



Identifying dust as the dominant source of exposure to heavy metals for residents around battery factories in the Battery Industrial Capital of China

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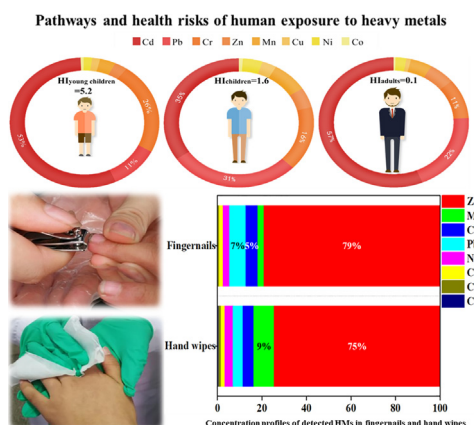
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HIGHLIGHTS

- Hand wipes and fingernails were collected from residents living around battery factories.
- Human exposure to heavy metals was found to be negatively correlated with age.
- Dust might be the main source of human exposure to heavy metals, especially for young children.
- Apparent non-carcinogenic risks were observed, with Cd, Cr and Pb as dominant contributors.

GRAPHICAL ABSTRACT



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ABSTRACT

Heavy metals (HMs) are constantly released into the environment during the production and use of batteries. Battery manufacturing has been ongoing for over six decades in the "Battery Industrial Capital" (located in Xinxiang City) of China, but the potential exposure pathways of residents in this region to HMs remain unclear. To clarify the exposure pathways and health risk of human exposure to HMs, hand wipe samples ($n=82$) and fingernail samples ($n=36$) were collected from residents (including young children (0–6 years old), children (7–12 years old) and adults (30–60 years old)) living around battery factories. The total concentrations of the target HMs (Zn, Mn, Cu, Pb, Ni, Cr, Cd, Co) in hand wipes ranged from 133 to 8040 $\mu\text{g}/\text{m}^2$, and those in fingernails ranged from 9.7–566 $\mu\text{g}/\text{g}$. HM levels in the hand wipe and fingernail samples both decreased with age, and higher HM levels were observed for males than females. The HM composition profiles in these two matrices represented a high degree of similarity, with Zn as the predominant element, and thus, oral ingestion and dermal exposure via dust were expected to be the most important HM exposure pathways for residents in this region. The non-carcinogenic risks (HQs) from dermal and oral ingestion exposure to Cd, Cr, and Pb were higher than those of the other five elements for all three populations, and the HQ_{derm} of Cd for young children was 2.1 ($HQ_{\text{oral}}=0.6$). Moreover, the hazard index (HI) values of $\sum_8\text{HMs}$ for young children ($HI_{\text{total}}=5.2$, $HI_{\text{oral}}=2.0$,

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$HI_{\text{dermal}}=3.2$) and children ($HI_{\text{total}}=1.6$, $HI_{\text{oral}}=1.3$, $HI_{\text{dermal}}=0.3$) exceeded the safe threshold (1.0). Therefore, young children and children should be prioritized for protection from HM pollution, and more attention should be paid to young children's dermal exposure to Cd in this region.

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1. Introduction

Heavy metals (HMs) are ubiquitous in the environment and can adversely impact human respiratory function, pulmonary function, and intellectual function throughout life (Madrigal et al., 2018; Zeng et al., 2016). HMs can accumulate in tissues and organs of the human body and are difficult to metabolize. For example, Pb can accumulate in the human brain, causing neurological diseases, and may also induce heart cerebrovascular disease; Ni may cause chronic lung lesions (e.g., idiopathic pulmonary fibrosis); the carcinogenic HMs including Cd, Cr, Ni and Pb can induce cancer. Hence, human exposure to HMs and the corresponding health risks have attracted continuous attention (Anyanwu et al., 2018; Koedrith et al., 2013; Zahra and Chemistry, 2017).

Humans are exposed to HMs through near-field exposure pathways, e.g., non-dietary dust ingestion, and far-field exposure pathways, e.g., food consumption (Li et al., 2019). Previous studies indicated that food ingestion is the primary exposure pathway for humans living near a typical HM-contaminated area due to the tendency for food self-sufficiency of local people (Cao et al., 2014; Cao et al., 2015; Du et al., 2019). However, a recent study from a fourth-tier city in China evaluated the patterns of human exposure to HMs through multiple pathways using various samples, including food, drinking water, soil, dust, and airborne particles (Zhang et al., 2019), indicating that the levels of HMs in daily food were low and inhalation exposure via airborne particles has become the main HM exposure pathway. Similarly, several other recent studies have also highlighted the significance of environmental matrices such as dust and atmospheric particles as significant HM vectors, and human exposure to HMs via these matrices should catch more concern (Cotter-Howells and Thornton, 1991; Day et al., 2007).

Dust is one of the most important carriers of HMs and has a smaller particle size than soil (Pan et al., 2017; Sutherland, 2003). HMs in dust can easily enter the human body by ingestion, inhalation and dermal absorption and can therefore contribute to human exposure to HMs. HM pollution in street dust (Glorennec et al., 2012; Hou et al., 2019) and indoor dust (Barrio-Parra et al., 2018; Cotter-Howells and Thornton, 1991) has increased dramatically in urban environments as a result of rapid urbanization and industrialization during the last few decades; such pollution has been extensively studied all over the world in recent years (Duan et al., 2016; Hu et al., 2020; Li et al., 2014). Almost all these studies evaluated human exposure to HMs using settled dust samples; however, a few studies have been conducted using the skin wipe approach, which has recently been applied to measure the contamination levels of chemicals on the human skin surface, which can reflect the characteristics of human exposure to contaminants more accurately than settled dust can (Cao et al., 2018; Cao et al., 2019b; Liu et al., 2017c; Taylor et al., 2013). Moreover, skin wipes, e.g., hand wipes, may be a better matrix than settled dust because they are easy to collect and can reflect integrated exposure from multiple environments and the effects of personal habits (e.g., touching and hand washing frequency) (Liu et al., 2018).

For long-term biomonitoring and understanding the adverse effects of HMs, human fingernails have been used as internal exposure indicators to HMs in several studies (Hussein Were et al., 2008; Parizanganeh et al., 2014; Wongsasuluk et al., 2018). On the one hand, concentrations of HMs in nails have been reported to be orders of magnitude higher than those in body fluids and other accessible tissues (Sukumar and Subramanian, 2007). On the other hand, as bio-indicators of HMs,

nails have distinct advantages because they can be collected, transported and stored easily and inexpensively. Thus, nails are more feasible than other matrices for the assessment of human retrospective exposure to HMs, and a growing number of studies have used human nails as internal indicators to explore HM levels in the human body (Gutierrez-Gonzalez et al., 2019; Hussein Were et al., 2008; Parizanganeh et al., 2014; Wongsasuluk et al., 2018).

