ).

The pretreatment method for gaseous PAHs is described in the literature.<sup>8–10)</sup> PUF plugs with backup filters were extracted with DCM for 24 hr using a Soxhlet apparatus. The concentrate was purified with 5 g of silica (deactivated by 5% distilled water) by gel column chromatography, and then concentrated to 0.5 ml as shown above. Silica gel (Wakosil C-200; 64–210  $\mu$ m, 80% up) and solvents were purchased from Wako Pure Chemical Industries Ltd. All chemicals used were residual-pesticide-free and of analytical grade.

using high-All samples were analysed resolution gas chromatography (GC)/highspectrometry (MS) (HP5890; resolution mass Agilent, Santa Clara, (CA, U.S.A.) JMS700D; JEOL, Tokyo, Japan) equipped with an SLB-5 ms capillary column (Supelco,  $30 \text{ m} \times 0.25 \text{ mm i.d.} \times$ 0.25 µm film thickness). The injection port was kept at 300°C, and 1 µl of each concentrate was injected in splitless mode. The column temperature was held at 70°C for 1.5 min, then programmed to increase at 15°C/min to 130°C and then at 6°C/min to 300°C before being held for 1 min. High-resolution GC/high-resolution MS analyses were conducted under high-resolution mode ( $R \ge 10000$ ). The recoveries of Ph- $d_{10}$ , Chr- $d_{10}$ , BaP- $d_{12}$ , BghiP- $d_{12}$ and Cor- $d_{12}$  were  $83 \pm 4\%$ ,  $96 \pm 6\%$ ,  $94 \pm 5\%$ ,  $90 \pm 7\%$  and  $81 \pm 8\%$ , respectively. The levels of individual PAHs in the blank sample were generally low and in most cases below the level of detection. Limits of detection (LODs) for individual PAHs, as derived from the  $3\sigma$  (standard deviation) value of replicate analyses of a standard solution (n = 5),<sup>33)</sup> ranged between 4 and  $64 \text{ pg/m}^3$ .

#### **RESULTS AND DISCUSSION**

## Recoveries of PAHs Retained on a QFF and Those Trapped within PUF Plugs and Backup Filters during 24 hr of Sampling

Table 1 lists the recoveries of 28 PAH compounds during 24 hr of sampling using the proposed sampler. Recovery of authentic PAH compound is defined as the amount of each compound retained on a OFF or trapped within PUF plugs and backup filters relative to that spiked on a QFF. The average recoveries of LMW (166-202) PAHs retained on a OFF were not detectable (ND) or occurred in trace amounts. In contrast, the recoveries of LMW PAHs trapped within PUF plugs and backup filters were 43-98% at 20°C and 42-108% at 35°C. Thus, at both temperatures, most of the LMW PAHs spiked on a QFF were vaporised from the filter during 24 hr and were trapped with PUF plugs and backup filters. Among the LMW PAHs, the average recoveries of fluorene trapped with PUF plugs and backup filters at 20 and 35°C (43% and 42%, respectively) were the lowest. In addition, the average recoveries of Ant at both temperatures were lower than those of Ph, although MW of Ant was as high as that of Ph. Similar trend was also observed between Py and Flu.

In the present study,  $Ph-d_{10}$  used as an internal standard for the LMW PAHs satisfactorily yielded approximately 83%, indicating that losses of LMW PAHs during extraction and clean-up procedures could be small. However, the vapor pressure of fluorene was roughly an order of magnitude higher than that of Ph (Table 1). Therefore, the lower recovery of fluorene might be attributable to its vaporisation during drying solvent at room temperature and/or analytical procedures. Other possible cause is breakthrough during sampling. In contrast, the vapor pressure of Ant was as high as that of Ph, and the value of Py was similar to that of Flu. Another factor that may explain the lower recoveries of Ant and Py are their high reactivity compared with those of Ph and Py.<sup>14, 34, 35)</sup> Therefore, the depletion of Ant and Py might depend on their reactivity. As shown above, we tried to minimize artifact formation in the recovery tests. However, our results suggest that it is difficult to completely eliminate artifact formation for reactive PAHs (e.g., Ant) using the proposed sampling system.

