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RESEARCH ARTICLE

Transferral of HMs pollution from road-deposited sediments to stormwater runoff during transport processes

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HIGHLIGHTS

- Ratio of turbidity and TSS (Tur/TSS) was used to characterize PSD of stormwater particles.
- Pb and Zn preferred to accumulate in finer RDS, while Cu, Cr and Ni in coarser RDS.
- HMs pollution in stormwater particles increased linearly with Tur/TSS.
- Dissolvability of HMs and PSD variations contribute to the differences between RDS and stormwater.

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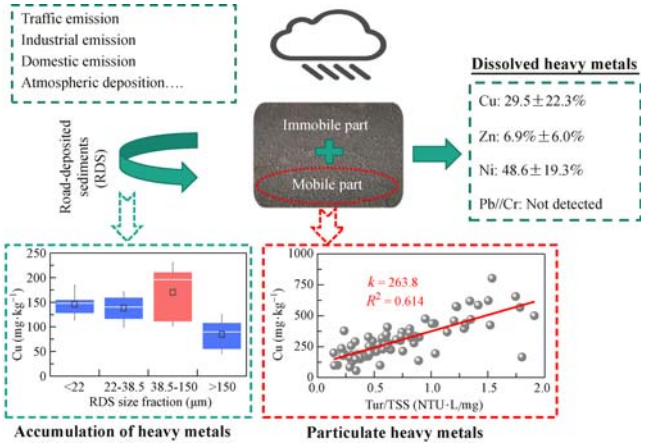
GRAPHIC ABSTRACT



ABSTRACT

Stormwater runoff, derived from the wash-off of road-deposited sediments (RDS), contains elevated heavy metal (HM) concentrations and, thus, imposes an increasing threat to urban aquatic ecosystems. In-depth understanding of the variations of HMs pollution from RDS to stormwater during transport processes facilitates the development of effective RDS and stormwater control strategies. Toward this end, the distribution of HMs (Cu, Pb, Zn, Cr, and Ni) in RDS and stormwater were investigated simultaneously. The results show a preferential accumulation of Pb and Zn in the finer (<38.5 μm) RDS, and Cu, Cr and Ni in the coarser (38.5–150 μm) RDS. For stormwater, n.d.~48.6% of HMs fractionated into the dissolved phase, and stormwater particles constitute the primary carriers of HMs. Furthermore, the accumulation of HMs in stormwater particles increased linearly with finer particle size distributions (PSD). Geoaccumulation index (I_{geo}) highlighted the predominant pollution of both RDS and stormwater particles by Cu, Pb and Zn. Nonetheless, Cu, Pb, and Ni mostly contributed the potential ecological risk of RDS, whereas Cu, Pb, and Zn mainly contributed that of stormwater particles. Moreover, contamination by Cu, Pb and Zn was significantly higher in stormwater particles than that in RDS. These differences are attributable to the solubility and size-dependent accumulation of HMs in RDS, as well as the PSD variations during transport processes. The study outcomes highlight the importance of very fine (nano- and submicron- scale) RDS in stormwater pollution and the necessity of control.

1 Introduction

Road-deposited sediments (RDS) in urban environments ubiquitously contain elevated heavy metal (HM) concentrations due to a variety of anthropogenic sources such as weathering of building and pavement surfaces, traffic, industrial and domestic emissions (Wei and Yang, 2010; Aminiyan et al., 2017; Lin et al., 2017). These RDS and associated HMs can be partly washed off from road

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surfaces and ultimately discharged into urban waterways without treatment during wet seasons. Due to the high toxicity, concealment, persistence and biological accumulation of HMs (Huang et al., 2016), the input of untreated stormwater poses an increasing threat to aquatic ecosystems. Therefore, it is important to investigate the HMs pollution of both RDS and stormwater to ensure better management of RDS and stormwater, and thus, preserve waterways effectively.

With the active control of point source pollution and increasing urbanization in China, stormwater pollution in urban areas has become an important source of river pollution. Consequently, the HMs pollution of both RDS and stormwater has been investigated individually and widely in the past decades. It has been recognized that the HMs accumulated in RDS are highly particle size-dependent, irrespective of the ubiquitous influence of traffic conditions, land uses and antecedent dry days (ADD), etc. (Yuen et al., 2012; Liu et al., 2015; Liu et al., 2016; Ziyath et al., 2016; Padoan et al., 2017; Zhang et al., 2017). During rainfall events, the HMs associated with RDS may be dissolved, desorbed and transported by stormwater, and thus contribute to stormwater in both particulate and dissolved forms (Zafra et al., 2017). Therefore, the concentrations (mg/L) of dissolved and particulate HMs in stormwater were normally considered, and found to be exceedingly influenced by rainfall characteristics, antecedent weather conditions and land uses (Beck and Birch, 2012; Li et al., 2012; Zhang et al., 2013b ; Peng et al., 2016). Nonetheless, the first flush phenomenon has been prevailingly observed during runoff processes (Furumai et al., 2002; Ying and Sansalone, 2010; Li et al., 2012). On the other hand, given the importance of particle size in pollutants entrainment, mobility, bioavailability and removal effectiveness, the HMs accumulated in size-fractionated stormwater particles were also investigated by a few researchers (McKenzie et al., 2008; Nie et al., 2008; Kayhanian et al., 2012). Furthermore, the wash-off of RDS was investigated by both simulated and field rainfall events, and was expectable to be greatly dependent on particle size (Zhao and Li, 2013b ; Zhao et al., 2016; Zafra et al., 2017). Finer RDS are easier transported into stormwater, and consequently, stormwater particles are primarily contributed by fine particles (Zhao et al., 2010; Wang et al., 2017). Thus, the particle size distribution (PSD) varies exceedingly from RDS to stormwater, and the PSD of stormwater particles is much finer than RDS (McKenzie et al., 2008). These research outcomes provide valuable information for understanding and management of RDS and stormwater pollution. However, there are still some inadequacies existed.

