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Characteristics of heavy metal pollution in highway runoff

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Abstract The rainfall–runoff flow rate, and heavy metal content (Cu, Zn, Pb, Cd, Ni, Cr) for highway runoff events were studied for three roads in Guangzhou, China. During the rainfall–runoff event, a distinct "first flush" of heavy metals was recorded. Their concentrations peaked at an early stage during rainfall and then decreased with the progression of the rainfall–runoff event. Heavy metal concentrations reached their lowest values when the runoff flow rate peaked, and then increased slightly again as the runoff flow rate decreased. Heavy metals in the runoff showed significant correlation with one another, as well as a clear correlation with the quantity of suspended solids in the runoff. Most heavy metals existed either as adsorbed to suspended solids or as free metallic particles. The degree of heavy metal pollution was found to be closely related to surrounding land use. Runoff from an urban road had the highest mean concentration of heavy metals per runoff event, whereas runoff from a suburban road and a road at the urban–suburban boundary had lower heavy metal concentrations, and were similar. Lead was identified as the main heavy metal pollutant in highway runoff.

Key words highway; rainfall; runoff; heavy metal pollution

INTRODUCTION

Heavy metals are released from vehicle traffic through various mechanisms, such as exhaust emissions, brake and tyre wear, and corrosion of metallic parts. The heavy metals released accumulate on highways during dry periods. When rainfall occurs, these heavy metals are transported by dissolution or washing from the highway as runoff. This results in direct pollution of neighbouring water bodies and the roadside soil. Studies of heavy metal pollution of highways have considered surface sediments, including their characteristics and the concentrations of metals (Legret & Pagotto, 2006), the particle size distribution and phase partition (Lee *et al.*, 2005; Momani, 2006), the morphologies of metal particles in the sediments, and their build-up on highways (Varrica *et al.*, 2003; Deletic & Orr, 2005). However, the migration of heavy metals under the washing action of rain, and their partition between solid and liquid phases, has not been studied intensively (Sansalone & Buchberger, 1997; Shinya *et al.*, 2000; Zhao *et al.*, 2001).

In this study, runoff on three representative highways in Guangzhou, China, was analysed during rainfall events. The rainfall and runoff flow rates were continuously monitored, and the runoff was sampled regularly. The objectives of the study were: (a) to understand better the migration of heavy metals under rain washing, (b) to determine the proportions of the washed-out heavy metals between the solid and liquid phases, and (c) to describe the discharge of these pollutants. Overall, this study provides baseline information for the informed management of heavy metal pollution resulting from highway runoff.

MATERIALS AND METHODS

Sampling sites

Sampling sites were selected from the representative sections of three highways in the urban and the northern suburban areas of Guangzhou, China. Site S, a viaduct section in the highway from the Guangzhou inner ring road to Shantou, was in the urban area. At this site, highway runoff collected in downspouts and then drained into underground storm drains. Site C, at the intersection between the northern section of the Guangzhou ring expressway and the Guangzhou-Shenzhen expressway, was at a boundary between urban and suburban areas. The embankment at this site was 7 m above the ground surface, and the runoff flowed along gutters to outlets and finally drained to roadside ditches. Site Y, the Yushatan section of the Beijing-Zhuhai expressway, was in the northern suburb of Guangzhou city. The catchment area for this section consisted of viaducts and runoff was collected by downspouts and drained onto the grass slopes under the viaducts. The sides of all road sections studied were fully closed. More details of the sites are listed in Table 1.

Table 1 Characteristics of the highway runoff sampling sites.

Site	S	C	Y
Drainage area (m^2)	135	110	115
Road surface material	Asphalt	Concrete	Asphalt
Imperviousness (%)	100	100	100
Number of lanes	3	3	4
Average daily traffic	22 170	43 200	31 000
Surrounding land use	commerce/traffic/residence	forest/traffic/residence	agriculture/villages

Sampling and monitoring

Monitoring equipment was placed at the runoff outlets. The equipment consisted of an automatic water sampler, a 60° triangular weir, and an ultrasonic flow sensor. The water height in the weir was detected by the flow sensor and transmitted to the sampler. This water height was processed by a microprocessor in the sampler and converted into flow rate. The runoff was sampled regularly, usually at intervals of 5–10 minutes during the early stage of rainfall and at intervals of 20 or 30 minutes at later stages, depending on the rainfall intensity. During each rainfall–runoff process, 3–8 runoff samples were collected using plastic containers (1-L) and immediately sent to the laboratory for pretreatment. The volume of rainfall was measured using raingauges.

