# Human Health Risk Assessment Based on Toxicity Characteristic Leaching Procedure and Simple Bioaccessibility Extraction Test of Toxic Metals in Urban Street Dust of Tianjin, China

# Binbin Yu<sup>1</sup>, Yu Wang<sup>2</sup>, Qixing Zhou<sup>1</sup>\*

1 Key Laboratory of Pollution Processes and Environmental Criteria (Ministry of Education), College of Environmental Science and Engineering, Nankai University, Tianjin, China, 2 Department of Agricultural and Biological Engineering, University of Florida, Gainesville, Florida, United States of America

### Abstract

The potential ecological and human health risk related with urban street dust from urban areas of Tianjin, China was quantitatively analyzed using the method of toxicity characteristic leaching procedure (TCLP) and simple bioaccessibility extraction test (SBET). In the study, Hakason index, Nemerow index (*P*), the hazard index (*HI*) and the cancer risk index (*RI*) were calculated to assess the potential risk. The sequence of potential ecological risk based on Hakason index was arsenic (As) > cadmium (Cd) > lead (Pb) > copper (Cu) > chromium (Cr), in particular, As and Cd were regarded as high polluted metals. While the results of extraction of TCLP were assessed using *P*, the sequence was As > Pb > Cd > Cr > Cu, which mean that As and Pb should be low polluted, and Cd, Cr and Cu would barely not polluted. For human health, total carcinogenic risk for children and adults was  $2.01 \times 10^{-3}$  and  $1.05 \times 10^{-3}$ , respectively. This could be considered to be intolerable in urban street dust exposure. The sequence in the hazard quotient (*HQ*) of each element was As > Cr > Pb > Cu > Cd. The *HI* value of these toxic metals in urban street dust for children and adults was  $5.88 \times 10^{-1}$  and  $2.80 \times 10^{-1}$ , respectively. According to the characters of chemistry, mobility, and bioavailability of metals in urban street dust, we estimated the hazards on the environment and human health, which will help us to get more reasonable information for risk management of metals in urban environment.

Citation: Yu B, Wang Y, Zhou Q (2014) Human Health Risk Assessment Based on Toxicity Characteristic Leaching Procedure and Simple Bioaccessibility Extraction Test of Toxic Metals in Urban Street Dust of Tianjin, China. PLoS ONE 9(3): e92459. doi:10.1371/journal.pone.0092459

Editor: Qinghua Sun, The Ohio State University, United States of America

Received December 9, 2013; Accepted February 21, 2014; Published March 20, 2014

**Copyright:** © 2014 Yu et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

**Funding:** This work was financially supported by the National Natural Science Foundation of China as a key project (grant No. 21037002) and the Ministry of Science and Technology, People's Republic of China as a 863 project (grant No. 2012AA101403-2). The funders had no role in study design , data collection and analysis, decision to publish, or preparation of the manuscript.

Competing Interests: The authors have declared that no competing interests exist.

\* E-mail: zhouqx@nankai.edu.cn

## Introduction

Along with rapid urbanization, many suburban lands are being converted to residential use, streets, commercial and industrial zones. The high population density leads to an increasing level of urban environmental pollution, industrial discharges, traffic emissions, and waste from municipal activities cause the major anthropogenic troubles [1–4]. Street dust is an important factor of urban pollution, and road activities often cause air pollution and adverse human health effects such as lung cancer, hypertension and cardiovascular diseases [5–9]. Due to the accumulation of metals in street dust with atmospheric deposition by sedimentation interception, human health may be adversely affected by air pollution if metal concentrations reach a level of being considered as toxic pollutants [10].

Many studies reported that the total concentration of heavy metals in street dust was regarded as an indicator of urban air pollution affecting urban environmental quality. More airenvironmental scientists described that not only the total concentration of heavy metals in street dust, but also the proportion of their mobile and bioavailable forms were important to environmental and human health risk of metal pollutants [11– 16]. Metals in urban street dust occur in variable forms, such as adsorbed or exchangeable. The forms of toxic metals could affect their mobility and bioavailability including uptake by living organisms, and result in potential risk to the environment and residents. To evaluate long-term impacts of toxic metals on urban environment and risks to residents, it was necessary to investigate chemical forms, mobility, and bioavailability of toxic metals in urban street dust.

Tianjin (39°07' N, 117°12' E) is a mega-city in northern China, which is adjacent to Beijing and Hebei Province. It is a municipality along the coast of the Bohai Gulf. There are four distinct seasons, characterized by cold, windy, dry winters affected by the vast Siberian anticyclone, and hot, humid summers due to the East Asian monsoon. The mean temperature is  $11.6-13.9^{\circ}$ C and the annual average wind speed is  $2-5 \text{ m s}^{-1}$ . Rapid expansion in Tianjin has made the city become one of the most densely populated regions in China, with the population size of over 1.27 million. Urbanization increases the population density and lots of human activities such as traffic, industry, commerce, petrol combustion, and waste disposal. Of the contaminants in the urban area, toxic metals have caused serious concern of both

researchers and governments for their characteristics of accumulation and degradation-resistant. As a crucial component of urban ecosystems, urban dust is subjected to continuous accumulation of contaminants [17–19], especially toxic trace metals [9,20], lots of investigations have been done on metal contamination in urban areas [15,21–25].

