



Ambient Air Heavy Metals in PM_{2.5} and Potential Human Health Risk Assessment in an Informal Electronic-Waste Recycling Site of China

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ABSTRACT

In this study, we characterized the concentration of heavy metals in PM_{2.5} in the community with e-waste dismantling, Guiyu, China and assessed potential public health risk associated with heavy metal composition of PM_{2.5} for local residents. Daily samples of PM_{2.5} were collected with Harvard Impactors on the roof of 3-story buildings from March 2012–April 2013 in Guiyu (n = 133) and seasonal samples were collected in a reference site, Haojiang (n = 33). The concentrations of PM_{2.5} mass and heavy metals were analyzed gravimetrically and by graphite furnace atomic absorption spectrometry, respectively. The geometric mean concentrations of PM_{2.5}, Pb and Cd in Guiyu were higher than in the reference area (PM_{2.5}: 49.9 μg m⁻³ vs. 37.6, p < 0.01; Pb: 160 ng m⁻³ vs. 69 ng m⁻³, p < 0.001; Cd: 5.7 ng m⁻³ vs. 3.4 ng m⁻³, p < 0.01), but Cr and Mn concentrations were not statistically different (Cr: 4.5 ng m⁻³ vs. 3.8 ng m⁻³, p > 0.05; Mn: 17 ng m⁻³ vs. 16 ng m⁻³, p > 0.05). The metal concentrations in PM_{2.5} from Guiyu were also higher when compared to other Asian cities. We observed higher heavy metal concentrations during winter and spring than summer and fall. Human health risk assessment showed that the total potential cancer risk for both adults and children are higher than the safe acceptable range recommended by the US EPA. Furthermore, the carcinogenic and non-carcinogenic elements in PM_{2.5} pose higher public health risk to children than adults. The results indicate that air pollution emitted from informal e-waste recycling activities might be affecting the health of local residents, especially children.

Keywords: E-waste; PM_{2.5}; Heavy metals; Risk assessment; Guiyu.

INTRODUCTION

Electronic equipment production and consumption has exponential growth in the last two decades, resulting in an increase of electronic waste (e-waste). E-waste includes end-of-life electronic products such as computers, printers, mobile phones, television sets, stereos, radios that contain persistent organic pollutants (polychlorinated biphenyls [PCBs], polybrominated diphenyl ethers [PBDEs]) and heavy metals which include lead (Pb), mercury (Hg),

chromium (Cr) and cadmium (Cd) (Wu *et al.*, 2010; Xu *et al.*, 2012). Guiyu, a southeast China town, is one of the largest e-waste destinations and recycling area in the world. It has a nearly 30-year history of e-waste recycling. The recycling is often performed by family-run workshops that use uncontrolled recycling methods which may pose a threat to the environment and human health (Huo *et al.*, 2007; Hahladakis *et al.*, 2013). Fine particulate matter (PM_{2.5}) in the atmosphere of the e-waste dismantling sites raised public concern in recent years. Many processes used within the informal e-waste recycling sector, including grinding, melting, roasting and open burning, release large amounts of dust, fumes and smoke into atmosphere. These emissions contain potentially carcinogenic and highly toxic metals such as chromium (Cr) and manganese (Mn) (Zheng *et al.*, 2013a), which may adversely affect human health. These metals, when deposited in the lower airways, can lead to acute and chronic toxicological effects in the lung (Bradshaw and Slater, 1998; Sobaszek *et al.*, 2000; Zheng *et al.*, 2013a).

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Cr and Cd contained in PM_{2.5} are carcinogenic and many other chemicals in e-waste are toxic (Betha *et al.*, 2013).

Pb and Cd are significant industrial and environmental pollutants, which are highly toxic to human. Although Cr and Mn are essential trace elements, excessive amounts of exposure also have toxic effects in human. Several studies conducted in Guiyu have reported high levels of toxic heavy metals in samples of dust, soil, river sediment, surface water, and groundwater (Deng *et al.*, 2006; Wong *et al.*, 2007a, b; Alabi *et al.*, 2012). Our previous studies showed that children living in Guiyu had significantly higher Pb, Cd, Cr and Mn levels in blood compared to the reference area (Huo *et al.*, 2007; Zheng *et al.*, 2008; Liu *et al.*, 2011; Yang *et al.*, 2013; Zheng *et al.*, 2013a; Xu *et al.*, 2015). Guiyu neonates also had higher Pb, Cd and Mn levels in blood (Li *et al.*, 2008a, b, 2011; Xu *et al.*, 2012). These findings highlight the importance of the assessment of heavy metal exposure and risk for people living in e-waste recycling area.

The exposure to airborne PM_{2.5} and heavy metals has been shown to pose public health risk (Greene and Morris, 2006; Diaz and Rosa, 2009). Therefore, it is essential to assess the human health risk of exposure to toxic metals in PM_{2.5} derived from e-waste recycling activities. Human health risk assessment is a tool for determining the likelihood of adverse health effects (carcinogenic and non-carcinogenic) occurring to a wide population after chemical exposure. Although heavy metals in some matrices (such as dust, water and soil) and the associated health risk from e-waste locations have been reported in studies (Leung *et al.*, 2008; Luo *et al.*, 2011; Fujimori *et al.*, 2012; Zheng *et al.*, 2013b), there is no comprehensive research on the contents of PM_{2.5} and health risk assessment for heavy metals. Hence, the monitoring data on the contents of PM_{2.5} in our study are valuable and significant to assess the potential health risks of heavy metal exposure in PM_{2.5} in an e-waste recycling area. Our major purposes of this study are as follows: (1) to monitor the concentrations of heavy metals in PM_{2.5} in Guiyu; (2) to determine the potential health risks of heavy metals as cumulative carcinogenic and non-carcinogenic risks via inhalation exposure for residents in the region.

METHODS

Sampling Sites

Guiyu town is located in Shantou, Guangdong Province, Southeast China. Guiyu has a total area of 52 km² and a population of 150,000 (Bi *et al.*, 2010; Alabi *et al.*, 2012; Ren *et al.*, 2013; Xu *et al.*, 2013; Liu *et al.*, 2014). It is a rice-growing countryside and its industry has been dominated by e-waste recycling since the early 1980s. Eighty percent of families in Guiyu are engaged with individual recycling workshops, with nearly 160,000 workers involved in recycling activities but without protective measures (Guo *et al.*, 2010; Wu *et al.*, 2010; Liu *et al.*, 2011; Wu *et al.*, 2011; Guo *et al.*, 2012; Wu *et al.*, 2012). The area has a sub-tropical climate, with an annual average temperature of 21.5°C, relative humidity of 80% and mean annual rainfall of 1721 mm (Deng *et al.*, 2006; Wong *et al.*, 2007b). The

prevailing wind is from the northeast except in the summer, when it is in the southwestern direction. In the northern part of Guiyu, there is a reservoir and a large area of hilly woodlands. E-waste recycling sites are mainly located in the residential areas and completely surrounded by farm land in the southern part of Guiyu.