Regarding PAHs with a MW of 228, the average recoveries of BaA and Trip + Chr retained on a QFF at 20°C were 92% and 84%, respectively, and

PAHs <sup>a)</sup>	MW	Vapor	Recovery (%) <sup>c)</sup>						
		Pressure b)	20°C				35°C		
		(Pa)	par-PAHs <sup>d</sup>	gas-PAHs <sup>e)</sup>	Total PAHs <sup>f</sup>	par-PAHs <sup>d</sup>	gas-PAHs <sup>e)</sup>	Total PAHs <sup>f</sup>	
fluorene	166	$4.08  imes 10^{-1}$	1 ± 1	43 ± 8	44 ± 7	$1 \pm 0$	42 ± 5	44 ± 5	
Ph	178	$7.04 \times 10^{-2}$	N.D.	67 ± 9	67 ± 9	$2 \pm 0$	$70 \pm 8$	72 ± 8	
Ant	178	$6.60 \times 10^{-2}$	N.D.	57 ± 7	57 ± 7	$1 \pm 0$	$59 \pm 10$	$60 \pm 10$	
4H-CdefP	190	—	$0 \pm 0$	$93 \pm 6$	$93 \pm 6$	N.D.	$108 \pm 8$	$108 \pm 8$	
1-MePh	192	—	$0 \pm 0$	89 ± 5	89 ± 5	N.D.	94 ± 8	94 ± 8	
2-MePh	192	—	$0 \pm 0$	$82 \pm 11$	$82 \pm 11$	N.D.	$88 \pm 11$	$88 \pm 11$	
3-MePh	192	—	$0 \pm 0$	$98 \pm 11$	$98 \pm 11$	N.D.	$98 \pm 6$	$98 \pm 6$	
4-+9-MePh	192	—	$0 \pm 0$	$96 \pm 10$	$96 \pm 10$	N.D.	$100 \pm 6$	$100 \pm 6$	
2-MeAnt	192	—	$1 \pm 0$	$74 \pm 11$	$75 \pm 11$	N.D.	$79 \pm 15$	$79 \pm 15$	
9-MeAnt	192	—	$1 \pm 0$	$78 \pm 8$	$79 \pm 8$	N.D.	82 ± 9	82 ± 9	
Flu	202	$6.95 \times 10^{-3}$	$0 \pm 0$	76 ± 8	76 ± 8	$0 \pm 0$	74 ± 8	$75 \pm 8$	
Ру	202	$4.45 \times 10^{-3}$	$1 \pm 1$	67 ± 9	68 ± 9	$0 \pm 0$	$67 \pm 10$	$67 \pm 10$	
BaA	228	$2.51 \times 10^{-4}$	$92 \pm 12$	$7 \pm 3$	$98 \pm 14$	$40 \pm 3$	$50 \pm 11$	90 ± 8	
Trip+Chr	228	$2.28\times10^{-4g)}$	$84 \pm 4$	8 ± 4	$92 \pm 3$	$46 \pm 5$	$56 \pm 4$	$102 \pm 3$	
		$2.31 \times 10^{-4 h}$							
7-MeBaA	242	—	$106 \pm 2$	N.D.	$106 \pm 2$	$87 \pm 3$	$17 \pm 6$	$104 \pm 5$	
BeP	252	$1.35 \times 10^{-5}$	$102 \pm 5$	N.D.	$102 \pm 5$	$95 \pm 4$	$5 \pm 1$	$100 \pm 5$	
BaP	252	$1.20 \times 10^{-5}$	87 ± 7	N.D.	87 ± 7	$80 \pm 1$	$3 \pm 3$	$83 \pm 4$	
perylene	252	—	$76 \pm 4$	N.D.	$76 \pm 4$	$75 \pm 4$	$3 \pm 2$	$79 \pm 4$	
BbF+BjF	252	$2.11 \times 10^{-5i}$	$114 \pm 9$	N.D.	$114 \pm 9$	$93 \pm 6$	$4 \pm 3$	$97 \pm 4$	
BkF	252	$2.08 \times 10^{-5}$	$89 \pm 8$	N.D.	89 ± 8	$83 \pm 3$	$6 \pm 4$	$89 \pm 7$	
7-MeBaP	266	—	$100 \pm 5$	N.D.	$100 \pm 5$	$86 \pm 2$	N.D.	86 ± 2	
INcdP	276	—	$93 \pm 3$	N.D.	$93 \pm 3$	$84 \pm 3$	N.D.	84 ± 3	
BghiP	276	—	87 ± 1	N.D.	87 ± 1	$100 \pm 3$	N.D.	$100 \pm 3$	
DiBahAnt	278		$93 \pm 5$	N.D.	$93 \pm 5$	$77 \pm 2$	N.D.	$77 \pm 2$	
Cor	300	—	$82 \pm 4$	$2 \pm 0$	83 ± 4	$89 \pm 2$	N.D.	89 ± 2	

