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Comparison of metal pollution and health risks of urban dust in Beijing in 2007 and 2012

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Abstract Urban dust in cities is a useful indicator of ambient environmental conditions and a sink for pollutants emitted through various natural and human activities. In this study, metal distributions in urban dust samples collected in 2007, using vacuuming, and 2012, using brushing, were compared. Experiments comparing the vacuuming and brushing methods were performed and translation equations were developed to correct the vacuuming results so that they could be compared with the brushing results. Cadmium concentrations were lower in 2012 than 2007; this could be because many industries moved out of the Beijing region after 2007. Concentrations of Cr, Cu, and Zn changed slightly, which could result from a combination of decreased industrial pollution and increased traffic pollution. A health risk assessment found that except for Cr, exposure to metals in urban dust in the Beijing study area would not cause serious health impacts on residents in 2007 or 2012. However, the health risk for children was higher than for adults in both years. Chromium had the highest hazard index (0.44) and the highest carcinogenic risk (4.16×10^{-6}).

Keywords Brushing · Metal · Risk assessment · Urban dust · Urban non-point source pollution

Introduction

Although a useful indicator of urban environmental conditions, urban dust in cities is also a sink for pollutants emitted via various natural and human activities (Zhao and Li 2013; Song et al. 2015; Li et al. 2016). High metal concentrations have frequently been detected in urban dust (Li et al. 2013a; Gunawardana et al. 2014; Liu et al. 2015; Yu et al. 2016), and the environment in China is deteriorating because of rapid industrialization and urbanization (Du et al. 2013). Metals in urban dust primarily originate from traffic-related activities (Kim et al. 2005; Ewen et al. 2009; Guney et al. 2010a; Soltani et al. 2015), industrial activities (Žibret 2012; Li et al. 2013b), urban construction, and the use of pesticides and fertilizers (Li et al. 2001). Atmospheric deposition consists of a combination of local primary sources and pollutants transported over long distances. Different sources emit unique metal pollution profiles. For example, abrasion of tires mainly releases dust with zinc (Zn) (Smolders and Degryse 2002). The brake systems of motor vehicles mainly discharge particles with copper (Cu), antimony (Sb), and barium (Ba) associated with them (Hopke et al. 1980; Adachi and Tainosho 2004; Grigoratos and Martini 2015).

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Chromium (Cr) is emitted through processes like stainless steel wear, auto part wear, and tool manufacturing (Li et al. 2016). Several studies have reported that mercury (Hg) is emitted from hospitals (Li et al. 2016). The smelting industry produces iron (Fe), cobalt (Co), manganese (Mn), and vanadium (V), and e-waste recycling contributes significant amounts of trace metals such as lead (Pb) and cadmium (Cd) to urban dust (Žibret et al. 2013; Lau et al. 2014). Except anthropogenic sources, natural source is one main source of nickel (Ni) as most studies have reported (Li et al. 2016; Yu et al. 2016). Because of these correlations with sources, urban dust contains important pollution source information that can be decoded using suitable mathematical methods (Li et al. 2013c). In this study, Cd, Cr, Cu, Hg, Ni, Pb, and Zn were investigated because they are typically from anthropogenic sources.

Urban dust is a pollutant to which people, especially children, are exposed in the urban environment (Guney et al. 2010b). Non-degradable and toxic pollutants, especially heavy metals in urban dust, may cause adverse effects on human health, including lung cancer, cardiovascular diseases, and high blood lead contents (Wang et al. 2014; Lin et al. 2015). Because of the short distances between residential buildings and streets, and high pollutant emissions in urban areas, the exposure risk posed by urban dust cannot be ignored (Zheng et al. 2010; Lu et al. 2014). Health risk assessments can be used to evaluate the potential risks from exposure to metals in urban dust and provide important information for residents and policymakers (Ferreira-Baptista and De Miguel 2005; Shi et al. 2011). Health risk assessments have been widely used to evaluate the impacts of many pollutants in various environmental media, such as water, soil, and the atmosphere (Guney et al. 2010b; Keshavarzi et al. 2015). Generally, health risk assessments include hazard identification, dose-response assessment, exposure assessment, and risk characterization. The US Environmental Protection Agency (USEPA) health risk assessment model has often been used (Lau et al. 2014). Specific pollutant concentrations, local social parameters, and USEPA-recommended parameters have been applied in previous studies. Using more local parameters improves the reliability of the model for local conditions.