Research concerning human exposure to HMs has been focused on people living in metropolises and industrial areas, such as coal and metal mines and coke plants (Augustsson et al., 2016; Du et al., 2019; Saha et al., 2017). In addition to these hotspots, battery factories are also significant HM emission source, and HMs can be released to the environment during the manufacturing of batteries. However, human exposure to HMs around battery factories have only been considered in a few studies (Cai et al., 2019; Johnston et al., 2019; Liu et al., 2017a; Wu et al., 2020). Although the battery industry is now developed in China, the HM exposure characteristics of people living near battery factories have rarely been explored, and relevant data are rather limited. Because the adverse health effects of HMs and their environmental pollution are well known by the Chinese government and the public, strict measures have been taken in China to prevent human exposure to HMs, especially through the food consumption pathway. Therefore, the main exposure pathways and relevant health risks from HMs for residents living in battery manufacturing areas in China are in urgent need to be clarified.

To fill these gaps, taking Xinxiang, the "Battery Industrial Capital" of China, as an example, this study analysed HMs (Zn, Mn, Cu, Pb, Ni, Cr, Cd, Co) in hand wipe and fingernail samples collected from young children, children and adults living around battery factories in this study. The main objectives were to 1) investigate the contamination characteristics of HMs in hand wipes and fingernails, as well as the potential health risk; 2) explore the association between HM occurrence in fingernail and hand wipe samples and the potential influencing factors of human exposure to HMs; and 3) illustrate the main source and pathway of human exposure to HMs in this region. The results of this study provide significant implications for local governments to conduct effective measures to ensure the health of local populations.

2. Materials and methods

2.1. Sampling information

The samples were collected in rural areas around battery factories located in Xinxiang, Henan province, a medium-sized city in central China, where more than 500 battery enterprises of all sizes are distributed, and all types of batteries, including lead-acid batteries, lithium batteries, and nickel-cadmium batteries have been manufactured liberally for more than 60 years. In this region, residents have been forbidden to grow crops on the local land because wheat produced in this region was found to be seriously contaminated with Cd several years ago (He, 2012; Jiang et al., 2020). All these policies help to ensure that food items consumed by residents in this region are safe and not contaminated by HMs. A total of 82 hand wipe samples (47 males, 35 females) and 36 fingernail samples (15 males, 21 females) were collected in the spring of 2018. To explore the influence of age, the sample providers were divided into three age groups, i.e., young children (0–6 years old; $n=34$ for hand wipes, $n=10$ for fingernails), children (7–12 years old; $n=25$

for hand wipes, $n=15$ for fingernails), and adults (30–60 years old; $n=23$ for hand wipes, $n=11$ for fingernails), and the detailed sampling information is presented in the Supporting Information (SI) Table S1. Participants were required not to wash their hands for at least 2 h prior to sampling, and ethical approval for this investigation was obtained from the Research Ethics Committee of Henan Normal University.

2.2. Sampling method

Hand wipe and fingernail samples were collected from young children and children at a local primary school, and adult hand wipe and fingernail samples were collected in the village. Ghost wipes were used to collect hand wipe samples, similar to previous studies (Taylor et al., 2015; Taylor et al., 2013). For each participant, the entire hand surface of two hands was wiped two times using one surface of a Ghost wipe and then wiped two additional times using the other side (Liu et al., 2017b). The surface area of human hands was referenced from Exposure Factors Handbook of Chinese Population (Wang and Duan, 2016; Zhao and Duan, 2013; Zhao and Duan, 2016). The Ghost wipes were then put back into a 60-mL, pre-cleaned (combusted at 450 °C for 6 h) brown glass jar. All 82 samples were stored in a refrigerator at -4 °C until analysis. Fingernails were cut from fingers with sterilized stainless steel scissors. A total of 36 fingernail samples were collected, and all samples were kept in plastic bags and stored in a -4 °C refrigerator prior to analysis. Relevant information on the age and sex of all participants was also recorded during sampling.

2.3. Sample analysis and detection

2.3.1. Hand wipe samples

Samples were dried at 40 °C for 1 h in a dryer to remove moisture. After drying, each sample was placed in a 100-mL polytetrafluoroethylene tank. A total of 8 mL of nitric acid and 2 mL of hydrofluoric acid were added in sequence, and the tanks were kept for 6 h at room temperature to prevent excessive foaming. Then, the samples were digested in a microwave digestion system for 10 min at 130 °C, then 10 min at 150 °C, followed by 15 min at 180 °C, and finally 15 min at 210 °C. After cooling, the extract was filtered with a 0.45 μ m polyethylene filter and dissolved in 50 mL deionized water (Cao et al., 2018). Finally, the HM concentrations of the samples were determined by inductively coupled plasma mass spectrometry (ICP-MS) similar to our former researches (Cao et al., 2018).

2.3.2. Fingernail samples

All fingernails were washed 3 times with detergent and deionized water with ultrasonic cleaning assistance for 10 min to remove the surface dirt. Then, the samples were kept in labelled vials and dried at 60 °C to a constant weight. After that, all samples were accurately weighed three times and transferred into 100-mL polytetrafluoroethylene tanks, and 6 mL of nitric acid was added to the tanks. Samples were predigested for 1 h at 100 °C and held for 5 min. Then, the samples were digested in a microwave digestion system for 7 min at 120 °C, then 10 min at 160 °C, and finally 30 min at 190 °C (Mehra and Juneja, 2005). After cooling, the extracts were filtered with a 0.45 μ m polyethylene filter and dissolved in 50 mL deionized water, and ICP-MS was used to detect the concentration of HMs.

2.4. Quality assurance and quality control

During the sampling process, all the items needed for sampling were regularly placed in an enclosed box to ensure that the sampling process was orderly and pollution-free. One standard reference material (Geochemistry reference matter GSS-2), one reagent blank (for fingernails) or one blank Ghost wipe was analysed per 10 samples to assure the accuracy and repeatability of the analysis procedure. For these 12 standard samples, the recoveries of all elements were in the range of 80% to 120%,

and the relative standard deviations were 8.5%, 7.6%, 7.4%, 7.3%, 7.0%, 5.6%, 5.1%, and 4.1% for Cd, Cu, Ni, Pb, Mn, Cr, Zn, and Co, respectively. All of the blanks ($n=12$) were below the detection limit for all elements. All tubes and bottles were previously soaked overnight in HNO_3 (20%) and rinsed thoroughly with distilled water before use. The limit of quantification (LOQ) was defined as 10 times the standard deviation of 10 runs of blank measurements, and the LOQs for Cd, Cu, Ni, Pb, Mn, Cr, Zn, and Co ranged from 0.1 to 0.6 $\mu\text{g/L}$.