 Table 1. Recoveries of 28 PAH Compounds during 24-hr Sapmling Procedure Using a Compact Sampler

*a*) Abbreviation of each PAH compound was shown in the main text. *b*) Values were obtained at 25°C. See Ref. 20). *c*) All data represent mean  $\pm$  S.D. (*n* = 3). N.D.: not detected. *d*) Particulate PAHs. *e*) Gaseous PAHs. *f*) Particulate plus gaseous PAHs. *g*) Trip. *h*) Chr. *i*) BbF.

the average recoveries for those trapped within PUF plugs and backup filters were < 10%. In contrast, at  $35^{\circ}$ C, the average recoveries of BaA and Trip + Chr retained on the QFF decreased to 40% and 46%, respectively; for PUF plugs and backup filters the corresponding values increased to 50% and 56%, respectively. The ratios of particulate PAHs to the sum of particulate and gaseous PAHs for all three compounds were > 90% at 20°C and approximately 50% at 35°C. Thus, the three PAH compounds spiked onto a QFF were largely retained over a period of 24 hr at 20°C, but half of the total PAHs were vaporised from the QFF and trapped within PUF plugs and backup filters at 35°C.

Table 1 also lists the results obtained for HMW (242–300) PAHs. The average recoveries retained on a QFF were 76–114% at 20°C and 75–100% at 35°C, while those trapped within PUF plugs and backup filters were ND or trace amounts at 20°C and ND or up to 17% at 35°C. Thus, at both

temperatures, HMW PAHs spiked on a QFF were largely retained on the filter for a period of 24 hr. In addition, at 35°C, the recoveries of 4–5-ring PAHs trapped with PUF plugs and backup filters increased to 17% for 7-MeBaA (4-ring) and 3–6% for BeP, BaP, perylene, BbF + BjF and BkF (5-ring). This finding suggests that the vapor pressure of 7-MeBaA is the highest among the HMW PAHs. The slight increase in the recoveries of 5-ring PAHs at higher temperature is in good agreement with the results of a previous study.<sup>18</sup>

With a few exceptions, we obtained satisfactory recoveries of PAH compounds using the proposed sampler. In addition, the obtained gas–particle partitions of PAHs are in agreement with those reported in previous studies.<sup>15–18)</sup> Therefore, the proposed sampler would be suitable for investigations of atmospheric PAHs.



Fig. 2. Temporal Changes in the Concentration of  $\Sigma$ 28PAH (a) Each PM fraction (PM<sub>>10</sub>, PM<sub>2.5-10</sub>, PM<sub>2.5</sub>) and (b) the gaseous phase during August 2006 and February 2007.