Air Sampling and Analysis

PM_{2.5} samples were collected on the roof of a 3-story building located on a street in Guiyu where there are open burning and other e-waste recycling operations (23°17'36.9"N, 116°22'14.9"E) (Fig. 1). For comparison, we also collected PM_{2.5} samples on the roof of a 4-story building from the reference area in Haojiang (23°20'20.6"N, 116°40'13.7"E), which lies about 50 km away from Guiyu and with no record of e-waste recycling. PM_{2.5} samples were collected on a 37 mm pre-weighed Teflon membrane filter (2 μm pore size; SKC Inc, Eighty-Four, PA) using Harvard-type PM_{2.5} impactors (MS and T Area Sampler; Air Diagnostics, Inc, Harrison, ME) at these two sampling sites. The flow rate was 10 ± 0.5 L min⁻¹, which was calibrated with a flow meter before and checked after each 24 h sampling. The sampling period was 4 seasons from March, 2012 to April, 2013. In Guiyu, PM_{2.5} samples were collected every 24 hours except rainy or stormy days. In reference site, PM_{2.5} samples were collected 1 week for each season. Some samples were voided, due to wet filters, torn filters, or unstable flow rate outside of the 9.5 to 10.5 L min⁻¹ range. The Teflon filters were analyzed for PM_{2.5} mass concentrations using gravimetric technique. In addition, metals were analyzed from PM_{2.5} filters using graphite furnace atomic absorption spectrophotometry (GFAAS).

For the metal analysis, the filters were placed in digestion bottles, and high-purity HNO₃ (3 mL 65%–68%) and HCl (1 mL 36%–38%) were added. The mixtures were left overnight in a fume chamber and then digested using a microwave digestion system (WX-4000, Shanghai Yiyao, China). After microwave digestion, the digested solutions were heated to almost dryness to remove acids. After the bottles were cooled, 1 mL of high-purity HNO₃ was added to the solution, filtered into 50 mL glass bottle and then rinsed with deionized (Milli Q water) water. The filtrate was diluted to 50 mL and kept at 4°C until analysis. The total concentrations of Pb, Cd, Cr, Mn in the filtrate were determined by GFAAS (Jena Zenit 650, Germany). The operating conditions for GFAAS are presented in Table S1. Ten percent (10%) of the samples were laboratory blanks and another 10% were field blanks to assure the validity of the sample results.

We compared the PM_{2.5} mass and Pb, Cd, Cr, and Mn concentrations between the e-waste recycling sites and the reference site using t-tests after natural logarithmic transformation. We conducted a sensitivity analysis of concurrent air samples collected during the sampling period of reference site. Further, we compared PM_{2.5} and air metals between the two sites for each of the four seasons during the sampling period. All statistical tests were two-sided and the significance level was at 0.05. SAS 9.4 (SAS Institute Inc., Cary, NC) was used for all statistical analyses.

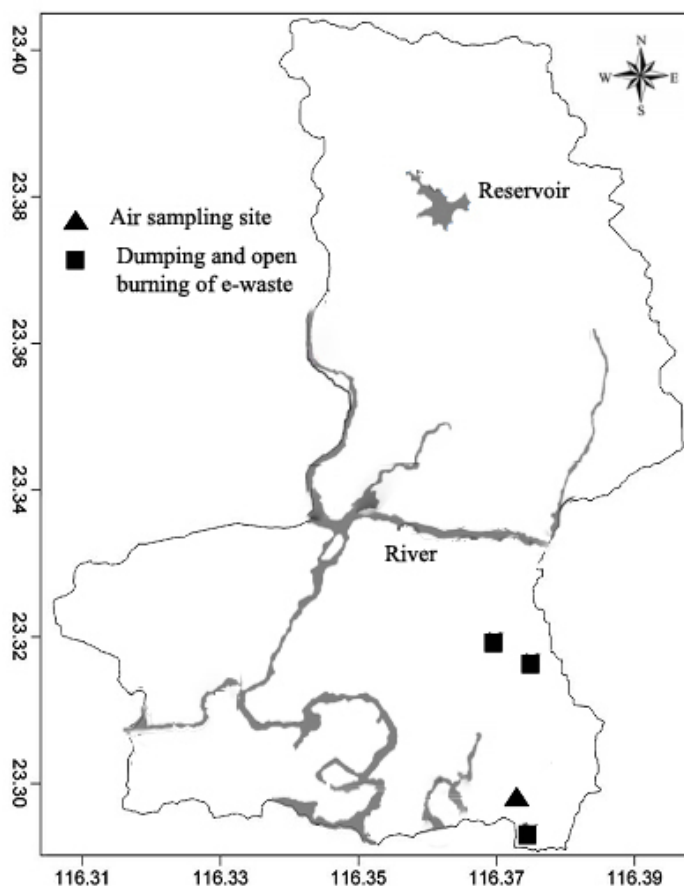


Fig. 1. Air sampling locations in Guiyu.

Human Health Risk Assessment for $PM_{2.5}$

Health risk assessment of respiratory exposure to $PM_{2.5}$ was carried out for residents living in Guiyu (See and Balasubramanian, 2006; Betha and Balasubramanian, 2011; Betha *et al.*, 2013). The chronic daily intake (CDI, $mg\ kg^{-1}\ day^{-1}$) of each metal was calculated from the following equations,

$$CDI (mg\ kg^{-1}\ day^{-1}) = \frac{Total\ dose\ (TD, mg\ m^{-3}) \times inhalation\ rate\ (IR, m^3\ day^{-1})}{Body\ weight\ (BW, kg)} \quad (1)$$

$$TD = C \times E \quad (2)$$

In the Eq. (2), C represents the geometric mean of the metal concentration in the $PM_{2.5}$ samples. E is the deposition fraction of particles by size and was calculated using a computer-based model, LUDEP 2.07 (ACJ and Associates, Inc., Richland, WA; ICRP, 1994), separately with parameters representing 5-year old child, 10-year old child, 15-year old boy and 15-years old girl, adult male and adult female. For calculation of the inhalation rate (IR), it was assumed that the subjects spent 80% of their time indoors and 20% outdoors. For the body weight (BW), we

