Characteristics of particle-associated PAHs in a first flush of a highway runoff

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Abstract Runoff monitoring of six rainfall events was carried out in a highway, Winterthur, Switzerland focusing on first flush (runoff volume up to 2.88 mm). Six runoff events were used to investigate the characteristics of particle-associated PAHs in first flush. The fine fraction (< 45 μm) had a relatively higher contribution than the coarse fraction. A significant contribution of the coarse fraction was observed at some periods when the runoff flow rapidly increased. Fluctuation of PAH content during a runoff event was significant in the coarse fraction and, in contrast, the PAH content in the fine fraction was less fluctuating. The weighted average PAH content in each event ranged from 17 to 62 μg/g in total SS, from 23 to 54 μg/g in the fine fraction and from 16 to 84 μg/g in the coarse fraction. The loading of particle-associated PAHs from the first flush of highway runoff ranged from 0.06 to 0.22 g/ha in a total of 12 PAH species.
Keywords First flush; highway runoff; PAH content; PAH profiles; suspended solids

Introduction

For the last few decades road/highway has been considered as one of the major contributing sources of diffuse pollution (Lee *et al.*, 1995; Barret *et al.*, 1998; Drapper *et al.*, 2000; Furumai *et al.*, 2002). During wet weather period, stormwater runoff carries many toxic pollutants such as polycyclic aromatic hydrocarbons (PAHs) (Pitt *et al.*, 1995; Boxall and Maltby, 1997). The PAHs are contained in vehicle exhaust gas as well as asphalt pavement and tire rubber. Since they are hydrophobic in nature, they are mostly attached to the solid particles and deposit on the road surface (Yang *et al.*, 1999).These PAHs are mainly discharged at an early period of runoff (Smith *et al.*, 2000). The phenomenon in the early period of stormwater runoff, in which the concentration of pollutants is substantially higher than in the later period, is called "first flush". For good management of pollution control, it is required to understand the first flush phenomenon (Hoffman *et al.*, 1984; Xanthopoulos and Augstin, 1992).

During runoff the solid particles of various sizes are remobilized and transported under different hydraulic conditions. One of the most important factors which control the transportation of particle-associated PAHs in runoff is particle size. Only a few studies discuss the behavior of PAHs in the first flush and the influence of different particle sizes (Krein and Schorer, 2000; Shinya *et al.*, 2000). The wash-off behavior of size fractionated SS and associated PAHs is less known. The current research work aims to investigate particle-associated PAH content in size fractionated SS and PAH composition in total SS at the early period of runoff (first flush) from a highway in six rainfall events.

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Materials and method

Study area

Runoff monitoring of six rainfall events was carried out at an inlet point of a retention pond facility for a highway drainage system covering an area of 8.4 ha in Winterthur, Switzerland from October to December 2000. Figure 1 provides the area of sample collection and Table 1 shows the outline of the sampling area. The highway traffic volume was 25,300–73,700 vehicles per day from and into Zurich. The average number of light duty vehicles (bike, car and van) in the area was 22,200–58,700 while the average number of heavy-duty vehicles (bus and trucks) was 4,200–7,500 on weekdays and 800–1,300 at the weekend. The average daily wind speed of the area ranged from 0.5 to 4.7 m/s (average 1.85 m/s).

Sample collection

The number of total rainfall events in the area was 166 in the year 2000. The continuous rainfall record was separated into discrete rainfall events by applying an inter event time definition (IETD) of 8 hours. The initial loss from the road surface was 0.7 mm from the field monitoring data using the rainfall runoff relationship. Thus, we considered effective rainfall (able to runoff) only when the rainfall height exceeded 0.7 mm and IETD greater than 8 hrs. The total effective rainfall was 121 in year 2000. The effective rainfall events were categorized into four groups according to the rainfall height (Figure 2a). Stormwater samples of six runoff events on Oct.26, Oct.31, Nov.3, Nov.14, Nov.17 and Dec.8 in 2000 were used to study the characteristics of particle associated PAHs in a first flush. Table 2 provides the characteristics of the six events. The collected runoff samples represented moderate/strong rainfalls as well as three antecedent dry weather period (ADWP) conditions (Figure 2b).

