

Dispersion and dry and wet deposition of PAHs in an atmospheric environment

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Abstract The atmospheric concentration and dry and wet deposition were measured for particulate matter (PM) and polycyclic aromatic hydrocarbons (PAHs) from August to December in Higashi-Hiroshima City, Japan. PM concentration of fine particles (0.6–7 μm) was 5.7–75.1 $\mu\text{g m}^{-3}$, and coarse particles (>7 μm) was 2.2–22.3 $\mu\text{g m}^{-3}$. Total PAHs concentration of fine particles was 0.14–16.3 ng m^{-3} , and coarse particles was 0.01–0.77 ng m^{-3} . Their concentration increased on non-rainy days and decreased rapidly on rainy days. For seasonal fluctuations of PAHs, their concentrations decreased from summer to winter, and the rate of decrease was more distinct for fine particles. For total (dry + wet) depositions, the PM flux was 1.9–11.2 $\text{mg m}^{-2} \text{d}^{-1}$, and the total PAHs flux was 1.9–97.2 $\text{ng m}^{-3} \text{d}^{-1}$. From these measurements, the yearly total loading of PAHs was estimated for the particle phase. Total loading was 28 $\mu\text{g m}^{-2} \text{y}^{-1}$ for the dry deposition and 52 $\text{mg m}^{-2} \text{y}^{-1}$ for the wet deposition. The loading of the wet deposition was comparable to those of the dry deposition for all ring numbers.

Keywords Atmospheric concentration; PAHs; particulate matter; polycyclic aromatic hydrocarbons; total deposition

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds composed of two or more fused aromatic rings. Several compounds of this class are believed to be human carcinogens. PAHs are emitted into atmospheric environments mainly due to incomplete combustion processes, deposited on ground surfaces, and discharged into aquatic environments. Many researchers have estimated PAH emissions on a nationwide scale, and the atmospheric concentrations and depositions have been measured (Baek *et al.*, 1991; Fukushima *et al.*, 2003). According to the results, vehicle emissions, especially diesel exhausts, are one of the major sources of PAH emissions in urban areas. Higher molecular weight PAHs are adsorbed into particulate matter (PM), and move with PM. In discussing the discharges from atmospheric environments into aquatic environments, the relation of the atmospheric condition and the deposition onto ground surface would be the major concern. These relations, however, have not been scientifically determined yet. Moreover, the estimation of temporal and spatial variations in the atmospheric concentration has made for basic uncertainties in discussing the total loading on a larger scale. In the present study, the atmospheric concentration and deposition of particulate matter and PAHs were measured in a suburban area. The measurements of atmospheric concentrations and depositions of particulate matter and PAHs formed the basis of a discussion on the temporal variations in the atmospheric concentration and ground surface loading.

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Experimental methods

Sampling campaigns

The sampling site was located at the Saijo campus of Hiroshima University in Higashi-Hiroshima, Japan (34°23'11"N, 132°43'00"E). Sampling apparatuses were put on the roof of an eight storey building in the campus (height: 30 m). The population of Higashi-Hiroshima is 1.2×10^5 . The city center district is located 3 km northeast from the sampling site. Atmospheric particulate matter was collected using a high-volume air sampler (HVS-500-5; Shibata Kagaku Co., Ltd.) with an impactor system followed by a glass fiber filter. Each sampling was conducted for 24 hours, and the sampling rate was 500 L min^{-1} . Using the impactor system, particles of $>7 \mu\text{m}$ (coarse particulate matter; CPM) were trapped on a stainless plate. After sieving, particles of $0.6\text{--}7 \mu\text{m}$ (fine particulate matter; FPM) were collected on a glass fiber filter (GB-100R, Advantec Co., Ltd.). Prior to the experiment, the stainless plate and glass fiber filter were precombusted at 110°C for 24 hours. The deposited particulate matter for total and wet deposition was collected in a bucket (24 cm in diameter and 35 cm height). For total deposition, the sampling tray was put in for 72 hours, and for the wet deposition, the sampling tray was put in during the rainy periods. At the end of the sampling for non-rainy periods, the bucket and stainless plate for holding coarse particle matters were rinsed with Milli-Q water (Millipore Co., Ltd.). Collected water was then filtered through a glass fiber filter (GF/C, Whatman Co., Ltd.), which was precombusted at 450°C for 4 hours. For both atmospheric and deposited particulate matter, each sampling began at 14:00 and lasted 24 hours. For rainy periods, dissolved PAHs were also measured. (The PAHs concentration dissolved from collected particles in the water used for rinsing the non-rainy period sampling was negligible and so this concentration was omitted.) Overall, the sampling session was performed from 10th August to 28th December, 2003. The periods of sampling of each item are shown below.