On the one hand, RDS and stormwater particles were traditionally size-fractionated by dry or wet sieving methods, which were only competent to separate particles within micron-scale (Kayhanian et al., 2012). Therefore, there are little knowledge on the HMs pollution of finer particles (e.g., nano- and micron-scale). McKenzie et al. (2008) adopted a cell sorter (or a flow cytometer) and a settling column to fractionate RDS and stormwater particles of diameter 0.1–1.5 and 2–63 μm, respectively. Fedotov et al. (2014) applied a new technique, sedimentation field-flow fractionation in a rotating coiled column to fractionate RDS into < 0.3, 0.3–1, 1–10 and 10–100 μm. These studies provide a glimpse of the HMs pollution of nano- and submicron-scale particles, though, in-depth investigation is necessary. On the other hand, the traditional size-fractionation methods overshadows the variations of HMs pollution from RDS to stormwater and during runoff processes result from the PSD differences during transport processes. These deficiencies may be supplemented by considering the bulk PSD of stormwater, by which the variations of HMs pollution related with PSD differences are accessible. Characterizing the weight and optical properties respectively, total suspended solids (TSS) and turbidity are also indicators related to the particle size of suspended solids. TSS is dominantly contributed by coarse particles, while turbidity is dominantly contributed by fine particles. Therefore, the PSD can be represented by their quotient (i.e. Tur/TSS), and has been proven to be effective in our previous study (Wang et al., 2018). The Tur/TSS value is negatively correlated with PSD, and thus, stormwater with higher Tur/TSS shows finer PSD.

In this study, the HMs pollution of stormwater related with PSD (represented by Tur/TSS) variations were analyzed, to elucidate the variations of HMs pollution from RDS to stormwater during transport processes. Therefore, the concentrations of HMs in both RDS and stormwater from the same catchment area were investigated simultaneously to: 1) determine the distributions of HMs in both RDS and stormwater; 2) evaluate the contamination and potential ecological risk of HMs in RDS and stormwater particles, and 3) discuss the transferal of HMs pollution from RDS to stormwater during transport processes. The research findings may provide further understanding of HMs pollution and guide effective RDS and stormwater management to preserve urban waterways.

2 Materials and methods

2.1 Study area and sampling site

The study area is located in Yixing, a county-level city with advanced economy in the west of Taihu Lake, East China. It is also a typical plain city with densely covered river, and belongs to the subtropical monsoon climate. The average annual rainfall and number of rainy days are 1177 mm and 137 d, with a strong seasonality. Rainfall is abundant in summer (June to August), followed by spring (March to May) and autumn (September to November), and is least in winter (December to February). The city has

a drainage system of rain and sewage diversions. During wet seasons, the stormwater generated was quickly discharged into nearby receiving water without treatment through rainwater drainage system.

Lvyuan road, a typical traffic road located in the industrial area of Yixing, was selected as sampling site of both RDS and stormwater (Fig. 1). Lvyuan road has a total of six traffic lanes in two directions and paved with asphalt. The traffic volume is about 12000 vehicles/d. The road surface is manually and mechanically swept at a daily frequency. This road was selected as a sampling site due to its ease of access, which facilitated field sampling and observation.

Fig. 1 Map of sampling site and surrounding environment (a) photographs on the right side present the RDS (b) and stormwater (c) sampling.

2.2 Sample collection and pretreatment

2.2.1 RDS samples

A total of five RDS samples were collected from the curbs of Lvyuan road with clean brushes and dustpans in spring and autumn seasons during March 2016 to March 2017. The RDS samples collected were representative of two typical periods: in spring, more RDS accumulate on the road surfaces after a long period of dry winter; while in autumn, most RDS have been washed away during the rainy summer. The ADD varied from 2 to 8 days. After sampling, the RDS samples were transported to laboratory as soon as possible, and then immediately dried at 25°C for 5 days. Given the dominant contribution of < 150 μm RDS to stormwater particles (Ferreira et al., 2013; Charters et al., 2015; Wang et al., 2017), each RDS sample was dry-sieved into three fine fractions (< 22, 22–38.5, 38.5–150 μm) and one coarse fraction (>150 μm) with clean stainless sieves. The debris larger than 2000 μm were separated out and discarded. All the RDS subsamples were preserved in a desiccator until laboratory analysis.

2.2.2 Stormwater samples

Time-interval stormwater samples were collected from the gutter inlet at the roadside of Lvyuan road during three typical rainfall events in spring and autumn of 2016, as presented in Table 1. It is noticed that RDS and stormwater samples were collected during the same seasons, which avoid the influences of seasonality of RDS and stormwater pollution. The rainfall events differ in amount, duration, intensity and ADD. The detail information of the stormwater sampling campaign is presented in our previous study (Wang et al., 2018). A total of 90 samples were obtained. After sampling, the samples were immediately transported to laboratory, and prepared for laboratory analysis. A tipping bucket rain gauge, installed in the vicinity of the sampling site, was used to record the rainfall data at a 1-min time interval.

2.3 Laboratory testing

The HM concentrations of size-fractionated RDS subsamples were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) after microwave-assisted acid digestion, according to EPA 3052: 1996 and EPA 6010c: 2007.