The early phase of runoff, corresponding to the first 2.88 mm rainfall, was captured for the “first flush” phenomenon. Autosamplers were set to collect the runoff samples into 24 bottles at an interval of 10 m^3 runoff volume (0.12 mm rainfall) in the drainage area. The sampling was carried out once the flow rate exceeded 8 L/sec and was stopped at below 5 L/sec. The collected runoff samples were filtered through the glass fiber filter (Whatman GF/C with pore size 1.2 μm) and SS was recovered. The filters with SS were dried below 40 °C and kept in a desiccator for a while. Then they were preserved in refrigerator till further analysis.

The SS on four runoff events (Oct.26, Oct.31, Nov.3 and Nov.14) was fractionated into two different particle sizes, 1.2–45 μm (fine) and 45–2,000 μm (coarse) using stainless steel mesh sieves (wet sieving). In case the SS concentration was low, the SS

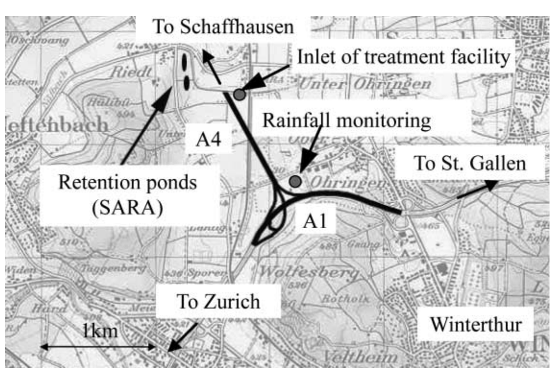

Figure 1 Sampling area

Table 1 Characteristics of highway

Highway route name	Length (km)	Area (ha)	ADT* (vehicles/day)
A1	1.8	5.5	57,500
A4	1.2	2.0	25,300
Ramp area	0.6	0.9	73,700
Total		8.4	

*ADT = Average daily traffic

samples in serial bottles were mixed together to recover a sufficient amount of suspended particles for the size fractionation.

Chemical Analysis

For PAH analysis, the SS samples were mixed with a solvent of dichloromethane and methanol (5:1 by volume). Three internal standards (phenanthrene-d10, chrysene-d12, and perylene-d12) were added into the mixture sample to correct the recovery rate of the analytes. The mixture was then applied to sonication for 30 minutes (50% cycles, 160 watt) for extraction of PAHs. The obtained extract was filtered through a glass fiber filter (GF-75, Advantec). The filtrate was evaporated to dryness below 40 °C. The dried extract was finally dissolved in dichloromethane and PAHs in the solution were analyzed using GC/MS (Hewlett Packard HP6890 GC coupled with HP 5973 mass selective detector) in SIM mode. The quantified PAHs were phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, and benzo(ghi)perylene. The PAH content reported in this paper is the sum of all individual target analytes.

Results and discussion

SS particle size variation in runoff

The size distribution of SS in runoff samples showed a significant fluctuation with runoff volume (Figure 3). In all four events, the fine fraction had a relatively higher contribution than the coarse fraction. Especially in the events on Oct.26 and Nov.3, the fine fraction showed its domination during the first flush period. The fine fraction contribution varied from 49% to 92% on Oct.26 and from 73 to 90% on Nov.3. In the events on Oct.31 and Nov.14, a significant contribution of the coarse fraction was observed when the flow increased rapidly. But a similar increase on Nov.3 did not give a significant rise of coarse fraction contribution. The antecedent condition (antecedent rainfall, wind speed in antecedent dry weather period, etc.) may give the difference as well as a variation of the fine/coarse ratio at the beginning of each event despite a similar flow rate.