Meteorological measurements

The meteorological data were collected from the meteorological data acquisition system (<http://home.hiroshima-u.ac.jp/hirodas>) in Hiroshima University. The observation point was at a 380 m distance from the PAHs sampling site.

PAHs extraction and analysis

For particulate matter, the filters collecting particles were dried for 2 days under dark conditions at room temperature and subsequently extracted with dichloromethane in a sonication water bath. For the dissolved phase, a silica column (Sep-Pak Plus C18, Waters Co., Ltd.) was used for extraction. The collected water was passed through the silica column for PAHs entrapment at the rate of 3 mL min^{-1} . After the entrapment, 10 mL DCM (dichloromethane) was passed for extraction at the rate of 1 mL min^{-1} . After the extraction, these DCM extracts were concentrated into 2 mL by N_2 . PAHs were then analyzed on a gas chromatograph (GC17A, Shimadzu Co., Ltd.) equipped with a mass selective detector (QP5050, Shimadzu Co., Ltd.) operated in the single-ion monitoring mode. Injection was split with detector and inlet temperatures at 230°C . The initial temperature was 80°C held 2 min, ramped at $30^\circ\text{C min}^{-1}$ to 210°C , ramped at 5°C min^{-1} to 295°C , and ramped at 2°C min^{-1} at 315°C . Sixteen unsubstituted PAHs were measured: acenaphthalene (Ace), acenaphthene (Act), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo(a)anthracene (B(a)A), chrysene (Chr), benzo(b)fluoranthene (B(b)F), benzo(k)fluoranthene (B(k)F), benzo(e)pyrene (B(e)P), benzo(a)pyrene (B(a)P), dibenzo(ah)anthracene (D(ah)A), benzo(ghi)perylene (B(ghi)P), and indeno(123-cd)pyrene (Ind(123)P). The detection limit was set at the

level of 3 in the SN ratio. Detection limits ranged from 1 to 5 ng for individual PAHs. Within this level, the CV ratio of each of the compounds was less than 20%. Quality of extraction was checked using dried marine sediments (HS-3B, National Research Council of Canada Institute for Marine Biosciences). The recovery averaged 50–80% for all PAHs, and the repetition error was 5–10%.

Results

Atmospheric concentrations

The climatic conditions and averaged atmospheric concentrations and deposition fluxes of PM and total PAHs in particulate matter are listed in Table 1. In the sampling periods, temperature and precipitation were moderate for this sampling site. For particulate matter, the atmospheric concentration of FPM (fine particulate matter) was 22.0–29.2 $\mu\text{g m}^{-3}$, and that of CPM (coarse particulate matter) was 7.0–11.1 $\mu\text{g m}^{-3}$. For total PAHs, the atmospheric concentration of PAHs in FPM was 0.80–5.16 ng mm^{-3} , and that in CPM was 0.04–0.17 ng mm^{-3} . For FPM and CPM concentrations, they were stable from summer to winter. For PAHs, on the other hand, the concentration in FPM increased from summer to winter. This seasonal fluctuation is commonly observed in many atmospheric measurements (Fukushima *et al.*, 2003; Ozaki, 2002; Wu and Fang, 2001; Panther *et al.*, 1999). For the concentration in CPM, on the other hand, no seasonal variation was observed. Effects of seasonal changes on PAHs in atmospheric environments would be different between FPM and CPM.

