Distribution of polycyclic aromatic hydrocarbons concentrations simultaneously obtained in gas, rainwater and particles

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Abstract This study reported the distribution of polycyclic aromatic hydrocarbons (PAHs) concentrations simultaneously obtained in gas/rain/particle in rain event from 2010 to 2012 in Osaka, Japan. A sampling method for rain and the materials of a rain collector were also surveyed. Benzene and a glass bottle were used to prevent the decrease of PAHs in rainwater. The average concentration of Σ9PAHs in rainwater ranged between 17.49 and 646.52 ng dm^{-3}. The mean ratio of these Σ9PAHs in gas versus particles was 77.9 and 68.3 % during rain and no rain, respectively. During rain, the PAHs in particles were scavenged by rain and were incorporated via washout by collision with each other. Therefore, the ratio of PAHs in rainwater was similar to that in particles. The low molecular weight LMW-PAHs from gas were recognized as being dissolved in rain but did not affect the ratio of PAHs in rain. Four rings PAH were dominant in gas/rain/particles. The seasonal variation of Σ9PAHs in rainwater was reported and discussed, and the PAHs levels during the winter and spring were higher compared with that of summer and autumn. Furthermore, the sampling method of PAHs in snow is also developed.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been identified as persistent organic pollutants and are found ubiquitously in the atmospheric environment. They have been a concern because of their carcinogenic and mutagenic properties (Rianawati and Balasubramanian 2009; Liu et al. 2006). PAHs are mainly formed by incomplete combustion processes and are also derived from industrial processes, burning natural gas, cooking gas, forest fire, and oil refining (Liu et al. 2006).

PAHs are transported and deposited in the atmosphere by the movement of clouds, aerosol, particles, and gas (Olivella 2006). Considering the differences in their physical properties, chemical properties, meteorological conditions, and source of emissions, the distribution of PAHs in gas, rain, and particles can vary. In Osaka, Japan, the concentrations of several PAHs in particles and gas have been investigated (Kishida et al. 2009b; Hien et al. 2007a; Kishida et al. 2011), but PAHs in rainwater have not been reported.

There are vast reports of PAH concentrations in solely rainwater, which showed the different concentration in different regions. The concentration of Σ16PAHs in Singapore was 5–162 ng dm^{-3} in rainwater (Basheer et al. 2003). A study at Brno, Czech Republic, showed that the concentration of Σ15PAHs in rainwater varied between 2.8 and 571 ng dm^{-3} (Škrdlíková et al. 2011). The concentrations of Σ17PAHs were quantitatively determined at two sites in Alsace (Eastern France) and varied between 1.6 and 968.1 ng dm^{-3} (Delhomme et al. 2007). The average concentrations of Σ13PAHs was between 72.90 and 94.24 ng dm^{-3} at Mount Taishan, China (Wang et al. 2010). Some previous studies

reported PAH concentration in gas/rain/particle but no simultaneous rain event. Gas and particle were collected during dry period, whereas rainwater was collected during rainy period using dry and wet deposition automatic sampler between 2 and 4 weeks (Park et al. 2001) and 15 days (Birgül et al. 2011). In other reports, they were investigated concurrently but not separating gas and particle (Sahu et al. 2004) or investigated during storm event (Poster and Baker 1995a). This study described distribution of PAH concentration in gas/rain/particle simultaneously collected during rain and discussed PAH concentration in gas and particles during rain and no rain.

Various methods were used to collect rain or storm water, and chemicals were sometimes added to avoid any decreases in PAH levels during sampling or storage. Generally, solid-state extraction is used to collect PAHs in rain. However, large amounts of rainwater are required to measure low concentrations of PAHs in rain, and therefore, a liquid–liquid extraction method was adopted. A wet-deposition sampler was sometimes used for PAHs sampling (Rianawati and Balasubramanian 2009; He and Balasubramanian 2010; Birgül et al. 2011; Cereceda-Balic et al. 2002; Park et al. 2001). The addition of Thymol (400 mg dm^{-3} $C_{10}H_{14}O$) or storage at 4 °C was used (Rianawati and Balasubramanian 2009; Olivella 2006; Huang et al. 2009). We also investigated the effects of the sampling methods on PAHs in rainwater and snow because some PAHs were known to evaporate during sampling or storage. We report here the more correct sampling method of PAHs in rainwater and snow. Furthermore, distribution of PAHs in gas, rainwater, and particles and removal process of PAHs from the atmosphere to the ground were discussed.

Experimental procedures

Sampling location and sampling

Gas, rainwater, and particles were collected on the roof of the B5 building, Nakamozu Campus, Osaka Prefecture University, Sakai, Japan, which is approximately 18 m in height. The campus is located in a residential area, not near any special industrial zones, and by one side of a two-lane national road. Twenty-six rainwater samples were collected from July 2010 to December 2012. During this time, 16 gas and particle samples were obtained during rain events, and 7 gas and particle samples were obtained when it was not raining.

