The chemical fractionation and potential source identification of Cu, Zn and Cd on urban watershed

Jin Zhang, Pei Hua and Peter Krebs

ABSTRACT

This study showcases the chemical fractionation and primary source identification of Cu, Zn and Cd in road-deposited sediment. Results show that Zn and Cd were identified as easily mobilised and biologically available metals that pose high risks to the receiving aquatic environments. However, Cu was released in substantial amounts only under relatively extreme conditions. With the assistance of principal component analysis and chemical fractionation, two primary contributors to heavy metals in road-deposited sediment were tentatively identified as vehicle-related sources (especially, auto brake pad erosion for Cu and tyre debris for Zn) and atmospheric deposition (especially for Cd).

Key words | chemical fractionation, heavy metal, integrated stormwater management, road-deposited sediment

Jin Zhang
Peter Krebs
Institute of Urban Water Management,
Technische Universität Dresden,
01062 Dresden,
Germany

Pei Hua (corresponding author)
Chair of Water Supply Engineering,
Institute of Urban Water Management,
Technische Universität Dresden,
01062 Dresden,
Germany
E-mail: pei.hua@hotmail.com

INTRODUCTION

With the rapid development of the economy and society, the process of urbanisation has increasingly caused urban runoff pollution problems in many countries (Sartor & Boyd 1972). Natural and anthropogenic pollutants are washed off urban watersheds and transported through sewers or directly into lakes, rivers and seas, ultimately contaminating receiving waters (Hillenbrand et al. 2005; Egodawatta et al. 2013). In this context, the urban watershed has been recognised as a leading diffuse pollution source in urban areas worldwide (Sartor & Boyd 1972; Loganathan et al. 2013). Therefore, a mitigation strategy for stormwater pollution should be based on the in-depth understanding of initial pollutant build-up on urban watersheds (Egodawatta et al. 2013; Zhang et al. 2015).

Among the priority pollutants abundant in both the urban watershed and stormwater runoff, heavy metals are known to be acutely toxic, carcinogenic, and persistent trace elements (Sartor & Boyd 1972). The knowledge on the metals in road-deposited sediment (RDS) is essential to assess the potential adverse effects of RDS on the stormwater quality and the potential performance of an integrated stormwater pollution management in eliminating heavy metals.

It has been reported that heavy metal concentrations in RDS are commonly at least an order of magnitude higher than those in neighbouring soils (Loganathan et al. 2013). However, the environmental and health effects of metals are dependent, at least initially, on the mobility and availability of their chemical fractionation, e.g. exchangeable, reducible, oxidisable, and residual fractions determined by a sequential extraction protocol (Davidson et al. 1998; Sutherland et al. 2012). The chemical fractionation of heavy metals in solid-phase concentration (mass of metals per unit mass of dry RDS) has been reported (Sutherland et al. 2012). However, less attention has been paid to the mass of heavy metal chemical fractionation per unit surface area, referred to as surface load, which describes the accumulation ability of RDS adsorbed toxic substances on urban watersheds and the total mass contribution to receiving aquatic environments (Lau & Stenstrom 2005).

Therefore, the focuses of this study were to (i) determine the chemical fractionation of RDS adsorbed heavy metals in the form of surface load and (ii) identify the primary source contributors of these metals.

MATERIAL AND METHODS

Sample collection

RDS samples were obtained from three urban roads with various surrounding land use types and traffic loads in the city of Dresden (51°02′55″ N, 13°44′29″ E), Germany. The characteristics of the sampling sites are shown in Table 1.

Table 1 │ The characteristics of sampling sites

Site	Abbr.	Road class	Pavement quality	Lane number	Average daily traffic[a] vehicle/day	Heavy traffic %	Vicinity land use
Walpurgis str.	W	Main road	Good	4	12,600	3–4	City commercial centre
Bannewitz	B	Federal highway	Average	2	15,900	5	Petrol and bus station
Noethnitz	N	Secondary road	Good	2	50	<1	Rural residential area

[a]The traffic loads were determined in one flow direction (www.dresden.de, accessed July 2012).

The sampling campaign was performed in July 2012. A professional vacuum sweeper (Puzzi 100 Super, Kärcher) with a water filtration system was employed for the sample collection. It has been proven to be more efficient in removing the fine materials within a typical pavement structure than mechanical broom sweepers and traditional domestic vacuum sweepers (Sartor & Boyd 1972; Egodawatta et al. 2013). The power requirement was provided by a generator (Honda EU30i, Rated power COP, 2.6 kW).