An example of the results of PM and PAH fluctuation is shown in Figure 1 (from 6th Nov. to 6th Dec.). By comparing these results with the precipitation profile, the dependencies of PM concentration on precipitation can be observed (Figure 1a). The FPM and CPM concentrations increased during non-precipitation periods and decreased rapidly during precipitation. This tendency is apparent for the period from 6th to 13th of November. When we compare the FPM and CPM, we see that the pattern of fluctuation is fairly similar (Figure 2; $R = 0.67$ for all the samplings). The concentration profile of total PAHs is shown in Figure 1b. Compared to the PM, the extent of fluctuation is larger in PAHs (the CV values of all the samplings were 43% and 49% for FPM and CPM, and 92% and 130% for PAHs in FPM and CPM) and a sharp increase was occasionally observed. In comparing the total PAHs in FPM and CPM, the fluctuation pattern was basically similar (the R of total PAH concentration between FPM and CPM was 0.72).

Total and wet deposition of PM and PAHs

Deposition samplings were conducted from 6th November to 5th December in 2003. During this period, precipitation occurred four times (9th to 10th Nov., 19th to 21st Nov., 26th to 28th Nov., and 5th Dec.). Figures 1c and 1d show the results of the PM and total PAH flux. (For wet deposition, the dissolved phase PAHs were not included in these results.) The PM total flux was 1.9–11.2 $\text{mg m}^{-2} \text{d}^{-1}$. The level of the total flux did not change significantly in the rainy periods. The deposition in the rainy periods was similar to those of the non-rainy periods.

In the third precipitation (26th to 28th Nov.), the bucket for collection was changed twice during the sampling. From this sampling, the first flush phenomenon was clearly observed. Also, the PM flux decreased after the precipitation, and increased in the non-rainy period. The fluctuation is, however, not so clear. This may be due to the sampling time duration (three days). The flux values were averaged over three days and the effects may be masked in these longer sampling periods. For atmospheric concentration, fairly clear oscillation was observed from the end of one precipitation to another (Figure 1a).

Table 1. Climatic condition and atmospheric concentration of PM and total PAHs

	August	September	October	November	December
Air temperature (°C)	25.4 (18.8 – 28.3)	22.6 (15.9 – 26.7)	14.5 (9.3 – 21.5)	11.9 (5.2 – 17.6)	4.6 (10.9 – 0.1)
Precipitation (mm)	114.5	59.5	12.5	130.0	44.0
Wind speed (m s ⁻¹)	0.6 (0.0 – 1.7)	0.3 (0.0 – 2.3)	n.d.	n.d.	n.d.
PM concentration	n = 28	n = 20	n = 12	n = 28	n = 28
FPM (µg m ⁻³)	22.0 (5.7 – 62.7)	22.9 (8.6 – 64.9)	29.2 (15.5 – 48.2)	22.7 (5.8 – 52.7)	25.7 (12.0 – 75.1)
CPM (µg m ⁻³)	7.0 (2.2 – 14.3)	7.7 (3.6 – 14.3)	11.1 (6.1 – 10.6)	8.4 (1.3 – 17.3)	8.8 (2.2 – 22.3)
Total PAHs	n = 20	n = 18	n = 0	n = 28	n = 8
in FPM (ng m ⁻³)	1.0 (0.14 – 5.0)	0.80 (0.17 – 2.88)	n.d.	4.1 (0.4 – 14.9)	5.16 (0.94 – 16.3)
in CPM (ng m ⁻³)	0.05 (0.01 – 0.02)	0.04 (0.02 – 0.05)	n.d.	0.17 (0.01 – 0.77)	0.06 (0.02 – 0.09)

Air temperature, wind speed: daily average; in the parenthesis is the min. to max.