In this study, we provided valuable information about toxic metals in urban dust, including chemical characters, mobility, and bioavailability of toxic metals in urban environment. According to the information, we estimated the hazards of toxic metals in street dust, in particular, adverse effects on the environment and human health. The key scientific problems related to street dust pollution were addressed as follows: (1) the spatial distribution of toxic metals; (3) the risk index (RI) and Nemerow index (P) based on chemical behaviors and mobility of toxic metals; (4) the hazards index and total cancer risk based on oral bioavailability of toxic metals; and (5) some environmental management advice to reduce dust pollution.

### **Materials and Methods**

# Sampling (No specific permits were required for this study)

Urban street dust samples were collected on pavements next to main roads at periods when no rain had occurred during the previous week, brushes and trays were used for sampling. Along the central line in Tianjin, we collected 87 samples ( $39^{\circ}09'$  N to  $39^{\circ}22'$  N,  $117^{\circ}14'$  E to  $117^{\circ}27'$  E). To uniform samples, the studying area was divided into regular grids of  $1 \times 1 \text{ km}^2$  and avoiding serious polluted areas (such as hospitals, gas stations, and bus stations). Each sample was at least 200 g and composed of 5–7 subsamples. Collected samples were put into clean polythene bags and taken to the laboratory as soon as possible. Each urban street dust sample was thoroughly mixed, sieved through a 63 µm nylon sieve, then one part was air-dried, other part was stored at 4°C. The detailed sampling information was depicted in Fig. 1.

#### Sample analyses

The pH values of urban street dust samples were measured with Milli Q water with a solid-to-solution ratio of 1:2.5 (w/v), organic matter (OM) contents were measured by the wet digestion method, the metals were measured by the microwave assisted acid digestion (US EPA 1996). 0.2 gram of the street dust sample was mixed with 8 mL 65% nitric acid, 5 mL 30% hydrogen peroxide and 3 mL 30% hydrofluoric acid and put into a microwave oven. The digestion procedure was described as follows: stage-1 (10 min to reach 150°C), stage-2 (10 min to reach  $180^{\circ}$ C) and stage-3 (15 min at  $200^{\circ}$ C). After cooling below  $100^{\circ}$ C, sample digestion solutions were evaporated near to dryness, added to 10 mL Milli Q water. Solutions were stored in 10 mL polyethylene vials at 4°C till analysis. Blank and control samples were used to check the accuracy and quality. The contents of arsenic (As), lead (Pb), cadmium (Cd), copper (Cu) and chromium (Cr) were measured by the inductively coupled plasma spectrometry (ICP-MS, DRC-e), the recovery of the metallic elements was in the 85.1-106.8% range.

## Toxicity characteristic leaching procedure (TCLP)

Leaching of hazardous metals from street dust samples were examined by means of a TCLP [26]. The pH values of dust samples were beyond 5, the extraction solution (HOAC,  $pH = 2.88 \pm 0.05$ ) was used, the solid - to - liquid ratio was 1:20, the temperature was  $23 \pm 2^{\circ}$ C, and the agitation time was 18 h in a

rotary tumbler. After extraction, the leaching solutions were filtered through a glass fiber filter (0.45  $\mu$ m). The filtrates were analyzed by ICP-MS immediately.

## Simple bioaccessibility extraction test (SBET)

Oral bioavailability of metals in street dust samples were measured by SBET [27–29]. Samples were extracted with glycine (0.4 M; pH=1.5±0.05, pre-adjusted with concentrated hydrochloric acid), the solid-to-liquid ratio was 1:100. Samples were extracted by rotating the samples end-over-end at 37°C for 1 h. The mixture solutions were centrifuged and the supernatant was filtered through 0.45  $\mu$ m cellulose acetate filter. The pH values of the mixed-solution should be within 0.5 pH units of the starting pH, otherwise the procedure has to be redone. The filtrates were stored in a refrigerator at 4°C until analyzed by ICP-MS in one week.

#### Pollution risk of total concentrations of urban street dust

Most researchers used potential ecological risk index (RI) as a method to assess the degree of metals pollution in soil. The method was originally introduced by Hakanson [30], according to the toxicity of heavy metals, assessed the response of metals to the environment.

$$C_f{}^i = C^i \div C_n{}^i \tag{1}$$

$$E_i = T_i \times C_f^{\ i} \tag{2}$$

$$RI = \sum_{i=1}^{m} E_i \tag{3}$$

Where  $C_f^i$  is the single metal pollution factor,  $C^i$  is the concentration of a metal in urban street dust,  $C_n^i$  is a reference value for a metal, in this study, which is the soil background value in Tianjin [31].  $E_i$  is the monomial potential ecological risk factor,  $T_i$  is the response coefficient for the toxicity of the single heavy metal, which for Cd is 30, As is 10, Pb and Cu are 5, Cr is 2 [30], RI is calculated as the sum of all five risk factors for heavy metals in urban street dust. Different categories of metal pollution about  $E_i$  and RI were delineated in Table 1.

# Assessment of pollution risk using the results of extraction of TCLP

To evaluate the toxicity of the mobile and soluble parts of urban street dust, via a TCLP test, Nemerow index (P) [32] was used to assess the degrees of dust contamination. The pollution index was defined as the ratio of metal concentration to geometric means of background concentration of the corresponding metal:

$$P_i = C_i / S_i \tag{4}$$

$$P = \sqrt{\frac{(C_i/S_i)^2_{\max} + (C_i/S_i)^2_{ave}}{2}}$$
(5)

and



Figure 1. The sampling sites of urban street dust in Tianjin, China. doi:10.1371/journal.pone.0092459.g001

Where  $P_i$  is the evaluation score corresponding to each sample,  $C_i$  is the value of extraction of TCLP,  $S_i$  is the maximum concentration  $(mg \cdot L^{-1})$  of a contaminant for toxicity characteristic, As for 5.0, Pb for 5, Cd for 1.0, Cu for 15, and Cr for 5 [33],  ${\it P}$  is the metal integrated pollution index,  $({\rm C_i}/{\rm S_i})_{\rm max}$  is the maximum and  $(C_i/S_i)_{\rm ave}$  is the average. There are five categories of metal pollution about P were displayed in Table 2.