Beijing, a rapidly developing mega-city, has experienced substantial economic growth over the past few decades. For example, the highest gross domestic product (GDP) growth rate occurred in 2007 (21 %) (Beijing Statistics Bureau 2008, 2013). The development rate has slowed since 2008, and Beijing's government has focused their attention on urban environment pollution control because of the global economic crisis and domestic macroeconomic control. The average GDP growth rate has remained at approximately 10 % since 2008, with the lowest rate observed in 2009 (9.3 %). Many industries moved out of the Beijing central urban area before the 2008 Beijing Olympic Games, and as such, local industrial pollution in central Beijing has been very low since 2008. But, the number of motor vehicles in Beijing increased from 3.1 million in 2007 to 5.2 million in 2012 (Beijing Statistics Bureau 2013), and the length of railways, highways, and roads has increased each year. We studied the characteristics of urban dust in 2007 and 2012 to understand the effects of urban pollution controls combined with rapid economic development. Based on previous studies, we chose to analyze Cd, Cr, Cu, Hg, Ni, Pb, and Zn concentrations. These metals are primarily from traffic, industry, and natural sources.

The objectives of this study were as follows: (1) to analyze changes in metal concentrations in urban dust related to the combination of pollution control measures and rapid economic growth; (2) to analyze the economic development factors affecting metal concentrations in urban dust; and (3) to determine the human exposure risk through ingestion, inhalation, and dermal contact of road dust metals for children and adults, as well as to analyze the differences (if any) in the exposure risk between 2007 and 2012.

Materials and methods

Sampling methods

Urban dust samples were collected by vacuuming and brushing in 2007 and 2012, respectively. Eight samples were collected using a Panasonic vacuum cleaner (Model: MC-CG663) in October 2007. To expand the study area and avoid the need for electricity, a brushing method was used in 2012. Thirty samples were collected between September and October 2012 using a plastic dustpan and a brush. The sampling locations shown in Fig. 1 were characterized as five functional areas: commercial, main roads (> four-lane dual carriageway), streets (≤ four-lane dual carriageway), parks, and residential. The 38 sampling sites were all in public areas,

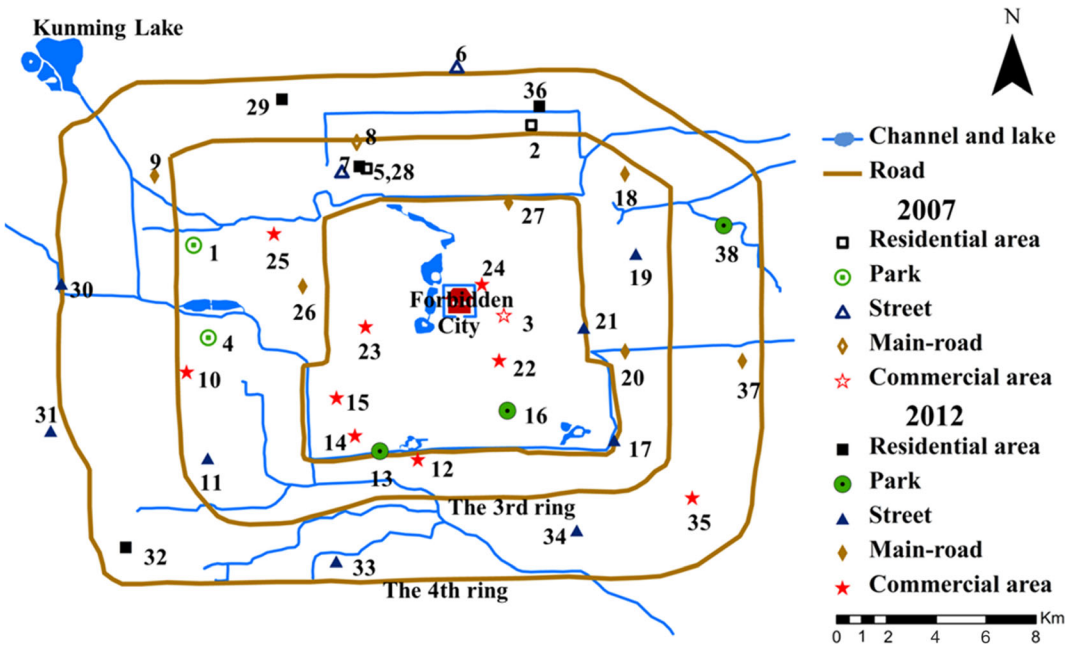

Fig. 1 Sampling site locations in Beijing in 2007 and 2012

and further site information is presented in Supporting Information Table S1. Sampling was conducted within 0.5 m of the road curb or edge, and the vacuuming or brushing processes were repeated at least three times to collect more surface dust. More than 300 g of dust was collected at each location. Sampling was conducted after a dry period of at least 7 days (Wicke et al. 2012). The collected samples were stored in self-sealing plastic bags and transported to the laboratory. Details of the vacuuming procedure have been reported by Xiang et al. (2010).