For stormwater samples, turbidity and TSS were first measured using a laboratory turbimeter (HACH 2100N) and gravimetric method, respectively. The ratio of turbidity and TSS were calculated to qualitatively represent the bulk PSD of stormwater particles. Subsequently, parts of stormwater samples were filtrated through 0.45 μm membranes to separate the solid and aqueous phase. The bulk stormwater samples and the filtrates were used to measure the concentrations (mg/L) of total and dissolved HMs, respectively. The HMs was determined by ICP-OES according to the national standard method (HJ 776-2015). Accordingly, the solid-phase concentrations (C_{SP}, mg/kg) of stormwater particles can be obtained by Eq. (1):

$$C_{SP} = \frac{V_T - V_D}{TSS} \times 10^6, \quad (1)$$

Table 1 Rainfall characteristics of monitored events over May to September 2016 in Yixing, China

Date	RA [a] (mm)	RD [b] (h)	ARI [c] (mm/h)	MRA [d] (mm/h)	ADD (d)	Rain type	Number of samples
May 2	7.2	5.3	1.4	12	6	Showery, light	31
May 31	7.4	0.5	13.9	36	4	Thunderstorm	19
Sept. 14	21.8	5.4	4.0	36	7	Moderate	40

Note: a) Rainfall amount; b) rainfall duration; c) average rainfall intensity; d) maximum rainfall intensity.

where: V_T and V_D are the concentrations of total and dissolved HMs in stormwater, respecetively, mg/L; *TSS* is the concentration of total suspended solids in stormwater, mg/L.

A quality control program, including reagent blanks, standard reference materials, 10% duplicates, and 5% spiked samples, was used to ensure the accuracy and precision of measurement. The recoveries of all HMs fell within the range of 70%–120%.

2.4 Assessment of pollution levels and potential ecological risk

Geoaccumulation index (I_{geo}) and potential ecological risk index (*RI*), initially designed for aquatic bottom sediments, have been widely used to evaluate the pollution levels and potential ecological risk of HMs associated with RDS to water, soil or river sediments (Muller, 1969; Hakanson, 1980). However, they have not been applied to stormwater particles yet. Since stormwater particles are one of the primary contributors of the river sediments, the I_{geo} and *RI* indexes were utilized in this study to evaluate HM pollution of both RDS and stormwater particles.

By comparing the HM concentrations in samples with the background values of unpolluted soils, I_{geo} evaluates the pollution levels of HMs and highlights the influences of anthropogenic activities. According to Muller (1969), I_{geo} can be calculated by Eq. (2):

$$I_{geo} = \log_2 \frac{C_i}{1.5B_i}, \quad (2)$$

where: C_i is the measured concentration of metal i in samples (mg/kg). B_i is the background concentration of metal i in unpolluted soils of the study area (mg/kg), which were 22.3 for Cu, 26.2 for Pb, 62.6 for Zn, 77.8 for Cr and 26.7 for Ni, respectively (Chinese National Environmental Monitoring Center, 1990). A factor of 1.5 was selected due to possible variations in the background concentrations of a given metal in the environment and the influence of human activities (Zhao and Li, 2013). According to Muller (1969), the I_{geo} for a specific metal can be classified into seven levels: G0, unpolluted (if $I_{geo} \leqslant 0$); G1, unpolluted/moderately polluted (if $0 < I_{geo} \leqslant 1$); G2, moderately polluted (if $1 < I_{geo} \leqslant 2$); G3, moderately/heavily polluted (if $2 < I_{geo} \leqslant 3$); G4, heavily polluted (if $3 < I_{geo} \leqslant 4$); G5, heavily/extremely polluted (if $4 < I_{geo} \leqslant 5$), and G6, extremely polluted (if $I_{geo} > 5$).

RI represents the sensitivity of the biological community to toxic metals and illustrates the potential ecological risk posed by the overall contamination. The *RI* index can be calculated with Eq. (3):

$$RI = \sum_{i=1}^{m} E_i = \sum_{i=1}^{m} T_r^i \times \frac{C_i}{B_i}, \quad (3)$$

where: *RI* is the overall ecological risk caused by all given metals; E_i is the potential ecological risk of metal i; T_r^i is the toxic response factor of metal i, and according to Hakanson (1980), the values for Cu, Pb, Zn, Cr and Ni are 5, 5, 1, 2 and 5, respectively. C_i and B_i have the same meaning as in Eq. (2), and m is the number of metal species. According to Hakanson (1980), the potential ecological risk can be classified as: G0, low risk (if $RI \leqslant 50$); G1, moderate risk (if $50 < RI \leqslant 100$); G2, considerable risk (if $100 < RI \leqslant 200$), and G3, high risk (if $RI > 200$).

3 Results and discussion

3.1 Distribution of HMs in bulk and size-fractionated RDS

The HM concentrations in bulk RDS and background values for local soils are presented in Table 2. Overall, the concentrations of all HMs in bulk RDS exceeded the

Table 2 HM concentrations (mg/kg) in bulk RDS, stormwater particles and local soils of Yixing, China

Items		Cu	Pb	Zn	Cr	Ni
RDS	Min	93.0	78.4	406.6	156.6	85.3
	Max	194.1	264.8	495.7	276.8	129.6
	Average	153.5	194.6	472.0	225.7	112.4
	SD	43.3	80.8	43.6	50.5	19.8
	CV	0.28	0.42	0.09	0.22	0.18
Stormwater particles	Min	55.8	87.4	350.0	40.6	19.8
	Max	802.5	1913.3	12538.9	800.0	413.9
	Average	297.2	412.2	2652.5	159.8	91.5
	SD	151.0	382.3	2569.1	162.2	64.2
	CV	0.51	0.93	0.97	1.01	0.70
Background soil (Chinese National Environmental Monitoring Center, 1990)		22.3	26.2	62.6	77.8	26.7

background values for local soils, highlighting the ubiquitous influences of human activities. More specifically, the average concentrations of HMs in bulk RDS were 6.9 (Cu), 7.4 (Pb), 7.5 (Zn), 2.9 (Cr) and 4.2 (Ni) times higher than that in the local soils, respectively. Altogether, the concentrations (mg/kg) of HMs in bulk RDS ranked as: Zn>Cr>Pb>Cu>Ni. The dominant accumulation of Zn was consistent with other previous reports (Zhang et al., 2013 a; Liu et al., 2015), confirming the ubiquitous accumulation of Zn in RDS worldwide. Moreover, slight to moderate variations in the concentrations of the various HMs were observed, which can be attributable to the differences in antecedent rainfall and dry conditions (Zhang et al., 2017).

