Estimation of river discharge loadings of PAHs in a suburban river in Hiroshima Prefecture, Japan

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ABSTRACT

The PAHs loadings on river discharge was estimated based on consecutive measurements during rainfall and non-rainfall periods at a river in a suburban area in Hiroshima Prefecture, Japan. The PAH concentrations ranged from 12 to 58 ng L⁻¹ for dissolved PAHs, and from 8 to 105 ng L⁻¹ for particulate PAHs on rainy periods. In non-rainy periods, they ranged from 10 to 58 ng L⁻¹ for dissolved PAHs, and from 4 to 418 ng L⁻¹ for particulate PAHs. PAH concentrations on non-rainy periods were stable for diurnal and seasonal terms. The dissolved PAH concentration was negatively correlated with EC and the particulate PAH concentration was negatively correlated with SS concentration. The yearly loading amount of PAHs was calculated with the data of river flow rate and PAH concentration, and the calculated yearly PAHs specific loading in the River on rainy days was 37 µg m⁻² year⁻¹ and the loading in non-rainy days was 29 µg m⁻² year⁻¹. The total loading was 66 µg m⁻² year⁻¹. From these estimations and our previous studies, the atmospheric loadings and river discharge were compared. From the comparison, the order of the loading from river basin area was comparable to this from atmospheric loadings.

Keywords: atmospheric deposition, PAHs, rainfall, river discharge.

INTRODUCTION

PAHs are a group of organic compounds consisting of two or more fused benzene rings, and they are noticed due to carcinogenicity and mutagen city (Dipple 1985; Vinggaard *et al*, 2000; Xue and Warshawsky, 2005). PAHs are mostly produced in the combustion process of fossil fuels and are emitted into the atmosphere. After dispersion, PAHs accumulate on ground surfaces and discharge into water bodies with rain. The behavior of PAHs has been extensively studied in atmospheric and aquatic environments (Takada *et al*, 1990; Baek *et al*, 1991; Sharma *et al*, 1994; Lee *et al*, 1995; Wan *et al*, 2006; Kumata *et al*, 2006). Still, the relation of the source and environmental fate has not been well clarified yet. In our previous study (Ozaki, 2006; Ozaki *et al* (2006, 2007)), the behavior of PAHs in Hiroshima Bay area was quantitatively investigated, and it was found that there was a major difference in PAHs loadings between the road traffic emission and the atmospheric deposition or the particle sedimentation on seabed. In order to consider the gap in PAHs loadings between road traffic loadings and environmental discharges, PAHs river discharges were investigated in this study. At a river in suburban areas in Hiroshima Prefecture, PAH concentrations were measured in rainy days and non-rainy days to examine the short- or long- term variations in PAH concentrations. Flow rate and other basic water qualities were also measured in the river, and their dependencies on PAH concentrations were investigated. From the measurements, the factors affecting the discharges were modeled for daily basis, and the total loadings were summed for one year. Further, from the comparison of the loadings

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of river discharge and other environmental loading stages, PAHs behaviors in atmospheric and water environments were discussed.

MATERIALS AND METHODS

Sampling campaigns

Water samples were taken at a point of Kurose River in Higashihiroshima City (population: 110,000, population density: 400 person km², average temperature: 13~14 °C, precipitation amount: 1200~1700 mm year⁻¹), Hiroshima Prefecture, Japan (Figure 1).

Figure 1 - The River Water Sampling Point and its basin area

The river basin area discharging into this sampling point was 121.45 km² (Higashihiroshima City, 2000). On rainy days in 2006, the samplings were performed on Jul. 23 and 24, Oct. 22 and 23, Nov. 10 and 12, Dec. 13 and 14, and in 2007 they were carried out on Jan. 16~18, Feb. 22 and 23, Apr. 30 and May 1, May 25 and 26, Jul. 20 and 21. For non-rainy samplings, samples taken before starting the rain were regarded as the non-rainy samples. And in addition to them, samples were taken on Dec. 11~17 and on Dec. 21~22 for non-rainy samplings. Those samplings were performed in order to know the diurnal and weekly fluctuations. For diurnal sampling, the sampling was started at 13:00 and conducted every three hours, and for weekly, the sampling was generally conducted at 13:00 everyday.

At every sampling, 2 to 4 L of water was taken for measuring the dissolved and particulate PAHs. Samples of the river were classified into dissolved and particulate phases by filtering with a glass fiber filter (pore size: 0.7 µm, GF/F, Whatman co. ltd.), which was precombusted at 450°C for 4 hours. After suction filtration, the glass fiber filter was dried for one week at room temperature in a desiccator in dark condition. Besides the PAHs, flow rate, EC, DOC, and SS were measured. Flow rate was determined by the H-Q curve method leading from flow velocity and depth.

