Runoff pollution impacts of polycyclic aromatic hydrocarbons in street dusts from a stream network town

Hongtao Zhao, Chengqing Yin, Meixue Chen and Weidong Wang

ABSTRACT

Runoff with contaminated street dusts has an environmental risk to the aquatic environment. An assessment of the diffuse pollution of polycyclic aromatic hydrocarbons (PAHs) from a small town and their risks to the township stream network was conducted at Yangtze River delta. This assessment is based on measurements of 16 PAHs from the US EPA priority list by GC-MS in stream water during rainy and dry season, street dusts with different particle sizes, river sediments and suspended solids of urban runoff. The maximum level of PAHs in the stream water (2,323–4,948 ng L⁻¹) were found during rainy season, while significantly lower PAHs concentrations (242–998 ng L⁻¹) were measured during dry season. The total PAHs ranged from 1,629 to 8,986 µg kg⁻¹ in the street dusts. Approximately 55% of the total PAHs were associated with street dust particles of diameters less than 250 µm and these accounted for 40% of the total. The town reaches sediments were rich in PAHs and it was suggested as the sink of street dusts. The research findings suggested that size of street dusts, the topographical and hydrological features of the landscape in the stream network were the important factors influencing PAH emitted to the receiving water. The contribution of urban surface runoff could significantly influence PAHs concentration in the stream water. To reduce the pollution of street dust into the stream network, the buffer zone along the hydrological pathway is suggested and the existing street cleaning methods should also be improved.

Key words | diffuse pollution, PAHs, stream network, street dust particle, urban runoff

Hongtao Zhao (corresponding author)

Chengqing Yin

Meixue Chen

Weidong Wang

State Key Laboratory of Environmental Aquatic Chemistry,

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Hongtao Zhao (corresponding author)

Graduate University of Chinese Academy of Sciences,

Beijing 100039, China

E-mail: htzhao@163.com

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) were a group of ubiquitous environmental pollutants some of which are known to be mutagenic or carcinogenic (Ravindra *et al.* 2008). Input of PAHs from point sources has gradually decreased because of enhanced discharge control (Schneider *et al.* 2001), while input of PAHs from urban stormwater runoff has been increasingly reported as one of the most frequent causes of surface water pollution (Murakami *et al.* 2004). Street dust particles in urban runoff act as a transport medium for PAHs (Brown & Peake 2006).

Spatial patterns within landscapes, such as the location, distribution and proportions of watershed areas can crucially affect pollutants export (Yin *et al.* 1993; Wang *et al.* 2005).

Stream network is one of the important water shapes, extensively existing in big river deltas (Saco & Kumar 2002), (Thomas *et al.* 2004). They have large land/water boundaries and most of polluted runoff can enter the water without buffer zones (Wiens 2002). The population density is usually heavy and these regions are under rapid urbanization. In China, most towns of stream network are rapidly industrializing and urbanization is increasing impervious areas. Abundant rainfall, and crisscrossed networks of canals accelerates the transport of street dust particles from the land surface to water bodies by surface runoff. In addition, the flow of water in stream networks is slow resulting in sediment accumulation (Salant *et al.* 2008). Unfortunately, some potential drinking

water sources in this area have become contaminated by micropollutants such as PAHs by stormwater runoff (Chen *et al.* 2007). Thus, the stream network area, which is one of the most developed areas in East China, suffers from severe contamination of PAHs from non-point urban sources.

The objectives of this study were (1) to find the important fractions of particle-bound PAH, (2) to look for the impact of street dust particle on receiving stream network.

MATERIALS AND METHODS

Study site description

The selected study site is Xincheng, a town on the Yangtze River delta and in Zhejiang Province in the southeastern

People's Republic of China (Figure 1). There is a warm and humid climate with four distinct seasons, sufficient sunshine and abundant rainfall. The mean annual temperature is 15.9°C, the mean annual sunlight is 1,800–2,200 hours and the average annual rainfall is 1,180 mm. Xincheng is a typical town on the delta with the stream density is 3.5 km/km².

Sample collection and size fractionating

The study was conducted during 2006–2007. Street dust particles were collected with a vacuum cleaner between 9 and 10 a.m. after sweeping on March 26th, 2006. The mass of street dust per unit of street surface was measured. The sampling sites for street dust particles were distributed in the following typical sites: 3 in main traffic road streets

Figure 1 | (a) Study area in Xincheng, a town with the dark shape in the stream network, the sediment sampling point at the Xincheng River, (b) a diagram of runoff in the stream network town with conduit flow and surface flow.