Analyses of runoff samples

The samples were preserved and analysed according to standard methods specified by China SEPA (China's State Environment Protection Agency, 2002). Suspended solids (SS) and six heavy metals (Cu, Zn, Pb, Cd, Ni, Cr) were analysed. The SS concentrations were determined by filtration through 0.45-μm filters, followed by drying and weighing of the residue (detection limit: 0.1 mg L^{-1}). Concentrations of Cu and Zn were determined using flame atomic absorption spectrophotometry (detection limits: 0.006 mg L^{-1}). Pb and Cd concentrations were determined using graphite furnace atomic absorption spectrophotometry (detection limits: 1.1 and 0.2 μg L^{-1}) and Cr and Ni concentrations were determined using inductively coupled plasma atomic emission spectrometry (detection limits: 2.0 μg L^{-1}). Some samples (below the detection limits in their original state) were pre-concentrated before analyses to allow heavy metal determination. Precision was checked using replicate samples, and accuracy by the analysis of standard samples.

RESULTS AND DISCUSSION

Hydrological parameters of rainfall–runoff events

The hydrological parameters of the monitored rainfall–runoff events are listed in Table 2. The runoff volumes were obtained by integration of the runoff flow rates recorded in the hydrographs.

Table 2 Hydrological characteristics of the monitored rainfall–runoff events.

Site	Date	Runoff volume (L)	Runoff duration (min)	Rainfall volume (mm)	Rainfall duration (min)	Antecedent dry period (days)
S	25/07/2006	1530.0	22.5	10.9	20	126
C	05/10/2006	1928.2	84.0	16.3	48	90
Y	05/10/2006	4621.7	58.5	47.0	61	90

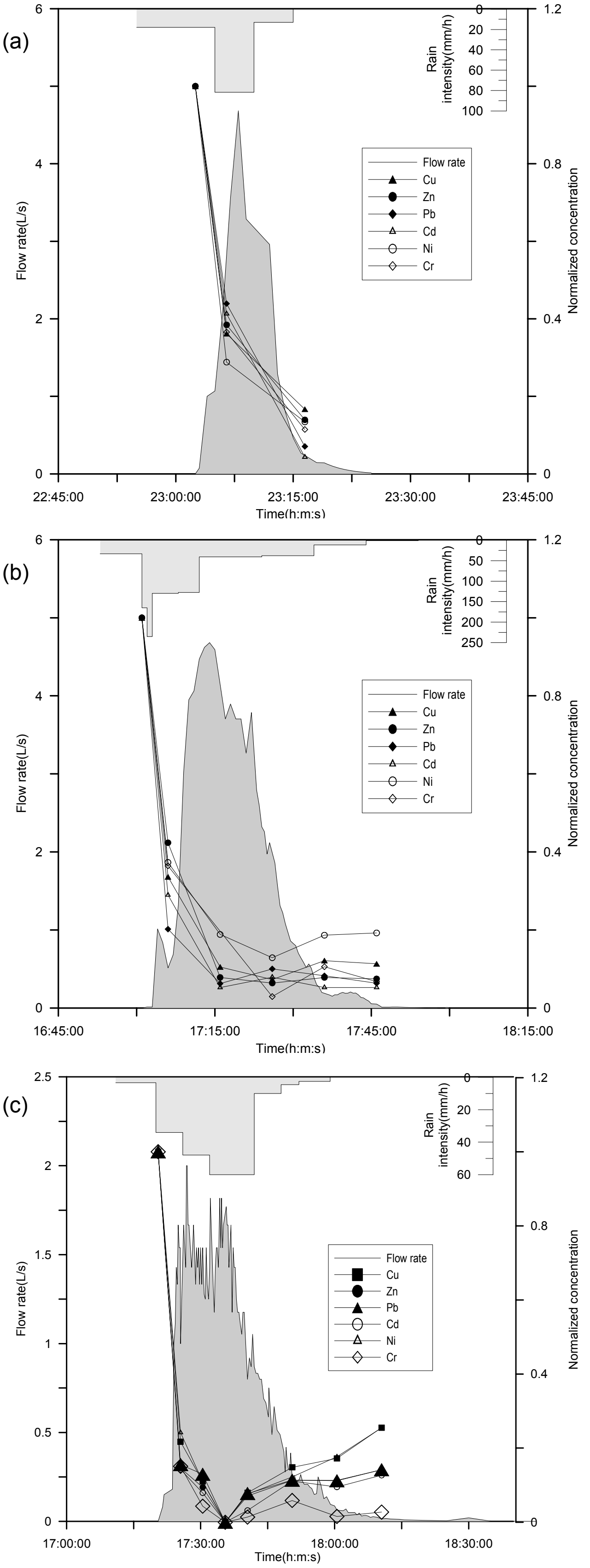

Fig. 1 Hydrographs showing the rainfall intensities, runoff flow rates, and heavy metal concentrations with monitoring time during the rainfall events at the three sampling sites S (a), C (b) and Y (c). See Table 1 for site details and Table 2 for hydrological details

The rainfall event monitored at site S was short and the rainfall level was low, but the duration of dry antecedent conditions prior to the event was relatively long. The rainfall events monitored at sites C and Y occurred in the same day and both lasted longer than the one recorded at site S. Moreover, the rainfall levels of both were high, although substantially different from one another due to location differences. Generally, all three rainfall events were unimodal.

