Understanding the relationship between heavy metals in road-deposited sediments and washoff particles in urban stormwater using simulated rainfall

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HIGHLIGHTS

- ▶ Heavy metal concentrations in washoff particles increased by 10–30% compared with RDS.
- ▶ Rainfall intensity and duration did not affect increased rate of metal concentrations.
- ▶ Grain size of RDS and washoff particles carrying most heavy metals was different.
- ▶ Metal concentrations in RDS washoff decreased along the urban–rural gradient.

GRAPHICAL ABSTRACT

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ABSTRACT

Understanding the relationship between heavy metals in road-deposited sediments (RDS) and washoff particles is essential to controlling urban runoff pollution. RDS and its associated heavy metals were investigated along the urban–suburban–rural gradient around Beijing, China. RDS washoff and its associated metal contaminants in different particle size fractions were evaluated using simulated rainfall. The results showed that the washoff percentage of RDS decreased along the urban–rural gradient. The Cu, Zn, Ni, Cr and Pb contents in washoff particles were 28.1%, 20.0%, 19.7%, 11.6%, and 11.4% higher than those in RDS, respectively. Additionally, different metals showed increases in different chemical fractions. RDS particles <105 μm accounted for 40% of the total mass in RDS, but 50%, 70% and 75% of the total metal content in RDS, washoff particle mass and washoff particle metal content, respectively. Rainfall intensity and duration affected the amount of metals in washoff, but did not lead to an increase in the percentage of metals with different chemical fractions in washoff particles. The findings presented herein will facilitate development of strategies for control of urban diffuse pollution from RDS.

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1. Introduction

Road-deposited sediments (RDS) on impervious surfaces are important carriers of heavy metal contaminants that often contain metals at elevated concentrations [1,2]. Heavy metals washoff from RDS is an increasing problem associated with rapid urbanization that results in urban diffuse pollution [3,4]. Because of the difficulty associated with using natural rainfall events to investigate rigorous RDS washoff processes [5,6], washoff is the least

understood among the three processes that occur before materials enter receiving waters (RDS buildup, washoff and transport) [7]. An in-depth understanding of these processes is essential to elucidation of the relationships of pollution between RDS and washoff particles [8,9].

Both toxicity issues and the amount of metals in washoff particles should be considered when assessing the ecological risk to urban runoff posed by RDS. Knowledge of total metal concentration is insufficient for assessment of environmental risk [10]. Chemical fractions are critical to the evaluation of potentially toxic metals in RDS and washoff particles [11–13]. The amount, particle size and particles mobility of RDS strongly affect their potential contribution to washoff particles. However, most

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Table 1
Characteristics of different administrative divisions along the urban–rural gradient.

Sampling sites ^a	Population density (person/km ²) ^b	Average daily traffic (vehicle/d/m) ^c	Total energy consumption (1000 tons of SCE) ^d	Street cleaning method ^e	Frequency of sweeping (times/d) ^f
UCA (11)	15,000	8900	960	M	3
UVA (6)	1200	115	346	H	<0.2
CSA (40)	3000–5000	6700	960	M	3–2
RTA (20)	1500–2000	1300	346	H	2
RVA (20)	1000	105	346	H	0.3

^a Sampling site areas: UCA = central urban area; UVA = urban village area; CSA = central suburban county area; RTA = rural town area; RVA = rural village area. The data in parentheses is the number of sampling sites.

^b Population density was estimated using the data from Beijing Municipal Bureau of Statistics in Beijing.

^c Average daily traffic was estimated using the data from Beijing Transportation Research. The data was divided by lane-width of road in order to compare each other.

^d The energy consumption refers to residential consumption, including coal, gasoline, diesel oil, liquefied petroleum gas, natural gas, heat, and electricity. It was estimated using the data from Beijing Municipal Bureau of Statistics in Beijing. Unit: 1000 tons of SCE refers to 1000 tons of standard coal energy (SCE). The SCE data are available for only categories: the urban and rural areas.

^e M = mechanical sweeper; H = hand-swept using straw brooms. Most sites on main traffic roads were paved with asphalt, but a few roads in the rural area were paved with concrete.

^f Street cleaning methods and frequency were based on our in situ investigation.

previous studies have investigated metal contaminants in RDS [14–16] and washoff particles [17–19] separately, or chemical fractions in RDS [20,21]. Indeed, few studies have investigated the pollutant chemical fractions of different particle sizes in RDS and washoff particles or their relationship. Accordingly, there is a clear need to investigate the relationship between the amount, particle size distribution and proportion of different metal chemical fractions in RDS with washoff particles, so that we can better understand how RDS affects heavy metal pollution through urban runoff.

The urban–suburban–rural gradient pattern is has been strongly affected by rapid urbanization in China, and in turn affects land use zoning, population density, proportion of impervious surfaces, traffic density, energy consumption, street cleaning methods, and spatial distribution of manufacturers [6,22]. Therefore, the urban–rural gradient could affect the amounts and proportions of different chemical fractions of heavy metals in RDS and washoff particles by influencing the particle size of RDS, the metals associated with RDS and the RDS washoff process. In this study, a washoff experiment was conducted using simulated rainfall and RDS samples collected from the studied area. Simulated rainfall provided greater flexibility and control of the fundamental rainfall parameters such as intensity and duration. Both RDS samples and washoff particle samples were analyzed for the amounts, particle size composition and concentrations of metals with different chemical fractions on each particle size. Specifically, we investigated how the RDS from an urban–rural gradient affect concentrations of heavy metals with different chemical fractions in washoff particles.