# Potential human health risk of metals in urban street dust

In order to assess both non-carcinogenic and carcinogenic risk for children and adults from ingesting urban street dust, the chronic daily intakes (CDI) of toxic metals and potential risks were used. According to the Exposure Factors Handbook [34], CDI  $(mg \cdot kg^{-1} \cdot day^{-1})$  of toxic metals via dust can be calculated using the following equation:

Ei	Ecological risk categories of single metal	RI value	Ecological risk categories of the environment
E <sub>i</sub> <40	Low contamination	RI<150	Low risk
$40 \le E_i \le 80$	Moderate risk	150≤RI<300	Moderate risk
80≤E <sub>i</sub> <160	Considerable risk	300≤RI<600	Considerable risk
160≤E <sub>i</sub> <320	High risk	RI≥600	Serious risk
E <sub>i</sub> ≥320	Serious risk		

**Table 1.** Potential ecological risk categories based on *E*<sub>i</sub> and *RI* values<sup>a</sup>.

<sup>a</sup>[30]. doi:10.1371/journal.pone.0092459.t001

P value	Ecological risk category	
P≤0.7	Safe	
0.7 <p≤1.0< td=""><td>Warily level</td><td></td></p≤1.0<>	Warily level	
1.0 <p≤2.0< td=""><td>Low contamination</td><td></td></p≤2.0<>	Low contamination	
2.0 <p≤3.0< td=""><td>Moderate contamination</td><td></td></p≤3.0<>	Moderate contamination	
P>3.0	Serious contamination	

<sup>a</sup>[31].

doi:10.1371/journal.pone.0092459.t002

$$CDI = C \times CF \times \frac{E_F \times E_D \times Ing_R}{BW \times AT}$$
(6)

Where C is the exposure site concentration (mg·kg<sup>-1</sup>), in this study, C is the mean concentration of SBET;  $E_F$  is the exposure frequency of 350 days·year<sup>-1</sup> [35–36];  $E_D$  is the exposure duration, in this study, 6 years for children and 24 years for adults;  $Ing_R$  is the ingestion rate at 200 mg·day<sup>-1</sup> for children and 100 mg·day<sup>-1</sup> for adults [34,37]; BW is average body weight, 15 kg for children and 60 kg for adults [35,38], and AT is average time (for non-carcinogens, AT =  $E_D \times 365$  days; for carcinogens, AT = 70 × 365 days); CF is conversion factor,  $1 \times 10^{-6}$  kg·mg<sup>-1</sup>.

The potential health risk of each element was calculated with equations (7–8). While Eq.7 is for non-carcinogenic risk, Eq.8 is for carcinogenic risk.

$$HQ = \frac{CDI \times RBA}{RfD_O} \tag{7}$$

and

$$CR = (CDI \times RBA) \times CSF_O \tag{8}$$

Where oral reference dose  $(RfD_o)$  and cancer slope factor  $(CSF_o)$  were obtained from regional screening levels [39], relative bioavailability (RBA) is the ratio of SBET/total contents.  $RfD_o$  for Pb has not established in US EPA, in this study,  $RfD_o$  for Pb is  $3.5 \times 10^{-3} \text{ mg} \cdot \text{kg}^{-1} \cdot \text{day}^{-1}$  calculated from the provisional tolerable weekly Pb intake limit ( $25 \ \mu\text{g} \cdot \text{kg}^{-1}$ -body weight) recommended by FAO/WHO for adults [24,40]. The toxicity of Cr depends on its valence state ( $Cr^{6+}$  and  $Cr^{3+}$ ), in this study,  $Cr^{6+}$  represented total Cr. The RBA,  $RfD_o$  and  $CSF_o$  values were listed in Table 3.

Though interactions between some metals might result in their synergistic manner, all metal risks were additive. The hazard index (HI) and total risk [41] were estimated with the following equations:

$$HI = \sum_{i=1}^{m} HQ \tag{9}$$

and

$$TotalRisk = \sum_{i=1}^{m} CancerRisk$$
(10)

If *HI* exceeds 1.0, there is a chance that non-carcinogenic effects may occur, with a probability which increases with an increase in the value of *HI*; and then, if *HI* is less than 1.0, it believed that there is no significant risk of non-carcinogenic effects [42]. Cancer risks (*CR*) estimates the incremental individual lifetime cancer risk for simultaneous exposure to several carcinogens, the acceptable or tolerable risk for regulatory purposes is in the range of  $1 \times 10^{-6}$ -  $1 \times 10^{-4}$ .