PAHs in particles and gas were collected using a Kimoto Electric Co. Model 120H high volume air sampler with a flow rate of ca. 1 m^3 min^{-1}. A quartz fiber filter (203×254 mm^2; Advantec MFS, QR 100) was used to collect particles. The filters were equilibrated in a desiccator at room temperature for 48 h and weighed before and after sampling. Each filter was wrapped in an aluminum foil envelope and placed in a

lockable polypropylene bag until extraction (Hien et al. 2007b). PAHs in the gas were collected by double polyurethane foams for dioxin (PUF; 4.7 cm in height×8.5 cm in diameter in each; Shibata Science Co., Ltd.), which were placed inside the high-volume air sampler. The PUF was wrapped in an aluminum foil envelope and placed in a lockable polypropylene bag until extraction. The sampling methods for rainwater are shown schematically in Fig. 1a. The maximum sampling time was 24 h. The rain sampler was rinsed with methanol and pure water and set outside just after a rain started, and collection was performed during the rain or just after the rain stopped. Before sampling the rainwater, 200 cm^3 of benzene was added to a 3-l brown bottle. Rainwater was collected in the bottle and transferred immediately to the laboratory for storage at 4 °C and was analyzed as soon as possible. The sampling period of gas and particles during rain was the same as that of rain.

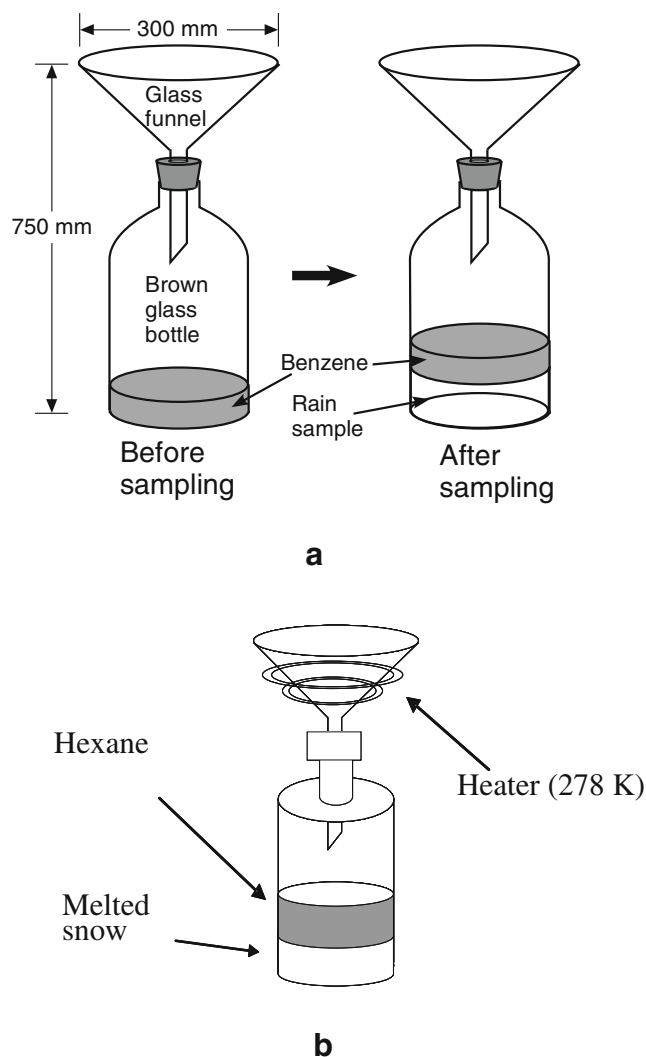A snow sampler is shown in Fig. 1b, and snow samples were collected in Fukui, Osaka in winter 2010 and winter

Fig. 1 Schematic diagram of the rainwater sampler (**a**) and snow sampler with heater (**b**)

2011. In order to investigate the evaporating PAHs from snow during melting and storage, two different experiments were conducted. One is for evaporation during sampling and melting, and one is for evaporation during melting and storages. In investigation of evaporating PAHs during sampling and melting snow was (1) directly collected in a stainless steel vat (20× 25×5 cm in height), (2) collected in a stainless steel vat (20× 25×5 cm in height) with hexane heated at 278 K(benzene cannot be used because its freezing temperature is approximately 279 K, 3) melted in a heated stainless steel funnel (30 cm in diameter at 278 K), and then melted sample was introduced to the vessel with hexane. In observing evaporation during storage, snow was collected and melted in vessels with and without addition of hexane.

Reagents

PAH standards were purchased from Supelco Standard Chemical. Pure water was prepared by Milli-Q Labo using distilled water (resistively, ≥18.2 MΩ cm). All solvents and chemicals used were purchased from Wako Chemical Ind., Ltd in high-performance liquid chromatography (HPLC) grade or reagent grade quality and used as received.

Extraction and determination of PAHs

In this study, nine PAHs with four to six aromatic rings (fluoranthene (Flr), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[ah]anthracene (DahA), and benzo[ghi]perylene (BghiP)) were investigated.

