Levels and Compositions of Polycyclic Aromatic Hydrocarbons in Rainwater and Their Implication for Aquatic Environments in Urban Area in Saitama, Japan

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ABSTRACT

In this study, we investigated concentrations and profiles of polycyclic aromatic hydrocarbons (PAHs) in rainwater and surface water samples collected in Saitama, an urban city located in Japan. The volume-weighted mean concentration of total PAHs in rainwater samples (dissolved + particulate) was 108.8 ng L⁻¹ with a range of 17.6–192.9 ng L⁻¹. Two and three benzene ring PAHs were predominantly detected, occupying 67.0% of the total concentration in rainwater samples. Individual PAH concentrations were negatively correlated with their $K_{ow}$ suggesting that low-molecular-weight PAHs are preferentially scavenged owing to the higher hydrophilicity. The toxic equivalent calculated based on the relative potencies of individual PAHs showed high toxic contributions by chrysene and benz[a]anthracene in the rainwater samples. Those PAHs levels in rainwater were comparable or higher than those in adjacent river water. Correlation coefficient of PAH signatures between rainwater and surface water samples was high particularly in the dissolved phase, supporting the source/sink relationships of PAHs between wet deposition samples and receiving waters. The mean deposition flux of PAHs was 2000 ng m⁻² and considered to increase with precipitation amounts.

ARTICLE HISTORY

Received 16 March 2021
Accepted 27 June 2021

KEYWORDS

Polycyclic aromatic hydrocarbons (PAHs); wet deposition; aquatic environments

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are composed of fused benzene rings and are a class of ubiquitous organic pollutants. Environmental pollution by PAHs in aquatic environments are of great concern from the view point of public health and environmental conservation because many are suspected to potentially exhibit mutagenicity and carcinogenicity. PAHs originate from numerous natural and anthropogenic environmental sources, such as incomplete combustion of fossil fuel, waste incineration, petroleum refining processes, and wild fires, with 520 Gg of estimated annual global atmospheric discharges. Owing to their widespread sources and persistent properties, PAHs have been detected in numerous environmental samples. Distribution of PAHs in aquatic environments have been widely reported in coastal sediments, lake and river surface water, seawater, and biota. Moreover, contentious exposure to parent PAHs lead to the biotransformation and accumulation of various hydroxylated metabolites in aquatic organisms. Surveys on historical trends of PAHs pollution levels have shown that PAHs have been
continuously discharged into aquatic environments\textsuperscript{4,11}. Therefore, the sources and fates of PAHs in aquatic environments remain problems that need to be addressed.

PAHs likely enter aquatic environments via various pathways including urban runoff\textsuperscript{12}, petroleum spill accidents\textsuperscript{13}, and industrial effluent discharges\textsuperscript{14}. Additionally, wet deposition, including washout and rainout, can be an alternative input pathway for PAHs in aquatic environments. Despite their hydrophobic properties, PAHs have been detected in precipitation samples, emphasizing the need for studies focused on migration processes of PAHs via wet deposition. For example, Skrdl\v{r}ková et al.\textsuperscript{15} detected PAHs in rainwater samples collected from the Czech Republic at mean concentrations of 93 ng L\textsuperscript{-1}. Moreover, PAHs have been detected at higher concentrations in precipitation samples compared to other organic pollutants, such as polychlorinated biphenyls, organochlorine pesticides, and polybrominated diphenyl ethers\textsuperscript{16–19}. Thus, investigating the transport behavior of PAHs via wet deposition processes is crucial to understanding their source and for controlling pollution in terrestrial and aquatic environments. The important and primary steps in evaluating migration processes of PAHs by wet deposition involve characterizing the concentrations, compositions, and fluxes of PAHs in precipitation. Although several studies have investigated the characteristics of PAHs wet depositions, it can differ as a function of meteorological and geographical conditions\textsuperscript{20,21}. Furthermore, the possible environmental effects of the input of PAHs in surface water should be considered\textsuperscript{22}. Many recent studies investigated wet deposition processes as a factor that contributes to mitigation and attenuation of air pollution. Thus, mechanisms and factors affecting the removal efficiencies of atmospheric PAHs by wet deposition have been discussed\textsuperscript{15,23–25}. Nevertheless, the available information on the possible implications of PAHs wet depositions on aquatic environments is still scarce, particularly in urban areas. Saitama City comprises complexed industrial and residential areas with approximately 1.2 million of population and it is located nearby the Tokyo metropolitan area. Due to the high anthropogenic activities, deposition of PAHs to aquatic environments is also concerned. Streams run through the city to reach the Tokyo bay, in which accumulation of PAHs and other micropollutants have been reported\textsuperscript{26,27}.