2. Materials and methods

2.1. Study area and RDS sampling

The administrative division in China has historically consisted of five practical levels: the province, prefecture, county, township, and village [23]. A province consists of a group of prefectures, a prefecture consists of a group of counties, a county consists of a group of townships, and a township consists of villages. This administrative division is defined by political boundaries but is not defined by any quantified criteria. The division in large cities follows similar patterns. In general, a large city in China is divided along urban, suburban, and rural areas as follows: urban district, suburban county, rural township, rural village and urban village. Legally, an urban district is equivalent to a county. An urban village is located within an urban area but is still more similar to a rural village in that it lacks urban infrastructure and services [24]. Such a division has

a remarkable urban–suburban–rural function gradient. Our RDS samples were collected from each of the administrative divisions in the Beijing metropolitan region. These administrative division units are called a central urban area (UCA) within the urban district, a central suburban county area (CSA) within a suburban county, a rural town area (RTA) within a rural township, a rural village (RVA) area and an urban village area (UVA) [6]. The series UCA, CSA, RTA, RVA and UVA has an urban–rural gradient feature with a gradient variation through different administrative divisions, and differ in characteristics such as population density, average daily traffic, total energy consumption, the method of street cleaning and street cleaning frequency (Table 1).

RDS samples were collected using a domestic vacuum cleaner (Philips FC8264) during September 2–10, 2009, which followed an antecedent dry period of about 2 weeks. This vacuum cleaner had high efficiency with an air filtration system and a cyclonic dustbin that effectively captures microscopic particulates. The RDS sampling sites were distributed along main traffic roads with the following urban–suburban–rural gradient: UCA, UVA, CSA, RTA, and RVA (Table 1). To account for variation in RDS characteristics on roads of areas, the number of sampling sites varied depending on our field investigation (Table 1). For example, we selected four main traffic roads as our sampling sites of the CSA for each of the ten suburban counties. We collected the RDS from all the ten suburban counties so that we could assure our sampling sites cover all suburban counties. The total sampling site number at the CSA was 10 CSA areas $\times$ 4 main traffic roads = 40 sampling sites. Based on our on-site investigation, we found that the characteristics of the UCA RDS had relatively lower variation. Eleven sampling sites were selected to represent the major roads of the UCA. Because of the smaller area of RTA and lower RDS variation of the RTA, RVA and UVA, we selected 20 (10 RTA $\times$ 2 main traffic roads), 20 (10 RVA $\times$ 2 main traffic roads) and 6 (3 UVA $\times$ 2 main traffic roads) sampling sites, for RTA, RVA, and UVA, respectively. We collected RDS samples (1) during a dry weather period of about 2 weeks; (2) at a time that was half-way between the last sweeping time and the next; (3) so that the collection of all RDS samples in the study were completed in as short a time period as possible (eight days in this study). For each RDS sample collection, a variable area was vacuumed from the central road marking to the curb, after which the sampling area size was measured with a ruler. All RDS samples were dried at room temperature for 7 days, and then weighed using an electronic scale. The sample mass ranged from 0.8 to 1.5 kg. Samples were sorted into particle size fractions of <44, 44–62, 62–105, 105–149, 149–250, 250–450, 450–1000 and >1000 μm using polyester sieves, which are typically referred to as silt and clay, very fine sand, fine sand, medium sand, coarse sand, and very coarse sand, respectively [3].

2.2. Experimental design of RDS washoff by rainfall simulation

The rainfall simulation was designed according to Herngren et al. (2005), Egodawatta et al. (2007), and Xie et al. (2008) [5,7,25]. The device consisted of two rainfall simulators. The four nozzles of the two rainfall simulators were equally distributed (with an interval of 1.1 m) along the swing nozzle boom, which stood at 2.5 m above the ground. The rainfall simulators were operated using an electronic control box that enabled calibration for different rainfall intensities. To reproduce natural rainfall characteristics as closely as possible, the water used in the simulated rainfall was measured and adjusted. The pH value and electrical conductivity (EC) of water used in the rainfall simulation was 6.0 ± 1.2 and $100 \pm 80 \mu\text{S/cm}$, respectively, which was close to that of natural rainfall in the Beijing region (pH: 5.50 ± 1.80 ; EC: $80 \pm 65 \mu\text{S/cm}$). The nozzles (Veejet 80100) generated uniform raindrops with medium sizes at a constant pressure of 0.04 Mpa. The two rainfall simulators generated a total uniform rainfall area of $1.5 \text{ m} \times 2.2 \text{ m}$. We selected an area of $1.5 \text{ m} \times 2.0 \text{ m}$ as our washoff test plot. A $1.5 \text{ m} \times 2.0 \text{ m}$ plastic frame was used to demarcate the plot boundary, which was sealed with a paved surface. One end of the plastic frame was kept open to affix the catch tray used for runoff collection.

The road selected for the RDS washoff experimental plot was paved with asphalt 2 years prior to the experiment, and its roughness and slope were 0.625 mm and 2.36° , respectively. The RDS was spread uniformly throughout the washoff plot prior to the test.

To obtain representative samples from our simulated runoff experiment, we used mixed RDS samples that were collected throughout the study area. Samples with an RDS fraction $<250 \mu\text{m}$ (<44 , 44–62, 62–105, 105–149, 149–250 μm) were obtained from the UCA and CSA sites, while those $>250 \mu\text{m}$ (250–450 and 450–1000 μm) were collected from the RVA and UCA sites. Further details regarding the experimental design are available elsewhere (Supporting Information; Zhao et al., 2011) [6].