To identify possible sampling efficiency differences between vacuuming and brushing (Herngren et al. 2006), comparison experiments were performed. Sites 5, 7, and 8 were selected for the comparison study. At each site, six consecutive grid cells of 10 m × 0.5 m were selected along the curb over a total length of 60 m. Vacuuming and brushing were conducted alternately to obtain three vacuuming and three brushing samples from each site. A total of nine vacuuming and nine brushing samples were obtained for further analysis.

Metal measurements

Each of the dust samples was air-dried for at least 15 days after being collected. The dried samples were screened through a 500-μm mesh nylon sieve to remove extraneous matter including leaves, small pieces of brick, cigarette butts, and other debris that could influence the metal concentrations measured in the dust. The screened samples were then sequentially sieved through nylon sieves with mesh openings of 500, 300, 120, 74, and 40 μm. These size ranges are commonly used in the literature (Li et al. 2016). The subsamples in each size range were weighed to calculate their proportional mass.

To reduce measurement costs and remove variance related to location, for the method comparison samples, the three parallel samples taken using the same method from each site were combined to form one bulk sample. Therefore, one bulk vacuuming sample and one bulk brushing sample were prepared for each of the three sites, resulting in a total of six bulk samples. The bulk samples were then sieved into the five size ranges discussed earlier, and their proportional masses were calculated. Samples were ground into powders less than 200 μm in diameter and stored at 4 °C prior to metal analysis.

Approximately 0.5 g of the ground sample powder was digested using hydrofluoric acid, nitric acid, perchloric acid, and aqua regia according to the national standard method from Environmental Quality Standard for Soils (National Environmental Protection Agency of China 1995). Concentrations of Cd, Cu, Ni, Pb, and Zn were determined using inductively coupled plasma-mass spectrometry (ICP-MS, American Thermo Electron Corporation X series II). Concentrations of Cr were determined using inductively coupled plasma-optical emission

spectroscopy (ICP-OES, American Thermo Electron Corporation IRIS Intrepid II). For Hg, aqua regia, potassium permanganate, and oxalate were used to digest the ground sample powder and cold vapor generation-atomic fluorescence spectrometry (CV-AFS, XGF-1011A) was used for its quantification.

The detection limits for Cu, Ni, Pb, Zn, Cr, Cd, and Hg were 1, 2, 2, 2, 5, 0.02, and 0.002 mg/kg, respectively. Duplicate samples (one duplicate sample for every 10 samples) and geochemical reference materials (one reference material for every 10 samples) were measured for quality control.

Health risk assessment model

Exposure dose

In this study, health risk assessment models developed by the USEPA were used to calculate the exposure of children and adults to metals in urban dust. The model was applied with the following assumptions: (1) human exposure to urban dust occurred through three main pathways, direct ingestion, inhalation through the mouth and nose, and dermal contact with urban dust particles that adhered to exposed skin; (2) intake rates and particle emissions were approximated using soil intake rates and particle emission parameters; (3) some human exposure parameters in the measurement areas were similar to those of the reference study area; and (4) the total non-carcinogenic risk was calculated for each metal (Cd, Cr, Cu, Hg, Ni, Pb, and Zn) by summing the individual risks obtained from the three exposure pathways.

Estimates of the daily doses received via the three exposure pathways were calculated using the following equations (USEPA 1989, 1996):

$$\mathrm{ADD}_{\mathrm{ing},m} = \frac{\mathrm{C}_m \times \mathrm{IngR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}_{\mathrm{noncan}}} \times 10^{-6} \quad (1)$$

$$\mathrm{ADD}_{\mathrm{inh},m} = \frac{\mathrm{C}_m \times \mathrm{InhR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{PEF} \times \mathrm{BW} \times \mathrm{AT}_{\mathrm{noncan}}} \quad (2)$$

$$\mathrm{ADD}_{\mathrm{derm},m} = \frac{\mathrm{C}_m \times \mathrm{SA} \times \mathrm{SL} \times \mathrm{ABS} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}_{\mathrm{noncan}}} \times 10^{-6} \quad (3)$$

where m is the metal element (Cd, Cr, Cu, Hg, Ni, Pb, Zn); $\mathrm{ADD}_{\mathrm{ing},m}$, $\mathrm{ADD}_{\mathrm{inh},m}$, and $\mathrm{ADD}_{\mathrm{derm},m}$ are the daily exposure amount of m through ingestion, inhalation, and dermal contact, respectively; C_m is the concentration of metal m in urban dust (mg/kg); IngR and InhR are the ingestion and inhalation rates, respectively; EF is the exposure frequency; ED is the exposure duration; BW is body weight; $\mathrm{AT}_{\mathrm{noncan}}$ is the average time for non-carcinogens; PEF is the particle emission factor; SA is the exposed skin area; SL is the skin adherence factor; and ABS is the dermal absorption factor. The units and parameter values used in Eqs. (1)–(3) are shown in Table 1.