### Application of the Proposed Sampler to Investigations of Atmospheric PAHs at a Roadside Site in Osaka, Japan

Figure 2 shows temporal changes in the concentrations of 28 PAH compounds ( $\Sigma$ 28PAHs) in size-fractionated PM fractions and the gaseous phase, as monitored at a roadside site in a heavy-traffic area in Osaka. The average values in each PM fraction (PM<sub>>10</sub>, PM<sub>2.5-10</sub> and PM<sub>2.5</sub>) and the gaseous phase were 0.53 ± 0.67, 1.19 ± 1.24, 9.86 ± 8.31 and 51.52 ± 25.97 ng/m<sup>3</sup>, respectively. The average  $\Sigma$ 28PAH concentration in the gaseous phase was approximately five times as high as the sum of those in the three PM fractions. Among the fractions, the  $\Sigma$ 28PAH concentration in fine particles (PM<sub>2.5</sub>) was roughly an order of magnitude higher than those in coarse particles (PM<sub>>10</sub> and PM<sub>2.5-10</sub>).

Figure 2 also shows that PAH concentrations in the PM fractions increased from summer to winter. Increases in PAH concentrations are generally caused by additional emission sources such as heating, intensification of PAH emissions from the main sources, and/or meteorological conditions.<sup>10, 29, 30)</sup> In terms of the present sampling site, there are no sources of PAHs (e.g., incinerators and factories) in addition to motor vehicles, and the use of vehi-

**Table 2.** Pearson Product-moment Correlation Coefficients between the Concentrations of Σ28PAHs and Meteorological Conditions

par-PAHs <sup>a</sup> )	gas-PAHs <sup>b)</sup>
$-0.85^{*}$	-0.61**
$-0.71^{*}$	-0.64**
-0.50	-0.37
-0.61**	-0.22
	<i>par</i> -PAHs <sup><i>a</i>)</sup> -0.85* -0.71* -0.50 -0.61**

*a*) Particulate PAHs (sum of PAH concentrations in  $PM_{>10}$ ,  $PM_{2.5-10}$  and  $PM_{2.5}$ ). *b*) Gaseous PAHs. \* $p \le 0.05$ , \*\*p < 0.01.

cles in this area shows no seasonal change.<sup>31)</sup> Therefore, the observed temporal change is attributable to meteorological conditions. Consequently, we calculated the Pearson product-moment correlation coefficients between the concentrations of particulate or gaseous  $\Sigma$ 28PAHs and meteorological conditions (Table 2). The sum of  $\Sigma$ 28PAH concentrations in the three PM fractions showed stronger negative correlations with ambient temperature and sunshine amount than with the other parameters. Therefore, the increase in PAH concentrations in PM fractions during winter is mainly attributable to a reduction in their photolytic degradation due to a decrease in sunshine amount and changes in gas–particle partitions.<sup>10, 17, 29, 30)</sup>

 $\Sigma$ 28PAH concentrations in the gaseous phase were also high in winter; however, a high concentration was also observed on 16–17th August, during summer. Indeed,  $\Sigma$ 28PAH concentrations in the gaseous phase showed negative correlations with ambient temperature and sunshine amount, although the relationships were weaker than those in the case of particulate PAHs (Table 2). As a result, the observed temporal changes in the concentrations of gaseous PAHs may have a weak relationship with meteorological conditions, as described previously in a study conducted at Herakleion, Greece.<sup>17</sup>)

We calculated the percentage of gaseous PAHs relative to the sum of the four fractions ( $PM_{>10}$ ,  $PM_{2.5-10}$ ,  $PM_{2.5}$  and gaseous phase) for each of the representative compounds considered in this study in order to understand their gas–particle partitioning (Fig. 3). Between August and February, LMW PAHs with 3–4 aromatic rings (e.g., fluorene, Ph, Ant and MePh isomers) occurred mainly in the gaseous phase, while HMW PAHs with 5–7 aromatic rings occurred mainly in the PM fractions. The other PAHs (e.g., Flu, Py, BaA and Trip + Chr) occurred in both the gaseous and PM fractions. These observations are in agreement with the find-