used values given by the International Commission on Radiological Protection (ICRP, 1994) for Chinese population (Table S2). The assessment of the non-carcinogenic risk, hazard quotient (HQ), was made using the equation,

$$HQ = CDI \times RfD \quad (3)$$

where RfD is the reference dose ($mg\ kg^{-1}\ day^{-1}$) for metals that are non-carcinogenic calculated from reference concentrations (RfC, $mg\ m^{-3}$) provided by the United States Environmental Protection Agency (USEPA). If the HQ is < 1 , then noncancerous effects are unlikely. If the HQ is ≥ 1 , then adverse health effects might be possible (U.S. EPA, 1993). If the HQ is > 10 , then it suggests high chronic risk (Leung *et al.*, 2008).

The assessment of the carcinogenic risk, excess lifetime cancer risk (ELCR), was made using the equation,

$$ELCR = CDI \times SF \quad (4)$$

where SF is the cancer slope factor, expressed in ($mg^{-1}\ kg\ day$). Cancer risk less than 1×10^{-6} is considered negligible (U.S. EPA, 2012).

Quality Assurance

The accuracy of the methods was checked by using both external assurance reference materials and internal quality

reference samples (Table 1). The method used in heavy metal analysis of PM_{2.5} filter samples was validated by determination of Pb, Cd, Cr and Mn in the Standard Reference Material, SRM3100, obtained from the National Institute of Standard and Technology (NIST). There was an excellent agreement between the experimental and the certified values for four metals in standard reference material, SRM3100. The recovery for the Pb, Cd, Cr and Mn in the certified standard reference material by GFAAS technique was greater than 95%. The precision for spiked filtrate with Pb, Cd, Cr and Mn was expressed as the relative standard deviation (RSD), which was less than 5%. The recovery for Pb, Cd, Cr and Mn in spiked filtrate also was greater than 94%.

RESULTS AND DISCUSSION

Air Monitoring

Table 2 presents concentrations of the four metals as well as PM_{2.5}. The geometric mean (GM) of PM_{2.5} concentrations in Guiyu (49.9 µg m⁻³) was significantly higher than that in the reference area (37.6 µg m⁻³). The GM PM_{2.5} concentrations obtained for both Guiyu and the reference site exceeded the current World Health Organization (WHO, 2014) 24h PM_{2.5} ambient air quality guidelines (25 µg m⁻³) and Chinese 2012 National Ambient Air Quality Standards Level I (NAAQS I, 35 µg m⁻³) (GB 3095-2012), but were lower than Chinese NAAQS, Level II (75 µg m⁻³). The GM PM_{2.5} concentrations in both sites also exceeded WHO annual ambient air quality standard (10 µg m⁻³) and Chinese NAAQS annual standards (15 µg m⁻³ and 35 µg m⁻³ for Level I and Level II, respectively). The metal analysis of the PM_{2.5} showed significantly higher values of Pb and Cd in Guiyu (160 ng m⁻³ and 5.7 ng m⁻³,

respectively) compared to the reference site (69 ng m⁻³ and 3.4 ng m⁻³, respectively). However, the GM concentrations of Cr and Mn in Guiyu (4.5 ng m⁻³ and 17 ng m⁻³, respectively) and in the reference site (3.8 ng m⁻³ and 16 ng m⁻³, respectively) were not significantly different. The high values of Mn and Cr in the reference area might be due to extensive use of coal by thermal power plant in this region (Jamil *et al.*, 2009; Pandey, 2012; Tian *et al.*, 2012; Duan and Tan, 2013). In order to gain a better understanding of the correlation structure between the heavy metals in PM_{2.5}, Spearman correlation coefficient matrix was calculated (Table 3). The concentrations of Pb and Cd in PM_{2.5} were strongly correlated (Spearman $r = 0.683$, $p = 0.000$). The correlation coefficient was more evident in Guiyu ($r = 0.723$, $p = 0.000$) than in the reference area ($r = 0.305$, $p = 0.085$), suggesting a common source or dependence of Pb and Cd in PM_{2.5} samples in Guiyu.

The sensitivity analysis by comparing the same sampling days between Guiyu and the reference area is shown in Table 4. It is a quality control check in order to eliminate the effects of uncertainty in different sampling dates by comparing data collected on two areas sampling at the same time. We analyzed the days that overlapped in both two groups and found that PM_{2.5}, Pb, and Cd are significantly different but not Cr and Mn, which is same as the results using data from all sampling days shown in Table 2.

Table 5 shows the comparison of metal concentrations in PM_{2.5} between Guiyu and other sites in Asia. The geometric mean PM_{2.5} concentration in Guiyu was higher than several Asian sites. Among the four metals, Pb concentrations in PM_{2.5} of Guiyu were much higher than in some other Asian areas. In our study, the concentrations of PM_{2.5} mass, Pb, Cd, Cr and Mn were lower than the results presented by Deng *et al.* (2006) for Guiyu. The difference may be

Table 1. External quality assurance and internal quality reference data for Pb, Cd, Cr and Mn.

	Measured	Certified	Recovery (%)	RSD (%)
(A) External quality control ^a				
Pb (µg)	25.7 ± 0.3	25.0 ± 0.5	102.8	
Cd (µg)	9.7 ± 0.5	10.0 ± 0.2	97.0	
Cr (µg)	10.4 ± 0.6	10.0 ± 0.1	104.0	
Mn (µg)	10.1 ± 0.2	10.0 ± 0.1	101.0	
(B) Internal quality control ^b				
Pb (µg/L)	66.7 ± 0.8	80.0	107.7	2.7
Cd (µg/L)	2.1 ± 0.1	1.0	94.5	2.1
Cr (µg/L)	34.2 ± 0.5	30.0	129.8	3.2
Mn (µg/L)	23.5 ± 0.8	20.0	103.7	3.4

^a Certified values are referred to NIST filter SRM3100; ^b Determined concentration in filtrate samples.

Table 2. Concentrations of PM_{2.5}, Pb, Cd, Cr, Mn in Guiyu and the reference area.