In our RDS washoff experiment, 20 g/m^2 of RDS sample for each individual RDS fraction from seven size fractions (<44 , 44–62, 62–105, 105–149, 149–250, 250–450 and 450–1000 μm) were washed off using three simulated rainfall intensities (12.87, 46.7 and 82.67 mm/h) applied for 1 h each (Table 2). Therefore, there were 21 different washoff scenarios.

During the washoff experiment, surface runoff samples were collected and their volumes were measured at set intervals for each simulated rainfall event (Table 2). Each size fraction of RDS in the runoff from the impervious surface was expressed as a percentage of the total RDS mass in the runoff with respect to the initial total mass of RDS on the surface. This was calculated by the following equation [6]:

$$F_w(\%) = \frac{M_{F_w}}{M_{\text{initial}}} \times 100\% = \frac{\int_0^1 C(t) \times Q(t) dt}{M_{\text{initial}}} \times 100\% \quad (1)$$

where F_w is the percentage of each RDS size fraction washed off the surface (%); M_{F_w} is the mass of the size fraction washed off the surface over the entire rain event (mg); M_{initial} is the initial mass of RDS with a corresponding particle size on the surface (mg); $C(t)$ is the mass of RDS with a corresponding particle size in the surface runoff water (mg/L) at each sampling time; and $Q(t)$ is the surface runoff flow rate at each sampling time (m^3/min).

F_w was used to calculate the amount and size composition of the washoff particles, as well as the concentrations of different chemical fractions of metals associated with the washoff particles. Because the washoff proportion of each RDS size fraction (F_w) was independent of the amount and particle size composition [26], we adjusted the amount and particle size composition of RDS to those in the corresponding sampling units to represent the RDS washoff scenarios in our washoff calculations. We applied F_w values of all individual RDS size fractions to deduce the RDS washoff amount for the RDS samples from urban–rural gradient units of UCA, UVA, CSA, RTA, and RVA.

2.3. Estimation of heavy metal loads in RDS

To determine the contribution particle sizes to the overall contamination of the RDS, we calculated the pollutant load percentage for each individual RDS sample. The particle size fraction load (GSF_{Load}) was calculated using the following equation [3]:

$$\text{GSF}_{\text{Load}} = \frac{C_i \times \text{GS}_i}{\sum_{i=1}^n C_i \times \text{GS}_i} \quad (2)$$

where C_i is the heavy metal level associated with a RDS sample for a given particle size (mg/kg); GS_i is the percentage by mass of the size fraction i in the total sample (%); and n is the number of particle size fractions.

2.4. Estimation of heavy metal concentration in washoff particles

There are many important factors that impact the potential contribution of RDS to surface runoff and runoff pollution. In the RDS runoff experiment, we focused on RDS particle size and particle size composition. The RDS percentage contribution for different particle sizes could be calculated from the combination of each particle size percentage. We used the following equation to calculate the concentration of heavy metal in washoff particles:

$$C_s = \frac{\sum_{i=1}^n M_i \times C_i \times F_{wi}}{\sum_{i=1}^n M_i \times F_{wi}} \quad (3)$$

Table 2

Simulated rainfall intensities, rainfall durations and particle size fraction of RDS in the RDS washoff experiment^a.

Rainfall intensity	Sampling interval ^b	Particle size fraction of RDS
12.87 mm/h	0–2, 2–4, 4–6, 6–8, 8–10, 10–15, 15–20, 20–30, 30–40, 40–50, 50–60 min	<44, 44–62, 62–105, 105–149, 149–250, 250–450, 450–1000 μm
46.7 mm/h	0–2, 2–4, 4–6, 6–8, 8–10, 10–15, 15–20, 20–30, 30–40, 40–50, 50–60 min	<44, 44–62, 62–105, 105–149, 149–250, 250–450, 450–1000 μm
82.67 mm/h	0–2, 2–4, 4–6, 6–8, 8–10, 10–15, 15–20, 20–30, 30–40, 40–50, 50–60 min	<44, 44–62, 62–105, 105–149, 149–250, 250–450, 450–1000 μm

^a In our previous study (Zhao et al., 2011), there was an obvious gradient in the RDS mass per unit area along the urban–rural gradient as follows: low (UCA, $21 \pm 24 \text{ g/m}^2$; CSA, $20 \pm 16 \text{ g/m}^2$), medium (RTA, $59 \pm 63 \text{ g/m}^2$), and high (UVA, $147 \pm 198 \text{ g/m}^2$; RVA, $147 \pm 112 \text{ g/m}^2$) mass per unit area. The higher level of RDS per unit area can be easily removed by improving the street cleaning method or increasing street cleaning frequency. So we selected the lower levels of RDS mass per unit area (20 g/m^2) in the RDS washoff experiment.

^b The washoff duration was one hour. The runoff samples were collected manually at 2 min intervals during the first 10 min, at 5 min intervals during the second and third 10 min, and at 10 min intervals thereafter until there was no more surface runoff.

Fig. 1. (a) Mean mass percentage of road-deposited sediment versus grain size fraction and (b) road-deposited sediment mass per unit area and the contribution of RDS to suspended solids in surface runoff after 60 min of simulated rainfall. Values are expressed as the mean $\pm$ standard deviation. UCA = central urban area; UVA = urban village area; CSA = central suburban county area; RTA = rural town area; RVA = rural village area. *The results for washoff particles were calculated using the F_w values determined with a rainfall intensity of 46.7 mm/h and duration of 1 h. The detailed method for calculation is provided in Section 2.3.

where C_s is the metal content in washoff particles (mg/kg); M_i is the initial mass of RDS with a corresponding particle size on the surface (mg); C_i is the heavy metal level associated with a RDS sample for a given particle size (mg/kg); F_w is the percentage of each RDS size fraction washed off the surface (%); and n is the number of particle size fractions.