For each land use, six sampling plots of 6 m² in close proximity were predefined. Since the majority of the sediments were assembled near roadside kerbs (Sartor & Boyd 1972), all the enclosed sampling plots were situated next to these areas. The RDS build-up process in each plot started at the same time period after the last substantial rainfall event. After the stipulated antecedent dry-weather period (ADP, the length of time which has elapsed since the last substantial rainfall event), i.e. 1, 2, 3, 4, 6, and 8 days, 13.9–72.7 g RDS were obtained from the respective sampling plots. During the sampling process, the vacuum nozzle was moved from the kerb to the bottom of the enclosed sampling plots at approximately 10 cm/s in parallel strips.

Due to the water filtration system used by the vacuum sweeper, the collected material was suspended in deionised water, which was used as a filtration reagent. The suspended RDS was then deposited into pre-cleaned 1 L amber-brown glass bottles with Bakelite caps before being transported to the laboratory. During the sample collection, around 0.5–0.8 L/m² deionised water was used. After sample collections at each site, about 6 L deionised water was passed through the sweeper three times to prevent cross-contamination. The vacuum nozzle and brush were cleaned with deionised water to remove all the remaining particles. Every effort was made to ensure consistent initial conditions for each RDS collection.

Laboratory analysis

RDS samples obtained from each site were fractionated into sub-samples and wet-sieved using nylon and stainless-steel sieves with mesh sizes of 1,000 μm, 400 μm, 100 μm and 63 μm in sequence. The particles passing through the 63 μm sieve were filtered by a 0.45 μm (classification diameter between soluble and particle) cellulose nitrite filter. The fractionated RDS samples were labelled, sealed and refrigerated at 4 °C in preparation for analysis.

A total of 68 bulk and size-fractionated RDS samples were tested for copper (Cu), zinc (Zn), and cadmium (Cd). The contents of metals were determined according to both a three-step sequential extraction protocol proposed by the Standards, Measurements and Testing Programme (SM&T, formerly BCR) of the European Commission, which has proved reproducible and gave good recoveries with respect to acid dissolution (Davidson et al. 1998) and a pseudo-total digestion protocol following the German Norm DIN 38406-8 (E8), DIN 38406-7 (E7), and DIN EN ISO 5961. The chemical extraction reagents and experimental protocol are given in Table 2. More details can be found elsewhere (Quevauviller et al. 1997).

The metal compounds of each fraction were determined in sequence by an atomic absorption spectrophotometer equipped with graphite furnace atomisation (Varian, SpectrAA 220 Fast Sequential AAS-220 Z). The samples were processed in triplicate throughout all the analyses and the results reported were the average values. To maintain the laboratory quality assurance and quality control, Cu (1.014 g/cm³, 20 °C), Zn (1.02 g/cm³, 20 °C), Cd (1.013 g/cm³, 20 °C) and multi-element standard solutions (23 elements in diluted nitric acid, 1.09 g/cm³, 20 °C), for each at 1,000 mg/L, were prepared (Merck KGaA, Darmstadt, Germany). A certified reference material of dry sewage sludge (KS 2/2006) from a European Union reference laboratory (Sächsische Landesanstalt für Landwirtschaft. Fachbereich 8 – Landwirtschaftliches Untersuchungswesen, Leipzig, Germany) was used. The recovery (the summation of the four fractions to the pseudo-total metals concentration) were in the range 98–116% for Cu, 109–124% for Zn, and 92–115% for Cd. The limits of detection were 1.0 μg/L for Cu, 20 μg/L for Zn, and 0.1 μg/L for Cd. The limits of quantitation were 0.5 μg/L for Cu, 10 μg/L for Zn, and 0.05 μg/L for Cd.