Pollutants (Unit)	Guiyu (n = 133)		Reference (n = 33)		P
	Geometric Mean	Range	Geometric Mean	Range	
PM (µg m ⁻³)	49.9	11–160	37.6	11.3–83.0	0.0088
Pb (ng m ⁻³)	160	9.1–1000	69	9.1–290	0.0000
Cd (ng m ⁻³)	5.7	0.40–56	3.4	0.28–23	0.0015
Cr (ng m ⁻³)	4.5	0.01–380	3.8	0.01–26	0.6750
Mn (ng m ⁻³)	17	0.71–140	16	0.71–85	0.7570

Table 3. Spearman correlation coefficient values between heavy metal concentrations in PM_{2.5}.

	Pb	Cd	Cr	Mn
Pb	1	0.683**	0.019	0.420**
Cd		1	-0.071	0.321**
Cr			1	0.324**
Mn				1

** p < 0.01.

because the study by Deng and colleagues collected air sample from an open burning site of e-waste recycling, but our study collected ambient air samples from the community setting. Therefore, our study can be used to represent the exposure of general population in the e-waste recycling community and the reference site.

Daily average PM_{2.5} concentration ranged from 11 µg m⁻³ to 160 µg m⁻³ in Guiyu. Concentrations ranged from 9.1 to 1000 ng m⁻³ for Pb, from 0.40 to 56 ng m⁻³ for Cd, from 0.01 to 380 ng m⁻³ for Cr, from 0.71 to 140 ng m⁻³ for Mn in Guiyu (Table 2). The variation in PM_{2.5} and metal concentrations throughout the study may be due to meteorological conditions, gas to particle conversion process favored by the high relative humidity and varying anthropogenic sources (Kulshrestha *et al.*, 2009). Seasonal variations were investigated with the sampling period spanning 4 seasons: spring (February–April), summer (May–July), fall (August–October) and winter (November–January). Variations among the seasons in the PM and heavy metals as presented by Duncan's test are shown in Figs. 2 and 3. The PM_{2.5} mass obtained in winter and spring were similar but significantly higher than summer and autumn, with the lowest value observed in summer (28.4 µg m⁻³). Observation similar to our study was reported for PM_{2.5} in the e-waste area of Taizhou (Gu *et al.*, 2010). We obtained the lowest and highest Pb, Cd, Mn values in summer and winter, respectively, while those of Cr were obtained in summer and fall, respectively. Cr was also found the most enriched metals in PM_{2.5} from Guiyu during August to September (Deng *et al.*, 2006), which may indicate more e-waste items containing Cr during this period. The average metallic species concentrations in PM_{2.5} have been found to be higher in winter season compared to summer seasons also in other studies (Srimuruganandam and Nagendra, 2011; Duan *et al.*, 2012; Duan and Tan, 2013; Wang *et al.*, 2013). The low concentrations in summer may be mainly attributed to the high temperature, rainfall and typhoon (Ho *et al.*, 2006; Duan and Tan, 2013; Wang *et al.*, 2013). Rainfall and

typhoon bring precipitation at high volume and frequency, then increases the wet deposition of atmospheric particles, thus providing effective self-purification of the air. So good atmospheric diffusion conditions decrease the concentrations of the pollutants (Wang *et al.*, 2013). Furthermore, seasonal industrial production and human activities contribute to the high concentration in winter (Wang *et al.*, 2013). Previous studies have shown that the PBDE concentrations in the gas and particulate phases of air samples in Guiyu are extremely high in winter, which may suggest more e-waste recycling in winter (Chen *et al.*, 2011).

Human Health Risk Assessment

Representative elemental components of PM_{2.5} were used to evaluate human health risk to trace metal exposure. The pertinent information of the CDI and RfD, HQ, SF and ELCR in female adults and 10 years old children are given in Table 6 and for the other population groups in Table S3 and S4.

For female adults, the levels of non-carcinogenic risk (total HQ) were estimated to be 3.6×10^{-1} for Guiyu and 3.2×10^{-1} for the reference area while the levels of carcinogenic risk (total ELCR) were 5.9×10^{-5} for Guiyu and 4.6×10^{-5} for the reference area. It implies that 59–60 female adults from Guiyu and 46–47 female adults from the reference area per million population can get cancer after exposure to the toxic heavy metals in PM_{2.5}. For both Guiyu and the reference area, total HQ was below acceptable levels (HQ = 1). However, total HQ was higher than 0.1, which has been reported to have potential for adverse health effects for children and adults (De Miguel *et al.*, 2007; Kong *et al.*, 2012). In the case of total ELCR for Guiyu and the reference area, the estimate risk was higher than the acceptable level (ELCR = 1×10^{-6}).

For children of 10 years, the levels of non-carcinogenic risk (total HQ) was estimated to be 5.5×10^{-1} for Guiyu and 5.0×10^{-1} for the reference area. While total ELCR was 9.0×10^{-5} for Guiyu and 7.1×10^{-5} for the reference area. It indicates that 90–91 children from Guiyu and 71–72 children from the reference area per million population can get cancer after exposure to the toxic heavy metals in PM_{2.5}. Total HQ in both e-waste exposed area and the reference area was above 0.1. In the case of total ELCR, the estimate risk was higher than the acceptable level (ELCR = 1×10^{-6}) in both areas. From the results it can be deduced that the non-carcinogenic risk indicated by total HQ and the carcinogenic risk indicated by total ELCR for adults and children were higher in Guiyu compared to the

Table 4. The sensitivity analysis by comparing the same sampling days between Guiyu (n = 22) and the reference area (n = 33).

Pollutants (Unit)	Guiyu	Reference	P
	Geometric Mean	Geometric Mean	
PM (µg m ⁻³)	53.0	37.6	0.0090
Pb (ng m ⁻³)	150	69	0.0012
Cd (ng m ⁻³)	5.5	3.4	0.0508
Cr (ng m ⁻³)	8.1	3.8	0.0865
Mn (ng m ⁻³)	24	16	0.2080

Table 5. Comparison of atmospheric concentrations of heavy metals between Guiyu and other sites in Asia.