The filter from the high-volume air sampler was cut into small pieces (exactly 1/8 of the sampling area). The filter was immersed in benzene/ethanol (3/1, v/v) solution and extracted by ultrasonication for 10 min; the extracted solution was then filtered. The filter was extracted again by ultrasonication in

hexane for 10 min, and the extracted solution was filtered. Both solutions were filtered using ADVENTEC PTFE filter, T050A047A (47 mm i.d. and 0.5 μm in pore size) to remove solid substances. The filtrate was purified using 100 cm^3 of 5 % NaOH aqueous solution, followed by 100 cm^3 of 20 % H_2SO_4 aqueous solution and then 100 cm^3 of pure water. The water remaining in the extract was removed by passing through 5 g Na_2SO_4 solid and was concentrated to approximately 3 cm^3 using a rotary evaporator. The extract was then dried under a gentle stream of nitrogen. Finally, 0.5 cm^3 of methanol was added and mixed for at least 4 min before injection to HPLC. Blank samples of quartz filters were quantitatively examined for contaminated PAHs. The results showed no contamination of PAHs from the filters.

The limits of detection, which are defined as three standard deviations of five measurements of 50 mm^3 injections of 5– 20 ng cm^{-3} PAHs standard samples into the HPLC, for all nine PAHs were between 0.03 and 0.38 ng; the recoveries were between 80.0 and 102.7 % (Supplementary information, Table S1).

For PAHs in the gas absorbed by the PUF, a Soxhlet system was used to extract the PAHs using 400 cm^3 hexane for 12 h. The extract was filtered using an ADVENTEC PTFE filter, T050A047A (47 mm i.d. and 0.5 μm pore size). The filtrate was treated as described above.

The benzene phase in the rainwater sample, the hexane phase in melted snow sample as described in "Sampling location and sampling" were collected and shaken in a separating funnel for 10 min. The extracted solvent was treated as described above.

For the pretreated solutions, 50 mm^3 were injected into an HPLC with a fluorescence detector (JASCO-FP 2020 plus). The program was set to detect fluorescence at the optimum exciting and emission wavelength for each PAH from 270 to 450 nm (Supplementary information, Table S1). An Inertsil HPLC column, ODS-P-5-μm 3×250 mm was used with a

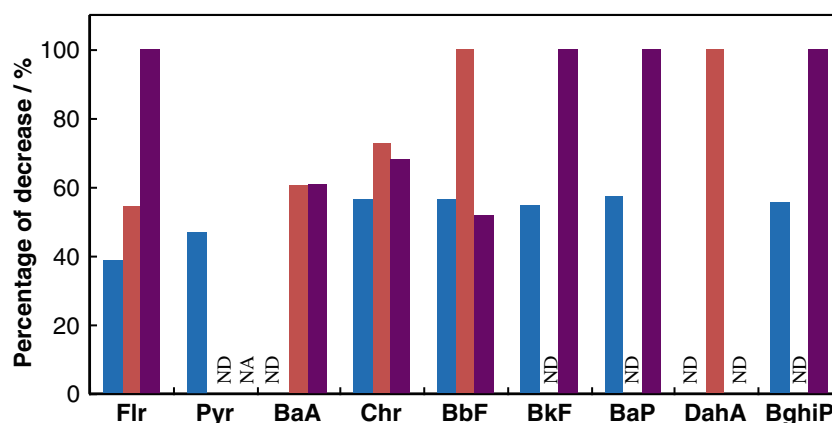**Fig. 2** The lost percentages of Σ9PAHs concentrations when benzene was not added to the rainwater. A volume of 200 cm^3 benzene was added to one of the sampling bottles before sampling, and no solvent was added to the other sampling bottle. *Blue bars*, 20 Jan 2010; *brown bars*, 28 Jul

2010; and *purple bars*, 13 Sep 2010. BaA and DahA from 20 Jan; Pyr, BkF, BaP, and BghiP from 28 Jul; and DahA from 13 Sep were all below the detection limits in the bottle with benzene added. *NA* not analyzed, *ND* not detected

Fig. 3 Recovery of PAHs from standard addition into natural rain samples. The samples were collected on 25th, 27th, and 29th August, 2008 at the Osaka Prefecture University. The volumes of the sample were 300, 220, and 1,180 cm^3, respectively. *Error bars* show 1 standard deviation
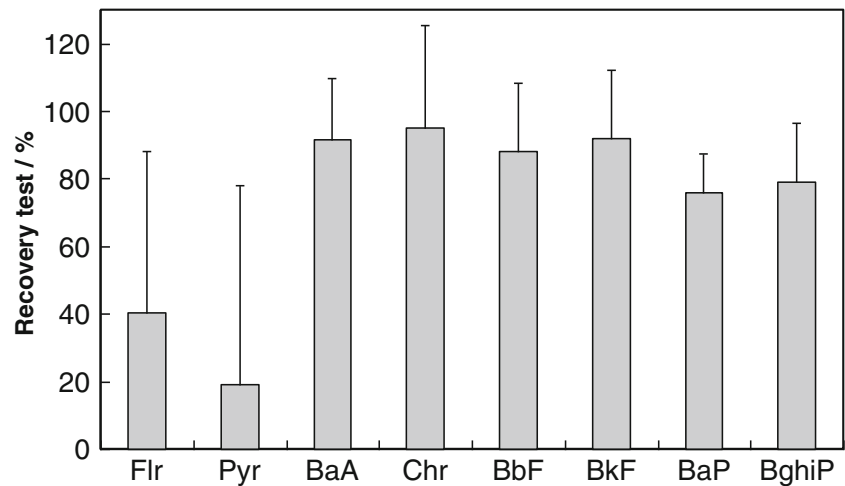
column oven (CTO-10AS-Vp Shimadzu) temperature of 40 °C. The mobile phase was a mixture of MeOH/H$_2$O (17:3, *v/v*). The flow rate of the mobile phase was 0.7 cm^3 min^{-1}.