Table 2 | Three-step sequential extraction (SM&T) and pseudo-total digestion protocols

Step	Fraction	Nominal target heavy metals	Chemical reagents and experimental protocols
F1	Exchangeable	Exchangeable, carbonate bound	A total of 40 mL 0.11 mol/L acetic acid (CH_3COOH, pH 2.85) was added to 1.0 g dry weight of RDS samples and shaken for 16 h. The mixture was centrifuged to separate the extract from the residue at 3,000 rpm for 20 min.
F2	Reducible	Iron, manganese oxide bound	A total of 40 mL 0.1 mol/L hydroxylammonium chloride ($NH_2OH \cdot HCl$, pH 1.5) was added to the residue from step 1 and the extraction performed as above.
F3	Oxidisable	Organically, sulphide bound	A total of 10 mL hydrogen peroxide (H_2O_2, 30%) was added to the residue from step 2 at room temperature for 1 h, and then evaporated at $85 \pm 2\,°C$ to dryness. Additional 50 mL 1 mol/L ammonium acetate (NH_4CH_3COO, pH 2) was added and shaken for 16 h. The extraction performed as above.
F4	Residual*	Remaining, non-silicate bound	With microwave assistance, the remaining material after step 3 was digested with 5 mL nitric acid (HNO_3), 5 mL ultrapure water and 1 mL hydrogen peroxide (H_2O_2, 30%). The digested samples were filtered through the cellulose nitrate membrane filter into a 50 mL Erlenmeyer flask and the leftover particles were removed.

*Digestion of the residual material is not a speciation of the SM&T three-step sequential extraction protocol, and is referred to as pseudo-total digestion.

Source apportionment

Principal component analysis (PCA) is one of the most classical source receptor approaches, which has been widely used to qualitatively identify the major sources of various environmental pollutants (Zhang et al. 2013). Its aim is to reduce a larger set of variables into a smaller set of artificial variables, referred to as principal components, which account for most of the variance in the original variables. In this study, a PCA receptor model with the assistance of chemical fractionation data was employed to qualitatively estimate the potential source apportionment of heavy metals.

RESULTS AND DISCUSSION

Heavy metal surface load in bulk RDS

As given in Table 3, the mean values of overall total surface load were: $Cu = 0.85 \pm 0.19$ mg/m^2 (mean ± standard error of the mean), $Zn = 1.70 \pm 0.31$ mg/m^2, and $Cd = 1.16 \pm 0.14$ μg/m^2. Compared with data from Queensland, Australia (Egodawatta et al. 2013), Cu overall mean surface load in the present study was high, and Zn overall mean surface load was comparable. Compared with data from Christchurch, New Zealand (Wicke et al. 2012), the presented Cu overall mean surface load was high, and the presented Zn

Table 3 | The present and reviewed heavy metal surface loads in bulk RDS

Study area	Mean surface load			No.[a]	Land use	Year
	Cu (mg/m^2)	Zn (mg/m^2)	Cd (μg/m^2)			
Present study	1.40	2.86	1.60	68	Commercial	2012
	0.88	1.64	0.68		Highway	
	0.15	0.39	1.22		Rural	
	0.85	1.70	1.16		Overall	
Queensland, Australia (Egodawatta et al. 2013)	0.15	1.43	n/a[b]	17	Residential	2013
Christchurch, New Zealand (Wicke et al. 2012)	0.21	2.72	n/a	11	Coarse asphalt	2012
	0.15	2.90	n/a		Smooth asphalt	
	0.18	2.81	n/a		Overall	
Santa Monica, California, USA (Lau & Stenstrom 2005)	4.10	16.71	53	18	Commercial	2005
	0.63	3.80	18		Residential	
	2.68	6.44	33		Industrial	
	2.47	8.98	35		Overall	

[a]No.: number of observations.
[b]n/a: not available.

mean overall surface load was low. All the presented metal contents were lower than the data from Santa Monica, California, USA (Lau & Stenstrom 2005).

With regard to land use, the urban commercial centre of site W had the highest mean surface loads, which was consistent with the findings of Lau & Stenstrom (2005) that the commercial area had higher metal surface loads than most of the other land uses. A plausible explanation is the prevailing anthropogenic and traffic activities at site W. In contrast, the rural area of site N which was only slightly influenced by traffic or anthropogenic activities had a very low value of mean surface loads.