2.5. Analytical methods

The BCR protocol developed by the Standard Measurement and Testing Program of the European Community [27,28] and the optimized BCR sequential extraction procedure developed by Sutherland and Tack (2002) [29] were used to fractionate the metals into the following target phases: acid-extractable (water soluble, exchangeable and bound to carbonate), reducible (bound to amorphous Fe- and Mn-oxides), oxidizable (bound to organic matter), and residual (bound to minerals). This procedure included four steps: (1) acid-extractable: extraction of 1.00 g RDS sample by adding 40 mL 0.11 M acetic acid; (2) reducible: addition of 40 mL 0.5 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ (pH $\approx$ 1.5); (3) oxidizable: addition of 10 mL H_2O_2 (pH 2–3) to the sample followed by incubation for 1 h at room temperature, and then at $85 \pm 2^\circ\text{C}$ for 1 h, after which 10 mL of H_2O_2 are added and the sample is incubated at $85 \pm 2^\circ\text{C}$ for 1 h and 50 mL 1 M NH_4OAc (pH 2) are added; (4) residual: addition of 3 mL distilled H_2O , 7.5 mL 6 M HCl, and 2.5 mL 14 M HNO_3 followed by overnight incubation at 20°C , then boiling under reflux for 2 h, cooling and filtration. After each of the first three steps, the suspension was shaken for 16 h at $22 \pm 5^\circ\text{C}$ and the extract was then separated from the solid residue by centrifugation at 3000 rpm for 20 min. Total metals were measured after digestion with HF-HClO_4 on a hotplate [30]. GBW07401(GSS-1) and GBW07402(GSS-2), which are the General Administration of Quality Supervision, Inspection and Quarantine of the PR China certified reference materials (CRMs) for soil, were used as the CRMs for digestion of RDS. The mass balance was evaluated by comparing the total metal content with the sum of the metal fractions. All solutions were stored at 4°C prior to analysis. The concentrations of Cr, Cu, Ni, Pb and Zn were determined using a PerkinElmer Elan 6000 ICP-OES. For heavy metal analysis, recoveries varied, but all fell within the range of 75–110%. The precision was nearly 90% with a confidence level of 95%.

3. Results

3.1. Particle size distribution of RDS and washoff particles

Particle size composition is critical to assessment of the role of RDS and washoff particles in heavy metal pollution of urban runoff. RDS particles with a particle size of 62–105 μm were the most abundant among the seven size fractions, accounting for $33 \pm 14\%$ of the total (Fig. 1a). When compared to the mass percentage of RDS with a corresponding particle size on the surface, washoff particles with less than 105 μm were present in higher proportions. Particles with particle sizes less than 105 μm in RDS particles and washoff particles accounted for 27–44% and 60–75% of the total mass of RDS particles and washoff particles, respectively. This resulted from washoff selectively transporting RDS of particular particle sizes.

The potential contribution of RDS washed off per unit area of impervious surface to runoff was determined by the amount of RDS per unit area. This value was calculated based on the simulated rainfall event (unit: mg/m^2) and found to be: RVA (18.4 ± 24.7) > UVA (16.0 ± 11.9) > RTA (7.6 ± 8.3) > UCA (3.0 ± 2.4) > CSA (2.8 ± 2.1) (Fig. 1b). In addition, the F_w (%) for entire particular particle sizes along the urban–rural gradient was estimated to be: UCA ($15.8 \pm 2.7\%$) > CSA ($14.2 \pm 1.6\%$) > RVA ($13.5 \pm 2.5\%$) > RTA ($12.7 \pm 2.2\%$) > UVA ($11.6 \pm 1.7\%$), which was determined based on the particle size composition of RDS collected from areas in five administrative units.

3.2. Comparison of heavy metal concentration with different chemical fractions in RDS and washoff particles

Comparison of the heavy metal distribution in RDS and washoff particles is important to understand runoff pollution as a result of RDS. Heavy metal concentrations with different chemical fractions in washoff particles were generally higher than those in RDS (Fig. 2). The percentage of total metals in washoff particles compared with that in RDS was as follows: Cu ($28.1 \pm 8.2\%$) > Zn ($20.0 \pm 11.7\%$) > Ni ($19.7 \pm 9.4\%$) > Cr ($11.6 \pm 7.4\%$) > Pb ($11.4 \pm 2.6\%$). The increases in total metal concentrations were attributed to increases of different chemical fractions. The residual, oxidizable, acid-extractable and residual, oxidizable and residual, acid-extractable and reducible chemical fractions were the main

Fig. 2. Comparison of heavy metal concentrations in different chemical fractions between RDS and washoff particles. Values are expressed as the mean $\pm$ standard deviation. UCA = central urban area; UVA = urban village area; CSA = central suburban county area; RTA = rural town area; RVA = rural village area. *The results for washoff particles were calculated using the F_w values determined with a rainfall intensity of 46.7 mm/h and duration of 1 h. The detailed method for calculation is provided in Section 2.3.

contributors to the increased percentage of total concentrations of Cr, Cu, Ni, Pb and Zn, respectively. The ratio of the mobile phase (the sum of acid-extractable, reducible, and oxidizable fractions) to the total concentration in RDS was in the following order: Zn ($72.1 \pm 5.2\%$) > Pb ($68.9 \pm 2.7\%$) > Cu ($63.3 \pm 14.4\%$) > Ni ($45.9 \pm 5.1\%$) > Cr ($34.6 \pm 4.9\%$), while those in washoff particles followed a similar pattern: Zn ($73.5 \pm 3.7\%$) > Pb ($69.7 \pm 4.3\%$) > Cu ($62.5 \pm 16.3\%$) > Ni ($45.7 \pm 4.7\%$) > Cr ($32.0 \pm 5.1\%$). The difference in pollutant distribution between RDS and washoff particles was caused by their particle size composition.