2.5. Statistical analysis

Statistical analyses were performed using the SPSS statistical software package, version 17.0 (SPSS Inc.). The Shapiro-Wilk test was used to examine whether the data were normally or log-normally distributed. The results revealed that all data were not log-normally distributed. As a consequence, nonparametric methods were used in the bivariate comparisons (Mann-Whitney U test), and Spearman's rank correlation tests were used to investigate bivariate correlations. For multivariate comparisons of HMs in hand wipes and fingernails, we used the Kruskal-Wallis test and principal component analysis (PCA).

2.6. Exposure models and parameters

Human exposure to HMs via dust particle adhered to hand surfaces occurs through two main pathways: dermal uptake and oral ingestion through hand-to-mouth contact. The human exposure dose are expressed in a daily average dose (DAD, $\mu\text{g/kg}\cdot\text{BW}\cdot\text{d}$) in this study. Oral ingestion exposure through hand-to-mouth contact was calculated from Eq. (1) (Liu et al., 2018). The dermal uptake doses of HMs can be estimated from Eq. (2) (Liu et al., 2018). In the equations, C_H ($\mu\text{g}/\text{m}^2$) is the concentration of the HMs on hand wipes; SA1 (cm^2/event) is the skin area contacted in each hand-to-mouth event, SA1 is 10% of SA2 (Stapleton et al., 2008); SA2 (cm^2) is the hand area; F (times/h) is the number of hand-to-mouth events per day; TE (%) is the transfer efficiency of HMs in hand-to-mouth event; ET (hours/d) is the exposure time; N (times/d) is the daily exposure frequency; BW (kg) is body weight; ABS (unitless) is the absorption factor. The parameter values for each population of people are shown in Table S2.

$$\text{DAD}_{\text{oral}} = \frac{C_H \times \text{SA1} \times F \times TE \times ET}{\text{BW}} \quad (1)$$

$$\text{DAD}_{\text{derm}} = \frac{C_H \times \text{SA2} \times \text{ABS} \times ET \times N}{\text{BW}} \quad (2)$$

2.7. Health risk assessment

The non-carcinogenic risk was evaluated by means of the hazard quotient (HQ) and hazard index (HI) (Cao et al., 2019a). HI corresponds to the sum of the individual HQs calculated for each element in the study. If the value of HI is ≤ 1 , it is believed that there is no significant risk of non-carcinogenic effects. If the value of HI is > 1 , it means that non-carcinogenic effects may occur, and the effects probably increase with an increasing value of HI. The non-carcinogenic risks via dermal contact and oral ingestion were estimated by the following equations (Eqs. (3) and (4)) (Cao et al., 2019a). The reference doses (RfDs) of heavy metals for the two exposure pathways ($\mu\text{g/kg}\cdot\text{BW}\cdot\text{d}$) are shown in Table S3.

$$Q = \frac{\text{DAD}_{\text{derm}}}{\text{RfD}_{\text{derm}}} + \frac{\text{DAD}_{\text{oral}}}{\text{RfD}_{\text{oral}}} \quad (3)$$

$$\text{HI} = \sum \text{HQ}_i \quad (4)$$

Table 1
Concentrations of detected HMs in hand wipes ($\mu\text{g}/\text{m}^2$) and fingernails ($\mu\text{g}/\text{g}$).

Element	Hand wipes ($\mu\text{g}/\text{m}^2$)						Element	Fingernails ($\mu\text{g}/\text{g}$)					
	Max	Min	Geomean	Mean	Median	CV		Max	Min	Geomean	Mean	Median	CV
Pb	486	3.0	43.7	79.1	47.5	1.21	Pb	130	0.2	6.3	15.5	8.3	1.54
Cr	408	0.0	17.4	43.9	28.8	1.50	Cr	8.0	0.1	1.4	2.1	1.5	0.86
Ni	318	1.4	37.4	67.8	51.0	0.93	Ni	29.7	0.2	2.4	4.5	2.6	1.36
Mn	736	4.4	90.9	160	161	0.86	Mn	28.6	0.2	2.3	4.0	2.4	1.25
Cu	519	1.7	48.9	99.2	79.0	1.05	Cu	22.7	0.4	4.6	6.2	5.5	0.75
Zn	7080	59.5	744	1320	956	1.07	Zn	507	7.3	67.2	98.6	81.3	0.93
Cd	93.0	0.0	10.1	20.2	16.0	0.97	Cd	5.7	0.0	0.6	1.1	0.8	1.02
Co	75.0	0.0	5.4	10.5	9.2	1.01	Co	1.7	0.0	0.1	0.2	0.1	1.48
$\sum_8\text{HMs}$	8040	133	1130	1810	1450	0.91	$\sum_8\text{HMs}$	566	9.7	93.1	132	118	0.82

CV: Coefficient of Variation.

3. Results and discussion

3.1. HM levels and profiles in hand wipes and fingernails

The concentrations and profiles of the 8 HMs in all hand wipes and fingernails are summarized in Table 1 and Fig. 1. The concentrations of $\sum_8\text{HMs}$ in the hand wipes and fingernails ranged from 133 to 8040 $\mu\text{g}/\text{m}^2$ and 9.7 to 566 $\mu\text{g}/\text{g}$, with geometric means (GMs) of 1130 $\mu\text{g}/\text{m}^2$ and 93.1 $\mu\text{g}/\text{g}$, respectively. For hand wipe samples, the concentrations of HMs ranked in decreasing order as follows: $\text{Zn} > \text{Mn} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Cr} > \text{Cd} > \text{Co}$, with GM values of 744, 90.9, 48.9, 43.7, 37.4, 17.4, 10.1, 5.4 $\mu\text{g}/\text{m}^2$, respectively, accounting on average for approximately $75 \pm 87\%$, $9 \pm 8\%$, $5 \pm 6\%$, $4 \pm 6\%$, $4 \pm 4\%$, $2 \pm 4\%$, $1 \pm 1\%$, and $1 \pm 1\%$ of $\sum_8\text{HMs}$. The concentrations of HMs in the fingernail samples presented a slightly different order of Zn (67.2 $\mu\text{g}/\text{g}$) $>$ Pb (6.3 $\mu\text{g}/\text{g}$) $>$ Cu (4.6 $\mu\text{g}/\text{g}$) $>$ Ni (2.4 $\mu\text{g}/\text{g}$) $>$ Mn (2.3 $\mu\text{g}/\text{g}$) $>$ Cr (1.4 $\mu\text{g}/\text{g}$) $>$ Cd (0.6 $\mu\text{g}/\text{g}$) $>$ Co (0.1 $\mu\text{g}/\text{g}$), contributing average proportions of $72 \pm 84\%$, $7 \pm 22\%$, $5 \pm 4\%$, $3 \pm 6\%$, $2 \pm 5\%$, $2 \pm 2\%$, $1 \pm 1\%$, and $0 \pm 0\%$ to $\sum_8\text{HMs}$, respectively.