Heavy metal surface load in size-fractionated RDS

As given in Table 4, the mean percentages of size fraction apportioned to total surface load were: Cu = 63–0.45 μm (39.8%), > 400–100 μm (32.6%) > 1,000–400 μm (15.6%) >

100–63 μm (12.0%); Zn = 63–0.45 μm (46.1%) > 400–100 μm (29.6%) > 1,000–400 μm (12.9%) > 100–63 μm (11.3%); and Cd = 63–0.45 μm (53.8%) > 400–100 μm (23.9%) > 100–63 μm (12.0%) > 1,000–400 μm (10.3%). It is obvious that the highest mean surface load dominated in the finest fraction of 63–0.45 μm for each metal, which is consistent with the common surface loads apportioning to size fractions (Lau & Stenstrom 2005; Sutherland et al. 2012; Loganathan et al. 2013). A possible explanation could be that the parameters favourable for metal adsorption to RDS, such as specific surface area, organic carbon content, effective cation exchange capacity and clay-forming mineral content, decrease with the increase in particle size. Therefore, special concern should be paid to the finer sediments, which can stay in suspension longer, be transported further by runoff than can larger sediments, and eventually result in a large amount of pollutant contribution to stormwater runoff.

Table 4 | Descriptive statistic of heavy metal surface loads in size-dependent RDS

Study area	No.[a]	Cu (mg/m²)		Zn (mg/m²)		Cd (μg/m²)	
		Mean	SD[b]	Mean	SD	Mean	SD
Commercial W							
1,000–400 μm	6	0.16	0.13	0.32	0.14	0.19	0.12
400–100 μm	6	0.57	0.27	1.07	0.52	0.47	0.27
100–63 μm	6	0.19	0.073	0.33	0.12	0.21	0.14
63–0.45 μm	6	0.47	0.23	1.14	0.47	0.72	0.28
Highway B							
1,000–400 μm	6	0.34	0.56	0.31	0.34	0.071	0.039
400–100 μm	6	0.24	0.23	0.54	0.30	0.18	0.11
100–63 μm	6	0.066	0.024	0.18	0.041	0.077	0.022
63–0.45 μm	6	0.23	0.11	0.61	0.26	0.35	0.12
Rural N							
1,000–400 μm	5	0.017	0.0083	0.049	0.018	0.12	0.037
400–100 μm	5	0.046	0.038	0.077	0.029	0.22	0.049
100–63 μm	5	0.014	0.006	0.035	0.0066	0.13	0.019
63–0.45 μm	5	0.070	0.032	0.23	0.078	0.76	0.085
Overall[c]							
1,000–400 μm	17	0.18	0.35	0.24	0.24	0.13	0.092
400–100 μm	17	0.30	0.30	0.59	0.53	0.29	0.21
100–63 μm	17	0.096	0.089	0.19	0.14	0.14	0.10
63–0.45 μm	17	0.27	0.22	0.68	0.49	0.60	0.063

[a]No.: number of observations.
[b]SD: standard deviation.
[c]Overall: indicates the contents regardless of land use (from all the sampling sites).

Heavy metal chemical fractionation in bulk RDS

The chemical fractionations of metals are shown in Figure 1. It shows that Cu presented considerable proportions in residual and oxidisable fractions. The proportion order of the four fractions decreased as residual (44.0 ± 4.22%) > oxidisable (41.1 ± 3.00%) > exchangeable (11.7 ± 1.36%) > reducible (3.3 ± 0.32%). The partitioning of Cu was comparable to a similar study performed at Murcia, Spain (Acosta *et al.* 2014). In terms of potential ecological risk assessment, the dominant Cu contents in residual fractions indicate that Cu contents in RDS were relatively stable and would not show significant transformation under various conditions when discharged into receiving waters by stormwater runoff. Meanwhile, Cu contents in the oxidisable fraction may be associated with various forms of organic material. The high affinity of Cu to organic matters should be due to the fact that Cu can easily complex with organic matter to form the high stability complexes of organic-Cu compounds (Sundaray *et al.* 2011; Li *et al.* 2013). These compounds could pose a comparably low ecological risk to the receiving waters, but would exist for longer periods. In terms of the build-up phenomenon, stable Cu components of residual and oxidisable fractions increased with an increasing duration of ADP at sites W and B.