3.3. Impacts of particle sizes on metal contamination in RDS and washoff water

The particle size composition of RDS and washoff particles also determines the contribution of particles with different particle sizes to the overall contamination. We estimated the contribution of particles with different particle sizes to the overall contamination of RDS and washoff particles using the GSF_{Load} (Fig. 3). For RDS, the order of the mean GSF_{Load} values for all total metals combined was $62-105 \mu m$ ($37 \pm 10\%$) > $149-250 \mu m$ ($19 \pm 8\%$) > $105-149 \mu m$ ($14 \pm 5\%$) > $250-450 \mu m$ ($10 \pm 6\%$) > $44-62 \mu m$ ($9 \pm 5\%$) > $450-1000 \mu m$ ($6 \pm 5\%$) > $0-44 \mu m$ ($4 \pm 2\%$), while for washoff particles the order was $62-105 \mu m$ ($48 \pm 13\%$) > $44-62 \mu m$ ($15 \pm 10\%$) > $0-44 \mu m$ ($12 \pm 4\%$) $\approx$ $149-250 \mu m$ ($12 \pm 9\%$) > $105-149 \mu m$ ($11 \pm 2\%$) > $250-450 \mu m$ ($2 \pm 2\%$) $\approx$ $450-1000 \mu m$ ($2 \pm 2\%$). RDS with a particle size <100 μm is commonly referred to as the particle size of suspended solids in runoff [31]. Consequently, the contribution of particles <105 μm

in diameter to the overall metal contamination of the RDS affected the potential release to runoff pollution. RDS particles <105 μm accounted for 40% of the total mass in RDS, but 50%, 70% and 75% of the total metals content in RDS, washoff particle mass and washoff particles, respectively. Street sweepers have been shown to be less efficient in picking up particles with low particle size, which implies that it is difficult to remove most of the metal load in stormwater runoff by conventional street sweepers [6,32,33].

The percentages of contributions of the RDS particle size fractions to the total mean GSF_{Load} of all metals were calculated along the urban-rural gradient (Table 3). For RDS and washoff particles, particles with a particle size <105 μm contributed 20–30% and 50–90% of the heavy metal loads including the four chemical fractions (acid-extractable, reducible, oxidizable, and residual), respectively. The above results were basically consistent with those of a previous study conducted by Sansalone and Ying (2008) that the finer particles generates the highest metal concentrations and the highest metal mass is associated with the coarser fraction [34]. The RDS and washoff particles with particle size <105 μm in UCA and UVA showed the largest and lowest GSF_{Load} values in the four chemical fractions, respectively, based on the particle size composition and pollutant distribution associated with them.

3.4. Estimation of amounts of metals from RDS in runoff

The potential heavy metal contribution of surface runoff is impacted by the mobility of RDS particles with different particle size and the metal distribution in the corresponding particle size. The metals mass per unit area varied widely as follows (unit:

Fig. 3. Percentages of heavy metals in different chemical fractions among varying grain size fractions. GSF_{Load} (%) represents the contribution of particles with different grain sizes to the overall contamination of the RDS. The detailed method for calculation is provided in Section 2.4. Values are expressed as the mean $\pm$ standard deviation. F1 = acid-extractable; F2 = reducible; F3 = oxidizable; F4 = residual. The dashed line above the figure represents the mass percentage with a corresponding size fraction in the total RDS.

$\mu\text{g}/\text{m}^2$): total Cr 400–3500, total Cu 80–4000, total Ni 200–4000, total Pb 200–4500 and total Zn 1500–25000 (Fig. 4). The proportion of potential contribution in surface runoff accounting for total metal load in RDS per unit area was approximately 10–25%. RVA and RTA had the largest metal load per unit area in RDS and washoff particles. However, the largest proportion of potential washoff metal load was observed in UVA and CSA. Approximately 60–75% Cu, Pb and Zn in washoff particles per unit area were stored in the mobile phase (the sum of acid-extractable, reducible, and oxidizable fractions). The above results implied that different controlling strategies for RDS pollution could be applied along the urban–rural gradient.

3.5. Impacts of rainfall intensity and duration on heavy metal concentrations with different chemical fractions in washoff particles

In our experimental design, the rainfall intensities of 12.87, 46.7 and 82.67 mm/h represented the typical rainfall intensity classes of moderate, intensive and highly intensive according to rainfall intensity class in Beijing, respectively. The rainfall durations of 0–10 and 0–60 min represent the periods of the first flush and the entire washoff process during a typical rainfall event, respectively. The results of a case study in a central urban area suggested that metal concentrations with different chemical fractions in washoff particles were basically coincident

during the washoff process (Table 4). The difference in metal concentrations between RDS and washoff particles with different chemical fractions was not affected by rainfall intensity or duration. These findings implied that the amount of washoff particles varied with different rainfall intensities and durations, but that the particle size composition of the washoff particles was not influenced.