The main purpose of this study was to characterize the migration processes of PAHs via wet deposition in an urban area, underlining the implications for aquatic environments. We analyzed 16 PAHs in rainwater samples collected in the Saitama City, to determine the levels, profiles, phase distributions, and toxic equivalents (TEQs). Additionally, surface water samples were also collected from an adjacent river. To estimate the potential effects of migration processes on aquatic environments, PAHs signatures in rainwater and surface water were compared. Specifically, we addressed the following issues: (a) What PAHs specifically accumulate in particulate and dissolved phase of rainwater in urban areas, and (b) do the rainwater PAHs to what extent involve PAHs accumulation in aquatic environments.

Materials and methods

Reagents and instruments

Dichloromethane, methanol, acetone, sodium chloride, and acetonitrile were purchased from Wako Pure Chemical Industries (Osaka, Japan). Anhydrous sodium sulfate was supplied by Yoneyama Yakuhin Kogyo (Osaka, Japan) and it was cleaned with dichloromethane prior to use. A PAHs standard mixture (200 µg mL\textsuperscript{-1} in dichloromethane: methanol = 1:1) containing the U.S. Environmental Protection Agency included 16 PAHs (naphthalene [NAP], acenaphthylene [ANTY], acenaphthene [ANTN], fluorene [FLU], phenanthrene [PHE], anthracene [ANT], fluoranthene [FLR], pyrene [PYR], benz(a)anthracene [B[a]A], chrysene [CHRY], benzo(b)fluoranthene [B[b]F], benzo(k)fluoranthene [B[k]F], benzo(a)pyrene [B[a]P], indeno(1,2,3-cd)pyrene [I[cd]P], dibenzo(a,h)anthracene [D[ah]A], and benzo(g,h,i)perylene [B[ghi]P]) and PYR – d\textsubscript{10}, 5662 K. SANKODA ET AL.
which was used as an internal standard, were obtained from Kanto Chemical (Tokyo, Japan). Surrogate standards (NAP – d₈, ANTN – d₁₀, PHE – d₁₀, CHRY – d₁₂, and perylene – d₁₂ in dichloromethane) were supplied by Supelco, Merck (Darmstadt, Germany). Glass fiber filters (GF/F class) were purchased from Whatman (Maidstone, UK). Then, 20-mm-long stir bars (Twister™) coated with a 0.5-mm film thickness layer (127 μL) of polydimethylsiloxane were obtained from Gerstel (Mülheim an der Ruhr, Germany). The quantification of 16 PAHs was conducted using a gas chromatograph mass spectrometer (GC/MS) GCMS-QP2010 (Shimadzu, Kyoto, Japan) by injecting 1 μL samples using the splitless mode at 300 °C. Chromatographic separations of the analytes were performed using a Select PAH column (Agilent, Santa Clara, USA) (15-m × 0.15-mm i.d. × 0.1-μm film thickness) operating in electron ionization and selective ion monitoring mode. The ionization voltage was set to 70 eV. The octanol–water partition coefficient (Kow) values of individual PAHs were estimated using EPI suite version 4.10 (Table S1).

**Sampling**

Rainwater and surface water samples were collected in Saitama, a Japanese urban area (Fig. S1). Saitama is located 30 km northwest of central Tokyo with an annual average (2010–2017) precipitation amount of 1292 mm². The sampling campaign for rainwater was performed from July 2017 to June 2018. Rainwater samples were collected on the balcony of the Research and Project building on the Saitama University campus, which is approximately 40 m above ground (St. R in Fig. S1). A main road with daily traffic density of 42,000 cars/day is approximately 0.27 km away from the sampling site. During rain events, a glass beaker with a stainless steel funnel was placed to collect precipitation. In total, 17 samples were collected as precipitation samples with different sample volumes (Table S2).

