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RESEARCH ARTICLE

Spatial distribution of heavy metal contamination in soils near a primitive e-waste recycling site

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Abstract The total concentrations of 12 heavy metals in surface soils (SS, 0–20 cm), middle soils (MS, 30–50 cm) and deep soils (DS, 60–80 cm) from an acid-leaching area, a deserted paddy field and a deserted area of Guiyu were measured. The results showed that the acid-leaching area was heavily contaminated with heavy metals, especially in SS. The mean concentrations of Ni, Cu, Zn, Cd, Sn, Sb and Pb in SS from the acid-leaching area were 278.4, 684.1, 572.8, 1.36, 3,472, 1,706 and 222.8 mg/kg, respectively. Heavy metal pollution in the deserted paddy field was mainly concentrated in SS and MS. The average values of Sb in SS and MS from the deserted paddy field were 16.3 and 20.2 mg/kg, respectively. However, heavy metal contamination of the deserted area was principally found in the DS. Extremely high concentrations of heavy metals were also observed at some special research sites, further confirming that the level of heavy metal pollution was very serious. The geoaccumulation index (I_{geo}) values revealed that the acid-leaching area was severely polluted with heavy metals in the order of Sb > Sn > Cu > Cd > Ni > Zn > Pb, while deserted paddy field was contaminated predominately by metals in the order of Sb > Sn > Cu. It was obvious that the concentrations of some uncommon contaminants, such as Sb and Sn, were higher than principal contaminants, such as Ni, Cu, Zn and Pb, suggesting that particular attention should be directed to Sn and Sb contamination in the future research of heavy metals in soils from e-waste-processing areas. Correlation analysis suggested that Li and Be in soils from the acid-leaching area and its surrounding environment might have originated from other industrial activities and from batteries, whereas Ni, Cu, Zn, Cd, Pb, Sn and Sb contamination was most likely caused by uncontrolled electronic waste (e-waste) processing. These results indicate the significant need for optimisation of e-waste-dismantling technologies and remediation of polluted soil environment.

Keywords E-waste · Heavy metals · Soil · Spatial distribution · Geoaccumulation index · Correlation analysis

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Introduction

Electronics manufacturing is the largest and most rapidly increasing manufacturing industry in the world (Liu et al. 2013). A large amount of waste electrical and electronic equipment (WEEE) is discarded due to the rapid development of information technology and the short lifespan of electronic products, resulting in a corresponding electronic waste (e-waste) (Yang et al. 2013), such as personal computers, TVs and mobile phones (Tang et al. 2010a, 2010b). It has been reported that e-waste is increasing at a rate of 4 % per year worldwide (Robinson 2009; Kahhat et al. 2008). Approximately 50–80 % of the e-waste collected for disposal in developed countries ends up in Asia, 90 % of which is illegally exported to China for processing and disposal (Leung et al. 2007; Shen et al. 2007). Moreover, 51.48 million home appliances and 4.48 million personal computers were generated in China in 2003 (Terazono et al. 2006). Uncontrolled e-waste-processing activities in China are causing increasing concerns because of both the importation of e-waste and the

swift growth of domestic production. In the past few years, intensive e-waste-recycling activities have taken place in a few regions in China, especially in Guangdong (Guiyu and Longtang) and Zhejiang (Taizhou) (Yang et al. 2012; Li et al. 2007a; Shen et al. 2007; Wong et al. 2007a). However, driven by profits, informal and primitive e-waste-recycling technologies, such as acid-leaching and open-burning of abandoned components, are carried out to reuse precious metals, including Au, Ag, Pd and Pt (Tang et al. 2010a; Zhao et al. 2009; Fu et al. 2008; Bi et al. 2007; Yu et al. 2006). A large number of toxic metals like Cr, Ni, Cu, Zn, Cd, Sn, Sb, Pb, etc. (Rath et al. 2012; Cui and Zhang 2008; Li et al. 2007b) and persistent organic pollutants, primarily including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated biphenyl ethers (PBDEs) and polychlorinated and polybrominated dibenzofurans (PCDD/F and PBDD/F), are released into the surrounding environment of e-waste-processing sites (Leung et al. 2007; Gullett et al. 2007; Deng et al. 2006). Subsequently, these contaminants may enter the soil environment through atmospheric deposition and water irrigation (Nan et al. 2002).

A comprehensive investigation on the status of heavy metal contamination in soil environmental surrounding e-waste-recycling sites is significant for the long-term improvement of public health. Previous heavy metal soil contamination investigations of e-waste-processing areas have included open-burning sites (Luo et al. 2008; Wong et al. 2007b), streets (Li et al. 2011), pond areas (Luo et al. 2011), paddy fields (Luo et al. 2011; Zhang and Min 2009), vegetable gardens and deserted areas (Luo et al. 2011). A survey by Wong et al. (2007b) showed that open-burning sites were severely polluted with Ni, Cu, Zn, Cd and Pb. Luo et al. (2011) reported that paddy fields and vegetable gardens were primarily contaminated by Cu and Cd, with mean values exceeding the target values of Dutch Standards (VROM 2000). Tang et al. (2010a) found that heavy metal contamination in agricultural surface soil surrounding e-waste-recycling workshops was very serious. The average concentrations of Ni, Cu, Zn and Cd for all soil samples were higher than grade II of environmental quality standards for soils (GB15618-1995) (pH<6.5) (SEPA 1995).