## Result and discussions

Sampling method of PAHs in rainwater

Typically, the rainwater sample was collected between 6 and 10 h, however, PAHs are semi-volatile and hydrophobic. Therefore, the loss of PAHs during sampling was investigated. Preliminary experiments confirmed the disappearance of PAHs from rain samples. Benzene was added into the sampling bottle. The contamination of gaseous and particulate PAHs into benzene were negligible during the rain sampling time of several hours had been confirmed. Experiments were carried out by two methods, with 200 cm^3 and without benzene added into sampling glass bottles. Figure 2 shows the

percentage decrease of nine PAH concentrations when benzene was not added. In the winter, the samples were collected on the 20th of January 2010 (average temperature was 4 °C), and individual PAH decreased from 38.85 to 57.32 %. In the summer, samples were collected on 28 July (average temperature was 25.1 °C) and 13 September (average temperature was 27.1 °C), 2010. Most of the Flr, BkF, BAP, and BghiP were lost from the sample when benzene was not added. Even the higher molecular weight PAHs were lost from the rainwater sample during sampling without the addition of benzene.

Decomposition of PAHs in water was investigated. As the temperature during summer is higher, the PAHs are then easily evaporated or decomposed. However, substantial decreases in PAH concentrations were not confirmed within a few days. We concluded that decreases in PAH levels in the rain sampler were not due to decomposition in water but due to evaporation. The decrease of PAH concentrations during several rain events using the same method with several kinds of organic solvent including hexane, toluene and benzene was investigated.

Fig. 4 Relative concentrations of PAHs measured after 24 h in the dark in a stainless bottle, a PTFE bottle, and a polypropylene bottle compared with those in a glass bottle. *Green bars*, stainless steel; *white bars*, PTFE; and *blue bars*, polypropylene
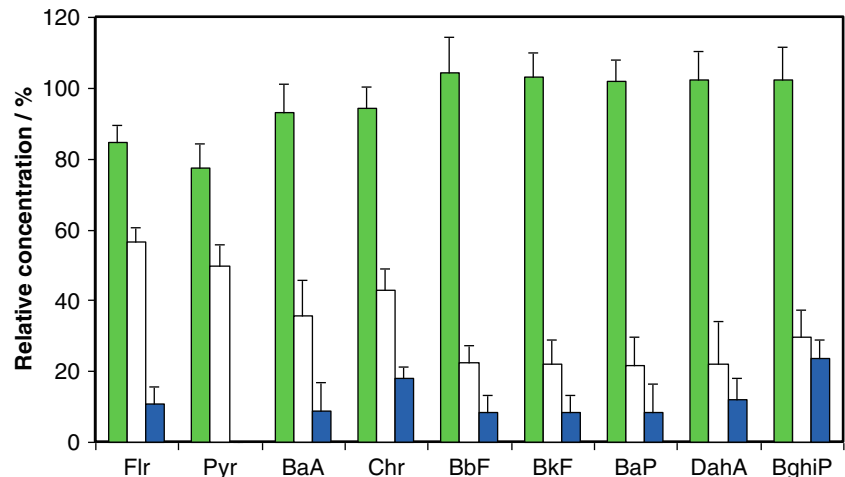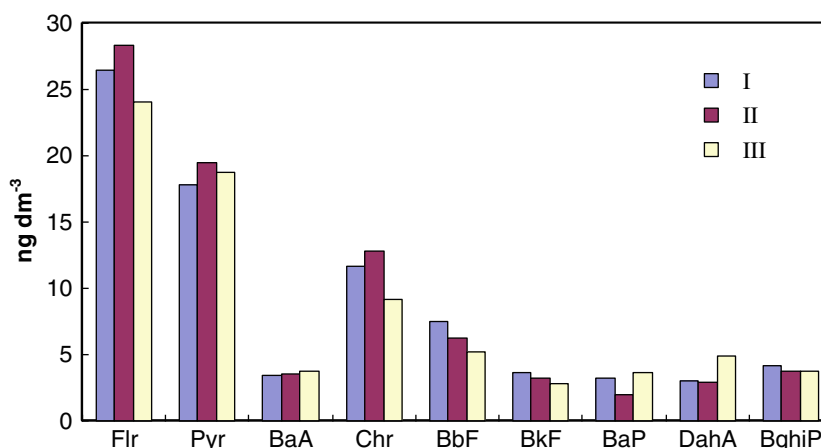
Fig. 5 Concentrations of PAHs obtained with three different sampling methods at Osaka Prefecture University on 14 February 2011. *I*, Collected snow sample directly with a stainless vat, added hexane, and then melted in a laboratory (volume of the sample was 2,104 cm^3). *II*, Collected snow sample with a stainless vat with hexane and melted in a laboratory (volume of the sample was 2,116 cm^3). *III*, Collected with melting snow sample with a heated funnel, and melted sample was kept in a bottle with hexane (volume of the sample was 745 cm^3)

Hexane is easy to evaporate so it cannot be used for long time sampling. Conversely, toluene is difficult to evaporate in clean-up and concentrated step. Therefore benzene should be added to minimize the evaporation of PAHs from rain samples during sampling.