In addition to rainwater, surface water samples were collected from a neighboring Kamo River (St. K), a tributary of Arakawa River, using a stainless bucket. The sampling campaign from St. K was performed from January to June 2018 (n = 13). The specific purpose of surface water sampling was to examine source/sink relationships by comparing PAHs signatures with rainwater and to evaluate the possible effects of direct input of precipitation.

**Analytical procedure**

The collected rainwater and surface water samples were passed through GF/F filters to separate the dissolved and particulate phases. A portion of the water samples was subjected to PAHs analysis in the dissolved phase by using the second step stir bar sorptive extraction (SBSE) method as proposed by Fujita et al. with slight modifications. First, surrogate standards were added to a sample solution (20 mL) containing 5% methanol. Then, SBSE was performed at 600 rpm at room temperature for 50 min. After the first step of extraction, sodium chloride was added to the samples at 2% and further stirred for 70 min. The stir bar was subjected to further ultrasonic extraction for 15 min with acetonitrile, and the internal standard, PYR-d₁₀, was added. In each batch for the SBSE procedure, the stir bars were cleaned after the experiments according to the method proposed by a previous study. Briefly, the stir bars were placed in a 2-mL vial with a mixture of dichloromethane and methanol (1:1, v/v) for 15 min at room temperature. Then, the stir bars were treated for 10 min via ultrasonication in a fresh mixture of solvents and dried under a N₂ stream for 3 min. The sonication repeated while the mixture was replaced by acetonitrile. The stir bars were kept until the next use. Blank experiments (n = 12) performed after the extraction of the environmental samples were performed to validate the cleaning procedure, which showed no detectable peaks for PAHs for the stir bars. For analysis of particulate phase PAHs, the filter samples were ultrasonically extracted for 15 min with dichloromethane (5 mL) after the addition of surrogate standards and anhydrous sodium sulfate (5 g). This extraction step was repeated by
adding the same amount of dichloromethane to the sample. Extracts were combined and centrifuged at 3000 rpm for 15 min and passed through a 0.45-μm PTFE syringe filter. Acetonitrile (190 μL) was added to the extracts of the particulate phase and concentrated by gentle N2 streams for solvent exchange. The samples were analyzed using a GC/MS system with PYR-d10 as the internal standard. The mean recovery rates (± standard deviation) of surrogate standards ranged from 50 ± 29% (NAP-d8) to 76 ± 30% (CHRY-d10) (n = 60). Concentrations of PAHs were corrected by the recovery rates of the surrogates according to their benzene rings. Quantification limits of the PAHs were calculated using the standard deviations of repeated measurements of the minimum level of standard solution (Table S1). In statistical analysis, Pearson correlation coefficients were applied with a significance level of p < 0.05.

3. Results and discussion

3.1. Characteristics of PAHs in rainwater

The volume-weighted mean concentrations and partitioning between the dissolved and particulate phases of the individual and total 16 PAHs in the rainwater samples are listed in Table 1. The mean concentration of the total 16 PAHs in all the rainwater samples (dissolved + particulate phase) reached 108.8 ng L⁻¹ with a range of 17.6–192.9 ng L⁻¹. The results indicated that the levels of PAHs in this study were the similar as previously reported PAHs concentrations in rainwater collected in Italy (102.9 ng L⁻¹) (∑14 PAHs)³² but lower than those in Turkey (785 ng L⁻¹) (∑16 PAHs)¹⁶ and India (2240.27 ng L⁻¹) (∑16 PAHs)³³. Moreover, Wei et al.²¹ detected a high concentration of total PAHs of 36.9 μg L⁻¹ in snow samples collected from northeast China, emphasizing the low PAHs levels found in this study. This may be due to differences in local pollution levels among the studied areas because emitted PAHs are shown to exclusively accumulate near emission sources³⁴. Moreover, Hayakawa et al.³⁵ atmospheric PAHs concentrations in Japanese cities have been decreasing in the recent decades. Of the individual PAHs, the highest concentration was found to be from NAP (mean: 28.9 ng L⁻¹), accounting for 29.9% of the total PAHs, followed by ANTY (12.6 ng L⁻¹) and PHE (11.2 ng L⁻¹). As shown in Table 1, these low-molecular-weight PAHs (LMW PAHs) with two and three benzene rings also showed high-detection frequencies, indicating ubiquitous distributions in rainwater. In contrast, many of the high-