(R1, R2, R3), 3 in industrial streets (I1, I2, I3), 3 in commercial streets (C1, C2, C3), 2 in old residential streets (OR1, OR2), 4 in new residential streets (NR1, NR2, NR3, NR4). Sites R1, R2, and R3 are paved with asphalt and the others with concrete. Polyester sieves were used for grain size fractionation. Samples were sorted into particle size fractions of <63, 63–125, 125–250, 250–900 and >900 μm . PAHs were analyzed for each particle size fractions, except the large fraction >900 μm , which could be efficiently removed by the street sweepers (Sartor & Boyd 1972; Lau & Stenstrom 2005).

Samples of the upper 15 cm of streambed sediment were collected using a stainless steel grab sampler, at three sites in the Xincheng River: upstream (sed1), within the town (sed2), and downstream (sed3) of Xincheng [Figure 1(a)], with two samples per site. Samples of the upper 10 cm of town soil were collected from four sites: roadside, kindergartens, public squares and fallow land. The content of town soil was an average value of the soils from the four sites (Table 1).

Samples of runoff water and river water were taken in June and August in 2007. 42 mm rain fell in 190 minutes on 6/13/2007, and 22 mm of rain fell in 30 minutes on

8/24/2007. Runoff samples were taken manually at catch basins in the streets with an interval of 3 minutes in the first 30 minutes followed by 10 minute intervals until runoff ceased. At the same time, river water samples were also taken from Xincheng River before and during the rain events. Runoff volume was measured using calibrated polythene barrel with 20 L for higher volumes and 5 L for smaller volumes during rainfall events. Water samples were collected in plastic bottles and were analyzed in the laboratory within 5 days of the sampling. Details of sampling were similar to that of Wang *et al.* (2005) and Zhao *et al.* (2007).

Event mean concentration (EMC) is used to estimate the pollution loads in the runoff. It is a flow-weighted average of constituent concentration to characterize runoff pollution (Sansalone & Buchberger 1997), and calculated as

$$\text{EMC} = \frac{\int_0^1 C(t) \times Q(t) dt}{\int_0^1 Q(t) dt}$$

where, EMC is the event mean concentration (mg/L); $C(t)$ is the time variable concentration (mg/L); $Q(t)$ is the runoff flow rate discharged at time (m^3/min).

Table 1 | Mass of street dust per unit area of street surface by grain size fraction for roads from several urban districts

Land use*	Mass of street dust per area (g/m^2)				
	>900 μm	250–900 μm	125–250 μm	63–125 μm	<63 μm
C1	0.4	0.9	0.5	0.4	0.3
C2	1.4	2.6	0.8	0.5	0.3
C3	5.2	7.5	2.5	1.7	0.6
I1	0.7	3.5	2.5	1.9	0.9
I2	9.5	10.3	2.6	1.3	0.5
I3	7.8	9.5	3.2	1.7	0.8
NR1	2.5	6.5	1.5	1.0	0.5
NR2	1.2	6.0	2.1	0.9	0.3
NR3	2.8	1.7	0.5	0.4	0.5
NR4	0.5	0.9	0.4	0.3	0.2
OR1	1.0	3.1	1.7	1.7	1.2
OR2	4.2	5.1	2.1	1.5	0.8
R1	1.0	2.5	1.1	0.5	0.1
R2	1.1	6.0	3.5	2.3	0.9
R3	8.1	7.5	3.0	1.8	0.6

*C, I, NR, OR and R represent: commercial, industrial, new residential, old residential streets and main traffic roads.

Analytical methods

The standards used were 16 USEPA priority PAHs [naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Fl), phenanthrene (Phe), anthracene (An), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (Inp), dibenzo[a,h]anthracene (DBA), and benzo[ghi]perylene (BgP)] in a solution of 2,000 $\mu\text{g}/\text{mL}$ and surrogate standards (acenaphthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12) in a mixture solution of 500 $\mu\text{g}/\text{mL}$. Both were purchased from Supelco (USA). All organic solvents of pesticide analytical grade were obtained from Fisher Co. (USA).