Even though numerous studies have been carried out to investigate heavy metal contamination in surface soils surrounding e-waste-processing regions, there is still a lacuna of information on the spatial distribution of contaminants in various soil layers. In addition, most studies have focused on principal contaminants, especially Ni, Cu, Zn, Cd and Pb, while reports are scarce regarding uncommon potential contaminants, such as Be, Sn and Sb. However, Be has been widely used in printed circuit boards and can induce chronic diseases, can damage lungs and may be a human carcinogen (Peng et al. 2009). Both Sn and Sb may be released from discarded printed circuit boards and solders within electronic devices (Li et al. 2011). Several studies have also illustrated that $SnCl_2$ could inhibit immune responses in rodents, alter gene expression and induce tumour generation in thyroid gland (Ferancová et al. 2007; Silva et al. 2002). Meanwhile, the genotoxicity of Sb may be very similar to As (III) (Tschan et al. 2009; Gebel 1997). Tschan et al. (2009) also found that antimonate $[Sb(OH)_6]^-$ was more toxic and more mobile in soil than Pb, and antimonate was also more soluble at higher pH and more easily taken up by plants. Therefore, it is important to pay more attention to these unconventional pollutants.

The objectives of this study were (1) to further investigate the spatial distribution of 12 heavy metals (Li, Be, V, Cr, Co, Ni, Cu, Zn, Cd, Sn, Sb and Pb) in soils near e-waste-processing sites (acid-leaching area, deserted paddy field and deserted area), (2) to comprehensively assess heavy metal pollution in an e-waste-processing village and the exposure risks to local residents and the soil environment and (3) to find correlations of heavy metals in soils and the sources of soil heavy metal contamination. It is hoped that the findings are useful for pollution prevention and soil remediation of heavy metal contamination in similar areas.

Materials and methods

Study area and sampling

Guiyu is a notorious e-waste-processing centre in China, located in the Chaozhou region of Guangdong Province, having been involved in e-waste-recycling for nearly 20 years. Based on the dominant land use patterns, all sampling sites can be classified as one of three types: an acid-leaching area, a deserted paddy field or a deserted area. Sites 1 to 5 were located in a deserted area. Sites 6 to 15 were located in an acid-leaching area with an area of approximately 7,000 m^2. Sites 16 to 23 were located in a deserted paddy field. Although the planting of rice was not taking place, the grazing of cattle and the breeding of geese were observed in a nearly 14,000 m^2 of deserted paddy field south of the acid-leaching area. A large number of strong acids (e.g. sulphuric acid, nitric acid and hydrochloric acid) were typically used to extract precious metals during the acid-leaching processes of e-waste in the past. The resulting waste acids and wastewater were then discharged into neighbouring rivers, while solid waste was sold or deposited onsite. Fortunately, these simple and traditional processing methods had already been abandoned by the local government (Li et al. 2011).

Sixty-nine samples of soils from the acid-leaching site (n=10×3), deserted paddy field (n=8×3) and deserted area (n=5×3) were obtained using a professional heavy metal sampler equipped with a polyvinyl chloride (PVC) liner in May 2013. Sampling methods were consistent with those described by Tang et al. (2010a). The locations of all sampling sites are

shown in Fig. 1. Three kinds of samples were collected from each site with a depth of 0–20 cm (surface soil, SS), 30–50 cm (middle soil, MS) and 60–80 cm (deep soil, DS), respectively. Five random SS samples from Guangzhou were also collected on the same day of sampling (not shown in Fig. 1). All samples were stored in polythene bags (Ziploc) and immediately transported to the lab. Upon arrival in the lab, all soils were refrigerated at 4 °C until pre-treatment.

Pre-treatment methods

All wet soil samples were dried at 80 °C for 2 days in an oven. After drying, a portion of each sample was crushed in an agate mortar, passed through a 100-mesh (d<0.154 mm) nylon sieve to remove stones, fine debris and coarse materials, thoroughly mixed and homogenised prior to analysis for heavy metals.