The accumulation of HMs in size-fractionated RDS is illustrated in Fig. 2(a). Evidently, the accumulation of HMs varies with particle sizes and metal species. For example, the concentrations of Cu, Cr and Ni were highest in the 38.5–150 μm RDS, followed by < 22 and 22–38.5 μm RDS. In contrast, the concentrations of Pb and Zn were highest in the 22–38.5 μm RDS, followed by < 22 and 38.5–150 μm RDS. The concentrations of all metals were lowest in the>150 μm RDS. One-way ANOVA analysis was performed to detect the significant differences of HM concentrations among various size RDS fractions. The results are presented by different color of the boxes in Fig. 2(a), and show significantly higher concentrations of Cu, Cr and Ni in 38.5−150 μm RDS, Pb in < 38.5 μm RDS and Zn in < 150 μm RDS. These results suggest the preferential accumulation of Pb and Zn in finer RDS, and that of Cu, Cr and Ni in coarser RDS.

3.2 Distribution of HMs in stormwater runoff

3.2.1 Dissolved and particulate HMs

RDS contribute HMs to stormwater in two pathways: Particulate HMs that adsorbed on the mobile RDS (i.e. stormwater particles) and dissolved HMs that released from both mobile and immobile RDS (Zafra et al., 2017). In this study, the concentrations of dissolved HMs were below the limit of detection for a majority of the stormwater samples, which were 51.1% (46/90) for Cu, 100% (90/90) for Pb, 60% (54/90) for Zn, 66.7% (60/90) for Ni and 100% (90/90) for Cr. The dissolved Pb and Cr concentrations were below the limit of detection for all stormwater samples. For the samples with concentrations above the limit of detection, the distribution of dissolved HMs was as follows: 29.5±22.3% Cu, 6.9±6.0% Zn and 48.6±19.3% Ni. The dissolvability of given metals ranked as Ni>Cu>Zn>Cr ≈ Pb. The results were similar to the findings of previous studies, which reported 3.3%–26.9% Cu, 0.1%–7.1% Pb, 5.8%–39% Zn, 1.1%–24.4% Cr and 7.3%–48.8% Ni in dissolved phase (Hallberg et al., 2006; Béchet et al., 2009; Helmreich et al., 2010; Joshi and Balasubramanian, 2010). The particulate forms of the various HMs dominated in the stormwater. Therefore, it forms an important factor for understanding the characteristics of HM accumulation in stormwater particles during runoff processes.

3.2.2 HM accumulation in stormwater particles during runoff processes

The solid-phase concentrations of HMs in stormwater particles during runoff processes are presented in Table 2. Overall, the concentrations of nearly all HMs exceeded the respective background values for the local soils, except for that of Cr and Ni in several samples. The average concentrations in stormwater particles were higher by 13.3 (Cu), 15.7 (Pb), 42.4 (Zn), 2.1 (Cr) and 3.4 (Ni) times than that in the local soils, respectively. Furthermore, the accumulation of Cu, Pb and Zn in stormwater particles were significantly higher than that in the bulk RDS by a factor of 1.9, 2.1 and 5.6, respectively. However, the concentrations of Cr and Ni in stormwater particles were comparable to that in the bulk RDS. Altogether, the HM concentrations of stormwater particles ranked as: Zn>Cu>Pb>Cr>Ni. Apart from the dominant accumulation of Zn, the order of HM accumulation in stormwater particles and bulk RDS were considerably disparate, demonstrating the variability of HMs pollution during transport processes from RDS to stormwater particles. The accumulation of Cr was prominent in RDS while those of Cu and Pb were more prominent in stormwater particles. These variations may be attributable to the differences in the distributions of Cu, Pb and Cr in the various RDS size fractions. Therefore, as the finer RDS are easier transported to stormwater, HMs preferring to accumulate in finer RDS present heavier pollution in stormwater particles (Zhao and Li, 2013b; Zhao et al., 2016). Moreover, significant variations in HMs accumulation were recorded for stormwater particles during runoff processes. The maximum concentrations of HMs recorded were 14.4–35.8 times higher than the minimum concentrations recorded. Given the considerable variations in HMs accumulation during runoff processes, stormwater control strategies should prioritize the stormwater with heavier pollution.

The distribution of HMs in stormwater particles with elevated Tur/TSS (i.e. finer PSDs) are illustrated in Fig. 2 (b). Linear regression analyses demonstrated that the concentrations of HMs increased linearly with Tur/TSS, suggesting a higher HMs accumulation in stormwater particles with finer PSDs. The slope (k) of the linear regression equation varied for the various HMs in the following order: Zn>Pb>Cu>Cr>Ni, showing decreasing influences of PSD. The coefficients of determination (R^2) ranged from 0.290 (for Ni) to 0.614 (for Cu), which were not very high due to several reasons. First, Tur/TSS was used as a substitute for PSD of stormwater particles.

However, apart from particle size, Tur/TSS is also affected by other factors such as the color of water, particle shape and composition (organic and inorganic) (Ying and Sansalone, 2010). Secondly, the build-up of HMs in RDS generally varies with the antecedent conditions (e.g., antecedent dry days and rainfall conditions) (Tian et al., 2009; Zhang et al., 2017). As the stormwater samples were collected during three rainfall events, the differences in RDS build-up during the antecedent dry periods may, consequently, contribute to the inter-event variability of HMs in stormwater particles, which was confirmed by the distribution of scatters from different events in Fig. 2(b). Additionally, the leaching of HMs from stromwater particles during transport processes also had influence on their relationships.