### Results

### Dust properties and metals spatial distribution

The urban street dust samples from Tianjin cover a wide range of pH and OM. The pH values varied from 7.50 to 10.77 with average of 8.28, OM from 0.56% to 4.25% with average of 2.32%. The concentrations of As, Pb, Cd, Cu and Cr in urban street dust varied from 17.18 to 203.78, 20.64 to 155.67, 0.22 to 1.38, 20.65 to 187.78, and 30.85 to 224.60 mg  $kg^{-1}$ , respectively, with the average concentration of 101.41, 60.11, 0.45, 55.47 and 71.85 mg·kg<sup>-1</sup>, respectively (Table 4). The sequence in the contents of toxic metals in urban street dust was As > Cr > Pb> Cu > Cd. The spatial distributions of metals (As, Pb, Cd, Cu and Cr) in urban areas of Tianjin were depicted in Fig. 2. As was strong contaminated in most sites of the urban areas, which was higher than Class III of National Soil Standards [43]. Pb and Cr were lower than Class II of National Soil Standards, while Cd and Cu were lower than Class II of National Soil Standards in most urban areas and only a few of sites were higher than Class III of National Soil Standards where near the sites were high population density, including stations, commercial zones and construction fields.

#### Metal mobility and relationship with dust properties

The mobility of toxic metals depends on their chemical forms. In this study, according to the method of TCLP extraction, the range of extraction efficiency of toxic metals varied widely among urban street dust, As is 0.24% to 21.22%, Pb is 0.04% to 26.73%, Cd is 0.24% to 75.35%, Cr is 0.54% to 5.64% and Cu is 0.15% to 7.12%. The sequence of average extraction efficiency of toxic metals is Cd (12.99%) > Pb (4.11%) > Cr (2.70%) > As (2.07%) > Cu (1.40%).

The mobility of toxic metals in urban street dust may be affected by metal-particles and other physiochemical properties of dust, such as pH, and OM. The stepwise multiple regression analysis showed that there were significant correlations among pH, OM, the total concentration and the TCLP-extraction (Cd, Pb and Cu) concentration (Table 5). Whereas for As and Cr in street dust, not obvious relationship was found.

# Metal bioaccessibility and relationship with dust properties

Many factors can affect metal bioaccessibility in dust, such as the interactions of metals, properties and constituents of dust. The range of bioaccessibility of metals varied widely among urban street dust, As is 4.94% to 37.60%, Pb is 4.49% to 33.22%, Cd is 8.81% to 43.13%, Cr is 6.70% to 80.70% and Cu is 4.21% to 36.92%. The sequence of average bioaccessibility of metals is Cr (22.63%) > Cd (21.73%) > Cu (19.01%) > Pb (15.04%) > As

PLOS ONE | www.plosone.org

Table 3. Heal	th risk from hea	avy metals in urban	street dust (n=87).						
Contaminant	رتا (95% UCL) mg·kg <sup>_1</sup>	<i>RfD<sub>o</sub><sup>b</sup></i> (mg/kg-day)	<i>CSF<sub>o</sub><sup>b</sup></i> (mg/kg-day) <sup>-1</sup>	Chemical daily in	ntake (mg/kg-day)	Child		Adult	
				<b>Children Adult</b>		РЙ	Carcinogenic risk	Ř	Carcinogenic risk
As noncanc.	101.41	3.00E-04		1.35E-03	6.76E-04	4.56E-01		2.28E-01	
As canc.	101.41		1.50E+00	1.11E-04	5.56E-05		1.69E-05		8.44E-06
Cr noncanc.	71.85	3.00E-03		9.58E-04	4.79E-04	6.60E-02		3.30E-02	
Cr canc.	71.85		5.00E-01	7.87E-05	3.94E-05		8.14E-06		4.07E-06
Cd (diet)	0.45	1.00E-03		6.00E-06	3.00E-06	1.33E-03		6.67E-04	
Cu	55.47	4.00E-02		7.40E-04	3.70E-04	3.22E-03		1.61E-03	
РЬ <sup>с</sup>	60.11	3.50E-03		8.01E-04	4.01E-04	3.25E-02		1.63E-02	
<sup>a</sup> 95% upper confic b[39]. <sup>c</sup> [40,24]. doi:10.1371/journa	dence limit of the m Lpone.0092459.t003	lean concentrations.							

Risk Assessment on Environment and Human

(14.42%). The bioaccessibility of metals (Pb 59%, and Cu 58%) in Hong Kong urban soils (pH 6.6, SOM 4.4%, clay 7%, and sand 76%) [16] was higher, those (As 27.3%, Pb 71.7%, Cr 5.6%, and Cu 40.4%) almost all higher except Cr in urban roadside soils from Xuzhou, China [44].

Metal bioavailability could be affected by the ingested heavy metal-particles and other physiochemical properties of dust, such as pH, and OM. The stepwise multiple regression analysis showed that there were significant correlation relationships among pH, OM, the total metal concentration and the SBET-extraction (As, Pb, Cd, and Cu) concentration (Table 6). Whereas for Cr in street dust, no obvious relationship was found.

#### Ecological risk assessment based on RI and P

To get better image of urban street dust pollution and related risks, the Hakanson's method and the Nemerow's method were applied in this study. The ecological risk assessment results of metals in urban street dust were summarized in Table 7. It was found that the sequence of risk indices  $(E_i)$  of single metal was As > Cd > Pb > Cu > Cr. As and Cd are considerable contaminated in urban street dust, the values of  $E_i$  were higher than 100, and less than 160. Pb, Cu and Cr were low contaminated, the values of  $E_i$ were lower than 40. According to the character of metals, the overall potential ecological risk of the observed metals was quantified. RI was calculated as the sum of all the five risk factors. RI in urban street dust was 283.72, which mean that the metals in urban street dust were contaminated in the moderate degree  $(150 \le RI \le 300)$ . The sequence of P index of each toxic metal was As > Pb > Cd > Cr > Cu (Table 7) in urban street dust. The ecological risk of As and Pb was low, whose value exceeded 1.0, and was less than 2.0. The ecological risk of Cd, Cu and Cr was barely not polluted, whose value was lower than 0.7. From the results, the potential ecological risk of the toxic metals in the extraction of TCLP was lower than that in the total concentrations, and As was the major contaminant in street dust.