FPM: fine particulate matter, DPM: coarse particulate matter

n: number of sampling, n.d: no data

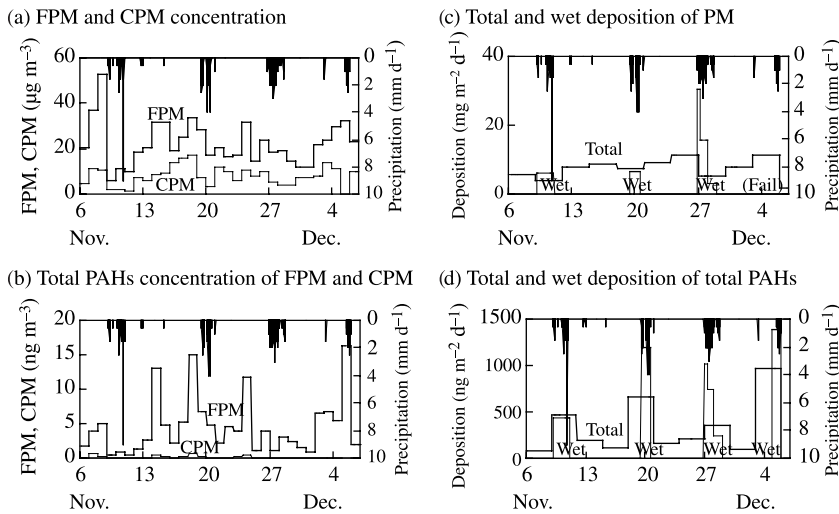


Figure 1 Profile of atmospheric and deposition PMs and PAHs (6 Nov. to 6 Dec. in 2003)

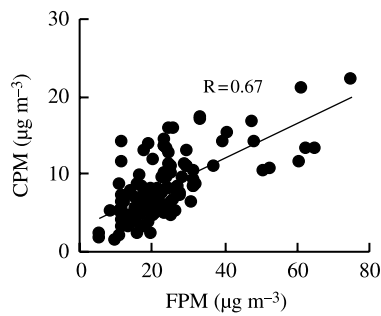


Figure 2 FPM vs. CPM concentration

It is reasonable to suppose that this oscillation affects the deposition. To elucidate this, the relation between the atmospheric PM (FPM + CPM) concentration and the dry deposition flux was shown (Figure 3; the three days average was taken for atmospheric PM in accordance with the period of deposition sampling). The dependence of the flux on the atmospheric concentration can be seen ($R = 0.51$; Figure 3), and further, more distinct dependence was observed for CPM concentration ($R = 0.79$).

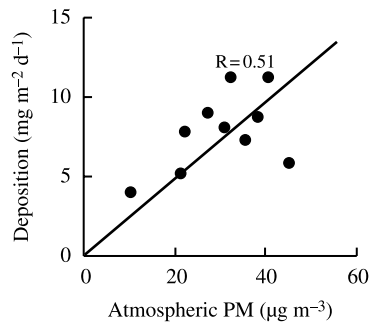


Figure 3 Atmospheric concentration and deposition

For the deposition of PAHs, the tendencies in the rainy periods are different (Figure 1d) from those of PM (Figure 4). The deposition increased sharply in the rainy periods. From this observation, it can be conjectured that the PM will have a different result of clean-up by precipitation than will PAHs.

Clean-up ratio of wet deposition

In order to estimate the effect of clean-up by precipitation, the mass balance was taken for before, during, and after precipitation. For the estimation of the total mass in the atmosphere, using the mixing height, the concentration profile in height was hypothesized as follows: from the ground level to the mixing height, the concentration is constant, and over the mixing height, the concentration is zero (Figure 4). From this hypothesis, the total mass per unit area in atmosphere can be calculated as follows:

$$\text{Total Mass in air [g m}^{-2}] = H_m \cdot C$$

where H_m : mixing height [m], C : atmospheric concentration [g m^{-3}]. The mixing height was calculated from the irradiation intensity for daytime (Kim *et al.*, 2001), and the monthly average value was taken for this study. The estimated averaged mixing height was 805–1,186 m and the value had seasonal fluctuation. (The value was higher in summer.) From this estimation, the mass balance of PM and PAHs was taken for ten major precipitations from 11th August to 6th November (Figure 5; the dissolved phase is excluded for the calculation). For estimation of PAHs, they were divided into four groups by ring number (3-rings: Ace, Act, Flu, Phe, Ant, 4-rings: Flt, Pyr, B(a)A, Chr, 5-rings: B(b)F, B(k)F, B(e)P, B(a)P, D(ah)A, and 6-rings: B(ghi)P, Ind(123)P) and they were summed for each group. Results of 3 and 6-rings were shown in Figure 5.