4. Discussion

Quantifying the relationship between RDS and washoff particles is important for estimation of the pollution load and assessment of the ecological risk that a waterway receives. Particle size composition is a critical factor in this relationship because surface washoff selectively transports RDS of particular particle sizes [12,13]. The washoff percentage of each RDS size fraction (F_w) varies with the particle size of RDS, with smaller particle sizes being associated with higher values of F_w . Washoff particles have higher proportions of smaller particle sizes than those in RDS. Previous studies suggested that RDS and washoff particles had either an exponential, rating curve, or other relationship depending on a range of parameters such as surface characteristics, rainfall intensity and duration, RDS particle sizes, land use, etc. [7,9,33–37]. However, it was unclear how particle size composition influenced the relationship of pollutants between RDS and washoff particles [38]. We compared heavy metals concentrations with different chemical

Fig. 4. Comparison of areal contribution of heavy metals in RDS with that in washoff particles. Log₁₀ values were used as arithmetic scaling of the Y-axis in Fig. 4. Values are expressed as the mean $\pm$ standard deviation. UCA = central urban area; UVA = urban village area; CSA = central suburban county area; RTA = rural town area; RVA = rural village area. Results for washoff particles in Fig. 4 were calculated using the specific F_w values determined with a rainfall intensity of 46.7 mm/h and duration of 1 h.

Fig. 5. Impacts of rainfall intensity and duration on the washoff percentage of each RDS size fraction (F_w , %).

Table 3GSF_{Load} of each metal fraction in RDS and washoff particles in different sizes along the urban–rural gradient (GSF_{Load}, %) ^a.

Metal fractions	Urban–rural gradient ^b	<105 μm		105–250 μm		250–1000 μm	
		RP ^c	WP	RP	WP	RP	WP
Acid-extractable	UCA	55.9 $\pm$ 28.2	78.2 $\pm$ 41.4	28.5 $\pm$ 19.8	18.0 $\pm$ 15.1	15.6 $\pm$ 10.2	3.8 $\pm$ 2.8
	CSA	44.5 $\pm$ 9.4	68.2 $\pm$ 18.2	45.1 $\pm$ 8.1	29.2 $\pm$ 7.6	10.4 $\pm$ 3.7	2.5 $\pm$ 1.0
	RTA	43.6 $\pm$ 17.5	74.3 $\pm$ 23.1	26.9 $\pm$ 10.9	16.5 $\pm$ 8.0	29.5 $\pm$ 18.8	9.3 $\pm$ 8.2
	RVA	50.1 $\pm$ 35.2	72.6 $\pm$ 33.4	35.1 $\pm$ 25.1	23.3 $\pm$ 19.0	14.8 $\pm$ 13.2	4.1 $\pm$ 4.1
	UVA	23.0 $\pm$ 2.7	51.5 $\pm$ 7.7	42.9 $\pm$ 9.7	36.1 $\pm$ 7.9	34.1 $\pm$ 1.8	12.4 $\pm$ 0.8
Reducible	UCA	52.5 $\pm$ 35.2	75.3 $\pm$ 49.6	27.7 $\pm$ 14.9	18.7 $\pm$ 12.8	19.8 $\pm$ 11.3	6.0 $\pm$ 5.4
	CSA	42.0 $\pm$ 14.9	66.6 $\pm$ 19.5	47.0 $\pm$ 11.2	30.7 $\pm$ 11.0	10.9 $\pm$ 3.6	2.7 $\pm$ 1.2
	RTA	39.7 $\pm$ 16.8	72.8 $\pm$ 19.4	29.6 $\pm$ 7.2	18.3 $\pm$ 6.0	30.7 $\pm$ 16.5	8.9 $\pm$ 6.1
	RVA	47.9 $\pm$ 34.0	71.3 $\pm$ 31.2	36.9 $\pm$ 21.2	24.5 $\pm$ 16.9	15.2 $\pm$ 11.5	4.1 $\pm$ 3.6
	UVA	29.0 $\pm$ 3.1	57.1 $\pm$ 5.2	46.6 $\pm$ 7.4	35.3 $\pm$ 5.2	24.3 $\pm$ 7.8	7.6 $\pm$ 3.4
Oxidizable	UCA	63.5 $\pm$ 32.7	86.2 $\pm$ 45.2	23.4 $\pm$ 3.7	11.1 $\pm$ 2.1	13.1 $\pm$ 6.6	2.7 $\pm$ 1.4
	CSA	48.6 $\pm$ 10.3	75.6 $\pm$ 14.3	39.1 $\pm$ 8.1	21.4 $\pm$ 5.4	12.4 $\pm$ 5.2	3.0 $\pm$ 1.6
	RTA	46.7 $\pm$ 18.8	76.6 $\pm$ 16.3	28.5 $\pm$ 14.8	16.6 $\pm$ 10.9	24.7 $\pm$ 16.1	6.8 $\pm$ 6.2
	RVA	44.1 $\pm$ 32.5	68.2 $\pm$ 31.5	37.4 $\pm$ 19.7	25.9 $\pm$ 17.0	18.5 $\pm$ 15.5	5.9 $\pm$ 6.3
	UVA	36.5 $\pm$ 11.6	63.6 $\pm$ 16.8	46.8 $\pm$ 13.5	32.0 $\pm$ 14.0	16.8 $\pm$ 2.0	4.4 $\pm$ 0.3
Residual	UCA	63.8 $\pm$ 24.2	86.5 $\pm$ 39.1	23.6 $\pm$ 6.6	10.9 $\pm$ 3.9	12.6 $\pm$ 3.2	2.6 $\pm$ 1.1
	CSA	48.0 $\pm$ 12.8	75.4 $\pm$ 22.1	42.7 $\pm$ 8.4	22.6 $\pm$ 4.1	9.3 $\pm$ 3.1	2.0 $\pm$ 0.6
	RTA	49.9 $\pm$ 20.6	77.9 $\pm$ 18.3	31.4 $\pm$ 21.9	17.4 $\pm$ 14.2	18.7 $\pm$ 10.0	4.7 $\pm$ 3.5
	RVA	54.0 $\pm$ 30.4	78.2 $\pm$ 29.7	30.7 $\pm$ 18.2	17.8 $\pm$ 12.1	15.2 $\pm$ 11.6	4.0 $\pm$ 3.9
	UVA	34.5 $\pm$ 10.0	63.3 $\pm$ 11.4	44.9 $\pm$ 10.2	30.9 $\pm$ 9.4	20.6 $\pm$ 3.7	5.7 $\pm$ 2.0
Total	UCA	63.0 $\pm$ 29.1	86.6 $\pm$ 43.8	23.9 $\pm$ 4.2	11.0 $\pm$ 1.9	13.2 $\pm$ 4.2	2.5 $\pm$ 0.7
	CSA	49.9 $\pm$ 7.6	76.5 $\pm$ 15.9	40.5 $\pm$ 5.1	21.4 $\pm$ 4.7	9.6 $\pm$ 3.6	2.1 $\pm$ 0.8
	RTA	47.8 $\pm$ 19.3	77.5 $\pm$ 17.0	29.3 $\pm$ 16.6	16.4 $\pm$ 11.5	22.9 $\pm$ 13.7	6.1 $\pm$ 5.2
	RVA	52.0 $\pm$ 31.6	76.4 $\pm$ 29.9	32.6 $\pm$ 18.4	19.6 $\pm$ 13.0	15.3 $\pm$ 12.0	4.1 $\pm$ 4.0
	UVA	33.7 $\pm$ 7.7	62.8 $\pm$ 11.0	46.2 $\pm$ 9.2	31.6 $\pm$ 9.3	20.1 $\pm$ 2.9	5.5 $\pm$ 0.7