# Human health risk assessment according to oral bioavailability

Metals are usually non-degradable in the environment, and homeostasis mechanisms are unknown. Thus, biological life would be threaten by any high levels of metals [45]. In an individual lifetime, the incremental risk probability of carcinogens is estimated as a result of exposure to the potential carcinogens. In this study, only As and Cr were assessed through the ingestion exposure modes of urban street dust, for children, As was  $1.50 \times 10^{-3}$ , and Cr was  $5.12 \times 10^{-4}$ , compared to adults, As was  $7.49 \times 10^{-4}$ , and Cr was  $2.56 \times 10^{-4}$ . The total cancer risk for children was  $2.01 \times 10^{-3}$ , and that for adults was  $1.05 \times 10^{-3}$ . The cancer risk was higher than  $1 \times 10^{-4}$ , which was considered to be high potential risk and indicated that the carcinogenic risk of As and Cr in urban street dust exposure cannot be tolerable.

Non carcinogenic risks of a metal in urban street dust is potential, and non-carcinogenic toxicity can occur with time, which is not expressed as the probability of an individual metal with an adverse effect. In this study, the HQ sequence of toxic metals was As > Cr > Pb > Cu > Cd ( $4.56 \times 10^{-1}$ ,  $6.60 \times 10^{-2}$ ,  $3.25 \times 10^{-2}$ ,  $3.22 \times 10^{-3}$  and  $1.33 \times 10^{-3}$ , respectively, for children; and  $2.28 \times 10^{-1}$ ,  $3.30 \times 10^{-2}$ ,  $1.63 \times 10^{-2}$ ,  $1.61 \times 10^{-3}$  and  $6.67 \times 10^{-4}$ , respectively, for adults) (Table 4). So the HQ values for toxic metals in this study were all lower than 1.0, which means that it was at the safe level. Non-carcinogenic risks were safe for children and adults. The hazards index (HI) for toxic metals to residents through the daily ingestion of street dust was  $5.88 \times 10^{-1}$ 

Ν

Pb mgkg-1 Pb concentrations <VALUE>

18. 5270977 - 35

35.00000001 - 350









Figure 2. Spatial distribution of metals (As, Pb, Cd, Cu and Cr) in urban street dust of Tianjin, China. doi:10.1371/journal.pone.0092459.g002

**Table 4.** A comparison of metal average concentration (mg kg<sup>-1</sup>) in street dust from some cities.

City (Ref.)	As	Pb	Cd	Cr	Cu
Tianjin	101.41	61.11	0.45	71.85	55.47
Beijing <sup>a</sup>	-	61	1.2	85.6	42
Shanghai <sup>b</sup>	8.01	236.62	0.97	264.32	257.63
Shenyang <sup>c</sup>	-	75.29	0.42	-	51.26
Nanjing <sup>d</sup>	13.4	103	1.10	126	123
Xi'an <sup>e</sup>	10.62	230.52	-	167.28	94.98
Hongkong <sup>f</sup>	66.8	120	-	124	110
National Standard- Class I <sup>g</sup>	15	35	0.20	90	35
National Standard- Class II <sup>h</sup>	25	350	0.60	250	100
National Standard- Class III <sup>i</sup>	40	500	1.0	300	400

<sup>a</sup>[22]. <sup>b</sup>[21].

<sup>c</sup>[44].

<sup>d</sup>[24].

<sup>e</sup>[50].

<sup>f</sup>[51].

<sup>g</sup>[43] Environmental quality standard for soils in China (National Environmental Protection Agency of China, 1995), and values in Class I are threshold levels of nationwide natural background.

<sup>h</sup>[43] Values in Class II are threshold values established to protect agricultural production and maintain human health.

<sup>i</sup>[43] Values in Class III are estalbished to maintain normal growth of plants, particularly the trees.

doi:10.1371/journal.pone.0092459.t004

for children, and  $2.80 \times 10^{-1}$  for adults. *HI* was less than 1.0, which means that human exposure to urban street dust was safe.

### Discussion

Street dust pollution in urban areas has an important impact on the environment, human health and life quality of residents. Meanwhile, the health of children and adults was affected by inhaling or ingesting street dust with the high metal contamination. It is important to identify the origin and distribution of toxic metals in street dust. The concentration of As in street dust was at the highest level, then followed by Cr, Pb, Cu and Cd. In most urban areas, it contaminated with As. Only the urban areas close to stations, commercial zones and construction fields, it contaminated with Cd and Cu. Compared with the average concentration of metals in street dust from different cities (Table 4), the average concentration of Pb, Cd, Cr and Cu in Tianjin was nearly same as that in Beijing, but lower than that in Shanghai [46], and the average concentration of Pb, Cu and Cd was almost at the same level in Shenyang [47].