Fig. 3. Average Ratio of PAH Concentration in the Gaseous Phase to the Sum of the Concentrations in Four Fractions (PM<sub>>10</sub>, PM<sub>2.5-10</sub>, PM<sub>2.5-10</sub>, PM<sub>2.5</sub> and the gaseous phase) for Each Representative Compound Error bars show 2 standard deviations (SDs).



**Fig. 4.** Average Ratio of the Concentration of Each PAH in PM<sub>2.5</sub> to the Sum of the Concentrations in Three PM Fractions Error bars show 2 SDs.

ings of previous studies.<sup>8–11, 14–19)</sup>

Figure 4 shows the percentages of PAHs associated with  $PM_{2.5}$  relative to the sum of  $PM_{>10}$ ,  $PM_{2.5-10}$  and  $PM_{2.5}$  for each representative compound, with the exceptions of fluorene, Ph, Ant and MePh isomers, which mainly occurred in the gaseous phase. The percentage of particulate PAHs in PM<sub>2.5</sub> shows a rough increase with increasing MW. In particular, the lowest values (approximately 65%) were observed for semi-volatile Flu and Py. Similar trends have been reported previously.<sup>4,6</sup>

To understand the gas-particle and particle-size distributions of semi-volatile PAHs (Flu, Py, BaA and Trip + Chr) in the PM and gaseous phases, we plotted their temporal changes (Fig. 5). On 16–17th August 2006, Flu and Py occurred mainly in the gaseous phase. From September onward, Flu and Py showed a gradual shift from the gaseous phase to the PM fractions, in accordance with decreasing ambient temperature, attaining similar levels in PM fractions to those recorded during winter, especially during January and February [Fig. 5 (a) and 5 (b)].

A similar trend was observed for BaA and Trip + Chr [Fig. 5 (c) and 5 (d)]. On 16–17th August, the contents of BaA and Trip + Chr in the gaseous phase were similar to those in the PM fractions. Subsequently, the content of BaA and Trip + Chr in the gaseous phase showed a gradual decrease with decreasing ambient temperature, attaining a value of approximately 20% on 13–14th February.

Regarding the size distribution, Flu and Py occurred mainly in fine particles (PM<sub>2.5</sub>) during summer and autumn. In particular, their concentrations on 16–17th August were 0.08 and 0.09 ng/m<sup>3</sup>, respectively, in fine particles and 0.01 ng/m<sup>3</sup> and ND, respectively, in coarse particles (PM<sub>>10</sub> and PM<sub>2.5–10</sub>). From September onwards, concentrations of Flu and Py in both fine and coarse particles showed a gradual increase, attaining (on 23– 24th January) 1.96 and 2.22 ng/m<sup>3</sup>, respectively, in fine particles and 1.09 and 1.11 ng/m<sup>3</sup>, respectively, in coarse particles. BaA and Trip + Chr occurred at much higher concentrations in fine particles than in coarse particles, although the concentration in





coarse particles did not show a marked increase over time. Hien et al.<sup>4)</sup> reported that the percentage of semi-volatile PAHs associated with fine particles  $(d_{ae} \leq 2.1 \,\mu\text{m})$  at a roadside site in Ho Chi Minh City (HCMC), Vietnam, was approximately 50-60% for Flu, Py and Trip in the dry and rainy seasons, and was approximately 60% for BaA and Chr in the dry season and 70-80% in the rainy season. Wu et al.<sup>6)</sup> investigated the percentages of PAHs associated with fine particles ( $d_{ae} \le 2.1 \,\mu\text{m}$ ) to those with  $PM_{10}$  ( $d_{ae} < 10 \,\mu$ m) during winter at a roadside site in Tianjin, China, yielding values of approximately 80% for Flu and Py, and approximately 90% for BaA and Chr. Thus, the above studies revealed different size-distribution characteristics in each city.