The exchangeable fraction (49.1 ± 2.34%) was the dominant phase of Zn, and followed the fraction order of residual (32.5 ± 3.01%) > oxidisable (9.22 ± 1.01%) > reducible (9.21 ± 0.51%). The results were consistent with the chemical fractionation pattern documented in the literature (Sutherland *et al.* 2012). As for the potential ecological risk assessment, metal content determined by the exchangeable extraction is considered to provide a reasonable approximation of the easily mobilised and biologically available metal content in RDS. The higher the proportion of metals in this fraction, the more mobile they are, and the higher the risk to the receiving aquatic environment (Sutherland *et al.* 2012). Therefore, the dominant Zn contents in the exchangeable fraction indicates that Zn contents in RDS could pose a considerably high ecological risk to aquatic biota when discharged into receiving waters. The results were consistent with previous findings in literature that Zn would be one of the most mobile and bioavailable of the anthropogenically impacted elements (Sutherland *et al.* 2012; Loganathan *et al.* 2013). In addition, Zn contents in the exchangeable fraction contributed significantly to the overall increasing tendency.

The Cd content was characteristically enriched in the exchangeable fraction. The mean proportion order of the four fractions decreased as exchangeable (59.0 ± 1.09%) > oxidisable (17.2 ± 1.35%) > reducible (19.4 ± 1.18%) > residual (4.4 ± 0.50%). The dominant content in the exchangeable
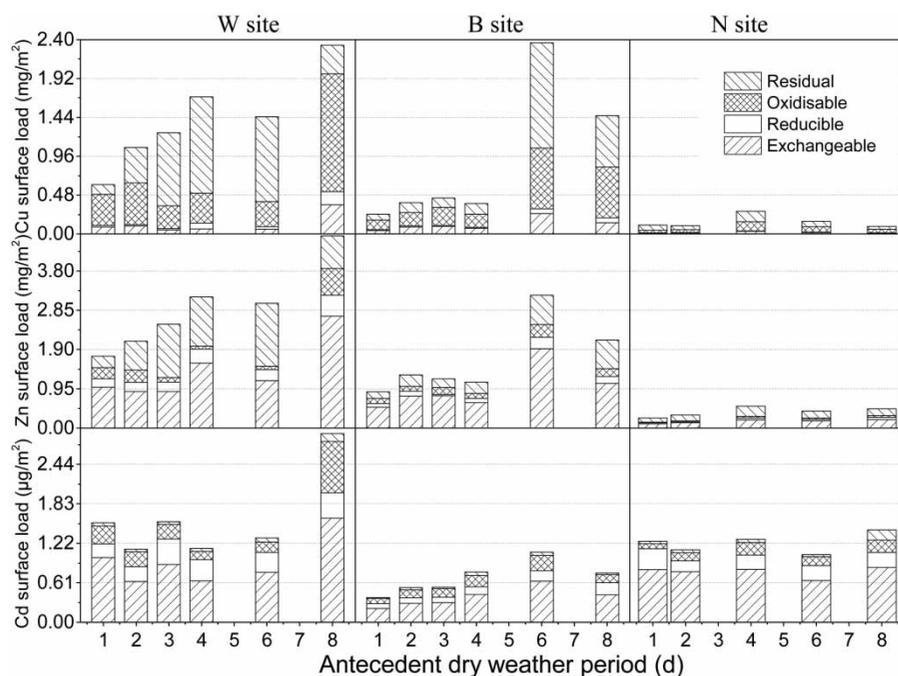

Figure 1 | Build-up patterns and chemical fractionation of Cu, Zn and Cd in bulk RDS.

fraction suggests that Cd is one of the most susceptible metals to be mobilised during stormwater runoff. Additionally, a comparably clear build-up pattern of Cd was found at site B, and was considerably attributed to the exchangeable fraction.

Heavy metal chemical fractionation in size-dependent RDS

To determine the mass percentage of chemical fractionation (P) in size-dependent RDS, according to Sutherland *et al.* (2012), the modified form of size fraction loading was applied in this study:

$$P = \frac{C_{i,j} \times M_i}{\sum_{j=1}^{m} C_{i,j} \times M_i} \times 100\% \tag{1}$$

where C_i is the surface load of metal in size fraction i in one of the four sequentially extracted chemical fractionations; M_i is the dry mass percentage of size fraction i; and m is the

number of given metal. Therefore, for a given metal, the summation of the four chemical fractionations in each size fraction = 100%.

As given in Figure 2, Cu surface loads in oxidisable and residual fractions were dominant due to the considerable contributions from the coarse size fractions (1,000–400 and 400–100 μm). All the size fractions contributed insignificantly to the unstable components of exchangeable and reducible fractions (ranging from 6.5–0.2%). Therefore, a considerable proportion of Cu in stormwater runoff could be more easily controlled and mitigated by removing coarse RDS from impervious surfaces.