Overall, similar HM profiles were observed in the two media, with Zn and Cu as the most abundant components (Fig. 1). Most HMs contributed similar proportions to $\sum_8\text{HMs}$ in these two media; however,

Mn contributed a much higher proportion to $\sum_8\text{HMs}$ in hand wipes (9%) than in fingernails (2%) ($p=0.000$). These data indicated that for most HMs, dust might be a significant human exposure source, while for Mn, other potential pathways might contribute more to human internal exposure. Our result was consistent with several former studies that found that the human exposure pathway to Mn was generally different from that for other HMs. For example, Zhang et al. (Zhang et al., 2019) indicated that human exposure to Mn was largely attributed to diet (72%), while exposure to HMs such as Zn, Pb, and Cd was ascribed to inhalation. Gutierrez-Gonzalez et al. also concluded that Mn in toenails was highly correlated with the Mn content in drinking water and respirable airborne particles, quite different from other elements (Gutierrez-Gonzalez et al., 2019).

3.2. Influence of age on HM exposure

The GM of $\sum_8\text{HMs}$ in the hand wipes of young children (2180 $\mu\text{g}/\text{m}^2$, $n=34$) was significantly higher than those of children (1100 $\mu\text{g}/\text{m}^2$, $n=25$, and $p=0.000$) and adults (310 $\mu\text{g}/\text{m}^2$, $n=23$, and $p=0.000$) (Table S4; Table S6). As shown in Fig. 2, great age-based

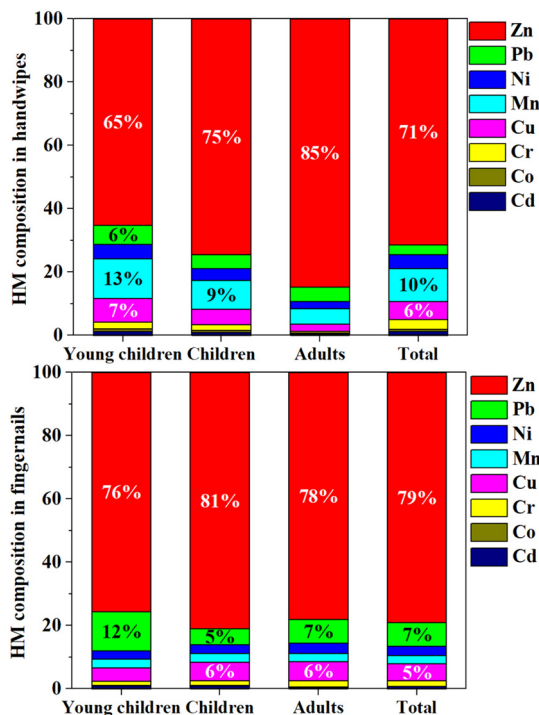


Fig. 1. Concentration profile of detected HMs in hand wipes and fingernails of young children, children, and adults.

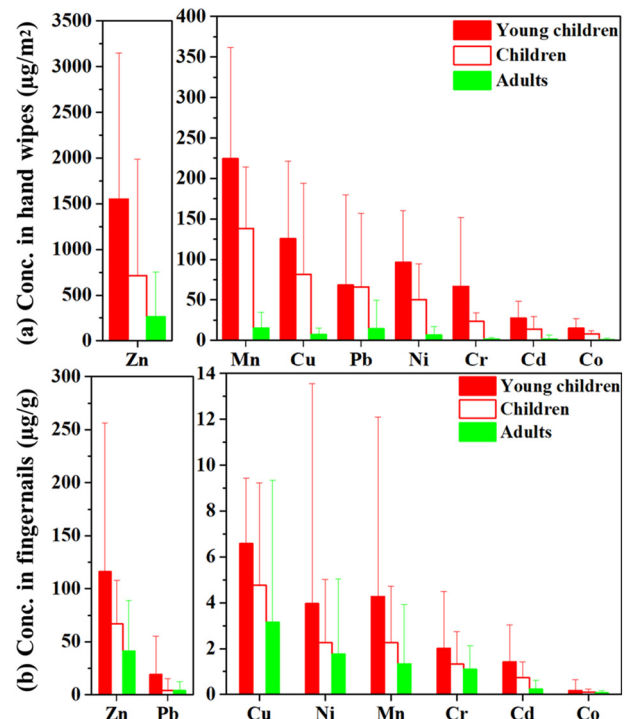


Fig. 2. Concentrations of detected HMs in hand wipes (a) and fingernails (b) of young children ($n=34$; $n=10$), children ($n=25$; $n=15$) and adults ($n=23$; $n=11$).

variations were found for most elements in hand wipes among the three populations, especially between young children and adults. In terms of Zn, the GM load on hands was 1550 $\mu\text{g}/\text{m}^2$ for young children, 2.2 times and 715 times higher than those for children and adults, respectively. The GM loads of Cd, Cr, Pb, Ni, Mn and Cu on hands were 27.5, 66.7, 68.3, 96.2, 126, and 224 $\mu\text{g}/\text{m}^2$ for young children, 1.9, 2.9, 1.0, 1.9, 1.5 and 1.6 times and 14.2, 23.3, 65.9, 50.5, 82.0 and 138 times higher than those for children and adults. Unconventionally, no significant difference between young children (68.3 $\mu\text{g}/\text{m}^2$) and children (65.9 $\mu\text{g}/\text{m}^2$) was found for Pb ($p=0.529$) (Table S6). Young children and children showed much higher HM loads on hands than did adults, which might be attributed to their distinct behavioural activities, e.g., frequent contact with all kinds of surfaces and settled dust (Miller et al., 2002; Van den Eede et al., 2015). Conversely, the hand wipes of adults, presenting the lowest HM levels, were in accordance with better hygienic habits and a lower risk of contact with dust.