It is believed that polyethylene, polypropylene, and other plastic bottles and tubing cannot be used to analyze organic compounds because of adsorption. The effect of materials on the PAHs collected from rain was confirmed. Figure 3 shows the recovery of PAH standards added to natural rain samples collected by a glass and a polyethylene bottles. Known amounts of PAHs were added to the glass and the polyethylene bottles including sampling. As shown in Fig. 3, the recovery of some PAHs was low; especially for Flr and Pyr, which were less than 50 %. Furthermore, benzene was added again to the bottles after the rain sample had been removed to examine whether the PAHs were absorbed to the wall of the bottle or not, and Flr and Pyr were detected in the extracted benzene. Polypropylene also

showed similar results. The adsorption of PAHs on several kinds of materials as a reservoir for storage was also investigated. Glass, stainless steel, polytetrafluoroethylene (PTFE) and polypropylene bottles were filled with 100–200 ng dm^{-3} of PAH standards in aqueous solution and left for 24 h in the dark. The relative concentrations of each PAH compared with those in the glass bottle are shown in Fig. 4. The recoveries of each PAH in a stainless steel bottle were good, but those in the plastic bottles, even PTFE, were very low. The glass or stainless steel is suitable for PAH sampling, and storage, but PTFE and polypropylene cannot be used for any analytical processing of PAHs.

Sampling method of PAHs in snow

The snow sample was collected on the vat and by using a funnel kept at 278 K in order to melt. In the latter stage, hexane was added in the collected bottle and the snow collected on the vat

Fig. 6 Percentage of decrease in PAHs concentrations in the snow samples melted with and without hexane addition on 16 January (Gifu Prefecture) and 11 March (Fuku Prefecture), 2010. The volume of gas collected ranged from 300 to 360 m^3. *Blue bars*, Σ4 rings; *brown bars*, Σ5 rings; and *white bars*, Σ6 rings
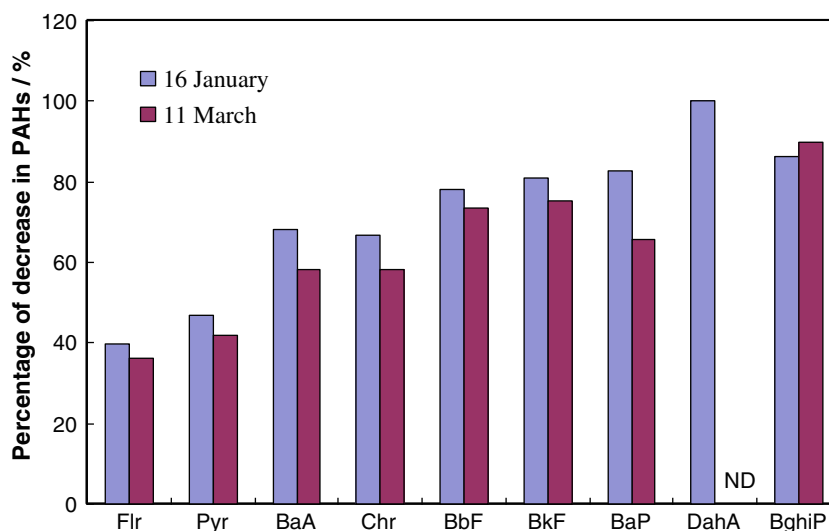
Table 1 The average concentration of Σ9PAHs during rain and no rain (nanograms per cubic meter)

PAHs	Particulate PAHs				Gaseous PAHs			
	Average	Max	Min	1σ	Average	Max	Min	1σ
Rain (n^a=16)								
Σ9PAHs	3.64	15.60	0.51	4.24	12.79	29.94	1.27	9.41
Σ4 ring	2.35	11.24	0.34	2.85	10.82	29.94	0.69	9.08
Σ5 ring	1.14	4.62	ND[b]	1.28	1.85	11.83	0.01	3.36
Σ6 ring	0.15	0.83	ND[b]	0.26	0.12	1.89	ND[b]	0.47
No rain (n^a=7)								
Σ9PAHs	1.64	0.42	0.71	0.92	3.27	7.70	1.32	2.12
Σ4 ring	0.97	2.88	0.39	0.86	3.23	7.70	1.26	2.11
Σ5 ring	0.55	0.95	0.32	0.21	0.04	0.13	ND[b]	0.05
Σ6 ring	0.12	0.79	ND[b]	0.30	ND[b]	ND[b]	ND[b]	ND[b]

The samples were obtained from 14 June 2011 to 28 December 2012, and the sampling volumes were 300 to 360 m³