PAHs extraction and concentration analysis

For dissolved PAHs, a surrogate spike with acenaphthene-d10, perylene-d10, chrysene-d10, and phenanthrene-d10 was added into the filtered water sample and entrapped at the rate of 1 mL min⁻¹ with a silica column (Sep Pak tC18, Waters). After entrapment and dehydration dryness of the silica column, dichloromethane was passed 10 mL for extraction at the rate of 1 mL min⁻¹. The dichloromethane was subsequently concentrated into 1.5 mL by N₂-gas, and a syringe spike with p-terphenyl-d14 and

2-fluorobiphenyl were added into it. For particulate PAHs, the glass fiber filter with suspended solids was put in a cellulose fiber cylindrical filter, and dropped into a 50 mL screw cap bottle. Dichloromethane was added to the screw cap bottle until the samples were soaked, and the PAHs were extracted with dichloromethane in an ultrasonic water bath for one hour without temperature rise. For the extraction, a surrogate spike of acenaphthene-d10, perylene-d10, chrysene-d10, and phenanthrene-d10 was added. The extract was concentrated into 2 mL by N₂-gas.

For both dissolved and particulate extracts, the PAH concentration was analyzed by using a gas chromatograph equipped with a mass spectrometer (GC-17A/MS-QP5050; SHIMADZU) and operated in the single-ion monitoring mode. Injection was split with the detector, and the inlet temperature was set at 230°C. The initial temperature was 80°C held for 2 min, ramped at 30°C min⁻¹ to 210°C, ramped at 5°C min⁻¹ to 295°C, and ramped at 2°C min⁻¹ to 315°C. In this study, the 16 PAHs were determined (Table 1).

Table 1 - 16 PAHs Analyzed in This Study.

PAHs	Abbrev.	MW	PAHs	Abbrev.	MW
Acenaphthylene	Ace	152	Chrysene	Chr	228
Acenaphthene	Act	154	Benzo(b)fluoranthene	B(b)F	252
Fluorene	Flu	166	Benzo(k)fluoranthene	B(k)F	252
Phenanthrene	Phe	178	Benzo(e)pyrene	B(e)P	252
Anthracene	Ant	178	Benzo(a)pyrene	B(a)P	252
Fluoranthene	Flt	202	Dibenzo(a,h)anthracene	D(ah)A	278
Pyrene	Pyr	202	Benzo(ghi)perylene	B(ghi)P	276
Benzo(a)anthracene	B(a)A	228	Indeno(1,2,3-cd)pyrene	Ind	276

The following presented PAHs values were the sums of these 16 PAHs. 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 40~70% for all PAHs, and the repetition error was 5~10%.

RESULTS AND DISCUSSION

Flow rate and runoff ratio

Flow rate and PAH concentrations were measured in rainy days and non-rainy days. The precipitation conditions and PAH concentrations and loadings were summarized in Table 2.

Table 2 - Precipitation Conditions, PAH concentration and Loading.

sampling date	precipitation (mm)	Rain interval (day)	Runoff ratio (%)	Number of sampling	PAH concentration			PAH loading	
					Dissolved	Particulate	Total	Rainy	Non-rainy
					EMC (ng L ⁻¹)			(g)	(g day ⁻¹)
2006	7/23~24	40	1	55	19	58	13	71	137
	10/22~23	5	21	2	6	19	8	26	2
	11/10~12	21	3	6	6	15	24	38	8
	12/13~14	18	3	15	8	19	47	66	25
2007	1/16~18	11	8	13	5	26	44	69	10
	2/22~23	9	3	6	4	17	105	122	40
	4/30~5/1	16	4	9	4	12	52	63	22
	5/25~26	29	6	34	6	19	42	60	96
	7/20~21	17	3	35	4	20	79	99	106
2006 (diurnal and seasonal terms)	12/11~17	0	1	0	5	18	28	46	0
	12/21~22	0	8	0	9	11	29	40	0

EMC: event mean concentration

Prior to the PAHs sampling, flow velocity and depth rate were measured during several precipitation events, and from the measurements, the H-Q curve was determined for Kurose River. Based on the obtained H-Q curve, the river flow at each sampling campaign was determined from the measurements of water depth. An example of the precipitation and flow rate was shown in Figure 2.

Figure 2 - Change in Flow Rate with Time (Dec. 13~14, 2006).