Year	Location	City	Character	Reference	Mass ($\mu\text{g m}^{-3}$)	Pb (ng m^{-3})	Cd (ng m^{-3})	Cr (ng m^{-3})	Mn (ng m^{-3})
2002	Indonesia	Bukit Tinggi	Tropical jungle	Maenhaut et al. (2002)	4.5	1.22	-	-	0.121
2002		Pontianak	Rural	Maenhaut et al. (2002)	9.4	8.7	-	-	0.34
2002		Pontianak	Rural	Fang et al. (2005)	23.6	26	-	-	-
2005	Korea	Seoul	Urban	Kim et al. (2003)	-	96.4	-	13.7	39
2001	Vietnam	Ho Chi Minh	Urban	Hien et al. (2001)	32	73	-	-	52
2002	Bangladesh		Semi-urban	Beguma et al. (2004)	22.4	89.4	-	6.3	6.7
2006	Japan	Kanazawa	Urban	Wang et al. (2006)	-	3.7	-	-	9.4
2003	Taiwan	Taichung	Urban	Fang et al. (2003)	42.8	283.1	4.3	33.5	19.1
2004–2005		Taichung	Harbor	Fang et al. (2006)	47.1	5.4	-	41.275	20.6
2001	China	Nanjing	Urban	Wang et al. (2002)	-	12.99	-	1.789	33.851
2003		Shanghai	University	Ye et al. (2003)	62.4	270	-	-	-
2003			Urban	Ye et al. (2003)	67.6	280	-	-	-
2006		Guiyu (Deng)	E-waste	Deng et al. (2006)	62.1	392	7.3	1152	25.4
The present study		Guiyu	E-Waste		49.9	160	5.7	4.5	17
		Haojiang	Suburbs		37.6	69	3.4	3.8	16

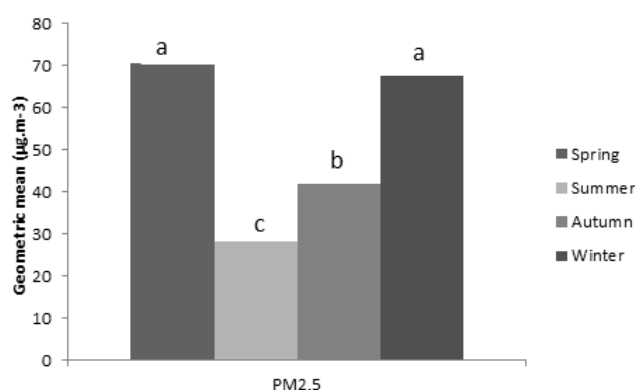


Fig. 2. Seasonal averages of PM_{2.5} mass in Guiyu.

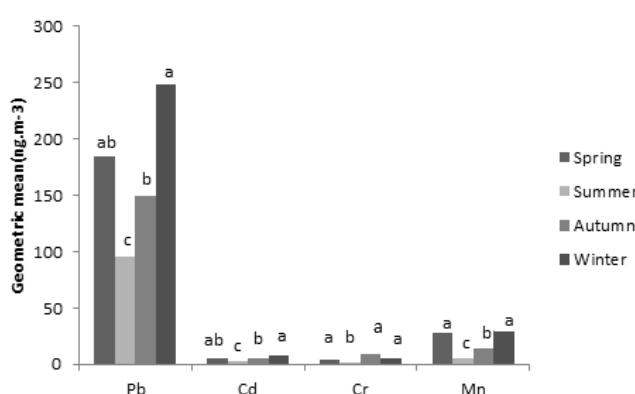


Fig. 3. Seasonal averages of heavy metals concentration in PM_{2.5} in Guiyu.

reference area. The results also showed that the carcinogenic and non-carcinogenic elements in PM_{2.5} may pose more serious public health risk to children than adults (Table 6, Table S3 and Table S4).

CONCLUSIONS

This is the first study that monitored PM_{2.5} for a long period and assessed potential health risks of air heavy metal exposure in e-waste recycling area. The concentrations of Pb, Cd, and PM_{2.5} mass in an informal e-waste recycling site were significantly higher than the reference site. Several metal concentrations in PM_{2.5} from Guiyu in our study were higher than other Asian sites. The results showed high concentrations of PM_{2.5} mass and heavy metals during winter months and lower concentrations in summer. The spread in the heavy metal concentration over the observation period suggests a high seasonal variability for heavy metal content in PM_{2.5}. We compared our results on human health risk to US EPA guidelines because there are no guidelines for risk assessment in China currently. In Guiyu and the reference site the total potential cancer risks for adults and children are above the safe acceptable range regulated by the US EPA. The results indicate that the carcinogenic and non-carcinogenic elements in PM_{2.5} may pose more public health risk to children than adults. The risk assessment results also showed that exposure to PM_{2.5}

Table 6. Health risk assessment of trace metals in PM_{2.5} for female adults and children (10 years) in two groups.

Metal	Female Adults			Children(10years)					
	CDI ^a	RfD ^a	HQ	ELCR	CDI ^a	RfD ^a	HQ	SF ^b	ELCR
(A) Guiyu									
Non-carcinogenic metals									
Pb	4.2 × 10 ⁻⁵	3.5 × 10 ⁻³	1.2 × 10 ⁻²		6.4 × 10 ⁻⁵	3.5 × 10 ⁻³	1.8 × 10 ⁻²		
Cr	1.2 × 10 ⁻⁶	2.9 × 10 ⁻⁵	4.1 × 10 ⁻²		1.8 × 10 ⁻⁶	2.9 × 10 ⁻⁵	6.2 × 10 ⁻²		
Mn	4.3 × 10 ⁻⁶	1.4 × 10 ⁻⁵	3.1 × 10 ⁻¹		6.6 × 10 ⁻⁶	1.4 × 10 ⁻⁵	4.7 × 10 ⁻¹		
Carcinogenic metals									
Cr	1.2 × 10 ⁻⁶			5.0 × 10 ⁻⁵	1.8 × 10 ⁻⁶			42	7.6 × 10 ⁻⁵
Cd	1.4 × 10 ⁻⁶			8.8 × 10 ⁻⁶	2.2 × 10 ⁻⁶			6.3	1.4 × 10 ⁻⁵
			Σ = 3.6 × 10 ⁻¹	Σ = 5.9 × 10 ⁻⁵			Σ = 5.5 × 10 ⁻¹		Σ = 9.0 × 10 ⁻⁵
(B) Reference									
Non-carcinogenic metals									
Pb	1.8 × 10 ⁻⁵	3.5 × 10 ⁻³	5.1 × 10 ⁻³		2.7 × 10 ⁻⁵	3.5 × 10 ⁻³	7.7 × 10 ⁻³		
Cr	9.7 × 10 ⁻⁷	2.9 × 10 ⁻⁵	3.3 × 10 ⁻²		1.5 × 10 ⁻⁶	2.9 × 10 ⁻⁵	5.2 × 10 ⁻²		
Mn	4.0 × 10 ⁻⁶	1.4 × 10 ⁻⁵	2.8 × 10 ⁻¹		6.1 × 10 ⁻⁶	1.4 × 10 ⁻⁵	4.4 × 10 ⁻¹		
Carcinogenic metals									
Cr	9.7 × 10 ⁻⁷			4.1 × 10 ⁻⁵	1.5 × 10 ⁻⁶			42	6.3 × 10 ⁻⁵
Cd	8.6 × 10 ⁻⁷			5.4 × 10 ⁻⁶	1.3 × 10 ⁻⁶			6.3	8.2 × 10 ⁻⁶
			Σ = 3.2 × 10 ⁻¹	Σ = 4.6 × 10 ⁻⁵			Σ = 5.0 × 10 ⁻¹		Σ = 7.1 × 10 ⁻⁵