For the precipitations of 8th Nov. and 18th Nov., the total mass before precipitation is considerably higher for both PM and PAHs. This is probably due to the error of the calculation of H_m . Except for these two events, the balance seems to have been successfully achieved. From the results, in order to discuss the relation of the atmospheric mass and precipitation loading, the clean-up ratio (CR) for the particulate phase was defined as follows:

$$\text{CR} = \frac{\text{Wet deposition}}{\text{Atmospheric Mass}(= \text{Atmospheric conc.} \times \text{Mixing height})}$$

The averaged CR value was 0.38, 0.86, 0.30, 0.07, and 0.11 for PM, 3-, 4-, 5-, and 6-ring PAHs respectively. The CR value can be supposed to change with the precipitation condition (e.g. the total precipitation mass, intensity). No clear relation, however, was found in this study.

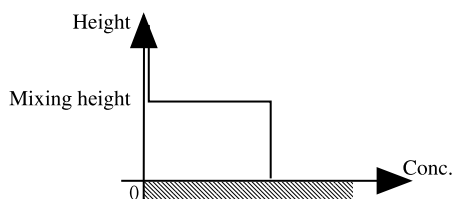


Figure 4 Hypothesis of concentration profile of PM and PAHs

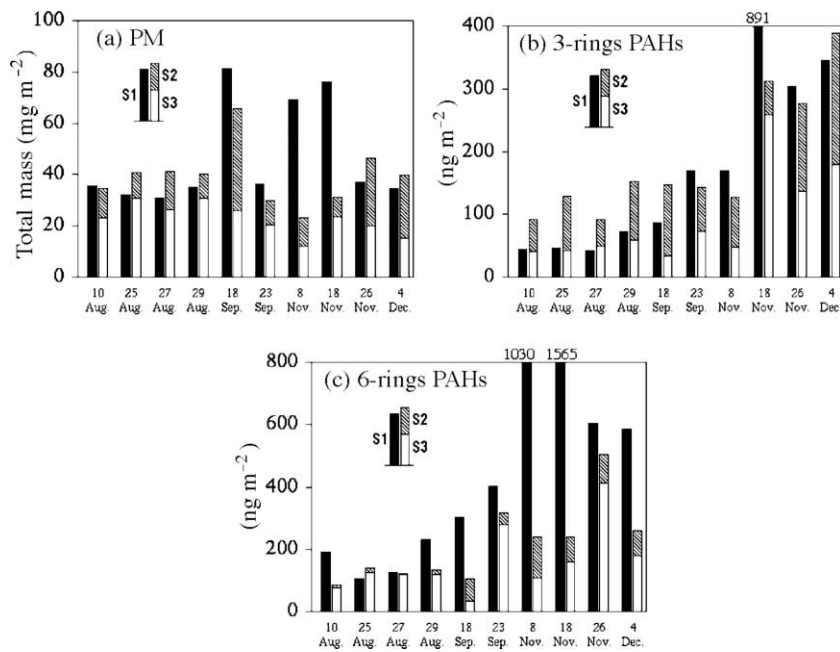


Figure 5 Mass balance of PM and PAHs in the precipitations. S1: total mass in the air before precipitation, S2: Precipitation load, and S3: total mass in the air after precipitation

Estimation of yearly total loadings of dry and wet deposition (particulate phase)

In order to estimate the yearly total loadings of the dry and wet deposition, the mechanisms of atmospheric concentration and deposition changes in time are hypothesized as follows (the scheme is described in Figure 6):

(a) *Atmospheric PM mass.* The atmospheric PM mass increases with time in the non-rainy period and decreases in the precipitation period. For the following calculations, the PM is defined as the sum of FPM and CPM (PM = FPM + CPM).