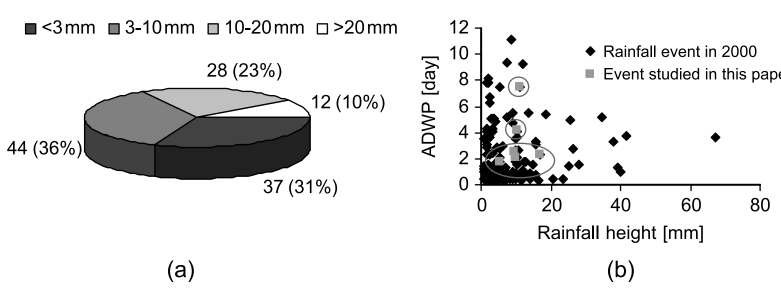

Figure 2 Characteristics of effective rainfall events (a) according to rainfall height and (b) ADWP (antecedent dry weather period) at Winterthur, Switzerland in 2000

Table 2 Characteristics of runoff events

	Whole event					First flush period	
	RH	Duration	PRV	ADWP	ADWP (2.88 mm)	RT	MRI
Oct.26	5.2	18.83	2.1	1.77	10.13	10.04	4.8
Oct.31	10.2	11.16	5.2	4.19	4.19	4.68	3.0
Nov.3	9.6	20.16	1.6	2.57	2.94	6.02	4.2
Nov.14	11.0	13.33	2.2	7.53	9.22	4.80	3.0
Nov.17	17.0	20.66	11.0	2.28	2.28	1.33	2.4
Dec.8	5.2	24.50	1.5	2.04	10.24	4.40	3.0

Note: RH = rainfall height [mm], Duration = rainfall duration [h], PRV = previous rainfall volume [mm], ADWP = antecedent dry weather period [day], ADWP (2.88 mm) = antecedent dry weather period when neglecting small rainfalls (< 2.88 mm) [day], RT = runoff time for 2.88 mm [h], MRI = maximum rainfall intensity in first 2.88 mm runoff [mm/h]

Content of PAHs in total SS and fractional SS

PAH content in runoff particles is shown in Figure 4 and Table 3. Fluctuation of the PAH content in the first flush period was significant in the coarse fraction and, in contrast, the PAH content in the fine fraction was less fluctuating (Figure 4 (bottom)). The fluctuation may be caused by the particle size distribution in the coarse fraction. In this study, the fractionation was conducted only at 45 μm and no further fractionation was done. According to Yang *et al.* (1999), the PAHs are mostly attached to the road dust particles of about 63 and 65.5 μm. Murakami *et al.* (2003) statistically showed that the PAH content was high in the road dust finer than 106 μm compared with coarser dust particles (> 106 μm).

The weighted average PAH content in each event ranged from 17 to 62 μg/g in total SS, from 23 to 54 μg/g in the fine fraction and from 16 to 84 μg/g in the coarse fraction. The PAH content in total SS on Oct.26 was highest among the six runoff samples.

Compared with other samples, the samples on Oct.26 and on Nov.14 had obviously high and low PAH content (Table 3). Both of the events had a long antecedent dry weather period (if small rainfalls were neglected as shown in Table 2). There are both possibilities to increase and to decrease the PAH content of runoff particles by a long