Street dust particles, sediment and soil samples were extracted with a Soxhlet apparatus. Each sample (10 g) was spiked with four surrogate standards (acenaphthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12), and then extracted with 200 mL of methylene chloride for 48 h, to which activated copper was added for desulphurization. The extract was pre-concentrated to 2 mL by a rotary

evaporator and the solvent was exchanged with hexane. The hexane extract was fractioned and cleaned up using an LC-Si SPE Tube (Supelco Co. Cat. No. SP7953C) capped with anhydrous sodium sulfate (1 cm). The tubes were eluted with 70 mL of methylene chloride/hexane (vol/vol = 3:7) to obtain PAHs. The PAH fraction was finally concentrated to 1 mL under a gentle stream of nitrogen.

The concentrations of PAHs in the extracts were determined using an Agilent 6890 gas chromatograph (GC) equipped with a splitless injector, HP-5 capillary column (30 m × 0.25 mm inner diameter × 0.25 µm film thickness) and a 5973 mass selective detector (MSD). The carrier gas was helium (ultra high purity) at a constant flow rate of 1 mL/min. The GC oven temperature was programmed from 50°C (2 min) to 200°C (2 min) at 20°C/min, then to 240°C (2 min) at 5°C/min before reaching 290°C at 3°C/min and held for 15 min. The injector and detector temperatures were 280°C and 300°C, respectively. Chromatographic data were collected and processed using HP Chemstation software. Detection limits were 1.1–5.3 µg/kg dry weight for PAHs. All the results were expressed on a dry weight basis.

Total organic matter (OM) was determined by ignition at 550°C for 2 h. The density of the street dust particles was measured with a pycnometer.

RESULT

The PAH contents in street dust particles, urban soil and river sediment

The contents of total PAHs in street dust particles (<900 µm) ranged from 1,629 to 8,986 µg/kg, with a mean of 4,130 µg/kg (Figure 2) in the Xincheng stream network. Of the five land use types, the dust particles collected from industrial area streets (I) had the highest PAH contents, while that from the new residential areas (NR) had the lowest. The magnitude of PAH contamination varied greatly in the sediments from different reaches of Xincheng River. Much higher total PAH concentrations were found in the town reach sediment (sed2). The town reach sediment (sed2) contained comparable amounts of PAHs to street dust particles, and the sediments from upstream and downstream reaches, and the town soil contained much lower PAH concentrations.

Figure 2 | Total PAHs contents in street dust particles, river sediments and urban soil. C, I, NR, OR and R represent: commercial, industrial, new residential, old residential streets and main traffic roads; sed1, sed2 and sed3: the sediments from the upstream, town section and downstream of the Xincheng River; soil: the town soil.

PAH contents of particle size fractions of street dust

The total PAHs and density in street dust particles with different size fractions showed a grain size gradient (Figure 3). Density varies from 1.62 to 1.85 g/cm³ in the four size-fractions. Higher contents of PAHs and smaller density occur in street dust particles with smaller grain size. It is suggested that they have high mobility in runoff and they are easily transported to the stream network (Murakami *et al.* 2005). Approximately 55% of total PAH were present in particles with diameters of less than 250 µm, accounting for 40% of the street dust particle weight.

Risk assessment and mobility of street dust particle to receiving water

To assess PAHs pollution in street dust particles and stream sediments, the results were interpreted using the effects range low (ERL) and the effects range median (ERM) values as defined elsewhere (Long *et al.* 1995). Table 2 shows that several PAH components contents in street dust, suspended sediment in runoff and streambed sediments are above the ERL and thus may moderately impact the biota health of stream network. Several PAHs in the street dust with the diameter less than 63 µm and suspended sediment of runoff are above the ERM, and these may severely impact biota health. The smaller street dust particles have even higher PAH content and it is expected that if the runoff

Figure 3 | The density of street dust particles and total PAH contents in the size-fractions of the street dust particles (C, I, NR, OR, R have the same meaning as in Figure 2).