Compared with the limited literature data (Table S7), the Pb level in hand wipes of young children in this study (68.3 $\mu\text{g}/\text{m}^2$) was much higher than that of undergraduates from the urban area of Xinxiang, China (6.4 $\mu\text{g}/\text{m}^2$) (Cao et al., 2018); slightly lower than that of 2-year-old children from the urban area of Birmingham, UK (158 $\mu\text{g}/\text{m}^2$) (Davies et al., 1990); much lower than that of children from the mining village of Winstar, UK (367 $\mu\text{g}/\text{m}^2$) (Cotter-Howells and Thornton, 1991); and much lower than that of South Australia children after playing in a playground near the Port Pirie lead smelter (the world's third largest lead-zinc smelter) (253–10,227 $\mu\text{g}/\text{m}^2$) (Taylor et al., 2013; Taylor et al., 2014).

The Cr level in hand wipes of young children in this study was 66.7 $\mu\text{g}/\text{m}^2$, which was much higher than that of undergraduates from the urban area of Xinxiang, China (4.9 $\mu\text{g}/\text{m}^2$) (Cao et al., 2018) and similar to those of Swedish carpenters (70 $\mu\text{g}/\text{m}^2$) (Liden et al., 2008), Swedish dental technicians (60 $\mu\text{g}/\text{m}^2$) (Kettelarij et al., 2016), and Swedish healthy participants (4.8–270 $\mu\text{g}/\text{m}^2$) (Erfani et al., 2017), while much lower than those of Swedish locksmiths (450 $\mu\text{g}/\text{m}^2$) (Liden et al., 2008), Danish adults who work with metals and leather (100–2000 $\mu\text{g}/\text{m}^2$) (Bregnbak et al., 2016), and cemented tungsten carbide workers (375 $\mu\text{g}/\text{m}^2$) from the southern United States (Day et al., 2009). The Cr level of children in this study (23.3 $\mu\text{g}/\text{m}^2$) was comparable with those of Swedish cashiers (30 $\mu\text{g}/\text{m}^2$) and secretaries (20 $\mu\text{g}/\text{m}^2$) (Liden et al., 2008).

To the best of our knowledge, participants in most studies focused on determining HM exposure associated with dust on hands generally live in highly HM-contaminated areas. Notably, HM doses in hand wipes might be strongly influenced by behavioural and individual differences (e.g., age- and population-dependent human exposure factors) and dust loads on hands but are not solely determined by the HM contamination level in dust (Glorennec et al., 2012). Hence, the elevated levels of HMs found in hand wipes generally reflect a combination of heavy HM pollution levels in dust and poor personal hygienic habits. Although related research is particularly limited, through the above comparison with the available literature data, it is generally concluded that the young children in the present study suffered a much higher risk of exposure to Cr and Pb through dust than did other populations, while the exposure risks for children and adults in this region were not prominent. However, for Co and Ni, the three populations in this study suffered lower exposure risks than did other subjects in the related literature (Table S7). Nevertheless, according to the literature, data on Cd, Cu, Mn and Zn in hand wipes are scarce, and we cannot compare the levels of Cd, Cu, Mn and Zn in hand wipes with literature data, which makes it difficult to evaluate the contamination levels of these elements in hand wipes in this study.

For fingernail samples, while the $\sum_8\text{HM}$ concentrations were higher for young children (177 $\mu\text{g}/\text{g}$, $n=10$) and children (86.3 $\mu\text{g}/\text{g}$, $n=15$) than adults (57.7 $\mu\text{g}/\text{g}$, $n=11$), no significant differences compared to the concentrations in hand wipes were observed considering the relatively small sample sizes ($p>0.05$), and similar patterns were also

reported in a former study (Mehra and Juneja, 2004) (Table S5; Table S6). Specifically, the concentrations of most elements in fingernails were ~ 2 times higher (except for Pb, which was 5 times higher) for young children than for children, and the HM concentrations for children was generally comparable with those for adults (except for Cd, which was ~ 3 times higher in children), indicating compared with adult exposure levels, the internal exposure levels of young children and children to Cd and Pb were distinct among the eight HMs.

To clarify the internal exposure levels to HMs of residents in this region, the data in this study were adequately compared with the literature (Table S8). Specifically, the Pb level in fingernails of young children in this study (19.2 $\mu\text{g}/\text{g}$) was much higher than those of smokers from Mansoura, Egypt (4.75 $\mu\text{g}/\text{g}$) (Mortada et al., 2002), adults from Katowice, the “coal capital” of Poland (11.2 $\mu\text{g}/\text{g}$) (Nowak and Chmielnicka, 2000), adults from an agricultural polluted area in Thailand (9.57 $\mu\text{g}/\text{g}$) (Wongsasuluk et al., 2018), businessmen from New Delhi, India (9.8 $\mu\text{g}/\text{g}$) (Sukumar and Subramanian, 2007), victims of As exposure from West Bengal, India (11.0 $\mu\text{g}/\text{g}$) (Samanta et al., 2004), Chinese centenarians (1.33 $\mu\text{g}/\text{g}$) (Li et al., 2011) and northern Swedish adults (1.06 $\mu\text{g}/\text{g}$) (Rodushkin and Axelsson, 2000); similar to the Pb levels in fingernails of children from typical industrial cities in Kenya (25.9 $\mu\text{g}/\text{g}$) (Hussein Were et al., 2008) and adults from Pakistan (20.1 $\mu\text{g}/\text{g}$) (Batool et al., 2015); but much lower than those of Indian smokers (92.3 $\mu\text{g}/\text{g}$), non-vegetarians (50.6 $\mu\text{g}/\text{g}$), and liquor users (33.7 $\mu\text{g}/\text{g}$) subjected to persistent exposure in battery factories and roadway workshops (Mehra and Juneja, 2005).

The Cr level in fingernails of young children in this study was 2.0 $\mu\text{g}/\text{g}$, which was much higher than those of adults from northern Sweden (0.76 $\mu\text{g}/\text{g}$) (Rodushkin and Axelsson, 2000) and Chinese centenarians (0.82 $\mu\text{g}/\text{g}$) (Li et al., 2011); higher than those of businessmen from New Delhi (1.4 $\mu\text{g}/\text{g}$) (Sukumar and Subramanian, 2007) and adults from LHR city, Pakistan (1.0 $\mu\text{g}/\text{g}$) (Batool et al., 2015); and much lower than those of adults from Katowice, Poland (18.1 $\mu\text{g}/\text{g}$) (Nowak and Chmielnicka, 2000), and Indian smokers (156 $\mu\text{g}/\text{g}$), non-vegetarians (136 $\mu\text{g}/\text{g}$), and liquor users (86.3 $\mu\text{g}/\text{g}$) subjected to persistent exposure in battery factories and roadway workshops (Mehra and Juneja, 2005).