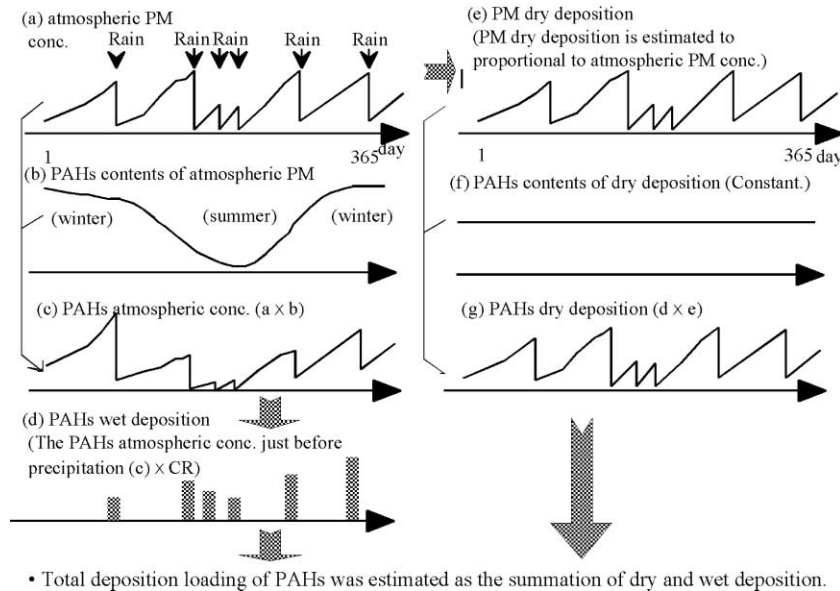


Figure 6 Scheme of estimation of yearly total deposition loading of PAHs

(a-1) The rate of increase of PM concentration is dependent on the wind speed (Figure 7).

(a-2) For the calculation of the rate of decrease of PM mass in precipitation, the averaged (1-CR) for PM applied. The precipitation event is defined on a daily basis, and when it exceeds 5 mm, it is recognized as “precipitation”. Consecutive precipitation over two days is recognized as one precipitation event.

(b) *The PAH contents of atmospheric PM.* The PAH contents of atmospheric PM are hypothesized to have seasonal fluctuation. The atmospheric concentration was measured one year from June 2000 to June 2001 at the identical sampling site (Ozaki, 2002). These obtained PAH values were summed for each ring number, log-normalized, and fitted with sine curves (Figure 8).

(c) *The PAH atmospheric mass.* The PAH atmospheric mass is the product of the atmospheric PM mass (a) and the PAH contents of atmospheric PM (b).

(d) *The PAH wet deposition.* The PAH wet deposition is calculated as the product of the PAH atmospheric mass (c) and the averaged CR values of each PAH ring group.

(e) *The PM dry deposition.* The PM dry deposition is hypothesized to be proportional to the PM concentration (Figure 3).

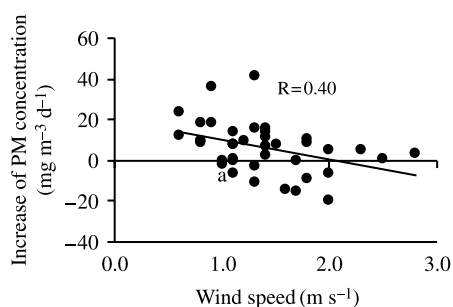


Figure 7 Wind speed and the increase of PM concentration

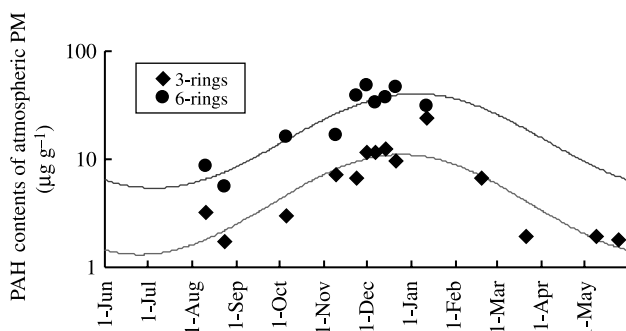


Figure 8 Yearly changes of PAH contents of atmospheric PM. The 3- and 6-rings PAH results are shown for example

(f) *The PAH content of dry deposition.* The PAH content of dry deposition is hypothesized to be constant. The value was estimated from the June 2000 to June 2001 measurements (Ozaki, 2002).

(g) *The PAH dry deposition.* The PAH dry deposition is the product of the PM dry deposition (e) and the PAH contents of dry deposition (f).