[a] Number of samples

[b] Not detected

Table 2 The solubility of the various PAH compounds in aqueous solution (http://www.ccohs.ca/oshanswers/legisl/msdss.html; http://www.inchem.org/)

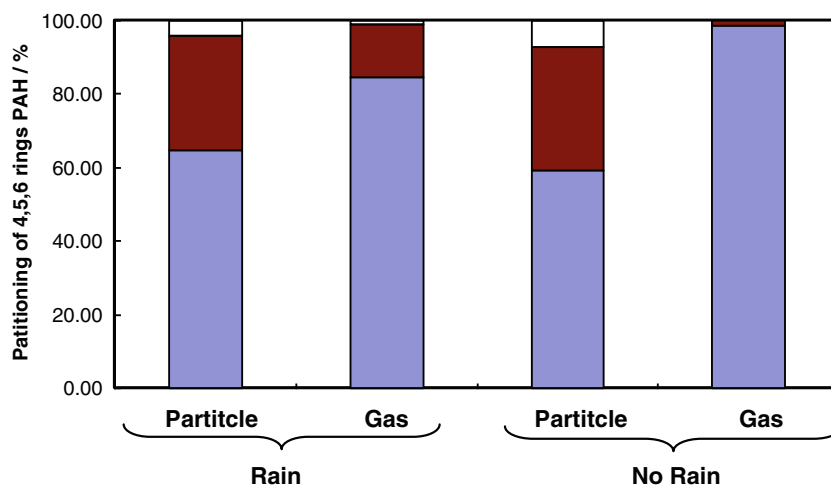| No.	PAHs compounds	MW (g mol⁻¹)	Boiling point (°C)	Solubility in water (μg dm⁻³)
1	FLr	202.3	375	265
2	Pyr	202.3	404	135
3	BaA	228.3	435	1.4
4	Chr	228.3	448	765
5	BbF	202.3	375	265
6	BkF	252.3	481	55
7	BaP	252.3	495	110
8	DahA	278.4	524	5.00
9	BghiP	276.3	500	0.26

was moved to the sealed vessel and melted after hexane was added in the vessel. As shown in Fig. 5, the results were almost similar. Conversely, the highest loss of PAHs was evaporated if hexane was not added in the vessel. It can be concluded that PAHs do not evaporate during sampling and melting but those evaporate during storage. Figure 6 shows the percentage of decrease in PAH concentrations in the snow samples melted with and without hexane addition. It can be concluded that hexane has to be added to melt snow and storage.

The difference in the PAH concentration in gas and particles between rain and no rain

Sixteen gas and particle samples were obtained during rain events, and 7 gas and particle samples were obtained when it was not raining, from 14 June 2011 to 28 December 2012.

Table 1 shows the results. The average concentration of the Σ9PAHs in particles during no rain was 1.64 ng m⁻³. This result was almost the same as the average concentrations measured in Osaka previously (Hien et al. 2007a; Kishida et al. 2011). The average concentration of the Σ9PAHs in the particles during rain was 3.64 ng m⁻³. The average concentration of the Σ9PAHs in the gaseous phase was 12.79 and 3.27 ng m⁻³ during rain and no rain, respectively. Distribution of the PAHs in the gaseous and particulate phases during rain differs from that in the case of no rain. The ratios of the Σ9PAH concentrations in the gaseous phase to those in particle phase are 3.51 and 1.99 during rain and no rain, respectively. During rain, the sunlight intensity is lower and photochemical reactions are decreased and decomposition of PAHs is less than during no rain. This is consistent with previous studies, which has been quantitatively reported that the most important process for the degradation of PAHs in the atmosphere is photochemical oxidation (F. DeWeist et al. 1981; Birgül et al. 2011). As a result, the concentrations of PAHs in both gaseous phase and particles during rain were higher than those during no rain (Franz and Eisenreich 1998; Panther et al.

Fig. 7 Partitioning of Σ4 rings, Σ5 rings, and Σ6 rings PAHs in gaseous phase and particles during rain and no rain from 14 Jun 2011 to 28 Dec 2012. The volume of gas collected ranged from 300 to 360 m³. *Blue bars*, Σ4 rings; *brown bars*, Σ5 rings; and *white bars*, Σ6 rings

Fig. 8 Distribution of individual PAH in rainwater, gas, and particle. Sixteen rain/gas/particle samples were collected between 30 Sep 2011 and 28 Dec 2012; 300 to 360 m³ gas and 185 to 1,275 cm³ rainwater were collected
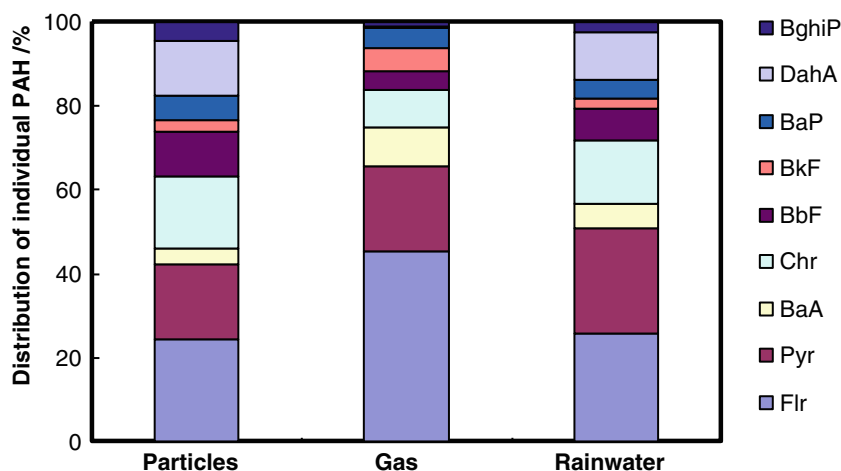
1999; Yang et al. 2010; Kishida et al. 2009a). It is speculated that gas and particle scavenging of PAHs by rain may not be considerably effective.