^a The percentage of contributions of the RDS particle size fractions to the mean GSF_{Load} of all studied metals was calculated by the combination of five metals percentage according the Eq. (2) in the section of materials and methods. Results for washoff particles in this Table were calculated using the specific F_w values from the scenario with rainfall intensity of 46.7 mm/h and duration of 1 h.

^b Urban–rural gradient: UCA = central urban area; UVA = urban village area; CSA = central suburban county area; RTA = rural town area; RVA = rural village area.

^c RP: road-deposited sediment particles; WP: washoff particles.

Table 4

Metal concentrations of different fractions in washoff particles under three rainfall intensities and two duration periods in the central urban area (mg/kg).

Heavy metal	Chemical fractions	Simulation rainfall intensities and durations						RDS
		12.87 mm/h		46.7 mm/h		82.67 mm/h		
		0–10 min	0–60 min	0–10 min	0–60 min	0–10 min	0–60 min	
Cr	Acid-extractable	3.0 ± 2.1	3.0 ± 2.2	3.3 ± 2.7	3.0 ± 2.3	3.1 ± 2.4	3.0 ± 2.3	2.6 ± 1.5
	Oxidizable	19.4 ± 22.4	19.8 ± 22.9	20.7 ± 25.3	20.0 ± 23.8	20.3 ± 24.8	19.9 ± 24.0	6.7 ± 3.4
	Reducible	12.1 ± 5.0	12.1 ± 5.0	13.4 ± 6.2	12.6 ± 5.5	13.1 ± 5.9	12.8 ± 5.6	13.3 ± 3.4
	Residual	63.8 ± 10.0	64.4 ± 10.0	69.5 ± 9.7	65.1 ± 10.1	66.0 ± 10.0	64.3 ± 9.8	51.9 ± 7.4
	Total	86.9 ± 2.2	87.7 ± 2.3	93.1 ± 3.2	88.5 ± 1.0	89.2 ± 0.4	87.4 ± 0.7	74.5 ± 5.8
Cu	Acid-extractable	3.1 ± 3.4	3.1 ± 3.3	3.6 ± 4.8	3.4 ± 4.0	3.7 ± 4.7	3.7 ± 4.4	2.6 ± 1.7
	Oxidizable	14.3 ± 9.4	14.1 ± 9.3	15.7 ± 15.2	14.6 ± 11.7	15.2 ± 13.6	15.2 ± 12.1	16.3 ± 1.3
	Reducible	53.8 ± 41.0	53.9 ± 40.9	63.3 ± 49.3	57.0 ± 44.2	59.7 ± 46.7	57.2 ± 44.3	61.4 ± 5.6
	Residual	21.5 ± 12.1	22.0 ± 12.5	24.0 ± 11.6	21.0 ± 10.7	20.1 ± 9.6	19.1 ± 9.5	16.1 ± 6.9
	Total	118.4 ± 2.2	118.5 ± 0.2	135.3 ± 24.7	123.2 ± 12.5	127.0 ± 21.3	122.5 ± 16.0	96.3 ± 7.0
Ni	Acid-extractable	5.8 ± 1.7	5.9 ± 1.7	6.7 ± 1.8	5.9 ± 1.4	5.9 ± 1.2	5.7 ± 1.2	4.5 ± 1.5
	Oxidizable	8.6 ± 9.3	9.1 ± 10.1	7.0 ± 6.1	8.7 ± 9.3	8.1 ± 8.2	8.4 ± 8.8	2.8 ± 1.6
	Reducible	3.2 ± 1.4	3.3 ± 1.5	3.6 ± 1.6	3.4 ± 1.5	3.5 ± 1.6	3.4 ± 1.6	2.1 ± 0.7
	Residual	11.4 ± 6.4	11.7 ± 6.6	12.6 ± 7.1	11.6 ± 6.4	11.5 ± 6.2	11.0 ± 5.9	8.74 ± 3.4
	Total	23.0 ± 5.6	23.4 ± 5.8	25.5 ± 5.4	23.5 ± 5.5	23.5 ± 5.3	22.7 ± 5.2	18.0 ± 2.8
Pb	Acid-extractable	7.6 ± 0.2	7.8 ± 0.0	7.4 ± 1.3	7.3 ± 0.9	7.1 ± 1.2	7.1 ± 0.9	6.3 ± 0.4
	Oxidizable	15.2 ± 5.8	15.2 ± 6.0	16.2 ± 6.6	15.2 ± 5.5	15.2 ± 5.2	15.0 ± 4.8	15.0 ± 4.4
	Reducible	17.2 ± 3.1	17.3 ± 3.0	19.8 ± 3.8	18.0 ± 3.9	18.7 ± 4.5	18.0 ± 4.4	14.1 ± 6.9
	Residual	15.7 ± 4.0	16.0 ± 3.9	15.9 ± 6.7	15.8 ± 4.3	15.2 ± 5.2	14.8 ± 4.6	14.2 ± 2.3
	Total	56.6 ± 8.2	57.2 ± 8.5	58.8 ± 6.6	56.7 ± 8.1	55.9 ± 7.2	54.7 ± 7.6	49.5 ± 13.9
Zn	Acid-extractable	128.5 ± 2.6	129.1 ± 2.9	139.3 ± 13.4	128.3 ± 5.5	128.2 ± 7.9	124.8 ± 5.2	112.3 ± 9.3
	Oxidizable	60.8 ± 27.2	61.4 ± 28.3	71.2 ± 25.2	62.3 ± 26.8	63.6 ± 24.9	60.3 ± 24.0	48.9 ± 18.8
	Reducible	75.5 ± 10.2	76.0 ± 10.9	86.0 ± 9.3	76.8 ± 6.3	77.6 ± 1.4	74.8 ± 5.1	76.0 ± 4.1
	Residual	80.4 ± 12.7	80.6 ± 11.9	89.9 ± 15.4	82.0 ± 14.8	83.6 ± 17.4	80.9 ± 17.2	67.4 ± 16.3
	Total	360.0 ± 17.2	362.9 ± 17.4	386.6 ± 4.7	360.6 ± 14.1	358.8 ± 8.8	349.3 ± 9.7	304.6 ± 6.3