Washing of heavy metals by highway runoff

Figure 1 shows rainfall intensities, runoff flow rates, and concentrations of the heavy metals (normalized against their peak values) recorded at the three sites during the rainfall–runoff events. The runoff flow rates were clearly positively related to rainfall intensities. The washing of heavy metals by runoff for all three highway sections demonstrated a similar "first flush", with concentrations of heavy metals peaking during the early stage of runoff followed by a steady decrease in concentration as the rainfall–runoff event progressed. These patterns are consistent with the results of other studies (Shinya *et al.*, 2000; Lee, 2003; Stenstrom & Kayhanian, 2005). Since most heavy metals that had accumulated during the dry periods were removed in the early stage of each rainfall–runoff event, the amount of heavy metals remaining on the highways, and thus their concentrations in the runoff, decreased over time. Metal concentrations reached minimum values with the peaking of runoff flow rates, and subsequently increased slightly as runoff flow rates decreased again (Fig. 1(b), (c)). This pattern was not observed at site S (Fig. 1(a)) as the number of samples was too limited. This change in concentration may be attributed to the vehicle traffic during rainfall. Although heavy metals accumulated during dry periods were diluted by the rainfall, the vehicles on the highways were still releasing heavy metals at a relatively stable rate. Thus, concentrations of heavy metals reached a minimum when runoff flow rates peaked (due to maximum dilution) and subsequently increased because the reduction in flow rate resulted in a relatively greater concentration of the freshly released metals.

Correlation among heavy metals and with suspended solids

The suspended sediment and heavy metal concentrations of the runoff samples were analysed using Pearson linear correlations (Table 3). The correlation coefficients between all metal pairs were high (r = 0.69–0.99), reflecting a common source. The extensive use of alloys in vehicle parts may explain this. For example, brass is an alloy of Cu, Zn and Pb (Legret & Pagotto, 2006). Varrica *et al.* (2003) analysed roadway dust particles by electron microscopy coupled with energy-dispersive spectroscopy (SEM/EDS) and also found a variety of metals in the wear particles released by vehicles.

The occurrence of heavy metals in highway runoff has important implications for the control of runoff pollution (Sansalone *et al.,* 1995). The coefficients of correlation between the metals and suspended solids ranged between 0.57 and 0.98, with Cr and Zn being high, followed by Ni, and then by Cu, Cd and Pb. This indicates a clear interdependency between suspended solids and heavy metals in highway runoff. This is consistent with previous studies (Han *et al.*, 2006).

To investigate this relationship further, the heavy metal contents of the suspended solids and the total heavy metal contents in the runoff samples were compared. Three samples collected from site S were filtered using 0.45-μm filters and the resultant residues and filtrates were analysed separately (Fig. 2). In samples 1 and 2, the six heavy metals found in the suspended solids accounted for more than 70% of their respective total contents in the runoff samples. Sample 3 had a lower suspended solid concentration and a lower ratio between suspended solids and total heavy metals. Overall, heavy metals were mainly adsorbed to suspended solids or existed as metal particles in the highway runoff.

Event-mean concentration (*EMC*)

EMC is defined as the ratio between the total pollutant mass discharged during a rainfall–runoff event and the total runoff volume during that event, and is expressed as:

Table 3 Correlation between heavy metals and suspended solids in highway runoff.

	Cu	Zn	Pb	Cd	Ni	Cr
SS	0.78	0.96	0.57	0.66	0.92	0.98
Cu		0.89	0.95	0.97	0.94	0.86
Zn			0.74	0.78	0.98	0.99
Pb				0.97	0.81	0.69
Cd					0.85	0.75
Ni						0.97

Note: $n = 16$.