Prior to the experiment, all glass tubes and plastic centrifuge tubes used in the experiments were thoroughly washed, soaked with 10 % (v/v) diluted nitric acid for more than 24 h and rinsed three times with distilled water and Milli-Q water (18.25 MΩ cm, 25 °C) produced by a water purification system. For each sample, an accurately weighted soil sample (≈0.2 g) was digested by mixed concentrated acids (HF/HNO_3/HCl=5:5:2) on a hot plate (ML-2-4, Beijing, China) at 200 °C. The digestion liquid was filtered and then diluted to 10 mL with Milli-Q water. The total concentrations of Li, Be, V, Cr, Co, Ni, Cu, Zn, Cd, Sn, Sb and Pb were determined using an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7700X, USA). To simplify the expression throughout the manuscript, a definition of 'heavy metals' was used in the present research: Li and Be were termed 'light metals', and Sb was termed 'metalloid'. For quality assurance/quality control protocols, reagent blanks, duplicates of 10 % total samples and standard reference materials (GBW07407 and GBW07429) were used. The recovery rates of 12 heavy metals in soils (GBW07407 and GBW07429) were approximately 90.4–121.6 %.

Data analysis

Geoaccumulation index

The geoaccumulation index (I_{geo}) was applied to assess the extent of heavy metal contamination in soils by comparing the current and original concentrations, although it is difficult to obtain original soils. The I_{geo} values of soils in study areas were calculated with the following formula:

$$I_{geo} = \log_2\left(\frac{C_i}{1.5B_i}\right)$$

where C_i is the concentration of heavy metals in soil at present and B_i is the geochemical background value. The national background values of soils in China, which are 1.95, 82.4, 61, 583, 12.7, 26.9, 22.6, 74.2, 0.097, 2.6, 1.21 and 26 mg/kg for Be, V, Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn, Sb and Pb, respectively, were adopted as references in the present study due to a lack of relevant background data in the study

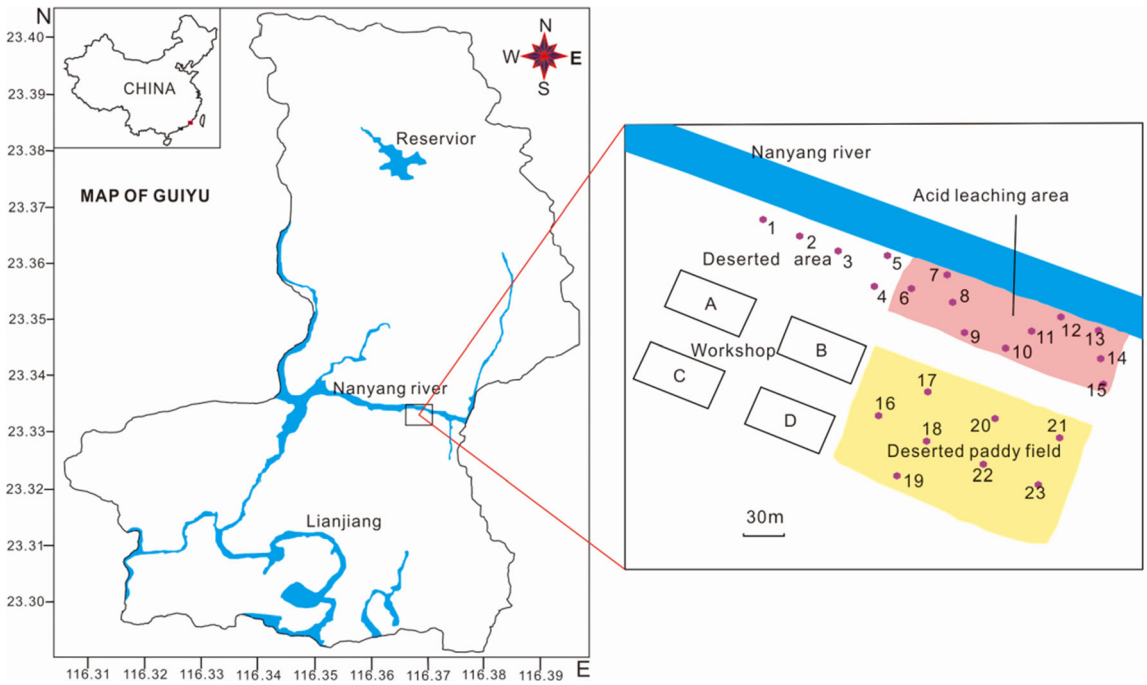

Fig. 1 The map of sample collection

area (Wei et al. 1991). The constant 1.5, a modified coefficient, was also used to represent the influence of deposition characteristics and geological characteristics and detect the effect of human activities. I_{geo} can be divided into seven classes (Muller 1969), as given in Table 1.

Statistical analysis

All statistical analyses were performed using Excel 2010 and Statistical Package for the Social Science software (SPSS statistics 17.0, USA). One-way ANOVA tests ($p<0.05$) were employed to examine the statistical significance of heavy metal concentrations among different sampling areas. Pearson coefficients were also used to find correlations for heavy metals in soils and to explore the homology of soil heavy metal contamination. The significant level was set at $p<0.05$ (two tailed).