Moreover, the concentration of Cd in fingernails of young children in the present study was 1.4 $\mu\text{g}/\text{g}$, which was much higher than those of adults from an agricultural polluted area in Thailand (0.024 $\mu\text{g}/\text{g}$) (Wongsasuluk et al., 2018), adults from an area with high natural background radiation in Serbia (0.063 $\mu\text{g}/\text{g}$) (Sahoo et al., 2015), Chinese centenarians (0.023 $\mu\text{g}/\text{g}$) (Li et al., 2011), northern Swedish adults (0.061 $\mu\text{g}/\text{g}$) (Rodushkin and Axelsson, 2000), victims of As exposure from West Bengal, India (0.32 $\mu\text{g}/\text{g}$) (Samanta et al., 2004), and children from a Kenyan industrial area (0.82 $\mu\text{g}/\text{g}$) (Hussein Were et al., 2008); similar to those of smokers from Mansoura, Egypt (1.44 $\mu\text{g}/\text{g}$) (Mortada et al., 2002), adults from Katowice, Poland (1.2 $\mu\text{g}/\text{g}$) (Nowak and Chmielnicka, 2000), and Indian non-vegetarian adults (1.31 $\mu\text{g}/\text{g}$) (Mehra and Juneja, 2005); and slightly lower than those of adults from LHR city, regarded as the most polluted area in Pakistan (1.7 $\mu\text{g}/\text{g}$) (Batool et al., 2015), New Delhi businessmen (2.1 $\mu\text{g}/\text{g}$) (Sukumar and Subramanian, 2007) and Indian adults including smokers (3.56 $\mu\text{g}/\text{g}$) and liquor users (2.01 $\mu\text{g}/\text{g}$) subjected to persistent exposure in battery factories and roadway workshops (Mehra and Juneja, 2005).

Conversely, the levels of Zn, Cu, Mn, Ni, and Co in fingernails of young children in this study (Zn: 116, Cu: 6.6, Mn: 4.3, Ni: 4.0, Co: 0.2 $\mu\text{g}/\text{g}$) were on the same order of magnitude as the literature data or relatively low compared with most of the literature (Table S8). These data indicated that young children in this area had higher internal exposure levels to Cd, Cr and Pb, which can derive from battery manufacturing. In the literature, elevated Cd, Cr and Pb emissions have been attributed to intensive battery production (Liu et al., 2017a; Yuan et al., 2019; Zhang et al., 2020). The lower levels of other HMs, including Zn, Cu, Mn, Ni, and Co, in fingernails could be due to a lack of contamination sources, e.g., traffic and industrial activities, in this region (Yang et al., 2016).

Generally, humans are exposed to HMs via diet, inhalation, dust ingestion and dermal uptake, and HMs can accumulate in the human body with age. Theoretically, if humans are predominantly exposed via diet or inhalation, the internal levels of HMs in humans should be proportional to age, similar to observed data for, e.g., polychlorinated biphenyls (PCBs) (Rylander et al., 1997; Thomsen et al., 2007). However, this study found that HM levels in fingernails, as an indicator of internal biological exposure, were negatively correlated with age, similar to the levels in hand wipes, which implies that exposure to dust, e.g., via hand-to-mouth contact, was possibly the dominant HM exposure source for residents living in this region. Otherwise, as HM contamination in soils of this region is well known and planting crops has been forbidden in this region, diet is expected to be a negligible human exposure pathway for HMs, similar to the findings of a recent study (Zhang et al., 2019). Our results verified that dust has become the most important human exposure source of HMs, which should arouse more concern from the government and residents in this region. Therefore, the higher HM levels here in young children and children than in adults may mainly be attributed to dust exposure. Different lifestyles and activities, including frequent contact with dust, hand-to-mouth contact, and not fully developed hygienic habits, might be the predominant reasons for the increased internal HM levels of young children and children. To further decrease human exposure to HMs, especially for young children and children in this region, measures and strategies related to decreasing dust exposure should be prioritized.

3.3. Influence of gender on HM exposure

Fig. 3 compares HM levels in hand wipe and fingernail samples between males and females. The Mann-Whitney *U* test was conducted to examine the influence of gender on HM concentrations (Table S9), and overall, no significant difference was observed between males ($1300 \mu\text{g}/\text{m}^2$ and $103 \mu\text{g}/\text{g}$, $n=47$ and $n=15$) and females ($938 \mu\text{g}/\text{m}^2$ and $86.9 \mu\text{g}/\text{g}$, $n=35$ and $n=21$) for $\sum_8\text{HMs}$ in both hand wipes ($p>0.05$) and fingernails ($p>0.05$) (Table S10; Table S11). Specifically, for hand wipe samples, Mn ($p=0.031$), Pb ($p=0.009$) and Cd ($p=0.019$) were significantly higher in males (119 , 57.8 , and $12.9 \mu\text{g}/\text{m}^2$) than in females (63.5 , 30.0 , and $7.3 \mu\text{g}/\text{m}^2$), whereas for the other five elements (Zn, Cu, Cr, Ni, and Co), no obvious gender differences were observed ($p>0.05$). For fingernail samples, although no significant differences were found, the concentrations of Zn, Cu, Mn, Cd, and Co were higher for males than for females ($p>0.05$), with GM values of 75.8 , 5.9 , 3.2 , 0.8 , and $0.1 \mu\text{g}/\text{g}$ for males, 1.2 , 1.5 , 1.7 , 1.6 , and 1.8 times higher than those for females, respectively, while Pb, Ni, and Cr presented higher concentrations of 7.1 , 2.6 and $1.5 \mu\text{g}/\text{g}$ for females ($p>0.05$), which were 1.4 , 1.1 and 1.2 times higher than those for males.

The differences could be attributed to the slightly different behaviour patterns between males and females. Males were generally found

to have more dust particles on their hands (24.2 mg) than females (17.8 mg) (Wang et al., 2015). For example, males may pursue more outdoor activities, e.g., playing or working, than females. On average, the levels of most HMs (Zn, Cu, Mn, Cd, and Co) in males were higher both in hand wipes and fingernails; these similarities also imply dust to be a dominant exposure source. However, for fingernails, higher concentrations of Pb, Ni, and Cr were found in females, which can be explained as follows. Females participate in more cooking activities than males. Studies have reported significant increases in indoor $\text{PM}_{2.5}$ levels and some HMs (e.g. Zn, Cu, Pb, Ni, and Cr) loaded in $\text{PM}_{2.5}$ from cooking activities. Fuel and cooking implements also release metals (e.g., Ni and Cr) during cooking activities (Li et al., 2015; Lu et al., 2019; See and Balasubramanian, 2008). Similar to results in previous studies from the U.S. and New Delhi, females also had higher Pb concentrations than males in shed deciduous teeth and nails collected from children living near a lead-acid battery smelter (Johnston et al., 2019) and adults living in urban areas (Sukumar and Subramanian, 2007). Moreover, according to the literature, Pb-contaminated soils can be an important contributor to household dust, and boys and girls have different soil Pb uptake patterns, which can cause females to be exposed to more Pb than males (Johnston et al., 2019).