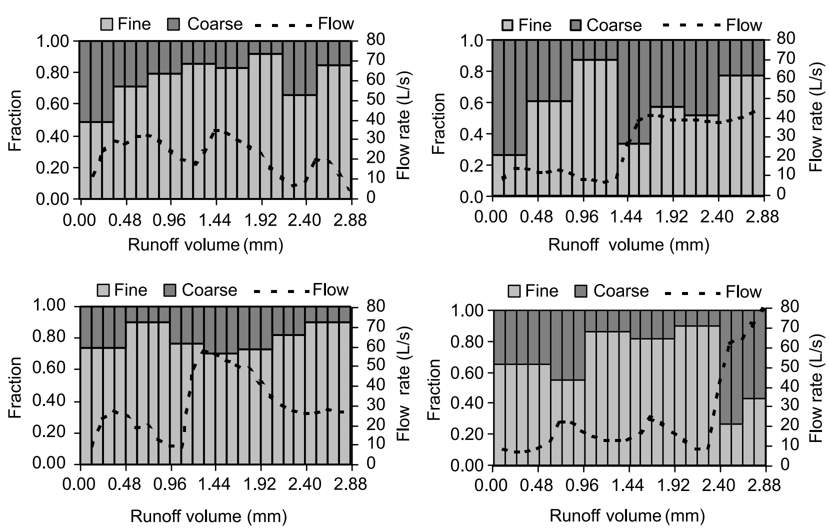

Figure 3 Fractional contribution by weight of fine and coarse particles during runoff on Oct.26 (top left), Oct.31 (top right), Nov.3 (bottom left) and Nov.14 (bottom right)

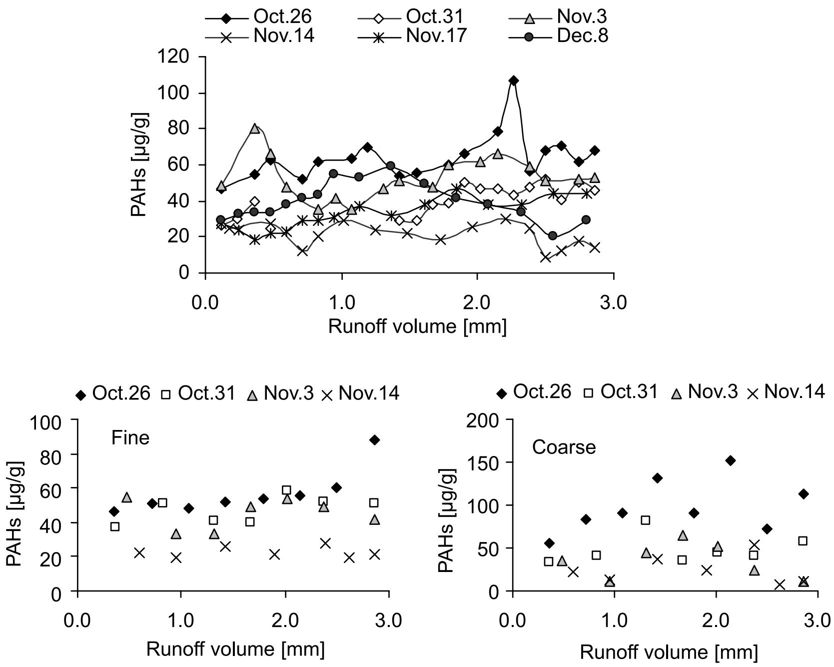

Figure 4 Variation of PAH content in total SS (top) and fractional SS (bottom)

exposure to antecedent dry conditions. Particles may be exposed repeatedly to the gas phase PAHs in a highway environment and it may increase PAH content. On the other hand, photodegradation of PAHs by sunlight during the antecedent dry weather period will decrease the observed PAH content. Wind may selectively remove fine particles which may have a specifically high/low content of PAHs. This field survey shows that the situation is too complicated and difficult to be generalized, and this means that a single/spot sampling is insufficient to understand the highway environment.

An average PAH profile (composition) of the runoff particles in each event is plotted in Figure 5. The PAH profiles were similar to each other but some difference was observed in the event on Oct.26 and on Nov.14, which had a long ADWP (2.88 mm) as already discussed. The contribution of 4-ring PAHs was high on Oct.26 and benzo(a)pyrene content was high on Nov.14.

The loading of particle-associated PAHs from first flush of highway runoff was calculated as shown in Table 4. The PAH load ranged from 0.06 to 0.22 g/ha in a total of 12 PAH species. Some major PAH species were benzo(k)fluoranthene, fluoranthene and pyrene. In this study, only the particle associated PAHs were measured and some of the low molecular weight PAHs must be present also in a dissolved form. Then this calculated load must be lower than the real load of total PAHs from the highway runoff.