Table 2 | Pollution criteria of PAH components for sediment matrix (μg/kg) suggested by Long *et al.* (1995) and Wang *et al.* (2005). Several PAH components are in the range between ERL and ERM where toxic effects were possible

Compound	ERL	ERM	sed1	sed2	sed3	SS1	SS2	<63 μm	125–63 μm	250–125 μm	900–250 μm
Nap	160	2,100	28	147	19	<u>393</u>	<u>410</u>	<u>322</u>	<u>365</u>	<u>389</u>	<u>223</u>
Acy	44	640	7	9	2	19	<u>96</u>	<u>86</u>	<u>83</u>	<u>72</u>	43
Ace	16	500	2	<u>36</u>	3	<u>27</u>	<u>58</u>	33	30	29	17
Fl	19	540	12	83	8	<u>245</u>	<u>211</u>	<u>158</u>	<u>139</u>	<u>123</u>	<u>73</u>
Phe	240	1,500	74	<u>576</u>	28	1,919	<u>768</u>	<u>1,022</u>	<u>1,035</u>	<u>858</u>	<u>587</u>
An	853	1,100	16	78	6	158	89	168	172	161	113
Flu	600	5,100	126	525	81	<u>2,249</u>	<u>836</u>	<u>925</u>	<u>698</u>	540	353
Pyr	665	2,600	102	454	109	<u>2,423</u>	<u>533</u>	645	483	395	271
BaA	261	1,600	92	<u>318</u>	62	7,956	<u>1,215</u>	<u>364</u>	<u>283</u>	218	167
CHr	384	2,800	125	457	122	<u>647</u>	<u>511</u>	<u>613</u>	<u>467</u>	366	195
BbF	NA	NA	153	585	156	4,657	1,020	917	736	531	224
BkF	NA	NA	53	234	38	2,003	685	315	227	124	76
BaP	430	1,600	113	358	95	78	236	<u>537</u>	370	246	157
InP	NA	NA	1	76	7	9,111	1,339	229	160	142	65
DBA	63	260	1	<u>222</u>	2	6,457	4,140	436	<u>208</u>	<u>176</u>	<u>180</u>
BgP	NA	NA	30	245	30	4,265	1,322	491	377	288	164
Total	4,000	44,792	934	4,402	767	42,608	13,470	7,261	5,835	4,660	2,909

NA: not available; The underlined data are above the ERL or ERM values.

continues washing the street dust particles into the river, the sediment PAH content would probably continue to increase.

Due to the slow flow of water in the stream network, street dust particles in urban runoff accumulate in the sediments close to the point of entry into the network. Figure 2 shows that the town reach sediment (sed2) had much higher total PAHs content than the sediments in the upstream and downstream reaches.

Surface runoff caused by rainfall contributes PAHs to the receiving water. This pollution is mostly in particulate form. Street dusts make a great contribution to the urban runoff particulate pollutants. The particle-bound PAHs account, on average, for 94.7% and 93.6% of total PAHs in two rainfall events in June and August in 2007 (Table 3).

The urban runoff water affects the water quality of Xincheng River markedly in the town reach during heavy rainfall events (Table 4) and the particle-bound PAHs account for the most. It was observed that the total PAHs concentrations in the stream increased 43%–62% during the rainfall events, and more than half of the increase was from particulate matter. Because the heavy rainfalls do not generate high flows in the stream networks, large-sized particles are deposited at runoff entry sites and accumulate there. This is probably the reason why the town reach

sediments (sed2) have much higher contents of PAHs than the sediments in the upstream and downstream reaches (Figure 2).

Buffer zones between the pollution sources and the receiving water can control pollutant transport (Lu *et al.* 2007). The distances between the sampling sites and the receiving water are small, and those distances and the pathways by which street dust particles enter the receiving water, are shown in Figure 1(b). The street dust mobilized by stormwater enters receiving water by either direct surface flow or conduit flow. The increasing size of impervious areas in the town could generate a high runoff. There are usually no buffer zones between the street and the receiving water in this town. The PAHs in street dust were quickly washed into the receiving water.