Results and discussion

Spatial distribution of heavy metals

Acid-leaching area

The mean concentrations of heavy metals at various depths (including SS, MS and DS) from the acid-leaching area and SS from Guangzhou are presented in Table 2, together with the background values of soils in China (Wei et al. 1991) and soil quality standards (China and Dutch) (SEPA 1995; VROM 2000). Environmental quality standards for soil (GB15618-1995) are more appropriately used in our study because they are Chinese Standards and our research area is in China as well. However, Chinese Standards have not provided the allowable concentrations of some uncommon pollutants, such as Sn and Sb. Therefore, both the Dutch Standards and environmental quality standards for soil (GB15618-1995) were used in this study.

Table 1 Seven classes of I_{geo} values

Classes	I_{geo} values	The quality of soils
1	$I_{geo}\leq 0$	Not polluted
2	$0<I_{geo}\leq 1$	Not polluted to moderately polluted
3	$1<I_{geo}\leq 2$	Moderately polluted
4	$2<I_{geo}\leq 3$	Moderately polluted to heavily polluted
5	$3<I_{geo}\leq 4$	Heavily polluted
6	$4<I_{geo}\leq 5$	Heavily polluted to extremely polluted
7	$I_{geo}>5$	Extremely polluted

I_{geo} values, the values of geoaccumulation index

No statistical significances were found between the concentrations of Li, V and Co at various depths of the acid-leaching area and the corresponding values in SS from Guangzhou ($p<0.05$), and the Cr level in the acid-leaching area was much lower than the background value in China. Thus, the acid-leaching area was not polluted with Li, V, Co or Cr. In addition, heavy metal pollution was mainly grouped in the SS and MS. The mean values of Ni, Cu, Zn, Cd and Pb in SS, MS and DS exceeded the limits of grade I of environmental quality standards for soils (GB15618-1995), and the average concentrations of Ni (278.4 mg/kg), Cu (684.1 mg/kg), Zn (572.8 mg/kg), Cd (1.36 mg/kg) and Pb (222.8 mg/kg) in SS were 7.0, 19.6, 5.7, 6.8 and 6.4-fold higher than the corresponding values of grade I, respectively. More seriously, very high concentrations of Sn and Sb were discovered in the acid-leaching area. The average values of Sn in SS (3,472 mg/kg) and MS (917.1 mg/kg) exceeded the indicative level for soil serious contamination of Dutch Standards (900 mg/kg), and the mean concentrations of Sb in SS, MS and DS (1,706, 804.6 and 480.5 mg/kg, respectively) exceeded the intervention value of Dutch Standards by 113.7, 53.6 and 32.0-fold, respectively. In view of its toxicity to humans and environments, extremely close attention should be directed towards reducing Sn and Sb contamination in future research of heavy metals in soil near dismantling areas of e-waste. In particular, the highest concentrations of Ni (822.6 mg/kg), Cu (2,782 mg/kg), Zn (3,667 mg/kg), Cd (3.61 mg/kg), Sn (8,756 mg/kg), Sb (3,654 mg/kg) and Pb (527.9 mg/kg) were found in the SS at site 7, the DS at site 8, the SS at site 9, the MS at site 6, the SS at site 8, the SS at site 8 and the SS at site 8, respectively (Table S1). The distribution characteristics of heavy metals again confirmed that the acid-leaching area was heavily contaminated by heavy metals.

Deserted paddy field

The mean concentrations of heavy metals in SS, MS and DS from the deserted paddy field are shown in Fig. 2. More detailed data are given in Table S2. On one hand, the mean concentrations of Cr and Zn were much less than the values of grade I of the Chinese Standard. Consequently, the deserted paddy field was not contaminated by Cr and Zn. On the other hand, similar to the acid-leaching area, heavy metal contamination in the deserted paddy field was mainly located in SS and MS. This could be explained by the fact that heavy metals in both SS and MS of these areas had been enriched in the past 20 years when e-waste-recycling activities were most extensive. The average concentrations of Li, Be, V, Co, Ni and Cu in the deserted paddy field were clearly higher than the corresponding values in SS of Guangzhou, and the concentrations of Cd, Sn, Sb and Pb were also higher than the background values of soils in China. This suggested that the deserted paddy field was polluted to some extent with Li, Be, V, Co,

Table 2 Heavy metal concentrations (mean) in SS, MS and DS from the acid-leaching area and SS collected from Guangzhou, mg/kg