Based on the change of flow rate with time, specific discharge was calculated for estimating runoff ratio of each measured precipitation event. Specific discharge is defined as the ratio of runoff loadings to the area of a river basin, and runoff ratio is defined as the ratio of specific discharge to precipitation amount. Runoff loadings were obtained by the subtraction of base flow from total flow in a rainfall event. For separation of base flow from the total river flow in the rainfall time, base flow was supposed to be constant throughout a precipitation event, and the level was thought to be equal to that measured just before precipitation began. Figures 3 and 4 showed the dependence of specific discharge and runoff ratio on precipitation amount for all the measured precipitation events. The obtained runoff ratio values increased with precipitation amounts, and maximum runoff ratio value was 55% at 40 mm of precipitation (Jul. 23~24 in 2006), although it was less than 15% when precipitation was less than 15 mm. It was suggested that the outflow would decrease almost into the negligible level owing to the percolation of the rainfall into the subsurface layer through permeable surface areas (forests, rice fields, and other fields), which accounts for 60 percent of the total land use in Kurose River basin area (Higashihiroshima City, 2000).

Figure 3 - Specific Discharge for Each Precipitation Event.

Figure 4 - Runoff Ratio for Each Precipitation Event.

PAH concentrations

PAH concentrations were measured several times during each precipitation event. Figure 5 shows an example of measurement results at a precipitation event. The graph shows the results of the sum of 16 PAHs concentration (sum of particulate and dissolved PAHs) changed through a precipitation. The PAH concentration was stable before precipitation began, and the PAH concentration increased with flow rate.

Figure 5 - Change in PAH concentration with Time (Dec. 13~14, 2006).

From all the measurements, the event-mean concentration (EMC) of PAHs was calculated for all the rainfall and non-rainfall samplings (Figure 6). On rainy days, the PAH concentrations ranged from 12 to 58 ng L⁻¹ for dissolved PAHs, and from 8 to 105 ng L⁻¹ for particulate PAHs. In non-rainy days, they ranged from 10 to 58 ng L⁻¹ for dissolved PAHs, and from 4 to 418 ng L⁻¹ for particulate PAHs.

(a) Rainfall (EMC)

(b) Non-rainfall

(For the samplings of Dec. 11~17 and 21~22, the simple average was taken.)

Figure 6 - PAHs concentration on Each Sampling Date.

In non-rainy days, besides the samplings before the precipitation, a 24-hours sampling (Dec. 21~22) and one-week sampling (Dec. 11~17) were conducted. From the measurements, PAH concentrations in non-rainy days were clarified to be stable for diurnal and weekly terms (Figures 7 and 8). During one-week samplings, it rained once (Dec. 13~14; corresponds to at 48 hours in Figure 7) and the higher concentration of particulate PAHs at this time would be due to this rainfall.

Figure 7 - PAH concentration on Dec. 11~17 ('06).

Figure 8 - PAH concentration on Dec. 21~22 ('06).

Relation to the basic water qualities

The relation of dissolved 16 PAHs concentration and EC, DOC was shown in Figures 9 and 10. The relation of particulate PAH contents (=PAH concentration/SS concentration) and SS concentration was shown in Figure 11. In this graph, the plots were separated into four seasons, and summer (Jun.~Aug.) and winter season (Dec.~Feb.) were shown. Firstly, dissolved PAHs were significantly negatively correlated to EC ($P < 0.05$; Pearson correlation test), but not to DOC. For particulate PAHs also, clear negative correlation with the SS concentration (Figure 11). Higher SS concentration occurred mostly during heavier rains, and this suggests rain soil SS discharges did not mainly contribute to the particulate PAHs loading. For seasonal variations, the particulate PAHs contents in winter season were higher than those of summer season in Figure 11. This result shows that particulate PAHs were contained more in winter season. For dissolved PAHs, on the other hand, significant differences in seasons were not observed in the measurements.

Figure 9 - Relation of EC and Dissolved PAH concentration.

Figure 10 - Relation of DOC and Dissolved PAH concentration.

Figure 11 - Relation of SS and Particulate PAHs Content.

PAH concentration profile

Averaged composition ratio of individual PAHs for all the samplings was shown in Figure 12. For both dissolved and particulate PAHs, the composition ratio of lower molecular PAHs (Ace~Pyr) was higher than that of higher molecular PAHs (Chr~Ind), and for particulate PAHs, higher molecular PAHs concentration was higher than that of dissolved PAHs.

(a) Dissolved PAHs

(b) Particulate PAHs

Figure 12 - Averaged Composition Ratio of Individual PAH
(Error bar represents standard deviation)

Loadings of PAHs

The loadings of PAHs for each precipitation event was calculated with the change in PAH concentration and flow rate with time. An example of the calculation scheme was shown in Figure 13.

Figure 13 - Change in Load of Particulate PAHs with Time (Dec. 13~14, 2006).