For carcinogens, only the carcinogenic risk from inhalation exposure was considered in the model. The lifetime average daily dose (LADD) for Cd, Cr, and Ni inhalation exposure was used to assess the risk of cancer according to the following equation (USEPA 1996, 2001):

$$\mathrm{LADD}_{\mathrm{inh},m} = \frac{\mathrm{C}_m}{\mathrm{PEF} \times \mathrm{AT}_{can}} \times \left(\frac{InhR_{\mathrm{child}} \times \mathrm{EF}_{\mathrm{child}} \times \mathrm{ED}_{\mathrm{child}}}{\mathrm{BW}_{\mathrm{child}}} + \frac{\mathrm{InhR}_{\mathrm{adult}} \times \mathrm{EF}_{\mathrm{adult}} \times \mathrm{ED}_{\mathrm{adult}}}{\mathrm{BW}_{\mathrm{adult}}} \right) \quad (4)$$

where, m is Cd, Cr, or Ni; $\mathrm{AT}_{\mathrm{can}}$ is the average time for carcinogens; $\mathrm{InhR}_{\mathrm{child}}$ and $\mathrm{InhR}_{\mathrm{adult}}$ are the inhalation rates for children and adults, respectively; $\mathrm{EF}_{\mathrm{child}}$ and $\mathrm{EF}_{\mathrm{adult}}$ are the exposure frequencies for children and adults, respectively; $\mathrm{ED}_{\mathrm{child}}$ and $\mathrm{ED}_{\mathrm{adult}}$ are the exposure durations for children and adults, respectively; and $\mathrm{BW}_{\mathrm{child}}$ and $\mathrm{BW}_{\mathrm{adult}}$ are the average body weights for children and adults, respectively. The units and parameter values used for Eq. (4) are also defined in Table 1. The arithmetic mean of metal concentrations in urban dust was used for the concentration term C_m (mg/kg) instead of the upper limit of the 95 % confidence interval of the mean (95 % UCL), which may overestimate the risk (Gržtić and Ahmed Ghariani 2008). The values of IngR, ED, $\mathrm{AT}_{\mathrm{noncan}}$, and $\mathrm{AT}_{\mathrm{can}}$ were set according to the USEPA suggestions (USEPA 1989, 2001), while values of EF, PEF, SA, SL, and ABS were provided by the Beijing Municipal Research Institute of Environmental Protection (BMRIEP 2009), as shown in Table 1. According to the Ministry of Environmental Protection of the People's Republic of China (MEPC 2013), the adult BW was set to be 60.6 kg and the adult InhR was set to be 15.7 m^3/day.

Table 1 Exposure factor definitions and values for the urban dust daily dose model

	Meaning	Unit	Child	Adult	Reference
$ADD_{ing,m}$	Daily exposure amount of metals through ingestion	mg/(kg·day)	–	–	–
$ADD_{inh,m}$	Daily exposure amount of metals through inhalation	mg/(kg·day)	–	–	–
$ADD_{derm,m}$	Daily exposure amount of metals through dermal contact	mg/(kg·day)	–	–	–
$LADD_{inh,m}$	Lifetime average daily dose	mg/(kg·day)	–	–	–
C_m	Metal *m* concentration in urban dust	mg/kg	Mean	Mean	This study
IngR	Ingestion rate	mg/day	200	100	USEPA (2001)
EF	Exposure frequency	d/a	233	300	BMRIEP (2009)
ED	Exposure duration	a	6	24	USEPA (2001)
BW	Average body weight	kg	15	60.6	USEPA (2001); MEPC (2013)
AT_{noncan}	Average time for non-carcinogens	day	365 × ED	365 × ED	USEPA (1989)
AT_{can}	Average time for carcinogens	day	70 × 365	70 × 365	USEPA (1989)
InhR	Inhalation rate	m^3/day	5	15.7	BMRIEP (2009); MEPC (2013)
PEF	Particle emission factor	m^3/kg	1.32×10^9	1.32×10^9	BMRIEP (2009)
SA	Exposed skin area	cm^2	1600	4350	BMRIEP (2009)
SL	Skin adherence factor	mg/(cm^2 day)	1	1	BMRIEP (2009)
ABS	Dermal absorption factor	–	0.001	0.001	BMRIEP (2009)