In terms of Zn and Cd, surface load in 63–0.45 μm dominated all chemical fractionations and especially the exchangeable fraction. This is notable because this is the size fraction most widely digested and assimilated by aquatic biota, especially benthic feeders. Therefore, the management of fine size fractions is a key issue in the potential mitigation of Zn and Cd in stormwater runoff.
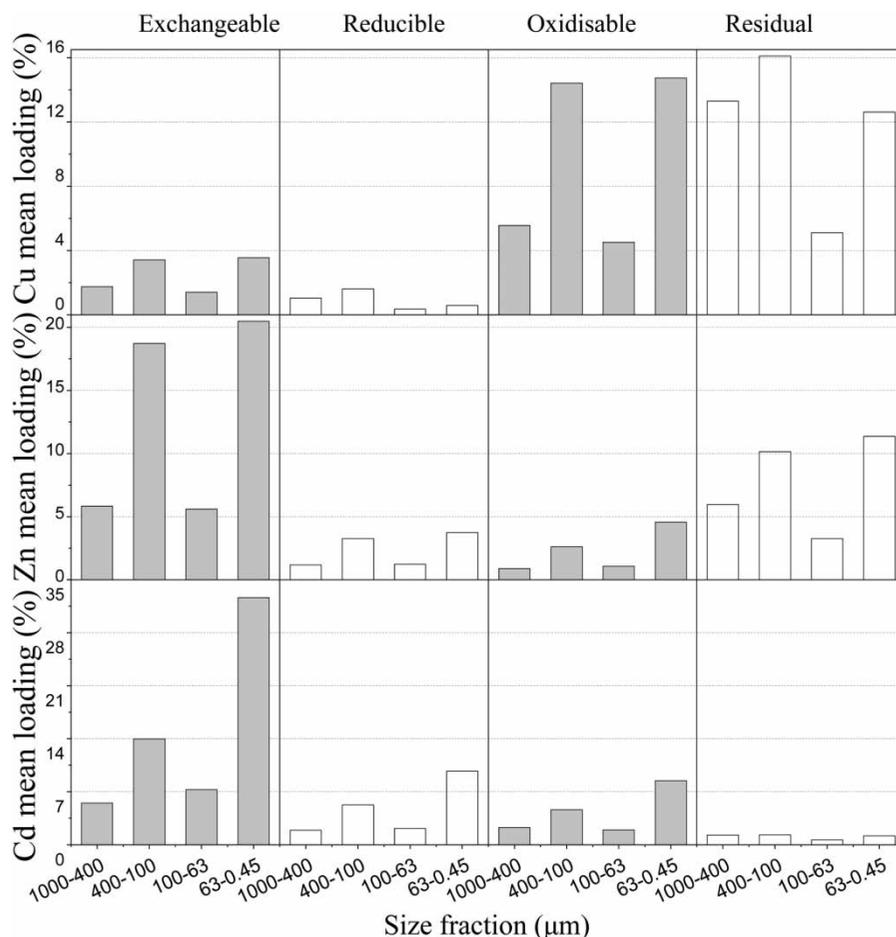

Figure 2 │ Size-dependent percentage contributions to heavy metal chemical fractionations.

Heavy metal primary source identification

The source identification of RDS-associated heavy metals is a complex research area. Heavy metals have a broad range of potential sources. Therefore, it is necessary to identify the primary contributors in order to facilitate source-oriented mitigation strategies for stormwater pollution. PCA was used to qualitatively identify the major sources of heavy metals. The purpose of PCA is to reduce the dimensionality of the original heavy metal data to a minimum number of principal components. Each principal component is a linear combination of the original variables. All the components are orthogonal to each other, which results in the smallest possible covariance. The principal components were computed using the varimax rotation method with Kaiser normalisation by SPSS Statistics 19. More details regarding analysis setting and other technical usage of PCA can be found elsewhere (Zhang *et al.* 2013; Banerjee *et al.* 2015).