^a mg kg⁻¹ day⁻¹;

^b mg⁻¹ kg day.

emitted from Guiyu may cause higher risk than PM_{2.5} emitted from the reference site. This study further shows the potential risk to human health associated with e-waste recycling activities. Limitations of our study include the lack of measurement of other pollutants, such as Persistent organic pollutants (POPs), which might co-exist in this PM_{2.5} and could add to the potential risk. Beside this, the risk was calculated only for inhalation exposure; if the other routes of exposure are considered (cutaneous and oral), the risk increases.

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SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

REFERENCES

- Alabi, O.A., Bakare, A.A., Xu, X., Li, B., Zhang, Y. and Huo, X. (2012). Comparative Evaluation of Environmental Contamination and DNA Damage Induced by Electronic-Waste in Nigeria and China. *Sci. Total Environ.* 423: 62–72.
- Beguma, B.A., Kimb, E., Biswasa, S.K. and Hopked, P.K. (2004). Investigation of Sources of Atmospheric Aerosol at Urban and Semi-Urban Areas in Bangladesh. *Atmos. Environ.* 38: 3025–3038.
- Betha, R. and Balasubramanian, R. (2011). Emissions of Particulate-Bound Elements from Stationary diesel Engine: Characterization and Risk Assessment. *Atmos. Environ.* 45: 5273–5281.
- Betha, R., Pradani, M., Lestari, P., Joshi, U.M., Reid, J.S. and Balasubramanian, R. (2013). Chemical Speciation of Trace Metals Emitted from Indonesian Peat Fires for Health Risk Assessment. *Atmos. Res.* 122: 571–578.
- Bi, X.H., Simoneit, B.R.T., Wang, Z.Z., Wang, X.M., Sheng, G.Y. and Fu, J.M. (2010). The Major Components of Particles Emitted during Recycling of Waste Printed Circuit Boards in a Typical E-Waste Workshop of South China. *Atmos. Environ.* 44: 4440–4445.
- Bradshaw, L.M. and Slater, T. (1998). Chronic Bronchitis, Work Related Respiratory Symptoms, and Pulmonary Function in Welders in New Zealand. *Occup. Environ. Med.* 55: 150–154.
- Chen, D., Bi, X., Liu, M., Huang, B., Sheng, G. and Fu, J. (2011). Phase Partitioning, Concentration Variation and Risk Assessment of Polybrominated Diphenyl Ethers (PBDEs) in the Atmosphere of an E-Waste Recycling Site. *Chemosphere* 82: 1246–1252.
- Deng, W.J., Louie, P.K.K., Liu, W.K., Bi, X.H., Fu, J.M. and Wong, M.H. (2006). Atmospheric Levels and Cytotoxicity of PAHs and Heavy Metals in TSP and PM_{2.5} at an Electronic Waste Recycling Site in Southeast China. *Atmos. Environ.* 40: 6945–6955.
- De Miguel, E., Iribarren, I., Chacon, E., Ordonez, A. and Charlesworth, S. (2007). Risk-Based Evaluation of the Exposure of Children to Trace Elements in Playgrounds in Madrid (Spain). *Chemosphere* 66: 505–513.
- Diaz, R.V. and Rosa, D.E. (2009). Health Risk by Inhalation of PM_{2.5} in the Metropolitan Zone of the City of Mexico. *Ecotoxicol. Environ. Saf.* 72: 866–871.
- Duan, J.C., Tan, J.H., Wang, S.L., Hao, J.M. and Chail, F.H. (2012). Size Distributions and Sources of Elements in Particulate Matter at Curbside, Urban and Rural Sites in Beijing. *J. Environ. Sci.* 24: 87–94.
- Duan, J.C. and Tan, J.H. (2013). Atmospheric Heavy Metals and Arsenic in China: Situation, Sources and Control Policies. *Atmos. Environ.* 74: 93–101.
- Fang, G.C., Chang, C.N., Chu, C.C., Wu, Y.S., Fu, P.P., Yang, I.L. and Chen, M.H. (2003). Characterization of Particulate, Metallic Elements of TSP, PM_{2.5} and PM_{2.5-10} Aerosols at a Farm Sampling Site in Taiwan, Taichung. *Sci. Total Environ.* 308: 157–166.
- Fang, G.C., Wu, Y.S., Huang, S.H. and Rau, J.Y. (2005). Review of Atmospheric Metallic Elements in Asia during 2000–2004. *Atmos. Environ.* 39: 3003–3013.
- Fang, G.C., Wu, Y.S., Lin, J.B., Lin, C.K., Rau, J.Y. and Huang, S.H. (2006). Characterization of Atmospheric Particulate and Metallic Elements at Taichung Harbor near Taiwan Strait during 2004–2005. *Chemosphere* 63: 1912–23.
- Fujimori, T., Takigami, H., Agusa, T., Eguchi, A., Bekki, K., Yoshida, A., Terazono, A. and Ballesteros, F.J. (2012). Impact of Metals in Surface Matrices from Formal and Informal Electronic-Waste Recycling around Metro Manila, the Philippines, and Intra-Asian Comparison. *J. Hazard. Mater.* 221–222: 139–146.
- GB 3095-2012. Ministry of Environmental Protection. Ambient Air Quality Standards, 2012. http://www.zzemc.cn/em_aw/Content/GB3095-2012.pdf.
- Greene, N.A. and Morris, V.R. (2006). Assessment of Public Health Risks Associated with Atmospheric Exposure to PM_{2.5} in Washington, DC, USA. *Int. J. Environ. Res. Public Health* 3: 86–97.
- Guo, Y., Huo, X., Li, Y., Wu, K., Liu, J., Huang, J., Zheng, G., Xiao, Q., Yang, H., Wang, Y., Chen, A. and Xu, X. (2010). Monitoring of Lead, Cadmium, Chromium and Nickel in Placenta from an E-Waste Recycling Town in China. *Sci. Total Environ.* 408: 3113–3117.
- Guo, Y., Huo, X., Wu, K., Liu, J., Zhang, Y. and Xu, X. (2012). Carcinogenic Polycyclic Aromatic Hydrocarbons in Umbilical Cord Blood of Human Neonates from Guiyu, China. *Sci. Total Environ.* 427–428: 35–40.
- Gu, Z.P., Feng, J.L., Han, W.L., Wu, M.H., Fu, J.M. and Sheng, G.Y. (2010). Characteristics of Organic Matter in PM_{2.5} from an E-Waste Dismantling Area in Taizhou, China. *Chemosphere* 80: 800–806.
- Hahladakis, J.N., Stylianou, M. and Gidarakos, E. (2013). Assessment of Released Heavy Metals from Electrical and Electronic Equipment (EEE) Existing in Shipwrecks through Laboratory-Scale Simulation Reactor. *J. Hazard. Mater.* 250–251: 256–264.