fractions in RDS and washoff particles using rainfall simulation and found increases in washoff particles when compared with those in RDS of 10–30%. Different metals showed increased percentages in different chemical fractions. Moreover, we found that the increased percentages of metals in washoff particles were not affected by rainfall intensity and duration. These findings implied that the particle size composition of washoff particles was not affected by rainfall intensity and duration, which could be attributed to the fact that the F_w of each particle size varied proportionally to the rainfall intensity and duration (Fig. 5). Although rainfall intensity and duration affected the amount of RDS and their associated metals in washoff water [5,6], solid phase concentrations of heavy metal in washoff particles did not vary throughout the entire washoff process. Clearly, our findings should contribute to quantification of the relationship between heavy metal pollutants in RDS and washoff particles.

The equation used in our washoff calculations was developed without considering the distance traveled by the RDS or the slope and roughness of the road. In a pre-experiment for RDS washoff, we found that smoothness of roads strongly affected the proportion of each particle size fraction of RDS, and that the amount and particle size composition of RDS also varied with road smoothness [39]. It is unknown how road smoothness and particle size composition interactively affect metal pollutants in washoff particles. The first flush could make a greater contribution to washoff pollution on smoother roads because of its higher F_w values. This is because rainfall is stronger at the start of the storm, but becomes a less important factor as the availability of easily detachable and transportable fractions of the surface pollutant decreases during the storm [40]. Future studies should consider how the road smoothness affects the relationship of heavy metals with different chemical fractions between RDS and washoff particles. In addition, all results of washoff particles in this study were based on simulated rainfall experiments; therefore, the findings presented herein should be verified based on natural rainfall in future studies [41].

5. Conclusion

We conducted a washoff experiment using simulated rainfall and RDS samples collected from a rapid urbanization area that had a clear urban–rural gradient pattern. Both RDS samples and washoff particle samples were analyzed for the amounts, particle size composition and metals concentrations in different chemical fractions for each particle size. The urban–rural gradient had an important impact on the relationships between pollutants in RDS and washoff particles via the quantity, particle size, particle mobility of RDS and pollutants associated with them. Along the urban–rural gradient, heavy metal concentrations with different chemical fractions in RDS and washoff particles and the percentage of RDS mobility caused by washoff decreased. The RDS and washoff amount per unit area increased along the urban–rural gradient. We found that heavy metal concentrations in washoff particles increased by 10–30% when compared with RDS because storm runoff selectively transported RDS with different particle sizes. However, the rate at which metals concentrations increased was not affected by rainfall intensities and durations due to the invariable particle size composition of the washoff. The contribution of particles with different particle sizes to the overall contamination differed between the RDS and washoff particles, with smaller washoff particles accounting for a larger proportion of particle size and heavy metal contribution than the corresponding particles in RDS. Overall, our findings will help explain the relationships between pollution in RDS and washoff particles along urban–rural gradients.

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