Figure 7 shows the partition of Σ4-, Σ5-, and Σ6-ring PAHs in gas and particles during rain and no rain. With four PAH compounds, the contribution of Σ4 rings are higher than Σ5 rings. One six-ring PAH was observed, but it is minor contribution in the atmosphere, especially in gaseous phase. During no rain, Σ4- and Σ5-ring PAH concentrations in the gaseous phase were 98.7 and 1.3 %, respectively, whereas Σ6-ring PAHs were not detected. During rain, Σ4-, Σ5-, and Σ6-ring PAHs concentrations in the gaseous phase were 84.6, 14.5, and 0.9 %, respectively. In contrast to observation in gaseous phase, the percentages of Σ4-, Σ5-, and Σ6-ring PAH concentrations in particles during rain and no rain were similar. Σ4-ring PAHs including Flr, Pyr, BaA, and Chr, which are LMW-PAHs are easier to dissolve in rain compared with high molecular weight HMW-PAHs, such as BbF, BkF, BaP, DahA and BghiP. Therefore, it is expected that the gaseous

phase LMW-PAHs contribution during rain becomes lower than that during no rain due to washout. Table 2 shows the solubility values of nine PAHs. Four-ring PAHs have higher solubility in water, and therefore, four-ring PAHs in the gaseous phase were dissolved in rain. As a result, PAH concentrations in gaseous phase decreased from 98.7 (no rain) to 84.6 % (rain).

Distribution of PAHs in gas, particle, and rainwater

Figure 8 shows the PAHs ratio in gas, rainwater, and particles during rain. The ratio in rain was similar to that in particles but differed from the ratio in the gaseous phase. This is likely because particles are incorporated into rain effectively while gaseous compounds pass through rain droplets with the air flow around them. Some LMW-PAHs in the gaseous phase can dissolve in rain because of diffusion, but most gaseous PAHs pass through the rain droplets. The contributions of the Σ4-ring PAHs were 64.7 and 73.4 % in particles and
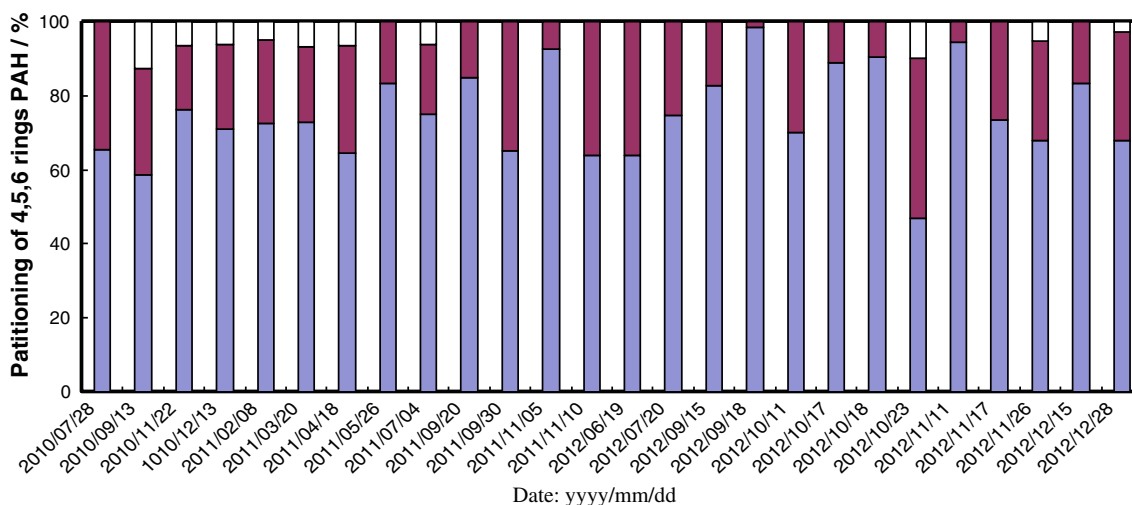