Risk characterization

The non-carcinogenic and carcinogenic risks of exposure to metals in urban dust were evaluated using the results of ADD_{ing}, ADD_{inh}, ADD_{derm}, and $LADD_{inh}$ based on the following equations:

$$HQ_{p,m} = \frac{ADD_{p,m}}{RfD_{p,m}}; \text{where } p = \text{ing, inh, derm; } m = \text{Cd, Cr, Cu, Hg, Ni, Pb, Zn} \quad (5)$$

$$HI_m = \sum\nolimits_p HQ_{p,m} \quad (6)$$

$$CR_{inh,m} = LADD_{inh,m} \times SF_{inh,m}; \text{where } m = \text{Cd, Cr, Ni} \quad (7)$$

where *m* represents the metals investigated in this study (Cd, Cr, Cu, Hg, Ni, Pb, Zn for non-carcinogenic risks and Cd, Cr, Ni for carcinogenic risks); the hazard quotient ($HQ_{p,m}$) represents the non-carcinogenic risk for metal *m* through exposure pathway *p*, which represents the three exposure pathways considered (direct ingestion ing, inhalation through the mouth and nose inh, and dermal contact with urban dust particles derm); the reference dose (RfD) was determined from the United States Department of Energy's RAIS compilation (United States Department of Energy 2004), BMRIEP (2009), and MEPC (2013) (Table 2); and the hazard index (HI_m) represents the non-carcinogenic risk for metal *m* through the three exposure pathways. If the HI_m (non-cancer risk) was <1, it was believed that there was no significant non-carcinogenic risk; however, if the HI_m was >1, there was a chance that non-carcinogenic effects might occur (USEPA 2001). $CR_{inh,m}$ represents the cancer risk from Cd, Cr, and Ni in urban dust through inhalation; $SF_{inh,m}$ is the cancer slope factor through inhalation. If the value of $CR_{inh,m}$ fell within the range of threshold values (10^{-4}–10^{-6}), the cancer risk was acceptable (Ferreira-Baptista and De Miguel 2005).

Results and discussion

Comparison of the two sampling methods

Vacuuming and brushing are two widely used sampling methods in urban non-point source pollution areas. However, the differences between these collection methods have seldom been investigated. To understand

Table 2 Values of RfD (mg/(kg·day)) and SF((mg/(kg·day))$^{-1}$) for metals

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
RfD_{ing}	1.00E−03	3.00E−03	4.00E−02	3.00E−04	2.00E−02	3.50E−03	3.00E−01
RfD_{inh}	1.00E−03	2.86E−05	4.02E−02	2.40E−05	2.06E−02	3.52E−03	3.00E−01
RfD_{dermal}	1.00E−05	6.00E−05	1.20E−02	3.00E−04	5.40E−03	5.25E−04	6.00E−02
SF	6.30	42.00			0.84		

and quantify the mass and pollutant concentration differences between samples collected using these 2 methods, 18 vacuuming and brushing samples were analyzed.

The mass proportion in each size range (<40, 40–74, 74–120, 120–300, 300–500 μm) was calculated for each of the 18 samples from the three sampling sites, as shown in Eqs. (8) and (9):

$$FV_{s,k,i} = \frac{MV_{s,k,i}}{\sum_i MV_{s,k,i}} \tag{8}$$

$$FB_{s,k,i} = \frac{MB_{s,k,i}}{\sum_i MB_{s,k,i}} \tag{9}$$

where s represents the sampling site number (5, 7, or 8); k represents the sequence number (1, 2, or 3) for consecutive samples using vacuuming or brushing at a specific site; i represents the five size ranges (<40, 40–74, 74–120, 120–300, and 300–500 μm); $MV_{s,k,i}$ and $MB_{s,k,i}$ are the masses of vacuuming and brushing sieved subsamples, respectively, collected from site s with sequence number k in size range i; and $FV_{s,k,i}$ and $FB_{s,k,i}$ are the mass fractions of the sieved subsamples from vacuuming and brushing, respectively. Values of $FV_{s,k,i}$ and $FB_{s,k,i}$ for the three sites are plotted in Fig. 2. Figure 2 shows that the sampling method had a substantial effect on the proportional mass in each of the size ranges. The particle mass fractions for particles <40 and 40–74 μm in diameter collected using the vacuuming method were generally higher than those using the brushing method at the same site. This indicated that vacuuming was more efficient at collecting smaller particles. For particles in the 74–120, 120–300, and 300–500 μm size ranges, the mass fractions using the brushing method were generally higher than those using the vacuuming method at each site, which indicated that the bushing method was more effective for collecting larger particles.

To compare the metal concentrations from the two sampling methods, the metal concentrations in each size range were quantified for each of the six bulk samples and the vacuuming to brushing metal concentration ratio, $CR_{s,i}$, was calculated using Eq. (10):

$$CR_{s,i,m} = \frac{CV_{s,i,m}}{CB_{s,i,m}} \tag{10}$$

where m is the metal element; $CV_{s,i,m}$ (mg/kg) and $CB_{s,i,m}$ (mg/kg) are the concentrations of metal m in the bulk sample of size range i from site s using the vacuuming and brushing methods, respectively; and $CR_{s,i,m}$ is the metal m concentration ratio between vacuuming and brushing in size range i and at site s.