3.4. Source and pathways of human exposure to HMs

Hand wipes are an indicator of external exposure, especially dust exposure, and fingernails are an indicator of internal exposure, reflecting integrated exposure. By analysing the correlation between HM occurrences in these two matrices, the human exposure pathways to HMs are illustrated as follows.

First, both in hand wipes and fingernails, significant correlations were found between most elements ($p<0.01$). Specifically, the Pb level was significantly correlated with Cd and Cu. The Cr level was significantly correlated with Cd, Co, Mn, and Ni; the Ni level was significantly correlated with Cd, Co, Cu, and Mn; the Mn level was significantly correlated with Cd, Co, Cu, and Zn; the Cu level was significantly correlated with Cd and Co; the Zn level was significantly correlated with Cd; and the Cd level was significantly correlated with Co (Table S12), indicating that HMs on human hands and fingernails might originate from the same exposure source, with dust as the most probable matrix. Moreover, according to the PCA results (Fig. S1), two similar factors were distinguished in both matrices. PCA1 for hand wipes and fingernails had heavy loadings of Cd, Co, Cr, Cu, Mn, Ni, and Zn. PCA2 showed a high loading of Pb, indicating dust to be a strong external source of residual HMs in fingernails. Furthermore, as discussed in the above sections, the 8 HMs shared similar composition profiles in hand wipe and fingernail samples, the concentrations of HMs showed a significant negative correlation with age, and males were generally exposed to more HMs. These differences can only be attributed to the different exposure patterns to dust of the three populations, considering that HM exposure via food might be similar between genders and among age groups. Overall, it is deduced that HMs in dust could be a significant source for human internal exposure to HMs in this region.

3.5. Exposure and health risk assessment

Based on the above analysis, we found that age is a major influencing factor for human exposure to HMs, while gender did not significantly affect human HM exposure. Thus, we calculated the HM exposure doses via oral ingestion and dermal uptake and related health risks for young children, children and adults, but a corresponding comparison between genders was not investigated. Generally, the GM ingestion doses of $\sum_8\text{HMs}$ for young children, children and adults via hand-to-mouth contact ($53.8 \mu\text{g}/\text{kg}\cdot\text{BW}\cdot\text{d}$, $32.5 \mu\text{g}/\text{kg}\cdot\text{BW}\cdot\text{d}$ and $0.5 \mu\text{g}/\text{kg}\cdot\text{BW}\cdot\text{d}$) were approximately 30, 180, and 2.5 times higher than the dermal uptake doses ($1.8 \mu\text{g}/\text{kg}\cdot\text{BW}\cdot\text{d}$, $0.2 \mu\text{g}/\text{kg}\cdot\text{BW}\cdot\text{d}$ and $0.1 \mu\text{g}/\text{kg}\cdot\text{BW}\cdot\text{d}$) (Fig. S2),

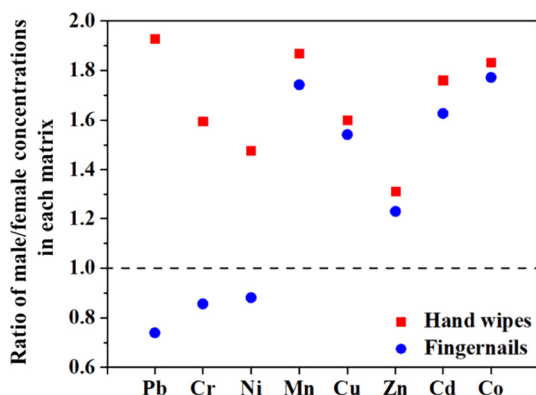


Fig. 3. Ratios of HM concentrations for males/females in hand wipes and fingernails.

indicating that young children had much higher HM exposure doses than children and adults and oral ingestion, rather than dermal uptake, was the dominant HM exposure route for all populations. The total GM daily average dose (DAD_{oral}) from oral ingestion among the diverse HMs decreased in the order of $Zn > Mn > Cu > Ni > Pb > Cr > Cd > Co$ for young children, $Zn > Mn > Cu > Pb > Ni > Cr > Cd > Co$ for children, and $Zn > Mn > Pb > Cu > Ni > Cr > Cd > Co$ for adults, among which the DAD_{oral} values of Zn and Mn were 35.5 and 5.1 $\mu g/kg \cdot BW \cdot d$ for young children, 18.5 and 3.6 $\mu g/kg \cdot BW \cdot d$ for children, and 0.4 and 0.02 $\mu g/kg \cdot BW \cdot d$ for adults, respectively. The order of the exposure doses to each HM for the three age groups via dermal uptake is similar to that of oral ingestion (Fig. S3).

Among these 8 HMs, Cd, Pb and Cr were the greatest contributors to the total human health risk (Fig. S4; S5). The HQ values of these three elements for the ingestion and dermal exposure pathways were 6.3×10^{-1} , 4.5×10^{-1} , and 5.1×10^{-1} and 2.1, 9.9×10^{-2} , and 8.5×10^{-1} for young children; 3.7×10^{-1} , 4.9×10^{-1} , and 2.0×10^{-1} and 2.0×10^{-1} , 1.8×10^{-2} , and 5.6×10^{-2} for children; and 2.4×10^{-3} , 6.1×10^{-3} , and 8.5×10^{-4} and 2.4×10^{-2} , 4.1×10^{-3} , and 4.3×10^{-3} for adults, respectively (Table 2). The HQ_{dermal} of Cd for young children (2.1) exceeded the threshold, implying the presence of non-cancer risks. In addition to depending on the exposure dose, the non-carcinogenic risk for HMs is also related to the toxicity or RfD value of the HMs. In this study, the toxicity of the eight HMs via dermal contact and ingestion decreased in the following order: $Cd > Cr > Pb > Mn > Ni > Cu > Co > Zn$ and $Cd > Cr > Pb > Ni \approx Co > Cu > Mn > Zn$, respectively (Table S3). For the two pathways, the exposure dose of Zn was highest among the eight HMs, but its non-carcinogenic risk was low, while the exposure doses of Cd, Cr and Pb were the highest due to their high toxicity and low RfD values.