Elements	Acid leaching area[a]			SS of Guangzhou[a]	Background values[b]	China[c]			Dutch[d]	
	SS	MS	DS			I	II pH<6.5	III	Target	Intervention
Li	22.4	30.5	35.2	14.2	*32.5*	–	–	–	–	–
Be	1.98	2.41	1.90	2.14	1.95	–	–	–	1.1	30[e]
V	52.9	61.09	62.1	52.4	82.4	–	–	–	42	250[e]
Cr	7.43	7.38	7.10	37.5	61.0	90	250	400	100	380
Co	11.9	18.0	13.6	3.78	12.7	–	–	–	9	240
Ni	278.4	349.9	225.7	12.8	26.9	40	40	200	35	210
Cu	684.1	855.8	789.5	20.7	22.6	35	50	400	36	190
Zn	572.8	484.4	189.7	115.8	74.2	100	200	500	140	720
Cd	1.36	1.41	1.12	0.40	0.10	0.2	0.3	1	0.8	12
Sn	3,472	917.1	760.1	8.91	2.60	–	–	–	–	900[e]
Sb	1,706	804.6	480.5	2.61	1.21	–	–	–	3	15
Pb	222.8	95.9	57.1	61.3	26.0	35	250	500	85	530

SS surface soils of 0–20 cm, *MS* middle soils of 30–50 cm, *DS* Deep soils of 60–80 cm, *I* the limits for protecting ecosystem, *II* the maximum allowable contents of metals in agriculture soil of China, *III* the upper limit values for regular growing of plants

[a] Data are given as average values

[b] From Wei et al. (1991)

[c] From SEPA (1995)

[d] From VROM (2000)

[e] Indicative level for soil serious contamination of Dutch Standards

Ni, Cu, Cd, Sn, Sb and Pb, especially with Sb. The concentrations of Sb in SS and MS exceeded the intervention value of Dutch Standards (15 mg/kg), with average values being 16.3 and 20.2 mg/kg, respectively. The deserted paddy field was extensively contaminated by many heavy metals. Because these contaminants may be transported to humans through the food chain (soils–plants–humans) (Fu et al. 2008; Zhang et al. 2012; Liu et al. 2011), and the grazing of cattle and the breeding of geese were still taking place in this area as illustrated in the study above, great attention must be paid to heavy metal contamination in deserted paddy fields.

Deserted area

The mean concentrations of heavy metals in SS, MS and DS from the deserted area are depicted in Fig. 3. Firstly, the concentrations of Li, Be, Cd, Sn, Sb and Pb in SS, MS and DS of the deserted area were significantly higher than the corresponding values of SS in Guangzhou ($p<0.05$) and the background values of soils in China. The Cu and Zn concentrations of soils in the deserted area were higher than the grade II limits of Chinese Standards. It can be inferred that the deserted area was primarily contaminated with Li, Be, Cu,

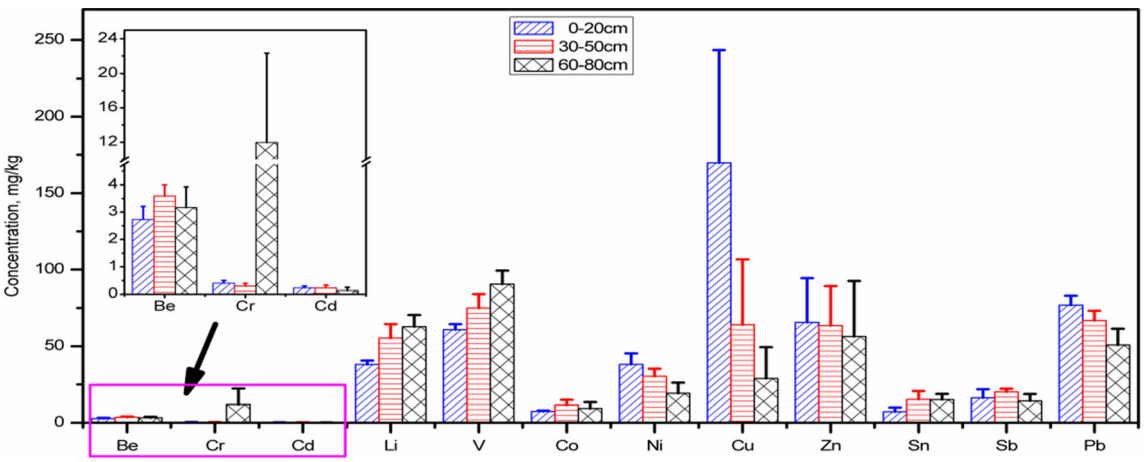

Fig. 2 Heavy metal concentrations in the deserted paddy field (mean±standard deviation)