Noticeably, HMs accumulation in stormwater particles differed with rainfall events (Fig. 2(b)). Due to the high intensity and short duration during thunderstorm, stormwater showed narrower and lower Tur/TSS values on May 31 than that on May 2 and Sept. 14. Accordingly, the Cu, Pb and Zn accumulation were lowest on May 31, while not for Cr and Ni. Cr and Ni accumulation were highest on Sept. 14 (moderate rain), followed by May 31 (thunderstorm), and were lowest on May 2 (showery, light rain), suggesting the greater influence of rainfall depth and intensity than PSD on Cr and Ni accumulation in stormwater particles. Pb and Zn accumulation on Sept. 14 were higher than that on May 2, which may be attributed to the seasonality of Pb and Zn build-up in RDS. To provide better guidance to stormwater management, further studies are needed to elucidate the inter-event variability of quantitative relationships between Tur/TSS and HMs accumulation. Nonetheless, HMs in stormwater particles increased with the finer PSD for both single and multiple events, and thus, pollution control should prioritize stormwater with high Tur/TSS.

3.3 Indicators of HMs pollution levels and potential ecological risk

3.3.1 Pollution levels

The pollution levels of five metals in bulk and size-fractionated RDS, as well as in stormwater particles with

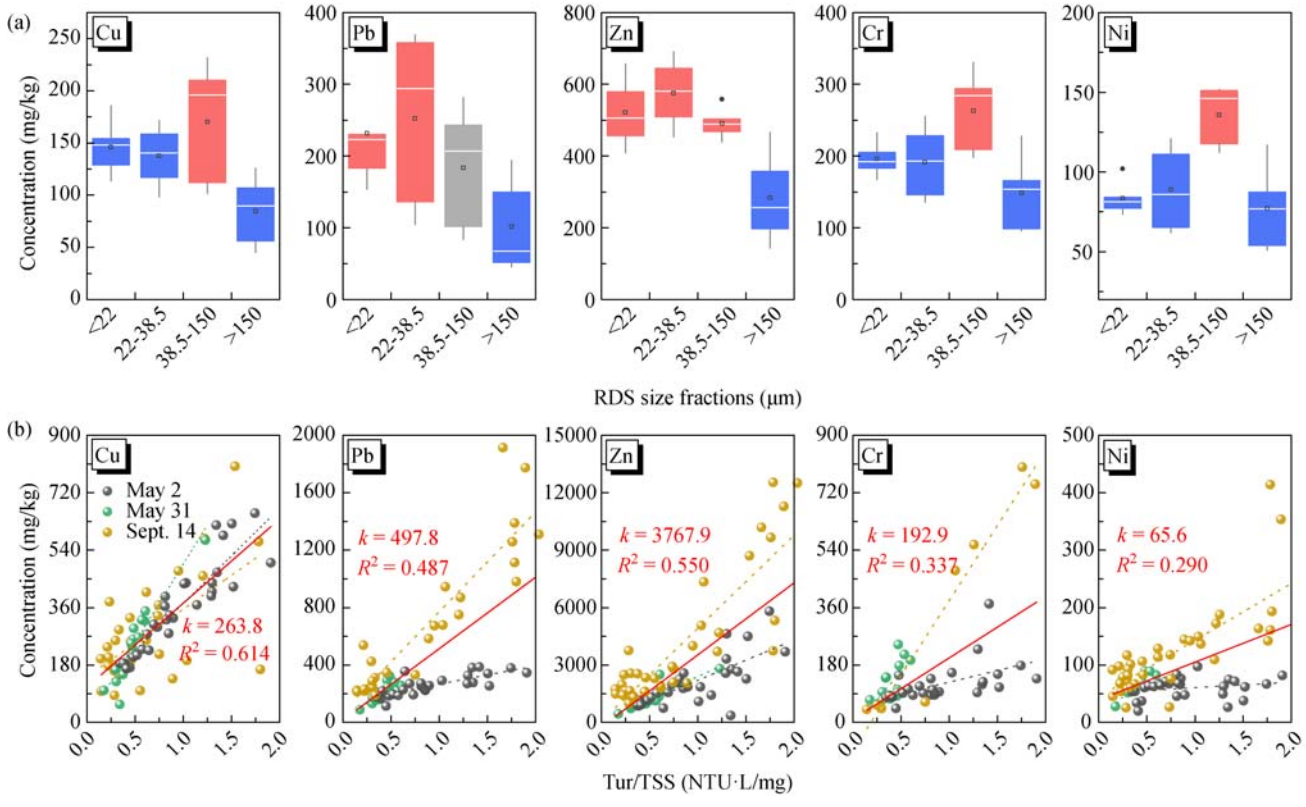

Fig. 2 Distribution of HM concentrations in (a) RDS of four size fractions, and (b) stormwater particles with elevated Tur/TSS (i.e. finer PSD). For (a), The bottom and top of the bigger box are the first and third quartiles; the bottom and top of the whiskers are the 1% and the 99% percentiles; the band and smaller box inside the bigger box are the median and mean; the gray circles are the outliers; and the colored boxes indicates the results of one-way ANOVA analyses, whereby similar colors denote no significant differences and vice versa. For (b), the gray, green and yellow scatters represent stormwater samples on May 2, May 31 and Sept. 14, respectively, and the colored dashed lines are corresponding results of linear regression analyses. The red solid lines show the results of linear regression analyses for all stormwater samples from three rainfall events. k and R^2 are the corresponding slope and coefficient of determination, respectively.

elevated Tur/TSS (i.e. finer PSD) were accessed by I_{geo} and given in Fig. 3. For bulk RDS (Fig. 3(a)), the I_{geo} of the five metals varied in the following order: Zn (2.1–2.4)>Pb (1.0–2.8)>Cu (1.5–2.5)>Ni (1.1–1.7)>Cr (0.4–1.2). Thus, these I_{geo} values fall within the levels of moderately/heavily (G3), unpolluted/moderately (G1) to moderately/heavily (G3), moderately (G2) to moderately/heavily (G3), moderately (G2), and unpolluted/moderately (G1) to moderately (G2) polluted, respectively. For the size-fractionated RDS, the I_{geo} values were highest in the 38.5–150 μm RDS for Cu, Cr and Ni; and highest in < 22 and 22–38.5 μm RDS for Pb and Zn, respectively. The I_{geo} values of all HMs were lowest in>150 μm RDS, which were approximately one or two grades lower than that in < 150 μm RDS.