Table 3 Weighted average content (µg/g) of PAHs in runoff particles

	Oct.26	Oct.31	Nov.3	Nov.14	Nov.17	Dec.8
Fine fraction	54	50	48	23		
Coarse fraction	84	40	78	16		
Total	62	44	48	17	32	37

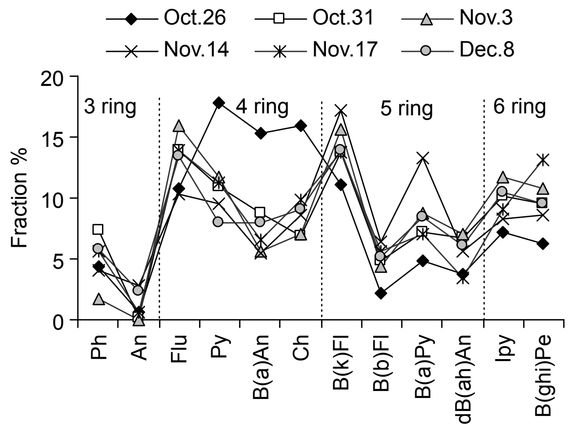

Figure 5 Average PAH profiles of six runoff events. Where, Ph-phenanthrene, An-anthracene, Flu-fluoranthene, Py-pyrene, B(a)An-benzo(a)anthracene, Ch-chrysene, B(k)Fl-benzo(k)fluoranthene, B(b)Fl-benzo(b)fluoranthene, B(a)Py-benzo(a)pyrene, Ipy-indeno(1,2,3-cd)pyrene, dB(ah)An-dibenzo(a,h)anthracene, B(ghi)Pe-benzo(ghi)perylene

Table 4 Loading (g/ha) of particle-associated PAHs from first flush of highway runoff

	Oct.26	Oct.31	Nov.3	Nov.14	Nov.17	Dec.8	Average load
Phenanthrene	0.0079	0.0093	0.0037	0.0025	0.0077	0.0097	0.0068
Anthracene	0.0012	0.0002	0.0000	0.0017	0.0011	0.0037	0.0013
Fluoranthene	0.0196	0.0161	0.0347	0.0064	0.0237	0.0235	0.0207
Pyrene	0.0305	0.0120	0.0254	0.0059	0.0143	0.0139	0.0170
Benzo(a)anthracene	0.0260	0.0095	0.0122	0.0034	0.0084	0.0134	0.0121
Chrysene	0.0268	0.0077	0.0149	0.0054	0.0126	0.0164	0.0140
Benzo(k)fluoranthene	0.0192	0.0171	0.0335	0.0105	0.0174	0.0237	0.0202
Benzo(b)fluoranthene	0.0040	0.0059	0.0091	0.0038	0.0072	0.0088	0.0065
Benzo(a)pyrene	0.0084	0.0090	0.0189	0.0080	0.0088	0.0140	0.0112
Dibenzo(a,h)anthracene	0.0062	0.0090	0.0157	0.0033	0.0043	0.0096	0.0080
Indeno(1,2,3-cd)pyrene	0.0125	0.0130	0.0254	0.0049	0.0114	0.0174	0.0141
Benzo(ghi)perylene	0.0112	0.0120	0.0233	0.0052	0.0166	0.0161	0.0141
Sum of 12 PAHs	0.17	0.12	0.22	0.06	0.13	0.17	0.15

Conclusion

A long term monitoring of a highway runoff was carried out. The particle-associated PAHs were subjected to analyses in total SS as well as in fractional SS. The following could be concluded.

- The fine fraction ($<45\,\mu$m) had a relatively higher contribution than the coarse fraction. A significant contribution of the coarse fraction was observed at some periods when the runoff flow rapidly increased.
- Fluctuation of PAH content during a runoff event was significant in the coarse fraction and, in contrast, the PAH content in the fine fraction was less fluctuating.
- The weighted average PAH content in each event ranged from 17 to 62 μg/g in total SS, from 23 to 54 μg/g in the fine fraction and from 16 to 84 μg/g in the coarse fraction.
- The loading of particle-associated PAHs from first flush of highway runoff ranged from 0.06 to 0.22 g/ha in a total of 12 PAH species.

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