In total, $\sum_8 HMs$ exhibited a higher HI for young children (5.2) than children (1.6) and adults (0.1) (Table 2), indicating that HMs posed a greater health risk to young children and children. According to the literature, it has been established that metal toxicity and absorption are elevated in children under six years of age compared to adults due to their not having fully developed nervous system and other organs (Hussein Were et al., 2008). Moreover, because the studied region is located in a rural area, the personal hygiene status of skin is relatively poor (e.g., there is a lower frequency of skin cleaning and higher load of dust on hands), which potentially increases the probability of human exposure to HMs, particularly for young children and children. Thus, we should pay more attention to HM exposure in young children and children in this region, and measures should be conducted to reduce HM pollution in dust, especially for Cd, Cr and Pb.

This study, to the best of our knowledge, has established an HM exposure database and age- and gender-based variation characteristics of HM exposure for residents around battery factories in China for the first time. The results highlight dust as a significant and even predominant contributor to human health risk from exposure

to HMs. Moreover, Cd, Cr, and Pb were found to be the HMs with the highest contamination levels, which is consistent with reports several years ago that wheat was polluted by Cd. All of this evidence indicates that diverse battery factories and battery manufacturing are the main source of HM pollution in this region. These findings will provide scientifically robust support for further facilitating the prevention and control of HM pollution and the abatement of HM emissions in the battery manufacturing industry in China. HM exposure levels, sources, routes, and health risk assessments can be combined to gain a better forecast of the HM influences on humans living near battery manufacturing facilities. However, on account of the difficulty of sample collection, due to limited cooperation, the sample size is relatively small in this pilot study, which may reduce the statistical power of the results. Variance during the sampling procedure was unavoidable, and it could bring about certain uncertainties in the results and conclusions of this study. Furthermore, samples collected at one time point are unable to represent residents' exposure to HMs over time. Additionally, dermal exposure risks were not fully estimated in the present study because the skin of only the hand, not the whole body, was considered. A more comprehensive and longitudinal study covering all types of environmental matrices including airborne particles, diet, and drinking water should be conducted to further clarify the exposure pathways and health risks to diverse HMs for residents in this region in the future.

4. Conclusions

This is the first study devoted to investigating the characteristics and influencing factors of human exposure to HMs in the "Battery Industrial Capital" of China. Generally, Zn presented the highest levels in both hand wipes and fingernails, and the HM levels in the two media were found to be affected significantly by age and human behaviour patterns, while gender had a weak effect on HM exposure. The levels of Cd, Cr and Pb in the fingernails of young children were higher than those of other relevant populations in most literature, and the levels of HMs in hand wipes from young children were much higher than those from children and adults. We first proposed that dust may be a dominant HM exposure source for residents near battery factories, and therefore, ingestion and dermal uptake via dust could be new dominant HM exposure pathways for residents in this area. The HI values of young children and children were 5.2 and 1.6, respectively, and that of adults was far below the safe level of 1, indicating that young children and children are more vulnerable to HM pollution than adults in this region and should be regarded as the priority for protection against HM contamination in dust. Moreover, Cd, Cr and Pb were major contributors to total health risks, and the HQ from dermal uptake of young children to Cd was greater than 1, indicating that Cd-induced health risks need to be given more attention and controlled in the near future.

Table 2
Non-carcinogenic risk from exposure to HMs for the three populations.

Element	Young children				Children				Adults			
	HQ_{oral}	Contribution	HQ_{dermal}	Contribution	HQ_{oral}	Contribution	HQ_{dermal}	Contribution	HQ_{oral}	Contribution	HQ_{dermal}	Contribution
Zn	1.2×10^{-1}	6%	2.0×10^{-2}	1%	6.2×10^{-2}	4%	1.7×10^{-3}	1%	1.3×10^{-3}	11%	6.5×10^{-4}	2%
Mn	1.1×10^{-1}	5%	9.3×10^{-2}	3%	7.6×10^{-2}	6%	1.1×10^{-2}	4%	4.8×10^{-4}	4%	1.2×10^{-3}	4%
Cu	7.2×10^{-2}	4%	8.0×10^{-3}	0%	5.3×10^{-2}	4%	9.8×10^{-4}	0%	2.6×10^{-4}	2%	8.6×10^{-5}	0%
Ni	1.1×10^{-1}	6%	1.4×10^{-2}	0%	6.6×10^{-2}	5%	1.4×10^{-3}	0%	4.9×10^{-4}	4%	1.8×10^{-4}	1%
Cr	5.1×10^{-1}	25%	8.5×10^{-1}	27%	2.0×10^{-1}	15%	5.6×10^{-2}	19%	8.5×10^{-4}	7%	4.3×10^{-3}	12%
Pb	4.5×10^{-1}	22%	9.9×10^{-2}	3%	4.9×10^{-1}	37%	1.8×10^{-2}	6%	6.1×10^{-3}	51%	4.1×10^{-3}	12%
Cd	6.3×10^{-1}	31%	2.1	66%	3.7×10^{-1}	28%	2.0×10^{-1}	70%	2.4×10^{-3}	20%	2.4×10^{-2}	69%
Co	1.7×10^{-2}	1%	7.1×10^{-4}	0%	1.1×10^{-2}	1%	7.4×10^{-5}	0%	5.9×10^{-5}	1%	7.3×10^{-6}	0%
HI	2.0		3.2		1.3		2.9×10^{-1}		1.2×10^{-2}		3.4×10^{-2}	
HI_{total}		5.2			1.6					0.1		

CRediT authorship contribution statement

Conceived and designed the experiments: Mohai Shen, Tingting Zhang, Zhiguo Cao.

Performed the experiments: Mohai Shen, Meihui Ren, Yange Wang, Fangfang Shen, Ruojin Du, Lijun Quan, Ya Wei, Jinghua Li, Guangxuan Yan, Jianbiao Peng.

Analysed and interpreted the data: Mohai Shen, Meihui Ren, Tingting Zhang, Zhiguo Cao.

Contributed reagents/materials/analysis tools: Yange Wang, Fangfang Shen.

Contributed to the writing of the manuscript: Mohai Shen, Meihui Ren, Zhiguo Cao.

Ethics

Ethical approval for this investigation was obtained from the Research Ethics Committee of Henan Normal University.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supporting Information: The SI contains additional detailed information on some additional tables and figures, as noted in the text. Supplementary data to this article can be found online at doi:<https://doi.org/10.1016/j.scitotenv.2020.144375>

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