With respect to stormwater particles (Fig. 3(b)), the I_{geo} of the five metals in stormwater ranked as Zn (4.4±1.0) >Pb (3.0±1.0)>Cu (3.0±0.8)>Ni (1.0±0.8)>Cr (0.1±1.0). These I_{geo} values fall within the levels of moderately (G2) to extremely (G6), moderately (G2) to extremely (G6), unpolluted/moderately (G1) to heavily/extremely (G5), unpolluted (G0) to heavily (G4), and unpolluted (G0) to moderately/heavily (G3) polluted, respectively. These pollution levels varied in a similar order with that in RDS, indicating that both RDS and stormwater particles were preferentially polluted by Cu, Pb and Zn rather than Cr and Ni. Furthermore, the average I_{geo} levels of Cu, Pb and Zn in stormwater particles were about one or two grades higher than that in RDS; while the I_{geo} levels of Cr and Ni were even slightly lower than RDS. The disparities may be attributable to differences of HMs in terms of dissolvability and size-dependent accumulation in RDS. For HMs of low dissolvability and with preferential accumulation in finer RDS, the contamination will be heavier in stormwater particles. Although the size-fractionation within micron-scale showed that the concentration of Cu was highest in 38.5–150 μm RDS, Cu may accumulate more in nano- or submicron-scale RDS. Consequently, the contamination of Cu, Pb and Zn exacerbated during transport processes from RDS to stormwater particles. On the other hand, it is noted that the I_{geo} of HMs in stormwater particles varied greatly during runoff processes and increased linearly with elevated Tur/TSS (i.e. finer PSD). The I_{geo} of stormwater particles with higher Tur/TSS were about three to four grades higher than that with lower Tur/TSS. Therefore, removal of stormwater with high Tur/TSS can effectively attenuate the contamination of Cu, Pb and Zn.

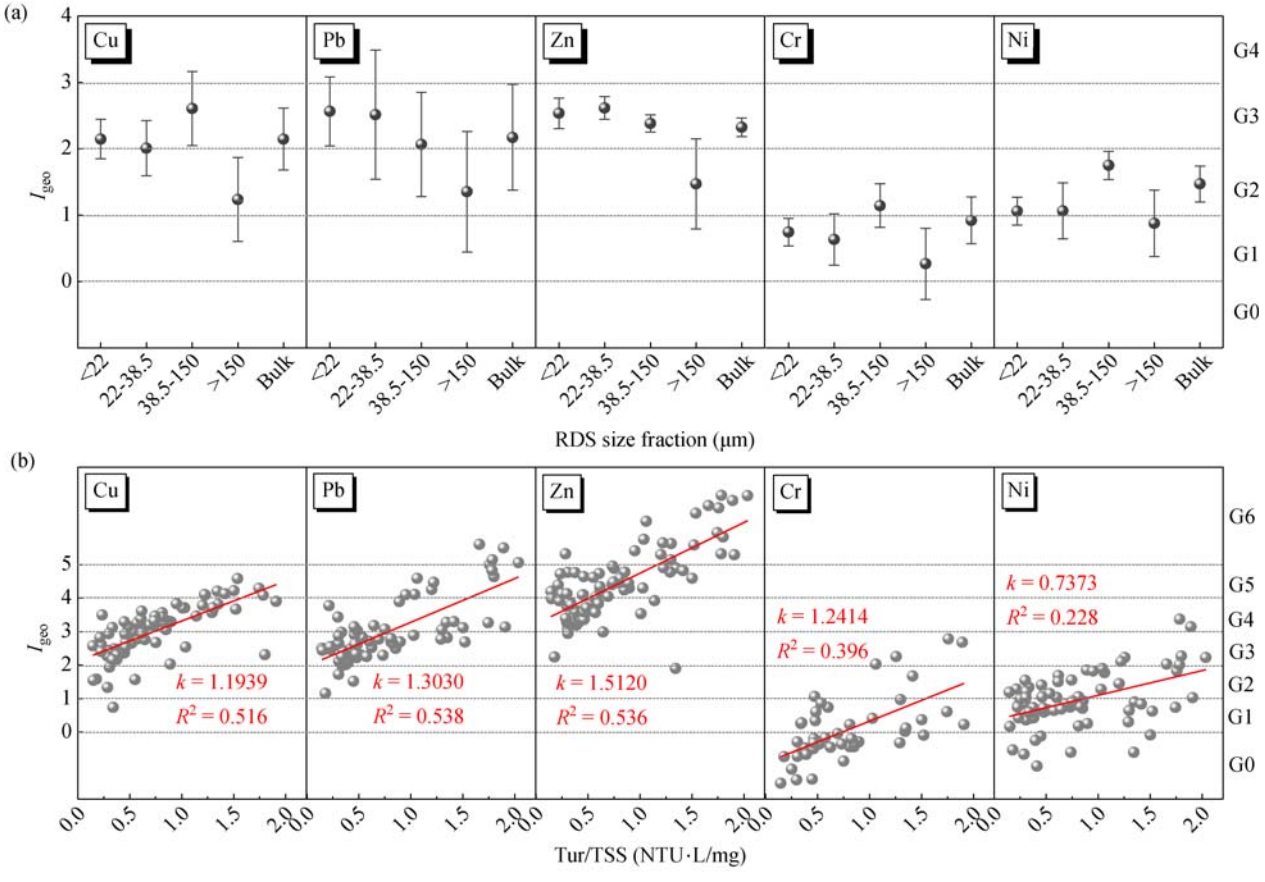

Fig. 3 Geoaccumulation index (I_{geo}) of HMs in (a) RDS of different size fractions, and (b) stormwater particles with elevated Tur/TSS (i.e. finer PSD). The red lines in (b) show the results of linear regression analyses.