A total of 15 concentration ratios for each metal were obtained for the three sites and five size ranges. The mean $CR_{s,i,m}$ value was 1.009 (±0.07). Therefore, the metal concentration in a subsample within a specific size range using one sampling method can be used to

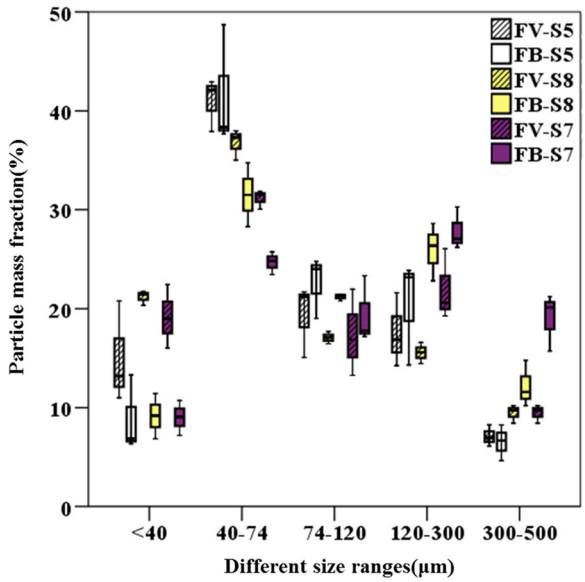

Fig. 2 Comparison of particle mass fractions in the different size ranges for the vacuuming and brushing methods

approximate the metal concentration of the same size range using the other method ($CV_{s,i,m} \approx CB_{s,i,m}$).

The comparative analysis demonstrated that metal concentrations in the same particle size range using the two methods were approximately the same. Therefore, Eqs. (11)–(13) were derived to covert the metal concentrations of the vacuumed samples to those of the brushed samples:

$$FV_{s,i} = \frac{MV_{s,i}}{\sum_i MV_{s,i}} \quad (11)$$

$$M(FB/FV)_i = \left(\sum_s \sum_{k=1}^{3} \frac{FB_{s,k,i}}{FV_{s,k,i}}\right)/9 \quad (12)$$

$$VB_{s,m} = \sum_i \left[CV_{s,i,m} \times FV_{s,i} \times M(FB/FV)_i\right] \quad (13)$$

where $FV_{s,i}$ is the particle mass fraction of sieved bulk samples from site s in size range i for vacuumed samples; $MV_{s,i}$ is the mass proportion in size range i from site s using vacuuming; $M(FB/FV)_i$ represents the mean mass fraction ratio of brushing to vacuuming for size range i, calculated from the 18 samples of the comparison study (Table 3); $CV_{s,i,m}$ (mg/kg) is the measured metal m concentration in the sieved bulk vacuuming samples from site s and particle size range i; and $VB_{s,m}$ (mg/kg) is the calculated brushing metal m concentration after converting the vacuuming results into brushing results for site s.

To evaluate the accuracy of the calculated brushing metal concentration, VB_s, the ratio between VB_s and the measured metal concentrations of the bulk brushing samples, CB_s, was calculated. The mean VB_s/CB_s for the three sites for Cd, Cr, Cu, Hg, Ni, Pb, and Zn were 0.929, 1.067, 1.144, 1.244, 1.153, 0.998, and 0.951, respectively. These mean ratio values demonstrated that the calculated values of $VB_{s,m}$ using Eq. (13) were close to the measured concentrations of bulk brushing samples at the same sites. Therefore, it was possible to use this method to convert the metal concentrations from vacuuming samples in 2007 into concentrations comparable to those found when then brushing collection method was used in 2012.

Table 3 Summary of mass fraction ratios of brushing to vacuuming

i (μm)	M(FB/FV)i (n = 9)		
	Mean	Min	Max
<40	0.495	0.337	0.641
40–74	0.888	0.759	1.134
74–120	1.206	0.809	1.758
120–300	1.370	1.005	1.837
300–500	1.421	0.668	2.516

Comparison of metal distributions in 2007 and 2012

To more accurately compare the vacuuming and brushing sampling results, the metal concentrations of the vacuuming samples in 2007 were transformed into calculated brushing metal concentrations, $VB_{s,m}$, using Eq. (13). The $VB_{s,m}$ values from 2007 and the measured brushing sample metal concentrations, $CB_{s,m}$, from 2012 for the different metals are shown in Table 4. The mean Cd concentration in 2007 was approximately 1.63 times the mean Cd concentration in 2012, which suggested that Cd pollution decreased substantially from 2007 to 2012. The most likely reason for this reduction in Cd concentrations is that most industries moved out of the Beijing urban area near the end of 2007. All of the heavy industry, such as Beijing Shougang (one of the largest steel plants), moved from the Beijing urban area to the Hebei province and is currently more than 150 km from the centre of Beijing. These industries likely contributed most of the Cd in the urban dust. The Ni concentrations in 2007 and 2012 were close to the background levels in Beijing (China National Environmental Monitoring Centre 1990; Chen et al. 2004), which indicated that a natural source could be the main source of Ni in the study area.