According to the component matrix in Table 5, two principal components (potential sources) were extracted. The sum of the variances of the first two components exceeded 98.73% of the total variance of the original data. The first component was responsible for 78.22% of the total variance. This component is heavily weighted by Cu and Zn. According to the source fingerprints (tracers) reviewed from literature, the dominant factor loadings of Cu and Zn have been suggested for vehicle-related sources (Sutherland *et al.* 2012; Loganathan *et al.* 2013). More explicitly, the elevated levels of Cu and Zn were usually regarded as source fingerprints of auto brake pad erosion and tyre debris, respectively (Banerjee *et al.* 2015).

In addition, the data of chemical fractionation further assist the potential source identification. As shown in Figures 1 and 2, Cu presented considerable proportions in residual and oxidisable fractions. In fact, Cu (Cu^0) is a component of brake pads with content up to 16% (www.copper. org, accessed July 2013). The considerable proportions of Cu in oxidisable and residual fractions are consistent with the Cu (Cu^0) speciation in brake pads, and further confirms the Cu contributor of brake pad erosion.

The exchangeable fraction was the dominant phase of Zn. Zn is added as Zn oxide (ZnO) to the tyre rubber as an activator to accelerate vulcanisation when manufacturing tyres. The tyre rubber contains 1.2% of ZnO for car tyres (min 0.4%, max 2.9%) and 2.1% (min 1.2%, max 4.3%) for truck tyres (Smolders & Degryse 2002). The high proportion of Zn in the exchangeable fraction and ZnO fractionation in tyre debris are highly linked, and further confirms the Zn contributor of tyre debris. Consequently, this component was tentatively attributed to the vehicle-associated sources.

The second component was responsible for 20.51% of the total variance. This component was characterised by high loading of Cd. The source apportionment of Cd is a much debated subject. Muhammad *et al.* (2012) found that Zn and Cd share a similar geochemical behaviour and often occur together as environmental pollutants in soils, sediments, plants, and other endpoints. However, Cu and Zn had negative loadings in this component, suggesting that Cd might have alternative sources compared with Cu and Zn.

Saeedi *et al.* (2012) reported that Cd in RDS does not have a local anthropogenic source. Fujiwara *et al.* (2011) stated that Cd is a component of petroleum and its concentration depends on the origin of petroleum, and generally it can be found at sub-ppm levels. Davis *et al.* (2001) have stated that the largest contributor (60%) to Cd pollution was atmospheric deposition. Banerjee *et al.* (2015) reported that Cd was usually considered as a source fingerprint of

Table 5 | Component matrix of heavy metals

Item	Component	
	1	2
Cu	0.941	−0.311
Zn	0.967	−0.214
Cd	0.726	0.688
% of variance[a]	78.22	20.51
Cumulative %[b]	78.22	98.73
Potential source	vehicle associated	atmospheric deposition

[a]The percentage of the total variability (initial eigenvalues) explained by each principal component.
[b]The amount of variance accounted for by each component.

vehicular and industrial emissions which are eventually released into the atmosphere. Accordingly, this component appeared to be highly indicative of atmospheric deposition attributed to the emissions of vehicles and/or industries.

In addition, the Cd content was characteristically enriched in the exchangeable fraction as shown in Figures 1 and 2, which was consistent with the chemical fractionation found in urban atmospheric aerosols whereby dominant components of Cd were in the exchangeable forms (Sun *et al.* 2014; Li *et al.* 2015). It would further lead to the suggestion that atmosphere deposition might be an alternative source for this component.

CONCLUSIONS

In this study, chemical fractionation determination and primary source identification of heavy metals in bulk and size-dependent RDS were conducted. Results show that the highest surface loads of heavy metals were consistently found in the finest size fraction of 63–0.45 μm. Zn and Cd were identified predominantly in exchangeable fractions, especially in 63–0.45 μm fraction, which can easily be mobilised and biologically incorporated. Cu posed a comparable low risk due to the high proportions of residual and oxidisable fractions. With the assistance of PCA and chemical fractionation, vehicle-related sources and atmospheric deposition were identified as primary source contributors to heavy metals in RDS. More explicitly, the potential source of Cu in RDS was identified as auto brake pad erosion. Zn was significantly attributed to tyre debris. The atmospheric deposition was tentatively identified as a significant source contributor for Cd.

The results reported herein could assist the potential integrated stormwater management designed to remove hazardous materials from roads, and could be used for source-oriented mitigation of rainfall-induced urban runoff pollution.

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