- Hien, P.D., Binh, N.T., Truong, Y., Ngo, N.T. and Sieu, L.N. (2001). Comparative Receptor Modelling Study of TSP, PM₂ and PM₂₋₁₀ in Ho Chi Minh City. *Atmos. Environ.* 35: 2669–2678.
- Ho, K.F., Lee, S.C., Cao, J.J., Chow, J.C., Watson, J.G. and Chan, C.K. (2006). Seasonal Variations and Mass Closure Analysis of Particulate Matter in Hong Kong. *Sci. Total Environ.* 355: 276–87.
- Huo, X., Peng, L., Xu, X., Zheng, L., Qiu, B., Qi, Z., Zhang, B., Han, D. and Piao, Z. (2007). Elevated Blood Lead Levels of Children in Guiyu, an Electronic Waste Recycling Town in China. *Environ. Health Perspect.* 115: 1113–1117.
- ICRP (International Commission on Radiological Protection) (1994). Human Respiratory Tract Model for Radiological Protection, ICRP Publication 66. *Annals of the ICRP* 24 (1–3).
- Jamil, S., Abhilash, P.C., Singh, A., Singh, N. and Behl, H.M. (2009). Fly Ash Trapping and Metal Accumulating Capacity of Plants: Implication for Green Belt around Thermal Power Plants. *Landscape Urban Plann.* 92: 136–147.
- Kim, K.H., Choi, G.H., Kang, C.H., Lee, J.H., Kim, J.Y., Youn, Y.H. and Lee, S.R. (2003). The Chemical Composition of Fine and Coarse Particles in Relation with the Asian Dust Events. *Atmos. Environ.* 37: 753–765.
- Kong, S., Lu, B., Ji, Y., Zhao, X., Bai, Z., Xu, Y., Liu, Y. and Jiang, H. (2012). Risk Assessment of Heavy Metals in Road and Soil Dusts within PM_{2.5}, PM₁₀ and PM₁₀₀ Fractions in Dongying City, Shandong Province, China. *J. Environ. Monit.* 14: 791–803.
- Kulshrestha, A., Satsangi, P.G., Masih, J. and Taneja A. (2009). Metal Concentration of PM_{2.5} and PM₁₀ Particles and Seasonal Variations in Urban and Rural Environment of Agra, India. *Sci. Total Environ.* 407: 6196–204.
- Leung, A.O., Duzgoren-Aydin, N.S., Cheung, K.C. and Wong, M.H. (2008). Heavy Metals Concentrations of Surface Dust from E-Waste Recycling and Its Human Health Implications in Southeast China. *Environ. Sci. Technol.* 42: 2674–2680.
- Li, Y., Huo, X., Liu, J., Peng, L., Li, W. and Xu, X. (2011). Assessment of Cadmium Exposure for Neonates in Guiyu, an Electronic Waste Pollution Site of China. *Environ. Monit. Assess.* 177: 343–351.
- Li, Y., Xu, X., Liu, J., Wu, K., Gu, C., Shao, G., Chen, S., Chen, G. and Huo, X. (2008a). The Hazard of Chromium Exposure to Neonates in Guiyu of China. *Sci. Total Environ.* 403: 99–104.
- Li, Y., Xu, X., Wu, K., Chen, G., Liu, J., Chen, S., Gu, C., Zhang, B., Zheng, L., Zheng, M. and Huo, X. (2008b). Monitoring of Lead Load and Its Effect on Neonatal Behavioral Neurological Assessment Scores in Guiyu, an Electronic Waste Recycling Town in China. *J. Environ. Monit.* 10: 1233–1238.
- Liu, J., Xu, X., Wu, K., Piao, Z., Huang, J., Guo, Y., Li, W., Zhang, Y., Chen, A. and Huo, X. (2011). Association between Lead Exposure from Electronic Waste Recycling and Child Temperament Alterations. *Neurotoxicology* 32: 458–464.
- Liu, W., Huo, X., Liu, D., Zeng, X., Zhang, Y. and Xu, X. (2014). S100 β in Heavy Metal-related Child Attention-deficit Hyperactivity Disorder in an Informal E-waste Recycling Area. *Neurotoxicology* 45: 185–191.
- Luo, C., Liu, C., Wang, Y., Liu, X., Li, F., Zhang, G. and Li, X. (2011). Heavy Metal Contamination in Soils and Vegetables near an E-Waste Processing Site, South China. *J. Hazard. Mater.* 186: 481–490.
- Maenhaut, W., De Ridder, D.J.A., Fernandez-Jimenez, M.T., Hooper, M.A., Hooper, B. and Nurhayati, M. (2002). Long-Term Observations of Regional Aerosol Composition at Two Sites in Indonesia. *Nucl. Instrum. Methods Phys. Res., Sect. B* 189: 259–265.
- Pandey, V.C. (2012). Phytoremediation of Heavy Metals from Fly Ash Pond by *Azolla caroliniana*. *Ecotoxicol. Environ. Saf.* 82: 8–12.
- Ren, Z., Bi, X., Huang, B., Liu, M., Sheng, G. and Fu, J. (2013). Hydroxylated PBDEs and Brominated Phenolic Compounds in Particulate Matters Emitted during Recycling of Waste Printed Circuit Boards in a Typical E-Waste Workshop of South China. *Environ. Pollut.* 177: 71–77.
- See, S.W. and Balasubramanian, R. (2006). Risk Assessment of Exposure to Indoor Aerosols Associated with Chinese Cooking. *Environ. Res.* 102: 197–204.
- Sobaszek, A., Boulenguez, C., Frimat, P., Robin, H., Haguenoer, J.M. and Edme, J.L. (2000). Acute Respiratory Effects of Exposure to Stainless Steel and Mild Steel Welding Fumes. *J. Occup. Environ. Med.* 42: 923–931.
- Srimuruganandam, B. and Nagendra, S.M. (2011). Chemical Characterization of PM₁₀ and PM_{2.5} Mass Concentrations Emitted by Heterogeneous Traffic. *Sci. Total Environ.* 409: 3144–57.
- Tian, H.Z., Cheng, K., Wang, Y., Zhao, D., Lu, L., Jia, W.X. and Hao, J.M. (2012). Temporal and Spatial Variation Characteristics of Atmospheric Emissions of Cd, Cr, and Pb from Coal in China. *Atmos. Environ.* 50: 157–163.
- U.S. EPA (1993). Description and Use in Health Risk Assessments, Background Document 1A, Integrated Risk Information System (IRIS); United States Environmental Protection Agency: Washington, DC. <http://www.epa.gov/iris/rfd.htm>.
- U.S. EPA (2012). Integrated Risk Information System. <http://www.epa.gov/irisU.S>.
- Wang, G., Huang, L., Gao, S., Gao, S. and Wang, L. (2002). Characterization of Water-Soluble Species of PM₁₀ and PM_{2.5} Aerosols in Urban Area in Nanjing, China. *Atmos. Environ.* 36: 1299–1307.
- Wang, J., Hu, Z.M., Chen, Y.Y., Chen, Z.L. and Xu, S.Y. (2013). Contamination Characteristics and Possible Sources of PM₁₀ and PM_{2.5} in Different Functional Areas of Shanghai, China. *Atmos. Environ.* 68: 221–229.
- Wang, X., Sato, T. and Xing, B. (2006). Size Distribution and Anthropogenic Sources Apportionment of Airborne Trace Metals in Kanazawa, Japan. *Chemosphere* 65: 2440–2448.
- Wong, C.S.C., Wu, S.C., Duzgoren-Aydin, N.S., Aydin, A.