Tianjin has a high demand on winter heating, from November to next March. As is known to be serious concentrated in coals, and coal combustion released many metals, such as As, Cr, Pb and Cu. Particularly, vehicle emissions are a major contributor to other metals in urban street dust, including Pb, Cu and Cd. Vehicle loadings were about 1.76 million in urban areas of Tianjin till 2011. In this study, Cd, Cu and Pb were the main source of auto transport activities, such as vehicle exhaust emissions. Without doubt, there are also a number of other sources of metals in urban street dust, including disintegration of vehicle brakes and tires, atmospheric deposition, road surface wear, municipal solid waste incineration, and residential heating. Besides, many residential buildings are close to streets, which result in the frequent exposure of inhabitants to urban street dust. To reduce the accumulation of toxic metals in street dust, we suggest that it should use clean energy at the heating period and increase green areas in urban areas.

The results of the potential ecological risk for urban street dust using Hakason index and Nemerow index methods were different. The RI values of As, Cd, Cu and Cr were higher than P, only the risks of Pb were the same. From the results, RI could characterize the sensitivity of the toxic metals, and moreover, represent ecological risk resulted from the all contamination in local ecosystems. RI estimated the risk in the chemical forms of toxic metals. The categories, concentrations and toxic characteristics of metals could affect the values of  $E_i$  and RI, and cause the different results. The P index was used to estimate the mobility of toxic

Table 5. Regression linear analysis of TCLP-extractable contents, total contents and selected dust properties (pH, and OM).

	Regression equation	R	Sig.
As	C=3.758-0.296pH+0.143OM-0.003Total	0.304	0.044
Cd	C = -0.059+0.004pH+0.001OM+0.197Total	0.547	0
Cr	C = 9.340-0.069pH+1.402OM+0.040Total	0.366	0.007
Cu	C=5.310-0.300pH+1.678OM+0.053Total	0.660	0.000
Pb	C = 7.939-0.786pH+2.582OM+0.019Total	0.622	0

doi:10.1371/journal.pone.0092459.t005

-			
	Regression equation	R	Sig.
As	C = -0.338+1.000pH+0.366OM+0.015Total	0.506	0
Cd	C = 0.071 - 0.009 pH + 0.020 OM + 0.131 Total	0.692	0
Cr	C = 9.340-0.069pH+1.402OM+0.040Total	0.366	0.007
Cu	C = 5.310-0.300pH+1.678OM+0.053Total	0.660	0.000
Pb	C = 7.939-0.786pH+2.582OM+0.019Total	0.622	0

Table 6. Regression linear analysis of SBET-extractable contents, total concentrations and selected dust properties (pH, and OM).

doi:10.1371/journal.pone.0092459.t006

metals in urban street dust. As and Pb were the major contaminants for the mobility and toxicity, then followed by Cd, Cr and Cu. Despite the concentration of Pb was not higher than Class III of the Chinese National Soil Standards, the P index of Pb was still at the low risk due to the low concentrations of Pb in most urban areas. The results of assessment of chemical forms and mobility of metals were different, because the mobility of metals could be reduced by organic matters in dust samples. In other words, the chemical forms and mobility of metals should be coupled in order to get better assessment of their potential ecological risk. Meanwhile, the properties of urban street dust also affect the mobility and bioaccessiblity of metals in street dust. Toxic metals such as As, Pb, Cd, Cr and Cu could continuously accumulate in urban environment due to their non-biodegradability and the longer residence time. Thus, the local government should pay more attention to the action of reckless and unconscious pollution of the environment, and work out some particular management strategies to achieve better urban environmental quality.

Metals may accumulate in fatty tissues of human bodies, have middle and long-term health risks, and can adversely affect their physiological functions, disrupt the normal functioning of internal organs, or act as cofactors in other diseases [48,49]. Meanwhile, metals could deposite in the circulatory system of people, and each element (As, Cr, Pb, Cu, or Cd) has a distinctive toxicological picture and a particular distribution in human bodies. For instance, Pb accumulates primarily in the liver and in the kidney, while Cd concentrates in the kidney. All these elements originate, following a chronic exposure, complex systemic alterations so that it seems to be quite short-sighted to reduce their toxicological effects to the central nervous system and the cardiovascular system. Metals in urban soils might be transferred to human bodies via ingestion, dermal contact, or breathing, especially to children due to the "hand to mouth" activity during outdoor activities in playgroud and recreational areas [50,51]. The total carcinogens risk was  $2.01 \times 10^{-3}$  for children, and  $1.05 \times 10^{-3}$  for adults. In other words, they were both higher than  $1 \times 10^{-4}$ . With the results, we considered to be high potential risk and indicated that carcinogenic risk of As and Cr in urban street dust exposure cannot be tolerable. HI for toxic metals were  $5.88 \times 10^{-1}$  for children, and  $2.80 \times 10^{-1}$  for adults, which means that exposure to urban street dust might be safe. Despite HI for children could be safe, low tolerance to toxins and the ingestion of dust through hand-to-mouth pathways, the hazards to children cannot be ignored. The ingestion of dust appears to be the main exposure to street dust, which results in health risk for As, Pb, Cd, Cr and Cu in street dust from anthropogenic sources. But if exposure frequency or ingestion rate is increased, street dust can still result in non-carcinogenic adverse effects on children. Therefore, the potential health risk for children cannot be ignored due to the exposure to the street dust.

Urban street dust receipt large amounts of metals originating from a variety of sources including materials, industrial waste, vehicle emissions, coal burning and other anthropogenic activities. Many metals could be remained in urban street dust for a long time, which may lead to further potential threat to ecosystems and human health. It is well known that chemical speciation of metals should be considered in addition to total concentration when evaluating the potential risk of metals in urban street dust. Therefore, we should consider the mobility and bioavailability of metals in urban street dust in order to offer an insight into potential ecological risk of urban street dust to the environment and human health.