| PAH   | Dissolved | Particulate | Total |
|-------|-----------|-------------|-------|
|       | Mean      | Range       | DF    | Mean      | Range       | DF    | Mean      | Range       | DF    |
| NAP   | 21.5      | ND-79.3     | 82.4  | 7.4       | ND-33.4     | 47.1  | 28.9      | ND-80.9     | 82.4  |
| ANTY  | 12.6      | ND-51.1     | 41.2  | ND        | 0           | 12.6  | ND-51.1   | 41.2         |
| ANTN  | 1.9       | ND-14.6     | 35.3  | 4.2       | ND-50.3     | 35.3  | 6.0       | ND-63.4     | 64.7  |
| FLU   | 7.4       | ND-32.8     | 41.2  | 0.96      | ND-4.1      | 35.3  | 8.4       | ND-36.4     | 58.8  |
| PHE   | 9.6       | ND-38.4     | 70.6  | 1.7       | ND-66.6     | 76.5  | 11.2      | ND-38.4     | 94.1  |
| ANT   | 4.5       | ND-38.3     | 23.5  | 1.3       | ND-9.5      | 35.3  | 5.8       | ND-38.3     | 58.8  |
| FLR   | 6.1       | ND-16.4     | 58.8  | 1.7       | ND-10.1     | 82.4  | 7.8       | ND-19.1     | 88.2  |
| PYR   | 3.7       | ND-14.2     | 70.6  | 1.4       | ND-10.2     | 94.1  | 5.1       | 0.7-15.5    | 100   |
| CHRY  | 1.2       | ND-9.4      | 35.3  | 0.48      | ND-3.0      | 17.6  | 1.7       | ND-9.4      | 47.1  |
| B[a]A | 0.67      | ND-7.7      | 5.9   | 2.1       | ND-9.9      | 11.8  | 2.8       | ND-9.9      | 17.6  |
| B[j]F | ND        | 0           | 1.5   | ND-5.8    | 17.6        | 1.5   | ND-5.8    | 17.6        |
| B[k]F | ND        | 0           | 0.90  | ND-4.4    | 5.9         | 0.90  | ND-4.4    | 5.9         |
| B[a]P | ND        | 0           | 0.98  | ND-4.5    | 11.8        | 0.98  | ND-4.5    | 11.8        |
| I[cd]P| 2.2       | ND-36.2     | 11.8  | 2.3       | ND-5.9      | 58.8  | 4.5       | ND-36.2     | 70.6  |
| D[ah]P| 7.2       | ND-67.0     | 11.8  | 0.15      | ND-0.75     | 5.9   | 7.4       | ND-67.0     | 17.6  |
| B[ghi]P| ND   | 0           | 3.1   | ND-8.4    | 58.8        | 3.1   | ND-8.4    | 58.8        |
| ΣPAHs | 78.6      | 11.6–162.1  | 30.2  | 0.43–70.7 | 108.8       | 17.6–192.9 | 5664 | K. SANKODA ET AL. |
molecular-weight PAHs (HMW PAHs), including five and six benzene ringed PAHs, were infrequently detected in samples and exhibited lower concentrations compared with LMW PAHs. Figure 1 shows the profile of PAHs based on the ring number in the dissolved phase, particulate phase, and whole rainwater samples. As depicted in Figure 1, the sum of the LMW PAHs showed a large contribution occupying 67.0% of the total PAHs concentrations in the rainwater. The PAHs profiles in rainwater samples are similar with previous studies. LMW PAHs are volatile, and they are likely much partitioning in atmospheric environments. Moreover, LMW PAHs have higher hydrophilicities. Figure 2 shows the relationship between the concentrations of individual PAHs in rainwater samples (ng L$^{-1}$) and their $K_{ow}$. LMW PAHs that have low $K_{ow}$ were found at high concentrations in samples, and there was a significant negative correlation between PAHs concentrations and log $K_{ow}$ values ($r = -0.70$, $p < 0.01$, $n = 16$).