- and Wong, M.H. (2007a). Trace Metal Contamination of Sediments in an E-Waste Processing Village in China. *Environ. Pollut.* 145: 434–442.
- Wong, M.H., Wu, S.C., Deng, W.J., Yu, X.Z., Luo, Q., Leung, A.O.W., Wong, C.S.C., Luksemburg, W.J. and Wong, A.S. (2007b). Export of Toxic Chemicals - A Review of the Case of Uncontrolled Electronic-Waste Recycling. *Environ. Pollut.* 149: 131–140.
- World Health Organisation (WHO) Ambient (Outdoor) Air Quality and Health, 2014, <http://www.who.int/mediacentre/factsheets/fs313/en/>.
- Wu, K., Xu, X., Liu, J., Guo, Y., Li, Y. and Huo, X. (2010). Polybrominated Diphenyl Ethers in Umbilical Cord Blood and Relevant Factors in Neonates from Guiyu, China. *Environ. Sci. Technol.* 44: 813–819.
- Wu, K., Xu, X., Liu, J., Guo, Y. and Huo, X. (2011). In Utero Exposure to Polychlorinated Biphenyls and Reduced Neonatal Physiological Development from Guiyu, China. *Ecotoxicol. Environ. Saf.* 74: 2141–2147.
- Wu, K., Xu, X., Peng, L., Liu, J., Guo, Y. and Huo, X. (2012). Association between Maternal Exposure to Perfluorooctanoic Acid (PFOA) from Electronic Waste Recycling and Neonatal Health Outcomes. *Environ. Int.* 48: 1–8.
- Xu, X., Yang, H., Chen, A., Zhou, Y., Wu, K., Liu, J., Zhang, Y. and Huo, X. (2012). Birth Outcomes Related to Informal E-Waste Recycling in Guiyu, China. *Reprod. Toxicol.* 33: 94–98.
- Xu, X., Yekeen, T.A., Xiao, Q., Wang, Y., Lu, F. and Huo, X. (2013). Placental IGF-1 and IGFBP-3 Expression Correlate with Umbilical Cord Blood PAH and PBDE Levels from Prenatal Exposure to Electronic Waste. *Environ. Pollut.* 182: 63–69.
- Xu, X., Chen, X., Zhang J., Guo, P., Fu, T., Dai, Y., Lin, S.L. and Huo, X. (2015). Decreased Blood Hepatitis B Surface Antibody Levels Linked to E-waste Lead Exposure in Preschool Children. *J Hazard Mater.* 298: 122–128.
- Yang, H., Huo, X., Yekeen, T.A., Zheng, Q., Zheng, M. and Xu, X. (2013). Effects of Lead and Cadmium Exposure from Electronic Waste on Child Physical Growth. *Environ. Sci. Pollut. Res. Int.* 20: 4441–4447.
- Ye, B., Ji, X., Yang, H., Yao, X., Chan, C.K., Cadle, S.H., Chan, T. and Mulawa, P.A. (2003). Concentration and Chemical Composition of PM_{2.5} in Shanghai for a 1-year Period. *Atmos. Environ.* 37: 499–510.
- Zheng, G., Xu, X., Li, B., Wu, K., Yekeen, T.A. and Huo, X. (2013a). Association between Lung Function in School Children and Exposure to Three Transition Metals from an E-Waste Recycling Area. *J. Exposure Anal. Environ. Epidemiol.* 23: 67–72.
- Zheng, J., Chen, K.H., Yan, X., Chen, S.J., Hu, G.C., Peng, X.W., Yuan, J.G., Mai, B.X. and Yang, Z.Y. (2013b). Heavy Metals in Food, House Dust, and Water from an E-Waste Recycling Area in South China and the Potential Risk to Human Health. *Ecotoxicol. Environ. Saf.* 96: 205–212.
- Zheng, L., Wu, K., Li, Y., Qi, Z., Han, D., Zhang, B., Gu, C., Chen, G., Liu, J., Chen, S., Xu, X. and Huo, X. (2008). Blood Lead and Cadmium Levels and Relevant Factors among Children from an E-Waste Recycling Town in China. *Environ. Res.* 108: 15–20.

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