The mean concentrations of Pb and Hg did not change substantially between 2007 and 2012. Slight changes in the concentrations of the rest of the elements were identified. The mean Cr concentration in 2012 was 1.23 times greater than that measured in 2007, which was not directly proportional to the increasing number of motor vehicles (almost twice of that in 2007). This suggests that both industry and traffic have strong influences on Cr concentrations in street dust and the influence of traffic could be slightly larger than that of industry in the study area. Mean concentrations of Cu

Table 4 A comparison between the calculated concentrations (VB) in 2007 and the measured concentrations (CB) in 2012 (mg/kg)

Mean	Cd	Cr	Cu	Hg	Ni	Pb	Zn
2007VBs	0.785	88.590	97.102	0.311	37.812	71.784	240.371
2012CBs	0.482	109.331	102.526	0.332	25.934	68.817	264.183
Background[a]	0.119	29.800	18.700	0.058	26.800	24.600	57.500

[a] China National Environmental Monitoring Center (1990) and Chen et al. (2004)

and Zn in 2012 were slightly higher than in 2007 and were much higher than the background values in Beijing. Higher Cu concentrations occurred near congested roads where braking systems are used more often, particularly on Wangfujing road and near railway stations. Hopke et al. (1980) showed that Cu has been used as brake friction material since the 1930s, and Cu is more easily accumulated in areas with increased braking. Zinc oxide is added as an activator during vulcanization of rubber for tires, and tire wear leads to zinc emissions. The fact that some industries had moved out of Beijing was not associated with decreased concentrations of most of the metals measured in street dust. It is likely that increasing vehicle pollution offset the decreasing industrial emissions.

Health risk assessment of metal exposure from urban dust

Non-carcinogenic risk of metals

The non-carcinogenic risk of exposure to metals in urban dust through the three exposure pathways considered was calculated using Eq. (10). The hazard index (HI), which was the sum of the risks from all three pathways, was also determined. The results are shown in Table 5. The non-carcinogenic risk associated with Cr, Cu, Hg, and Zn in urban dust in 2012 was higher than in 2007, similar to the changes in the metal distributions between 2007 and 2012. The non-carcinogenic risk for children was nearly an order of magnitude higher than for adults, meaning that children faced greater health risks from exposure to metals in urban dust in 2007 and 2012. For the non-carcinogenic risk for children in 2007 and 2012, direct ingestion was the main pathway for Cd, Cr, Cu, Hg, Ni, Pb, and Zn. For adults, dermal contact was the main exposure pathway to urban dust containing Cd and Cr, while direct ingestion was the main pathway for Cu, Hg, Ni, Pb, and Zn.

Among the 7 metals, the non-carcinogenic risk of exposure to Cr was the highest for both children and adults, up to 100 times higher than for other metals. The second highest non-carcinogenic risk was from Pb. For the non-carcinogenic risk for children, the HIs decreased in the following order: Cr > Pb > Cu > Ni > Cd > Hg > Zn and Cr > Pb > Cu > Ni > Hg > Zn > Cd in 2007 and 2012, respectively. The decreased Cd non-carcinogenic risk was related to the lower Cd concentrations in 2012. For adults, the HIs decreased in the following order: Cr > Pb > Cd > Cu > Ni > Hg > Zn and Cr > Pb > Cu > Cd > Ni > Hg > Zn in 2007 and 2012, respectively. Although the Zn concentration was high, its lower RfD values resulted in lower non-carcinogenic risk. HIs for children and adults in 2007 and 2012 were all less than 1, indicating that there was no substantial risk of non-carcinogenic effects from exposure to urban dust in the study area.

Carcinogenic risk of Cr, Cd, and As

The lifetime average daily doses through inhalation and the carcinogenic risks for Cr, Cd, and As in urban dust were calculated using Eqs. (4) and (7), and the results are shown in Table 6. Chromium can exist in two different valence states and this process can happen under many conditions. Some species, such as organic matter, Fe-Mn oxides, and indigenous microorganisms, can convert Cr (III) to Cr (IV). This oxidation process is also facilitated under high pH conditions or the presence of a strong oxidant. The total concentration of Cr, instead of just Cr (IV), was used in this study to calculate risk because the calculated risk would provide a more conservative value, supporting improved health risk assessment (Hu et al. 2011). The $LADD_{inh}$ and CR_{inh} for Cd and Ni in 2007 were higher than in 2012. Conversely, Cr exhibited a higher carcinogenic risk in 2012. The carcinogenic risk levels for Cd and Ni were all less than 10^{-6}, which were within the acceptable range. However, Cr exhibited higher values of 3.37×10^{-6} in