Phase distributions between the dissolved and particulate phases in rainwater are important not only to reveal contamination levels but also prove their environmental outcome. PAHs in dissolved phase were detected at high concentrations compared with those in the particulate phase. The mean concentrations of 16 PAHs in the dissolved and particulate phase were 78.6 (11.6–162.1) ng L$^{-1}$ and 30.2 (0.43–70.7) ng L$^{-1}$, respectively. Contributions of LMW PAHs were particularly higher in the dissolved phase with 73% compared with particulate phase (57%). A possible reason for the high concentrations in dissolved phase would be the presence of PAHs associated with particles that cannot be captured in filtering processes. Moreover, large
contributions of dissolving gaseous PAHs to rainwater would be another reason, since Wang et al.24 reported that atmospheric PAHs in gas phase were efficiently scavenged during clouding processes. LMW PAHs predominantly exist in the gas phase, while HMW PAHs that have low vapor pressures generally tend to associate with particles in atmospheric environments36,39. Greater contributions of rainwater LMW PAHs in dissolved phase than particulate phase would support that scavenging of atmospheric gaseous PAHs plays important roles in accumulation of PAHs in the dissolved phase37. Thus, different partition trends of PAHs according to the molecular size may be due to their different environmental behaviors.

The isomeric ratios of selected PAHs in samples, which is also known as diagnostic ratios, such as ANT/(ANT + PHE), FLR/(FLR + PYR), and B[a]A/(B[a]A + CHRY), have been used to probe potential sources of detected PAHs40. For example, an ANT/(ANT + PHE) higher than 0.1 implies the influence of pyrolytic sources (combustion of organic matter), whereas a value less than 0.1 suggests pollution by PAHs originating from petrogenic sources. Similarly, a FLR/(FLR + PYR) greater than 0.4 indicates contribution of combustion. In this study, ANT/(ANT + PHE) and FLR/(FLR + PYR) were applied as diagnostic ratios considering their high-detection frequencies in rainwater samples. The mean values of ANT/(ANT + PHE) in the dissolved phase, particulate phase, and whole rainwater were 0.32, 0.46, and 0.27, respectively. The ratios for FLR/(FLR + PYR) in the dissolved phase, particulate phase, and whole rainwater were 0.62, 0.52, and 0.59, respectively. These results indicate the important contribution of combustion as a PAHs source. In addition, Naser et al.41 concluded that diesel exhaust is the main source of PM2.5- and PM10-associated atmospheric PAHs in Saitama City. Thus, the emission sources of PAHs in the dissolved and particulate phases are similar to the main contribution of pyrolytic-related processes, including diesel exhaust.

To assess the potential toxicological implications posed by the exposure of PAHs to rainwater, the TEQ was calculated based on the relative potencies (REP) of individual PAHs determined in yeast assay experiments using the following equation42,43,

\[
TEQ = \sum [C_i] \times \text{REP}_{\text{B[a]P},i} / 60,
\]

where \([C_i]\) represents the concentrations of individual PAHs in the samples and \text{REP}_{\text{B[a]P},i} refers to the toxic potencies of PAHs reported in the literature43. The TEQ concentrations in the rainwater samples were 0.16–24.0 ng-TEQ L\(^{-1}\) (mean: 9.6 ng-TEQ L\(^{-1}\)). CHRY and B[a]A predominantly contributed to the TEQ concentration, showing 44% and 41% contributions, respectively. This was because HMW PAHs generally exhibit a higher \text{REP}_{\text{B[a]P}} compared with LMW PAHs. These results indicate that the toxicological implications of PAHs in rainwater in terms of TEQ may be dependent on the abundances of HMW PAHs, which tend to accumulate in the particulate phase. Indeed, PAHs detected in the particulate phase showed a slightly high contribution by the TEQ concentration on an average basis (55%).