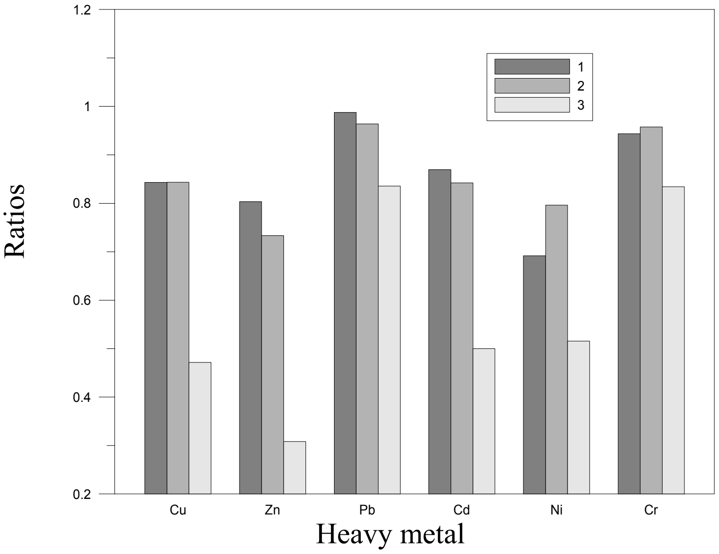

Fig. 2 Ratios of the heavy metals associated with suspended solids to the total heavy metal contents of runoff for three samples (1, 2, 3) collected from site S. A value of 1 indicates that 100% of the heavy metal was sediment-associated.

$$EMC = \frac{M}{V} = \frac{\int_0^{t_r} c(t)q(t)\mathrm{d}t}{\int_0^{t_r} q(t)\mathrm{d}t} \tag{1}$$

where M (mg) is the total pollutant mass discharged, V (L) is the total runoff volume, $c(t)$ (mg L^{-1}) is the time-variable concentration of the pollutant, $q(t)$ (L s^{-1}) is the time-variable volumetric flow rate, and t (s) is time. Because the measured flow rate and pollutant concentration are collected as discrete data, and the flow rate data usually far outnumber the pollutant concentration data, the following equation is generally used for the calculation of EMC:

$$EMC = \frac{M}{V} = \frac{\sum_1^{\mathrm{i}} c(t_i)Q_i}{\sum_1^{i} Q_i} \tag{2}$$

where $c(t_i)$ is the pollutant concentration at the ith time interval (mg L^{-1}), and Q_i is the volumetric flow rate at that time interval (L).

The EMC of heavy metals in the runoff was calculated using equation (2) (Table 4). The concentrations of heavy metals in the rain water were very low (Table 4) and their contribution to the runoff pollution was negligible.

Among the three sampling sites, site S had the highest EMC values for heavy metals, and the difference between sites C and Y was only moderate. This indicated that heavy metal pollution in the runoff was more serious in urban roads than in suburban ones. The pollutant concentrations in highway runoff are affected by many factors, e.g. the length of the dry period before rain, the

Table 4 Initial concentrations (*IC*) and event-mean concentrations (*EMC*) during the rainfall–runoff events.

Site	Concentration	Cu (mg L^{-1})	Zn (mg L^{-1})	Pb (μg L^{-1})	Cd (μg L^{-1})	Ni (μg L^{-1})	Cr (μg L^{-1})
S	*IC*	0.318	5.986	319.7	4.6	95.4	173.6
	EMC	0.104	1.935	100.6	1.3	26.5	52.7
C	*IC*	0.247	2.81	424.9	3.8	52	68.1
	EMC	0.041	0.476	51.3	0.5	11.9	8.7
Y	*IC*	0.290	2.120	469.9	6.3	47.5	51
	EMC	0.047	0.286	70.5	0.7	7.6	4.3
Rain		0.006	0.093	0.2	0.2	ND	ND

ND, not detected.

traffic volume, the characteristics of the rainfall and the runoff, the use of roadside land, and the nature of the pollutants. Typically, one single factor alone cannot account for all differences in pollutant concentrations in the runoff (Deletic & Orr, 2005). The comparison of the three sampling sites may reflect the fact that site S had a longer dry period before rain than sites C and Y, since its traffic volume and runoff flow rate were not the highest of the three sites. Nonetheless, site S was in an urban area and the roadside land was used for commercial and/or traffic purposes, and had a high concentration of highway runoff. In comparison, sites C and Y were in suburban areas and roadside land mainly consisted of forest or agricultural areas, which would facilitate the diffusion and dilution of heavy metal pollutants. These differences could, therefore, result in higher heavy metal concentrations in runoff from urban highways than from suburban ones. Thus use of roadside land can be an important factor in determining heavy metal pollution in highway runoff.

CONCLUSION

(a) The highway runoff clearly shows a “first flush” of heavy metal pollutants during the onset of rainfall. Heavy metal concentrations peaked during early stage rainfall and then steadily decreased as rainfall–runoff progressed. The concentrations reached minimum values during peak runoff flow rates, and then slightly increased as runoff flow rates decreased again.

(b) There were significant intra-correlations amongst heavy metal concentrations. Metal concentrations were also correlated with suspended solid concentrations in the runoff. The heavy metals existed mainly adsorbed to suspended solids or as metallic particles.

(c) The extent of heavy metal pollution was closely related to the use of roadside land. The event mean concentrations (EMC) of heavy metals in runoff were higher for urban highways than for either suburban highways or highways at the urban-suburban boundary. The difference between the latter two was insignificant. Lead was identified as the most important heavy metal pollutant found in highway runoff.

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