From the calculations, the total runoff load of PAHs in each rainfall event was calculated and the relation between precipitation and the load of PAHs during each rainfall event was shown in Figure 14. This tendency was basically similar to that of the runoff ratio (Figure 4). So it could also be deduced that the outflow of PAHs did not happen easily when there was less than a certain amount of precipitation. The load of PAHs increased with precipitation amount and reached 130 g at 40 mm of precipitation. Similarly, the load of PAHs on non-rainy days was calculated for all samplings (Figure 15). The range of them was from 4 to 18 g day⁻¹ (average: 9.6 g day⁻¹). The load of PAHs was fairly stable throughout the measurements, and no clear seasonal fluctuation was observed. From the obtained load of PAHs, the yearly PAHs loadings were estimated using the meteorological data of 2006. The meteorological data was obtained from the Japan Meteorological Agency, and the data at Higashihiroshima was used for this calculation. The daily precipitation data was used for this calculation. For the summation of PAHs loadings of rainfall, the loadings were supposed to follow the precipitation amount with a linear relation depicted in Figure 14. In this relation, loading becomes less than zero at <3.5 mm of precipitation. In this case, loading was assumed to be zero. Also, this relation is not validated more than 40 mm of precipitation experimentally. Since there were 12 precipitation events more than 40 mm occurred in this period, the calculation should include this uncertainty. For the calculation of each rainfall event, one rainfall event was hypothesized to continue one day, and even in the case when the actual rainfall continued over two days, it was regarded as two different rainfall events occur in each day (in 2006, 53 days of rainfall occurred, and consecutive rainfall occurred 11 times, and the maximum duration of consecutive rainfall was 2 days).

For the summation of the loadings of non-rainfall days, the loadings were supposed to be constant throughout each day, and the mean PAHs loadings were obtained by the average of all the measurements (Figure 16). The non-rainy loading was supposed to occur at rainy days, also.

Figure 14 - Relation of Load of PAHs on Each Rainy Day and Precipitation Amount.

Figure 15 - Load of PAHs on Each Non-rainy Day.

The calculated yearly PAHs specific loading in the Kurose River was $37 \mu\text{g m}^{-2} \text{ year}^{-1}$ on rainy days, and $29 \mu\text{g m}^{-2} \text{ year}^{-1}$ on non-rainy days. The total loading was $66 \mu\text{g m}^{-2} \text{ year}^{-1}$.

For comparing the river discharge loading, the yearly loadings arisen from road traffic and atmospheric deposition were estimated in this river basin area. The road traffic loadings and atmospheric deposition were investigated in our previous studies (Ozaki *et al* 2006 and 2007). In these studies, road traffic loading was calculated for this river basin area with an atmospheric diffusion simulation model developed by the National Institute of Advanced Industrial Science and Technology (AIST-ADMER). Atmospheric deposition was calculated for the same area for dry and wet deposition for one year (2003) by our group. From these calculations, the PAHs river discharge obtained in this investigation can be compared to the road traffic and the atmospheric deposition in this area (Figure 17; in order to compare with the road traffic loading, the loading for 10 PAHs (Pyr~Ind) was also calculated similarly because the road traffic was calculated was only for 10 PAHs). The load of the Kurose River was higher than that of the traffic loading, and comparable to that of the atmospheric deposition. From the comparison, the underestimation of the road traffic, or the existence of other major sources than traffic activities was suggested.

Figure 16 - Estimated Monthly PAHs Loading in Kurose River Basin Area.

Figure 17 - Yearly PAHs Loadings in Kurose River Basin Area.

CONCLUSIONS

This study primarily obtained flow rate of water and change in PAH concentration with time measured on rainy and non-rainy days in the Kurose River. On rainy days, the PAH concentrations ranged from 12 to 58 ng L^{-1} for dissolved PAHs, and from 8 to 105 ng L^{-1} for particulate PAHs. On non-rainy days, they ranged from 10 to 58 ng L^{-1} for dissolved PAHs, and from 4 to 418 ng L^{-1} for particulate PAHs. From the results of non-rainy samplings, it was shown that PAH concentrations were stable during the non-rainy periods through a year. For the relations to the basic water qualities, the negative correlation was obtained between EC and dissolved PAH concentration. For particulate PAHs, their content was negatively correlated with SS concentration, suggesting that PAHs were not included mainly in soil particles running into rivers on rainy days. Using flow rate of water and change in PAH concentration with time, yearly PAHs loadings were calculated. This study obtained 66 $\mu\text{g m}^{-2}\text{ year}^{-1}$ of PAHs loading in the Kurose River, and loading on rainy days and that on non-rainy days was clarified to be in the same order. The yearly PAHs loadings were compared to road traffic and atmospheric deposition in the river basin area. The value of the yearly load was comparable with that of atmospheric deposition. From the comparison, the underestimation of the road traffic, or the existence of other major sources than traffic activities was suggested.

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