#### Statement

Our sampling sites belong to local government departments, do not involve the use of private land. The whole sampling was finished in the public land, did not involve the destruction of the vegetation and biological species.

#### **Author Contributions**

Conceived and designed the experiments: QZ YW. Performed the experiments: BY. Analyzed the data: BY. Contributed reagents/materials/analysis tools: BY. Wrote the paper: BY. Guided the work as the supervisor and revised the manuscript many times: QZ. Improved the experimental scheme and made an elementary polishing and correction in English: YW.

Contaminant	E <sub>i</sub>	Risk degree	RI	Р	Risk degree
As	108.81±7.18	Considerable	283.72 Moderate degree	1.40	Low
Pb	15.03±0.67	Low		1.36	Low
Cd	148.54±6.59	Considerable		0.51	Clean
Cu	9.63±0.48	Low		0.16	Clean
Cr	1.71±0.08	Low		0.40	Clean

Table 7. The potential ecological risk indexes.

doi:10.1371/journal.pone.0092459.t007

#### References

- Wong CSC, Li XD, Thornton I (2006) Urban environmental geochemistry of trace metals. Environmental Pollution 142(1): 1–16.
- Liu R, Zhou QX, Zhang LY, Guo H (2007) Toxic effects of wastewater from various phases of monosodium glutamate production on seed germination and root elongation of crops. Frontiers in Environmental Science & Engineering in China 1(1): 114–119.
- Zhou QX, Wang ME (2010) Adsorption-desorption characteristics and pollution behavior of reactive X-3B red dye in four Chinese typical soils. Journal of Soils and Sediments 10(7): 1324–1334.
- Zhang L, An J, Zhou QX (2012) Single and joint effects of cadmium and galaxolide on zebrafish (Danio rerio) in feculent water containing bedloads. Frontiers in Environmental Science & Engineering in China 6(3): 360–372.
- Al-Khashman OA (2004) Heavy metal distribution in dust, street dust and soils from the work place in Karak Industrial Estate, Jordan. Atmospheric Environment 38(39): 6803–6812.
- Arslan H (2001) Heavy metals in street dust in Bursa, Turkey. Journal of Trace and Microprobe Techniques 19(3): 439–445.
- Chen B, Shand CA, Beckett R (2001) Determination of total and EDTA extractable metal distributions in the colloidal fraction of contaminated soils using SdFFF-ICP-HRMS. Journal of Environmental Monitoring 3(1): 7–14.
- Harrison RM, Laxen DPH, Wilson SJ (1981) Chemical associations of lead, cadmium, copper, and zinc in street dusts and roadside soils. Environmental Science & Technology 15(11): 1378–1383.
- Li XD, Poon CS, Liu PS (2001) Heavy metal contamination of urban soils and street dusts in HongKong. Applied Geochemistry 16(11–12): 1361–1368.
- Ferreira-Baptista L, Miguel DE (2005) Geochemistry and risk assessment of street dust in Luanda, Angola: a tropical urban environment. Atmospheric Environment 39(25): 4501–4512.
- Chang EE, Chiang PC, Lu PH, Ko YW (2001) Comparison of metal leachability for various wastes by extraction and leaching methods. Chemosphere 45: 91–99.
- Ge Y, Murray P, Hendershot WH (2000) Trace metal speciation and bioavailability in urban soils. Environmental Pollution 107(1): 137–144.
- Kim JY, Kim KW, Ahn JS, Ko I, Lee CH (2005) Investigation and risk assessment modeling of As and other heavy metals contamination around five abandoned metal mines in Korea. Environmental Geochemistry and Health 27(2): 193–203.
- Poggio L, Vrscaj B, Schulin R, Hepperle E, Marsan FA (2008) Metals pollution and human bioaccessibility of topsoils in Grugliasco (Italy). Environmental Pollution 157(2): 680–689.
- Lu SG, Bai SQ (2010) Contamination and potential mobility assessment of heavy metals in urban soils of Hangzhou, China: relationship with different land uses. Environmental Earth Sciences 60(7): 1481–1490.
- Lu Y, Gong ZT, Zhang GL, Burghardt W (2003) Concentration and chemical speciations of Cu, Zn, Pb and Cr of urban soils in Nanjing, China. Geoderma 115(1-2): 101-111.
- Tang L, Tang XY, Zhu YG, Zheng MH, Miao QL (2005) Contamination of polycyclic aromatic hydrocarbons (PAHs) in urban soils in Beijing China. Environment International 31(6): 822–828.
- Thornton I, Farago ME, Thums CR, Parrish RR, McGill RAR, et al. (2008) Urban geochemistry: research strategies to assist risk assessment and remediation of brownfield sites in urban areas. Environmental Geochemistry and Health 30(6): 565–576.
- Zhou QX, Luo Y (2011) Pollution Eco-chemistry (in Chinese). Science Press, Beijing, China 541pp.
- Luo XS, Yu S, Li XD (2011) Distribution, availability, and sources of trace metals in different particle size fractrions of urban soils in Hong Kong: Implications for assessing the risk to human health. Environmental Pollution 159(5): 1317–1326.
- Shi G, Chen Z, Bi C, Li Y, Teng J, et al. (2010) Comprehensive assessment of toxic metals in urban and suburban street deposited sediments (SDSs) in the biggest metropolitan area of China. Environmental Pollution 158(3): 694–703.
- Zheng N, Liu JS, Wang QC, Liang ZZ (2010) Health risk assessment of heavy metal exposure to street dust in the zinc smelting district, Northeast of China. Science of the Total Environment 408(4):7 726–733.
- Mahanta MJ, Bhattacharyya KG (2011) Total concentrations, fractionation and mobility of heavy metals in soils of urban area of Guwahati, India. Environmental Monitoring and Assessment 173(1–4): 221–240.
- Hu X, Zhang Y, Luo J, Wang TJ, Lian HZ, et al. (2011) Bioaccessibility and health risk of arsenic mercury and other metals in urban street dusts from a mega-city, Nanjing, China. Environmental Pollution 5(159): 1215–1221.