Table 5 Non-carcinogenic risk for each metal and exposure pathway

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
2007 child							
ADD_{ing}	6.68E−03	2.51E−01	2.07E−02	8.83E−03	1.61E−02	1.75E−01	6.82E−03
ADD_{inh}	1.27E−07	4.99E−04	3.89E−07	2.09E−06	2.96E−07	3.29E−06	1.29E−07
ADD_{dermal}	5.34E−03	1.01E−01	5.51E−04	7.07E−05	4.77E−04	9.31E−03	2.73E−04
HI	1.20E−02	3.52E−01	2.12E−02	8.91E−03	1.66E−02	1.84E−01	7.09E−03
2012 child							
ADD_{ing}	4.11E−03	3.10E−01	2.18E−02	9.42E−03	1.10E−02	1.67E−01	7.50E−03
ADD_{inh}	7.78E−08	6.16E−04	4.11E−07	2.23E−06	2.03E−07	3.15E−06	1.42E−07
ADD_{dermal}	3.29E−03	1.24E−01	5.82E−04	7.54E−05	3.27E−04	8.93E−03	3.00E−04
HI	7.39E−03	4.35E−01	2.24E−02	9.50E−03	1.14E−02	1.76E−01	7.80E−03
2007 adult							
ADD_{ing}	1.06E−03	4.01E−02	3.29E−03	1.41E−03	2.56E−03	2.78E−02	1.09E−03
ADD_{inh}	1.27E−07	5.00E−04	3.90E−07	2.09E−06	2.96E−07	3.29E−06	1.29E−07
ADD_{dermal}	4.63E−03	8.71E−02	4.77E−04	6.12E−05	4.13E−04	8.07E−03	2.36E−04
HI	5.70E−03	1.28E−01	3.77E−03	1.47E−03	2.98E−03	3.59E−02	1.32E−03
2012 adult							
ADD_{ing}	6.54E−04	4.94E−02	3.48E−03	1.50E−03	1.76E−03	2.67E−02	1.19E−03
ADD_{inh}	7.78E−08	6.17E−04	4.11E−07	2.23E−06	2.03E−07	3.15E−06	1.42E−07
ADD_{dermal}	2.85E−03	1.08E−01	5.04E−04	6.53E−05	2.83E−04	7.73E−03	2.60E−04
HI	3.50E−03	1.58E−01	3.98E−03	1.57E−03	2.04E−03	3.44E−02	1.45E−03

2007 and 4.16×10^{-6} in 2012, as shown in Table 6. These values were higher than the internationally accepted precautionary value of 10^{-6}, suggesting that more attention should be paid to control of this pollutant.

The CR_{inh} for Cr was more than 100 times higher than the values for Cd and Ni. The high risks associated with Cr in this study may be related to the substantial accumulation of Cr in urban dust and its high SF_{inh}. For Cr, the SF_{inh} was 42, which was much higher than the values for Cd and Ni. The high health risk posed by Cr should be given increased attention in the future.

With the exception of Cr, exposure to metals in urban dust in 2007 and 2012 would not cause serious non-carcinogenic or carcinogenic health impacts in the study area. Some measures should be taken to reduce Cr pollution and protect residents from its carcinogenic health impacts. This study did not include all metals or all exposure pathways, so the overall risk from metal exposure cannot be determined. As such, risks associated with exposure to urban dust should not be ignored.

Table 6 Carcinogenic risk of metals

	$LADD_{inh}$ (mg/(kg·day))		CR_{inh}	
	2007	2012	2007	2012
Cd	7.1025E−10	4.36601E−10	4.47E−09	2.75E−09
Cr	8.01714E−08	9.89415E−08	3.37E−06	4.16E−06
Ni	3.42187E−08	2.34696E−08	2.87E−08	1.97E−08

Conclusions

The mean concentration of Cd in Beijing's urban dust in 2007 was 63 % greater than that measured in 2012 and the mean concentration of Cr in urban dust was slightly higher in 2012 than in 2007. Pb, Cu, Hg, and Zn varied slightly between 2007 and 2012. The results obtained were likely the result of industry moving away from Beijing combined with increased economic growth and vehicle ownership. A health risk assessment suggested that Cr exhibited the highest non-carcinogenic and carcinogenic risks in both children and adults, followed closely by Pb. With the exception of Cr, exposure to urban dust metals in the Beijing study area likely did not

cause serious non-carcinogenic or carcinogenic health impacts in both 2007 and 2012. The non-carcinogenic risks of Cr, Cu, Hg, and Zn and the carcinogenic risk of Cr were higher in 2012 than that in 2007.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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