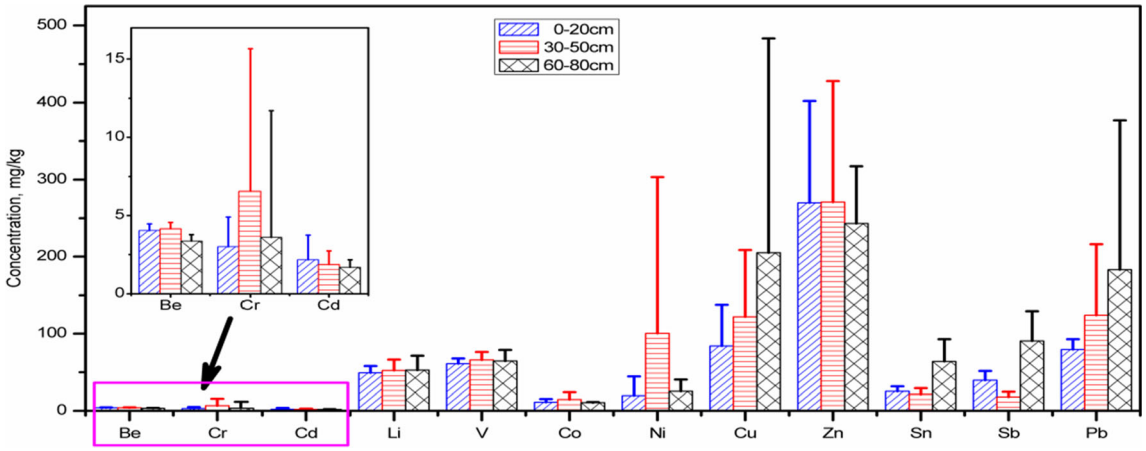

Fig. 3 Heavy metal concentrations in the deserted area (mean±standard deviation)

Zn, Cd, Sn, Sb and Pb. In addition, the concentrations of Li, Cu, Sn, Sb and Pb in DS were higher than those in SS and MS. It was obvious that the level of heavy metal contamination in DS of the deserted area was more serious than that in SS and MS. The reason for this might be that polluted soils in this area may have been recently covered by relatively unpolluted soils. Simultaneously, the highest concentrations of Ni (464.1 mg/kg), Cu (699.5 mg/kg), Zn (453.7 mg/kg), Cd (4.93 mg/kg) and Pb (531.4 mg/kg) were observed in site 4 or site 5 (MS of site 5 for Ni, DS of site 4 for Cu, SS of site 5 for Zn, SS of site 5 for Cd and DS of site 4 for Pb, respectively) (Table S3). We can deduce that the level of heavy metal contamination increased with the reduction of physical proximity between sampling sites and the acid-leaching area. It should be noted that it is still unclear whether the pollution characteristics vary with the distance between pollution sources and research areas.

Comparison

The mean concentrations of 12 heavy metals in different sampling areas are listed in Table 3. Comparing the three sampling areas, as expected, the acid-leaching area had the most serious heavy metal contamination, with mean values being 284.7 mg/kg for Ni, 776.5 mg/kg for Cu, 415.6 mg/kg for Zn, 1,716 mg/kg for Sn and 997.1 mg/kg for Sb, respectively. The mean concentration of Sn (1,716 mg/kg) in the acid-leaching area exceeded the indicative level for soil serious contamination of Dutch Standards (900 mg/kg). The average value of Sb (997.1 mg/kg) was more than 66.5 times that of the intervention value of Dutch Standards (15 mg/kg). To our surprise, the deserted area had the highest concentrations of Be (3.84 mg/kg), Cd (1.90 mg/kg) and Pb (129.0 mg/kg), indicating that the heavy metals released from e-waste-processing may enter the adjacent environment through water irrigation and atmospheric deposition. The results were similar to those of the previous report (Luo et al. 2011). In comparison with the acid-leaching area and the deserted area, the extent of heavy metal contamination in the deserted paddy field was relatively low. It was obvious that the pollution level of heavy metals in soils decreased in the order of acid-leaching area > deserted area > deserted paddy field.

Very few investigations have evaluated the extent of heavy metal contamination in MS and DS. Hence, it is difficult to compare our data with other studies due to the lack of appropriate comparable information. In the present study, only the results in SS (0–10, 0–15, 0–20 and 0–30 cm) collected from other e-waste-recycling centres or Guiyu in the past were compared with our data, as showed in Table 2, Figs. 2 and 3. From a report by Li et al. (2011), the concentrations of some common heavy metals (Cr 7.43 mg/kg, Ni 278.4 mg/kg and Cu 684.1 mg/kg) in the acid-leaching area (in the present study) were lower than the corresponding values (Cr 2,600 mg/kg, Ni 480 mg/kg and Cu 4,800 mg/kg) in soils/dusts collected around the abandoned workshops that had used acids to extract materials from e-waste. It was reported that the Ministry of Environmental Protection of China has taken measures to forbid informal e-waste processing (Li et al. 2011). This could partly explain why lower concentrations of Cr, Ni and Cu were found in the present research. The concentrations of Ni, Cu and Pb in the deserted paddy fields in Guiyu were very similar to those in Longtang (another e-waste-recycling centre in China) (Luo et al. 2011), while Zn and Cd were less than those in Luqiao and Longtang (Luo et al. 2011; Zhang and Min 2009). It seems that the pollution level of heavy metals in the deserted paddy fields of Guiyu was lower than those in Luqiao and Longtang.