3.3.2 Potential ecological risk

The potential ecological risks of HMs in the bulk and size-fractionated RDS, as well as in stormwater particles with elevated Tur/TSS (i.e. finer PSD) were accessed by *RI* and illustrated in Fig. 4. For bulk RDS (Fig. 4(a)), the *RI* ranged from 62.3 to 131.5, falling into the moderate (G1) to considerable (G2) risk levels. The contribution of each metal to *RI* ranked as follows: Pb (33.7±6.9%)>Cu (32.6±0.8%)>Ni (20.6±3.5%)>Zn (7.5±2.0%)>Cr (5.6±0.7%). More than 85% of risks were contributed by Cu, Pb and Ni. For the size-fractionated RDS, the *RI* values were highest in 38.5–150 μm RDS, and comparable for that in < 22 and 22–38.5 μm RDS. However, the average *RI* values of < 150 μm RDS fractions were evidently high compared with that of>150 μm RDS.

With respect to stormwater particles (Fig. 4(b)), the *RI* ranged from 53.2 to 328.8, falling into the moderate (G1) to high (G3) risk levels. The *RI* in stormwater particles varied significantly during runoff processes and were found to increase linearly with elevated Tur/TSS (i.e. finer PSD). Therefore, stormwater with high Tur/TSS should be of great concern due to its high risk. The contribution of each metal to the *RI* of stormwater particles ranked as follows: Cu (41.4±7.1%)>Pb (30.2±4.7%)>Zn (18.1±5.0%)>Ni (8.2±3.0%)>Cr (2.1±1.0%). Approximately 90% of the risks were contributed by Cu, Pb and Zn. The primary sources of risk were slightly different between RDS and stormwater particles. The contribution of Cu and Zn to ecological risk increased, while that of Ni decreased evidently during transport processes. Since RDS primarily exert ecological risk to urban waterways in terms of stormwater, attenuation of Cu, Pb and Zn pollution should be prioritized in RDS source and stormwater control measures.

Compared to bulk RDS, the *RI* of HMs in stormwater particles (moderate to high risk) were higher than that in RDS (moderate to considerable risk). Although different methods were used, the results were similar to that reported by Zhao and Li, (2013a), who modified the *RI* index by integrating the mobility and amount of RDS. Likewise, the assessment indicated the results of the modified *RI* (moderate to considerable risk) were higher than that of the original *RI* (low to moderate risk) for RDS in central Beijing (Zhao and Li, 2013 a). The heavier HM pollution in stormwater particles emphasizes the importance of controlling finer particles in both RDS and stormwater to limit the metal risk.

3.4 Insight into the transferral of HMs pollution from RDS to stormwater runoff

Originating from a variety of sources such as traffic, atmospheric deposition, industrial and human emissions, RDS accumulate on road surfaces during dry periods. The RDS retain elevated HM concentrations, which normally bond to carbonate, Fe-Mn oxide, sulphide, organic or mineral components, and thus, present different dissolvability (Sutherland et al., 2012; Świetilik et al., 2015). Consequently, part of the HMs associated with RDS dissolve into stormwater during rainfall events. In this study, it is found that 29.5% Cu, 6.9% Zn and 48.6% Ni is transported in the dissolved form with stormwater, and nearly all Pb and Cr were entrained by stormwater particles. Stormwater particles constitute the primary carriers of HMs in stormwater. The discharge of untreated

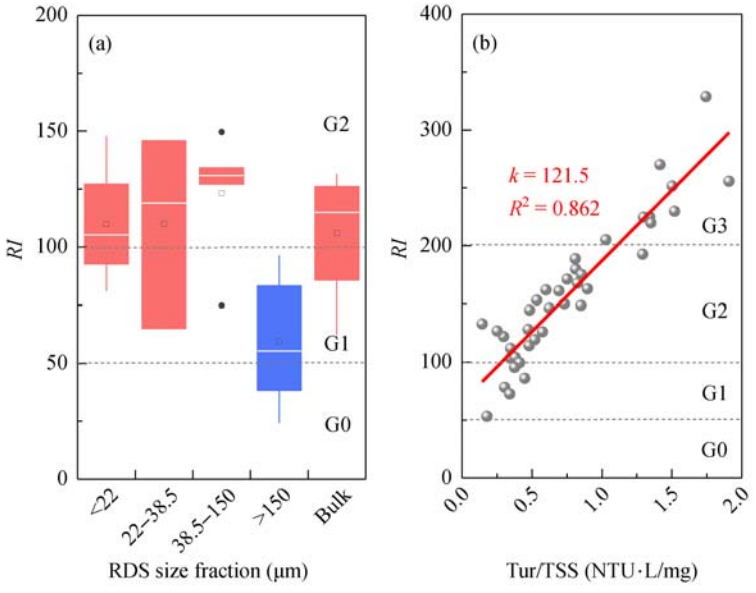

Fig. 4 Potential ecological risks (*RI*) of HMs in (a) RDS of different size fractions, and (b) stormwater particles with elevated Tur/TSS (i.e. finer PSDs). The boxes in (a) and line in (b) have the same meaning with Fig. 2.