Stream networks in large river deltas have special hydrological characteristics. In this area, the plain land is divided into many small pieces by the stream channels. The slope of streams is very low and the flow velocity is affected by many factors. Because there are many flow routes and wetlands in the stream network, the peak velocity is greatly reduced after rainfall. It was observed that there was small flow, no flow or back flow in Xincheng River, even during rainfall events. The mean levels of PAHs in the water in May and July ranged from 1,956 to 2,582 ng/L while in

Table 3 | Event mean concentration (EMC) of total suspended sediment (TSS) and PAHs contents in runoff water during two rainfall events

Date of rain event	Land use	PAHs forms	2 + 3 ring (%)	4 ring (%)	5 + 6 ring (%)	ΣPAH ng/L	TSS mg/L
6/13/2007	R	Dissolve	47	28	24	1,675	425
		Particle	15	29	56	30,195	
		Total	17	29	54	31,870	
8/24/2007	R	Dissolve	32	25	42	811	283
		Particle	23	22	55	5,686	
		Total	30	22	48	6,497	
	C	Dissolve	31	22	47	738	455
		Paritcle	14	29	57	18,099	
		Total	18	29	54	18,837	
	I	Dissolve	26	37	37	630	585
		Particle	17	30	52	27,852	
		Total	14	29	57	28,482	
	NR	Dissolve	19	26	56	611	292
		Particle	26	36	38	8,115	
		Total	18	29	53	8,717	

Table 4 | Total suspended sediment (TSS) and total PAHs contents (in ng/L) in Xincheng River before and during two rainfall events

Date of rain event	PAHs forms	TSS		2 + 3 ring		4 ring		5 + 6 ring		ΣPAHs	
		B.R	D.R	B.R	D.R	B.R	D.R	B.R	D.R	B.R	D.R
6/13/07	Particle			346	484	91	153	145	522	582	1,159
	Dissolve	35	131	723	975	117	219	392	347	1,232	1,542
	Total			1,070	1,459	208	372	537	869	1,815	2,701
8/24/07	Particle	38	230	286	532	54	281	796	1,105	1,136	1,918
	Dissolve			181	283	39	67	166	198	386	547
	Total			467	814	93	348	962	1,303	1,522	2,465

November and January significant lower PAHs concentrations were measured (311–475), which suggested that PAHs contamination in water was heavier during rainy season than during dry season (in Table 5). One of possible explanations could be the increased surface runoff and atmospheric deposition in rainy season.

DISCUSSION

The size of the street dust particles is a critical factor affecting the pollutant's mobility and remove efficiency. The behavior of street dust in runoff depends on its grain size-distribution (Furumai *et al.* 2005; Murakami *et al.* 2005). Street dust makes a great contribution to the runoff pollutant load (Stone & Marsalek 1996; Walker *et al.* 1999; Rocher *et al.* 2004). The smaller street dust particles have

higher PAHs contents due to greater surface area per volume and to higher organic matter contents, indicative of pollutant adsorption onto dust particles (Hoffman *et al.* 1982; Roger *et al.* 1998; Andral 1999).

Street dust has environmental impact to receiving waters and management actions should be taken to reduce the pollution at the sources. However, Xincheng town streets are swept with a push broom. The previous researchers found that this method is only effective for removal of large particles and is ineffective for small particles with high PAHs contents.

In this research, it was found that the PAHs contents in suspended sediment in runoff were even higher than less than those in less than 63 μm fraction, suggesting that the diameter of suspended sediment particles in runoff was probably much smaller. Larger dust particles are deposited onto the bed sediment; smaller particles remain in suspension longer and could be transported to the drinking water plant farther downstream in the Xincheng River, bringing a health threat to local communities. For this reason, we suggest actions should be considered to reduce the transport of street dust pollution to the stream network.

CONCLUSION

Smaller street dust particle had higher content of total PAHs, and lower densities, higher mobility and PAHs contamination during urban runoff. The high density of channels in the area, short distance between the streets and the receiving waters and the absence of buffer zones accelerated the street dust particles transfer from the streets into the stream network.

Table 5 | PAHs contents in Xingcheng River during rainy and dry seasons (ng/L)

Sampling time		Compound	2 + 3 ring	4 ring	5 + 6 ring	ΣPAHs
Rainy season	Jul	Particle	62	29	9	1,555
		Dissolve	45	45	10	1027
		Total	55	35	9	2,582
	May	Particle	70	23	7	1,420
		Dissolve	76	22	2	562
		Total	71	23	6	1,956
Dry season	Jan	Particle	52	40	8	154
		Dissolve	89	9	2	158
		Total	71	24	5	311
	Nov	Particle	58	29	13	213
		Dissolve	82	16	2	262
		Total	72	22	7	475

Urban runoff was one of the import reasons for higher PAHs concentration in the stream water in rainy season.

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