Atmospheric PAHs generally originate from combustion sources that produce fine particles; consequently, PAHs may occur in the gaseous phase and/or ultrafine particles immediately after PM is emitted into the air.<sup>4-6)</sup> Among the PAHs, LMW compounds with relatively high volatility may associate with larger particles via vaporisation from fine particles followed by their condensation on coarse particles, whereas HMW compounds are largely retained on fine particles because of their low vapor pressure.<sup>4-6)</sup> The redistribution behavior of semivolatile PAHs is complicated, and affected by factors such as ambient temperature, relative humidity and sunshine quantity.<sup>4-6)</sup> The observed low contents of semi-volatile PAHs in coarse particles during summer may also reflect their insufficient LODs. The measured concentrations of Flu and Py in coarse particles on 16-17th August were similar to or lower than their LODs (Flu and Py: 0.01 and 0.01 ng/m<sup>3</sup>, respectively). Thus, the analytical sensitivity of the proposed sampler appears to be insufficient in terms of determining low levels of semi-volatile PAHs in coarse particles, especially during summer. This problem is easily addressed by extending the sampling time from 24 hr to several days, taking care to avoid artifact formation, as reported previously,<sup>4, 6, 12</sup>) whereby filters are changed every 24 hr and at each stage all the filters are submitted to an extraction procedure.

In the present study, we used a new sampling device to measure temporal changes in the gas– particle and particle-size distributions of PAHs in the Osaka area, Japan. To date, only a small number of samples have been obtained with the aim of gaining a detailed understanding of the behavior of atmospheric PAHs. Further studies are underway in this regard.<sup>36</sup>

Acknowledgements This study was supported by the Commerce and Industry Promotion Office, Department of Commerce, Industry and Labor, Osaka Prefectural Government. We also thank the staff of the Examination Center for Environmental Pollution and Health, Higashi-Osaka City, for their corporation.

#### REFERENCES

- 1) Waller, R. E. (1952) The benzpyrene content of town air. *Br. J. Cancer*, **6**, 8–21.
- 2) Agency for Toxic Substances and Disease Registry (ATSDR) (1995) *Toxicological Profile for Polycyclic Aromatic Hydrocarbons*.
- 3) Kawanaka, Y., Matsumoto, E., Sakamoto, K., Wang,

N. and Yun, S. (2004) Size distributions of mutagenic compounds and mutagenicity in atmospheric particulate matter collected with a low-pressure cascade impactor. *Atmos. Environ.*, **38**, 2125–2132.