From these hypotheses, the dry and wet precipitation can be estimated. From 1st January to 31st December, the yearly profile was calculated. The yearly profile of estimation dry and wet deposition for PM is depicted in Figure 9. Along with the estimated values, the measured values are also shown in Figure 9a. The PM concentration does not have seasonal variations (Figure 9a). The PAH concentration is, on the other hand, higher in winter (Figure 9d). In accordance with this, PAH dry deposition is stable in seasons (Figure 9e), and wet deposition has seasonal fluctuation (Figure 9f). The total mass of PAHs is summarized and shown in Figure 10. The total PAH loading was $28 \mu\text{g m}^{-2} \text{yr}^{-1}$ for dry deposition, and $52 \mu\text{g m}^{-2} \text{yr}^{-1}$ for wet deposition. From the

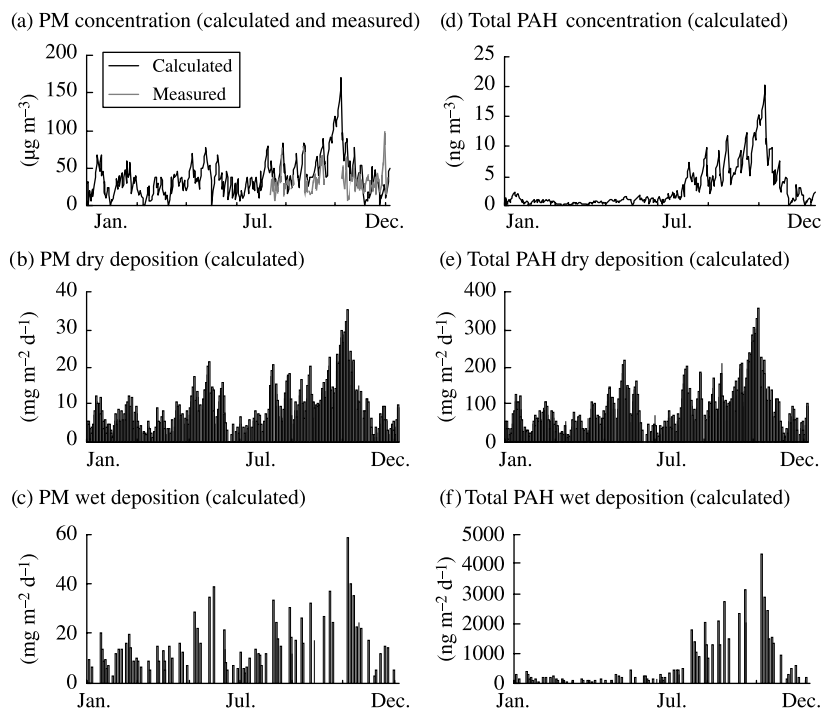


Figure 9 The calculated yearly profile of PM and PAH atmospheric concentration and deposition

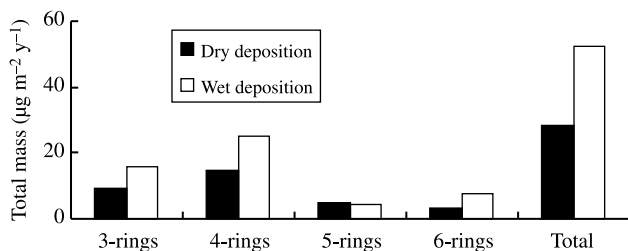


Figure 10 The yearly total loading of PAHs

results, the loading for each PAH ring group was in the same order, and the wet deposition was higher than the dry deposition.

Conclusions

From the measurement of the atmospheric PAH concentration at the sampling site of a suburban area, the dispersion and deposition profile were clarified. Using the data, a model describing the atmospheric concentration and deposition profile was established and the yearly total atmospheric loading was estimated. The total PAH loading was $28 \mu\text{g m}^{-2} \text{yr}^{-1}$ for dry deposition, and $52 \mu\text{g m}^{-2} \text{yr}^{-1}$ for wet deposition. From the results, the loading for each PAH ring group was in the same order, and the wet deposition was higher than the dry deposition.

This study focused on particle PAHs, and the load from the vapor phase and the dissolved phase were not estimated due to the lack of sampling of the vapor phase in the atmosphere. The contribution of the dissolved phase may be higher especially for lower molecular-weight PAHs. In our measurements, the load of wet deposition in the dissolved phase was in the same order as those of the particulate phase for 3- and 4-rings PAHs (not shown). For further study, in order to establish a more accurate estimation, the contribution of the dissolved phase should be considered.

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