Fig. 9 Partitioning of aromatic rings number in rainwater. Twenty-six rainwater samples of 185 to 1,275 cm³ in volume were collected between 28 Jul 2010 and 28 Dec 2012. *Blue bars*, Σ4 rings; *brown bars*, Σ5 rings; and *white bars*, Σ6 rings
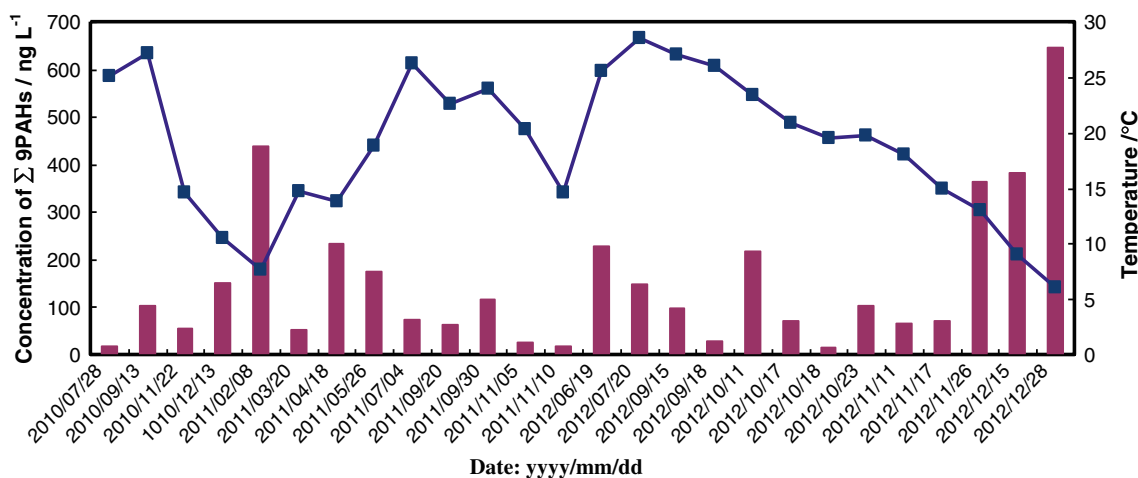
Fig. 10 Σ9PAHs concentrations in rainwater and temperature variation. Twenty-six rainwater samples of 185 to 1,275 cm^3 in volume were collected between 28 Jul 2010 and 28 Dec 2012. *Brown bars*, Σ9PAHs concentration and *blue squares and line*, temperature

rainwater, respectively, whereas those of the Σ5-ring PAHs were 31.2 and 24.7 %, and the contribution of the Σ6-ring PAHs were 4.1 and 1.9 %, respectively. The composition of PAHs in rainwater was similar with that in particles, and this could be due to the fact that the main source of PAHs in rainwater is particles, and only small amounts of PAHs in gaseous phase contribute to PAHs in rainwater. As mentioned above, particles are effectively incorporated by washout as a result of collision with each other, while gaseous compounds are not effectively washed-out by rain because they pass through the rain droplets with the air flow. The same conclusion has been reported by Poster and Baker (1995b). Σ4-ring PAH concentration was dominant with concentration of 84.6 %, whereas the Σ5- and Σ6-ring PAH concentrations were 14.4 and 1 % in the gaseous phase, respectively. The vast reported indicated that LMW-PAHs as four-ring PAHs were main component of PAHs in the atmosphere, because its sources were caused by vehicle emission and human activities. Therefore, four-ring PAHs were the highest concentration in the gaseous phase even in the rain (Sahu et al. 2004; Birgül et al. 2011).

Seasonal and temperature variation of PAHs in rainwater

Twenty-six rainwater samples were collected from 28 July 2010 to 28 December 2012. The partitioning of PAHs in the water is shown in Fig. 9. The concentration of Σ4-ring PAHs ranged from 66.8 to 98.5 %, the Σ5-ring PAH concentrations ranged between 1.5 and 43.3 %, and the Σ6-ring PAH concentrations ranged from lower than detection limit to 12.6 %. The partitioning of four-, five-, and six-ring PAHs in rain were similar to that shown in Fig. 8. Furthermore, the seasonal variation did not appear to significantly affect the results.

The Σ9PAH concentration in rainwater ranged from 17.49 to 646.52 ng dm^{-3}. This was lower than the Σ16PAH concentration of 1,218.1 (He and Balasubramanian 2010) and 375–

4,239 ng dm^{-3} (Rianawati and Balasubramanian 2009) measured in Singapore City, and the Σ14PAH concentration of 590 ng dm^{-3} in urban rain in Switzerland (Leuenberger et al. 1988). However, these concentrations were higher than the Σ14PAH concentration of 27.5 ± 2 and 75.4 ± 9 ng dm^{-3} in particles and dissolved phases, respectively, found in Northern Italy (Olivella 2006). Figure 10 shows that the Σ9PAH concentration in the rain during summer and autumn are lower than those during winter and spring. The highest concentration was obtained on 28 December 2012 when the temperature was the lowest (6 °C). During summer, the sun light is strong, and as a result the reaction with OH radical is active and leads to photolysis process. This causes the concentration of the PAHs to decrease. This result is in agreement with Chetwittayachan et al. (2002), who measured particulate PAHs concentration at traffic and normal sites in Tokyo, Japan These results showed a sharp decrease in the daytime and a gradual increase in the nighttime. Furthermore, for heating purposes, the thermal power plant using fossil fuels and heating using natural gas are increase in the winter those are one of the emission sources of PAHs.

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