Geoaccumulation index

Table 3 shows the I_{geo} of 12 heavy metals in the research areas. The mean concentrations of heavy metals in the acid-leaching area, deserted paddy field and deserted area were

Table 3 I_{geo} of soils from the acid-leaching area, deserted paddy field and deserted area

Elements	Concentrations of heavy metals[a]			Background values[b]	I_{geo}		
	Acid-leaching area	Deserted paddy field	Deserted area		Acid-leaching area	Deserted paddy field	Deserted area
Li	29.4	52.1	51.3	32.5	−0.73	0.10	0.07
Be	2.1	3.18	3.84	1.95	−0.48	0.12	0.39
V	58.7	75.4	63.9	82.4	−1.07	−0.71	−0.95
Cr	4.93	3.99	3.40	61	−4.21	−4.52	−4.75
Co	13.9	9.41	12.1	12.7	−0.46	−1.02	−0.65
Ni	284.7	28.6	48.1	26.9	2.82	−0.50	0.25
Cu	776.5	87.6	137.5	22.6	4.52	1.37	2.02
Zn	415.6	61.82	261.3	74.2	1.90	−0.85	1.23
Cd	1.30	0.19	1.90	0.10	3.16	0.38	3.71
Sn	1,716	12.53	36.8	2.6	8.78	1.68	3.24
Sb	997.1	16.9	49.4	1.21	9.10	3.22	4.77
Pb	125.2	65.0	129.0	26	1.68	0.74	1.73

[a] Data are given as average values

[b] From Wei et al. 1991

chosen as the current concentrations of elements in corresponding areas, while the background values of soils in China measured by Wei et al. (1991) were selected as geochemical background values, for calculating I_{geo} values. First, the acid-leaching area was polluted with heavy metals most seriously, especially with Sb and Sn, which had I_{geo} values of 9.10 and 8.78 (>5, extremely polluted), respectively. The I_{geo} values for Cu, Cd and Ni were also greater than 2 (moderately polluted to heavily polluted). In summary, the level of heavy metal contamination in the acid-leaching area decreased in the order of Sb > Sn > Cu > Cd > Ni > Zn > Pb. In addition, in comparison with the acid-leaching area, heavy metal contamination was lower in the deserted area and deserted paddy field. The I_{geo} values for all selected metals in these areas were less than 5. In the deserted area, only the I_{geo} values of Sb, Cd and Sn were higher than 3 (heavily polluted). Lastly, the deserted paddy field was predominantly polluted with Sb, Sn and Cu, with the I_{geo} values being 3.22 (heavily polluted), 1.68 (moderately polluted) and 1.37 (moderately polluted), respectively; the I_{geo} values for Pb, Cd, Be and Li were beyond 0 as well. Therefore, close attention must be paid to heavy metal contamination in the deserted paddy field because the grazing of cattle and the breeding of geese were still taking place in these fields. The results were very similar to the findings in the present research described above. In summary, effective measures should be immediately taken to remediate the most heavily polluted areas and agricultural soils.

Correlation analysis (Pearson)

Pearson correlation analysis has been widely applied to explore the relativity among various pollutants in soils (Borůvka et al. 2005; Zhang et al. 2006; Tang et al. 2010a). Correlation analyses of V, Cr and Co were not performed because the I_{geo} values of these metals were less than 0 (not polluted). As presented in Table 4, a significant correlation between Li and Be was observed at the level of 0.01. The Pearson coefficient was 0.654 between Li and Be, which revealed that these metals most likely had a common source. Strong correlations among Ni, Cu, Zn, Cd, Sn, Sb and Pb (with the

Table 4 Correlation coefficients among different metals in soils from Guiyu

Element	Li	Be	Ni	Cu	Zn	Cd	Sn	Sb
Be	0.654**							
Ni	−0.084	0.168						
Cu	−0.583	−0.375	0.375**					
Zn	−0.031	0.174	0.669**	0.287*				
Cd	−0.018	0.385**	0.561**	0.332**	0.521*			
Sn	−0.415	−0.310	0.288*	0.348**	0.274*	0.200		
Sb	−0.485	−0.314	0.340**	0.594**	0.294*	0.314**	0.868**	
Pb	−0.294	−0.009	0.217	0.241*	0.306*	0.377**	0.734**	0.650**

*Correlation is significant at the level of 0.05 (two tailed)

**Correlation is significant at the level of 0.01 (two tailed)

exception of Ni-Pb and Cd-Sn) were also evident at the levels of 0.01 or 0.05, suggesting that these metals might originate from common sources as well. Many previous reports have confirmed that most e-waste is composed of a mixture of heavy metals, plastics and ceramics (Li et al. 2011; Lehner and Vikdahl 1998; Cui and Zhang 2008; Robinson 2009; Pant et al. 2012; Kantarelis et al. 2011), and generally, most e-waste contains higher contents of Ni, Cu, Zn, Cd, Sn, Sb and Pb although the chemical composition of e-waste varies with the types of obsolete components (Robinson 2009). Consequently, we can further infer that the contamination of heavy metals in soils from Guiyu could principally originate from uncontrolled e-waste dismantling, while Li and Be contamination might arise from other industrial activities and battery disposal.