- 4) Hien, T. T., Thanh, L. T., Kameda, T., Takenaka, N. and Bandow, H. (2007) Distribution characteristics of polycyclic aromatic hydrocarbons with particle size in urban aerosols at the roadside in Ho Chi Minh City, Vietnam. *Atmos. Environ.*, **41**, 1575–1586.
- 5) Zielinska, B., Sagebiel, J., Arnott, W. P., Rogers, C. F., Kelly, K. E., Wagner, D. A., Lighty, J. S., Sarofim, A. F. and Palmer, G. (2004) Phase and size distribution of polycyclic aromatic hydrocarbons in diesel and gasoline vehicle emissions. *Environ. Sci. Technol.*, **38**, 2557–2567.
- Wu, S. P., Tao, S. and Liu, W. X. (2006) Particle size distributions of polycyclic aromatic hydrocarbons in rural and urban atmosphere of Tianjin, China. *Chemosphere*, **62**, 357–367.
- Ohura, T., Amagai, T., Sugiyama, T., Fusaya, M. and Matsushita, H. (2004) Characteristics of particle matter and associated polycyclic aromatic hydrocarbons in indoor and outdoor air in two cities in Shizuoka, Japan. *Atmos. Environ.*, 38, 2045–2054.
- 8) Kishida, M., Imamura, K., Takenaka, N., Maeda, Y. and Viet, P. H. (2006) Atmospheric polycyclic aromatic hydrocarbons in air samples of Hanoi. In Annual Report of FY 2006: Joint research on environmental science and technology for the earth, The core university program between Japan Society for the Promotion of Science and National Centre for Natural Science and Technology (Fujita, M. and Viet, P. H., Eds.), Osaka, Japan, pp. 35–40.
- 9) Kishida, M., Imamura, K., Takenaka, N., Maeda, Y., Viet, P. H. and Bandow, H. (2008) Concentrations of atmospheric polycyclic aromatic hydrocarbons in particulate matter and the gaseous phase at roadside sites in Hanoi, Vietnam. *Bull. Environ. Contam. Toxicol.*, **81**, 174–179.
- 10) Kishida, M., Mio, C., Imamura, K., Kondo, A., Kaga, A., Shrestha, M. L., Takenaka, N., Maeda, Y., Sapkota, B., Fujimori, K., Shibutani, Y. and Bandow, H. (2009) 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**, 67–82.
- Park, J. S., Wade, T. L. and Sweet, S. (2001) Atmospheric distribution of polycyclic aromatic hydrocarbons and deposition to Galveston Bay, Texas, USA. *Atmos. Environ.*, **35**, 3241–3249.
- 12) Sanderson, E. G. and Farant, J.-P. (2005) Atmospheric size distribution of PAHs: evidence of a

high-volume sampling artifact. *Environ. Sci. Tech*nol., **39**, 7631–7637.

- Sun, Q., Alexandrova, O. A., Herckes, P. and Allen, J. O. (2009) Quantitative extraction of organic tracer compounds from ambient particulate matter collected on polymer substrates. Talanta, 78, 1115– 1121.
- 14) Cotham, W. E. and Bidleman, T. F. (1995) Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in air at an urban and a rural site near Lake Michigan. *Environ. Sci. Technol.*, 29, 2782–2789.
- 15) Mandalakis, M., Tsapakis, M., Tsoga, M. and Stephanou, E. G. (2002) gas-particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece). *Atmos. Environ.*, **36**, 4023–4035.
- 16) Tsapakis, M. and Stephanou, E. G. (2003) 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, 4935–4944.
- 17) Tsapakis, M. and Stephanou, E. G. (2005) Occurrence of gaseous and particulate polycyclic aromatic hydrocarbons in the urban atmosphere: study of sources and ambient temperature effect on the gasparticle concentration and distribution. *Environ. Pollut.*, **133**, 147–156.
- 18) Yamasaki, H., Kuwata, K. and Miyamoto, H. (1982) Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.*, 16, 189–194.
- Yamasaki, H., Kuwata, K. and Miyamoto, H. (1978) Collection of atmospheric polycyclic aromatic hydrocarbons using polyurethane foam plugs. *Bunseki Kagaku*, 27, 317–321 (in Japanese).
- 20) Yamasaki, H. (1986) Futarusanesuteru oyobi takanhokozokutankasuiso niyoru taikiosen ni kansuru kisotekikenkyu, Ph. D. Thesis, Osaka Prefecture University, Osaka, Japan (in Japanese).
- 21) Galarneau, E., Haener, T., Shoeib, M., Kozma, M. and Lane, D. (2006) A preliminary investigation of sorbent-impregnated filters (SIFs) as an alternative to polyurethane foam (PUF) for sampling gas-phase semivolatile organic compounds in air. *Atmos. Environ.*, **40**, 5734–5740.
- 22) Araki, Y., Tang, N., Ohno, M., Kameda, T., Toriba, A. and Hayakawa, K. (2009) Analysis of atmospheric polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in gas-particle phases separately collected by a high-volume air sampler equipped with a column packed with XAD-4 resin. J. Health Sci., 55, 77–85.