### 3.2. PAHS in surface water and implication of deposition

The residual PAHs concentrations in surface water samples collected from the Kamo River (St. K) were also determined. The concentrations of PAHs in the samples are shown in Table S3. The mean total concentrations of 16 PAHs in the river surface water samples were 49.9 ng L\(^{-1}\). The observed PAHs concentrations in the surface water samples were similar level compared with those reported in Japanese suburban area (26–122 ng L\(^{-1}\))44. NAP was the most predominant PAHs in the surface water samples with a mean concentration of 16.7 ng L\(^{-1}\), followed by PHE (7.8 ng L\(^{-1}\)) and ANTY (6.3 ng L\(^{-1}\)).

To explore source/sink relationships of PAHs in receiving areas, comparisons of the PAHs signatures among the different types of samples have been used as key information32,45. In this study, PAHs signatures in rainwater and surface water were calculated by normalizing the individual PAHs
concentrations to the total PAHs concentrations. As shown in Figure 3, PAHs signatures of rainwater and surface water in dissolved phases were similar and showed a strong correlation ($r = 0.91$). These results suggest that source/sink relationships of PAHs between rainwater and receiving river water are important for dissolved phase. On the other hand, the obtained correlation of signature from particulate phases was relatively lower compared with that of dissolved phase ($r = 0.79$). The decreased correlation in particulate phase would be due to PAHs in particles are largely affected by other sources, such as urban street road runoff that contains particulate phase PAHs. Concentrations of dissolved phase PAHs in the river surface water (45.8 ng L$^{-1}$) were relatively low compared with those of the rainwater. This would mean that river surface water is likely susceptible to direct input of PAHs via rainwater, especially for the dissolved phase PAHs.

Furthermore, to characterize the deposition fluxes of PAHs by precipitation, the wet deposition of PAHs were calculated for each rain event by multiplying the determined concentration of PAHs (ng L$^{-1}$) in rainwater samples by the total precipitation amounts (mm) during the sampling periods. The estimated mean wet deposition of the total 16 PAHs by precipitation events was 2000 ng m$^{-2}$ with a range of 50.4–6280 ng m$^{-2}$. Generally, higher PAHs wet deposition fluxes were found when higher amounts of precipitation were observed. The amount of wet deposition for the 16 total PAHs showed a significant correlation with precipitation amounts (mm) during the sampling periods ($r = 0.89$, $p < 0.01$) (Fig. S2). These results suggest that the amount of precipitation is one of the most important factors that affect the deposition fluxes of PAHs in our studied area. The findings regarding the PAHs depositions are consistent with those of Wang et al. and Olivella et al., where increased PAHs wet deposition fluxes with increasing precipitation amounts were reported. The PAHs flux patterns observed in this study are likely explained by the ubiquitous distribution of PAHs and their emission sources in the ambient area. Based on the diagnostic ratios, the emissions of PAHs are expected to be associated with routine anthropogenic activities, including combustion of fossil fuels. Owing to the ubiquitous sources, PAHs are likely emitted continuously into environments even during rain events. Although wet deposition plays an important role in mitigation of atmospheric pollution, it would not sufficiently effective to rapidly scavenge atmospheric PAHs. Thus, contentious precipitation would result in higher deposition amounts of PAHs to terrestrial and aquatic environments.

**Conclusion**

In this study, PAHs in rainwater were characterized by the predominance of LMW PAHs. Similar PAH signatures between wet deposition samples and surface river water suggested source/sink
relationships of the PAHs especially in dissolved phase. Moreover, PAHs were detected in rainwater at levels that were relatively high than river surface water collected in the urban area. The burden to aquatic environments would increase with amounts of precipitation. Further studies are required to clarify the environmental risks of PAHs in aquatic systems posed by wet deposition processes.

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