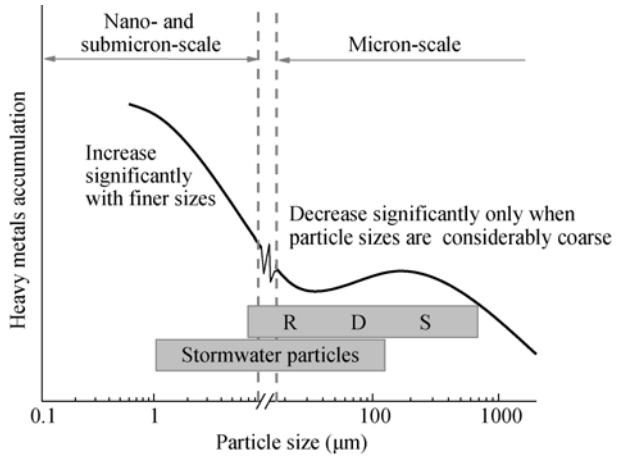

Fig. 5 Accumulation of HMs in RDS and stormwater particles with particle sizes. The figure was plotted using data obtained from McKenzie et al. (2008), Zhao et al. (2010), Kayhanian et al. (2012), Fedotov et al. (2014) and this study.

stormwater into receiving water will deteriorate the aquatic ecosystems via a variety of pathways, such as clog the river beds, attenuate the light penetration, damage the respiratory system, and pose toxicity to biological community by HMs (Blecken et al., 2012; Charters et al., 2015).

In previous studies, RDS were mostly size-fractionated within micron-scale to investigate the relationships between HM accumulation and particle sizes. It has been generally acknowledged that fine RDS carry relatively more HMs than coarse RDS. For example, Kayhanian et al. (2012) reported that the HMs accumulated in < 125 μm RDS were significantly higher than >125 μm RDS from highway road in California. Similarly, Zhao et al. (2010) reported that the HMs accumulated in < 250 μm RDS were significantly higher than >250 μm RDS in Beijing. The current study yielded similar results as the HMs accumulated in < 150 μm RDS were normally higher than that in the >150 μm RDS. However, a more detailed analyses by Fedotov et al. (2014), who fractionated RDS into nano- (< 1 μm), submicron- (1–10 μm) and micron-scale (10–100 μm) fractions found evident decreases of HM accumulation with coarser RDS. With respect to stormwater particles, only a few studies were conducted to investigate the HM accumulation in size-fractionated stormwater particles, which can be partly attributable to the laborious and inconvenient process of size fractionation. Nonetheless, Kayhanian et al. (2012) found that the size dependent trends in HM accumulation were less apparent according to the micron-scale size fractionation of stormwater particles. Conversely, McKenzie et al. (2008) reported increasing HM concentrations with finer particles within 0.1–1.5 μm ranges for highway runoff in California. Similarly, the HM accumulation in stormwater particles were found to increase linearly with finer PSD in this study. It seems, therefore, that the relationships between HMs accumulation and particles sizes depend on the scale of size fractionation of RDS and stormwater particles. As illustrated in Fig. 5, for nano- and submicron-scale (< 10 μm) particles, HM accumulation normally increases with finer sizes. However, for micron-scale particles (>10 μm), the HM accumulation decreases significantly only when particle sizes are considerably coarse. In this study, RDS samples were size-fractionated within micron-scales, with only small amounts of very fine (nano- and submicron-scale) particles in the RDS. Consequently, the influence of these very fine particles on HMs accumulation was overshadowed. Nevertheless, as the finer RDS are easier transported by runoff, the nano- and submicron-scale particles accounted for a considerable proportion of the stormwater particles (Yun et al., 2010; Charters et al., 2015; Wang et al., 2017). Thus, these finer RDS predominantly influenced the HMs accumulation in stormwater particles. Consequently, the HMs pollution of stormwater particles was observed to increase with Tur/TSS, an indicator positively correlated with the proportion of nano- and submicron-scale particles (Wang et al., 2018). It is noteworthy that the accumulation of HMs in particles within nano- and submicron-scale are significantly high than that in micron-scale, which is reasonable for HMs preferring to accumulate in finer particles (i.e. nano- and submicron-scale), such as Cu, Pb and Zn in this study. However, for HMs preferring to accumulate in coarser particles, such as Cr and Ni in this study, the accumulation of HMs in particles within nano- and submicron-scale may be comparable or slightly lower than that in micron-scale.

In addition, the dissolvability and accumulation of HMs in RDS of different size fractions also have impact on the transferral of HMs pollution from RDS to stormwater particles. Altogether, the HMs with preferential accumulation in finer RDS and of low dissolvability (e.g., Cu, Pb and Zn in this study) shows heavier contamination in stormwater particles; whereas those that preferentially accumulate in coarser RDS or of high dissolvability (e.g., Cr and Ni in this study) shows comparable or lower contamination potential in stormwater particles. HMs showing preferential accumulation in finer RDS are the primary sources of risk posed by stormwater particles to aquatic ecosystems. Therefore, stormwater control strategies should focus on these very fine (e.g., nano- and submicron- scale) particles in both RDS and stormwater. Nonetheless, the HMs of high dissolvability (e.g., Ni) should also be of great concern due to their higher bioavailability and needs to be attenuated before rainfall events.

4 Conclusions

Variations of HMs pollution from RDS to stormwater during transport processes are elucidated. The accumulation of HMs in RDS significantly depend on particle sizes. Pb and Zn preferentially accumulate in finer (< 38.5 μm)

RDS, whereas Cu, Cr and Ni preferentially accumulate in coarser (38.5–150 μm) RDS. In stormwater, n.d.~48.6% of the HMs fractionate into dissolved phases, and 51.4%–100% in the particulate phase. Stormwater particles constitute the primary carriers of HMs, and the associated concentrations increase with the finer PSD. Geoaccumulation index (I_{geo}) highlighted the predominant pollution of both RDS and stormwater particles by Cu, Pb and Zn. Nonetheless, Cu, Pb and Ni mostly contribute the potential ecological risks of RDS while Cu, Pb and Zn mainly contribute that of stormwater particles. Altogether, contamination by Cu, Pb and Zn can be significantly higher in stormwater particles than RDS. Variations in the pollution originate from the solubility and particle size-dependent accumulation of HMs in RDS. Therefore, the control of HMs pollution in stormwater particles should prioritize the removal of very fine (nano- and micron- sacle) particles in both RDS and stormwater. Nonetheless, the control of coarse RDS may also assist the attenuation of dissolved HMs pollution.

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