- 23) Sugiyama, T., Amagai, T., Matsushita, H. and Soma, M. (1999) Size distribution of indoor airborne particulates collected by a low flow rate cascade impactor. *Indoor and Built Environment*, 8, 361–369.
- 24) Kameda, T., Akiyama, A., Toriba, A., Tang, N. and Hayakawa, K. (2010) Determination of particulateassociated hydroxynitropyrenes with correction for chemical degradation on a quartz fiber filter during high volume air sampler. *Int. J. Environ. Anal. Chem.*, (in press).
- 25) Lohmann, R., Harner, T., Thomas, G. O. and Jones, K. C. (2000) A comparative study of the gas-particle partitioning of PCDD/Fs, PCBs, and PAHs in the U.K. atmosphere. *Environ. Sci. Technol.*, **34**, 4943– 4951.
- 26) Kishida, M., Imamura, K., Takenaka, N., Maeda, Y., Viet, P. H., Kondo, A. and Bandow, H. (2010) Characteristics of the abundance of polychlorinated dibenzo-*p*-dioxin and dibenzofurans, and dioxinlike polychlorinated biphenyls in sediment samples from selected Asian regions in Can Gio, Southern Vietnam and Osaka, Japan. *Chemosphere*, **78**, 127– 133.
- 27) Kishida, M., Imamura, K., Maeda, Y., Lan, T. T. N., Thao, N. T. P. and Viet, P. H. (2007) Distribution of persistent organic pollutants and polycyclic aromatic hydrocarbons in sediment samples from Vietnam. *J. Health Sci.*, **53**, 291–301.
- 28) Saito, N., Sasaki, K., Harada, K., Yoshinaga, T. and Koizumi, K. (2003) Perfluorooctane sulfonate concentrations in surface water in Japan. *Arch. Environ. Contam. Toxicol.*, 45, 149–158.
- 29) Kishida, M., Mio, C., Fujimori, K., Imamura, K., Shibutani, Y. and Bandow, H. (2009) Temporal change in atmospheric polycyclic aromatic hydro-

carbons in particulate matter from an urban location of Osaka, Japan: estimation of causes of a significant increase in their concentrations in the winter season. *Journal of Environmental Chemistry*, **19**, 543–553.

- 30) Hien, T. T., Nam, P. P., Sadanaga, S., Kameda, T., Takenaka, N. and Bandow, H. (2007) Comparison of particle-phase polycyclic aromatic hydrocarbons and their variability causes in the ambient air in Ho Chi Minh City, Vietnam and in Osaka, Japan, during 2005–2006. *Sci. Total Environ.*, **382**, 70–81.
- 31) Department of Urban and Public Works, Osaka Prefectural Government (2005) *Traffic Census* (in Japanese).
- 32) Japan Meteorological Agency, Government of Japan, Kisho Tokei Joho (in Japanese), http://www. data.jma.go.jp/obd/stats/etrn/index.php
- 33) Ministry of the Environment (MOE), Government of Japan (2008) Manual for the determination of atmospheric hazardous chemicals (in Japanese).
- 34) Perraudin, E., Budzinski, H. and Villenave, E. (2007) Kinetic study of the reactions of ozone with polycyclic aromatic hydrocarbons adsorbed on atmospheric model particles. *J. Atmos. Chem.*, **56**, 57– 82.
- 35) Perraudin, E., Budzinski, H. and Villenave, E. (2005) Kinetic study of the reactions of NO2 with polycyclic aromatic hydrocarbons adsorbed on silica particles, *Atmos. Environ.*, **39**, 6557–6567.
- 36) Research Institute of Environment, Agriculture and Fisheries, Osaka Prefectural Government *Results* of evaluation of research subjects performed in 2008 (in Japanese), http://www.epcc.pref.osaka.jp/ reaf/hyouka/h20kadaihyouka.pdf