- Wang G, Oldfield F, Xia DS, Chen FH, Liu XM, et al. (2012) Magnetic properties and correlation with heavy metals in urban street dust: A case study from the city of Lanzhou, China. Atmospheric Environment 46: 289–298.
- US EPA (1992) Toxicity characteristic leaching procedure. http://www.epa. gov/wastes/hazard/testmethods/sw846/pdfs/1311.pdf.
- Oomen AG, Hack A, Minekus M, Zeijdner E, Cornelis C, et al. (2002) Comparison of five in vitro digestion models to study the bioaccessibility of soil contaminants. Environmental Science & Technology 36(15): 3326–3334.
- US EPA (2007) Guidance for evaluating the oral bioavailability of metals in soils for use in human health risk assessment.
- US EPA (2008) Standard operating procedure for an in vitro bioaccessibility assay for lead in soil. http://www.epa.gov/superfund/bioavailability/pb\_ivba\_ sop\_final.pdf.
- Hakanson L (1980) An ecological risk index for aquatic pollution control. A sedimentological approach. Water Research 14(8): 975–1001.
- China National Environmental Monitoring Centre. The element background values of soil in China [M], Beijing: China Environmental Science Press.
- Nemerow NL, Hisashi S (1970) Benefits of water quality enhancement. Syracuse University, Syracuse, NY, Report No. 16110 DAJ, prepared for the US EPA.
- Sun YF, Xie ZM, Li J, Xu JM, Chen ZL, et al. (2006) Assessment of toxicity of heavy metal contaminated soils by the toxicity characteristic leaching procedure. Environmental Geochemistry and Health 28(1–2): 73–78.
- US EPA (1997) Exposure factors handbook. EPA/600/P-95/002F. Washington, DC: Environmental Protection Agency, Office of Research and Development.
- BMEPRI (2007) Guidance of Site Environmental Assessment. Municipal Environmental Protection Bureau, Beijing.
- Peng C, Chen WP, Liao XL, Wang ME, Ouyang ZY, et al. (2011) Polycyclic aromatic hydrocarbons in urban soils of Beijing: status, sources, distribution and potential risk. Environmental Pollution 159: 802–808.
- Calabrese EJ, Kostecki PT, Gilbert CE (1987) How much dirt do children eat? An emerging environmental health question. Comments Toxicol 1: 229–241.
- Shi GT, Chen ZL, Bi CJ, Wang L, Teng JY, et al. (2011) A comparative study of health risk of potentially toxic metals in urban and suburban road dust in the most populated city of China. Atmospheric Environment 45: 764–771.
- US EPA (2010) Region 9, Regional Screening Levels Available online at. http:// www.epa.gov/region9/superfund/prg/index.html.
- Ostapczuk P, Valenta P, Rützel H, Nürnberg HW (1987) Application of differential pulse anodic stripping voltammetry to the determination of heavymetals in environmental samples. Science of the Total Environment 60: 1–16.
- US EPA (2007) Available: http://www.epa.gov/superfund/bioavailability/bio\_ guidance.pdf.
- US EPA (2001) Risk Assessment Guidance for Superfund: Volume III d Part A, Process for Conducting Probabilistic Risk Assessment. US Environmental Protection Agency, Washington, D.C. EPA 540-R-02-002.
- GB 15618-11995. Available: http://www.nbepb.gov.cn/UploadFiles/lan2/ 200575165235193.pdf.
- Wang XS, Qin Y, Chen YK (2007) Leaching Characteristics of Arsenic and Heavy Metals in Urban Roadside Soils Using a Simple Bioavailability Extraction Test. Environmental Monitoring and Assessment 129(1–3): 221–226.
- Tong STY, Lam KC (2000) Home sweet home? A case study of household dust contamination in Hong Kong. Science of the Total Environment 256: 115–123.
- Tanner PA, Ma HL, Yu PKN (2008) Fingerprinting metals in urban street dust of Beijing, Shanghai and Hong Kong. Environmental Science & Technology 42(19): 7111–7117.
- Sun YB, Zhou QX, Xie XK, Liu R (2010) Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China. Journal of Hazardous Materials 174(1–3): 455–462.
- Nriagu JQ (1988) A silent epidemic of environmental metal poisoning? Environmental Pollution 50: 139–161.
- Mehmet Y (2006) Comprehensive comparison of trace metal concentrations in cancerous and non-cancerous human tissues. Current Medicinal Chemistry 13(21): 2513–2525.
- Han YM, Du PX, Cao JJ, Posmentier ES (2006) Posmentier, Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. Science of the Total Environment 355: 176–186.
- Yeung ZLL, Kwok RCW, Yu KN (2003) Determination of multi-element profiles of street dust using energy dispersive X-ray fluorescence (EDXRF). Applied Radiation and Isotopes 58(3): 339–346.