It should be noted that even though the I_{geo} analysis and Pearson correlation analysis used in the present study offer significant information of pollution status of heavy metals, better geochemical and statistical tools are essential to identify the natural and anthropogenic sources of heavy metal contamination (Hu et al. 2013). In addition, chemical species analysis and ecological risk assessment are necessary for evaluating the impact of pollutants in soil on animals.

Conclusions

Clearly, accumulations of heavy metals were found in the soil environment of the acid-leaching area, deserted paddy field and deserted area due to uncontrolled e-waste processing. Heavy metal contamination in the acid-leaching area and deserted paddy field was mainly focused on SS and MS. This could be explained by the fact that heavy metals in both SS and MS of these areas had been enriched in the past 20 years when e-waste-recycling activities were most extensive. The level of heavy metal contamination in the acid-leaching area decreased in the following order: Sb > Sn > Cu > Cd > Ni > Zn > Pb, while the deserted paddy field was mainly polluted with heavy metals in the order of Sb > Sn > Cu. It was evident that the pollution levels of Sn and Sb in both the acid-leaching area and the deserted paddy area were higher than that of Ni, Cu, Zn, Cd and Pb. More attention should be paid to Sn and Sb in the future research of heavy metal contamination in soils. However, heavy metal pollution in the deserted area was principally concentrated in DS because the deserted area has likely been covered by unpolluted soils. Correlation analysis suggested that Ni, Cu, Zn, Cd, Pb, Sn and Sb most likely originated from uncontrolled e-waste processing, while Li and Be pollution might be attributed to other industrial activities and battery waste. The acid-leaching area may be a source of contamination for its surrounding soil environments due to its extremely high concentrations of heavy metals. The remediation and management of this area are a matter of urgency.

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References

Bi X, Thomas GO, Jones KC, Qu W, Sheng G, Martin FL, Fu J (2007) Exposure of electronics dismantling workers to polybrominated diphenyl ethers, polychlorinated biphenyls, and organochlorine pesticides in South China. Environ Sci Technol 41(16):5647–5653

Borůvka L, Vacek O, Jehlička J (2005) Principal component analysis as a tool to indicate the origin of potentially toxic elements in soils. Geoderma 128(3):289–300

Cui J, Zhang L (2008) Metallurgical recovery of metals from electronic waste: a review. J Hazard Mater 158(2–3):228–256

Deng WJ, Louie PKK, Liu WK, Bi XH, Fu JM, Wong MH (2006) Atmospheric levels and cytotoxicity of PAHs and heavy metals in TSP and PM2.5 at an electronic waste recycling site in southeast China. Atmos Environ 40(36):6945–6955

Ferancová A, Adamovski M, Gründler P, Zima J, Barek J, Mattusch J, Wennrich R, Labuda J (2007) Interaction of tin (II) and arsenic (III) with DNA at the nanostructure film modified electrodes. Biogeosciences 71(1):33–37

Fu J, Zhou Q, Liu J, Liu W, Wang T, Zhang Q, Jiang G (2008) High levels of heavy metals in rice (*Oryza sativa* L.) from a typical e-waste recycling area in southeast China and its potential risk to human health. Chemosphere 71(7):1269–1275

Gebel T (1997) Arsenic and antimony: comparative approach on mechanistic toxicology. Chem Biol Interact 107(3):131–144

Gullett BK, Linak WP, Touati A, Wasson SJ, Gatica S, King CJ (2007) Characterization of air emissions and residual ash from open burning of electronic wastes during simulated rudimentary recycling operations. J Mater Cycles Waste Manag 9(1):69–79

Hu Y, Liu X, Bai J, Shih K, Zeng EY, Cheng H (2013) Assessing heavy metal pollution in the surface soils of a region that had undergone three decades of intense industrialization and urbanization. Environ Sci Pollut Res 20(9):6150–6159

Kahhat R, Kim J, Xu M, Allenby B, Williams E, Zhang P (2008) Exploring e-waste management systems in the United States. Resour Conserv Recycl 52(7):955–964

Kantarelis E, Yang W, Blasiak W, Forsgren C, Zabaniotou A (2011) Thermochemical treatment of e-waste from small household appliances using highly pre-heated nitrogen-thermogravimetric investigation and pyrolysis kinetics. Appl Energy 88(3):922–929

Lehner T, Vikdahl A (1998) Integrated recycling of non-ferrous metals at Boliden Ltd. Ronnskar smelter. IEEE International Symbosium on Electronics & the Enviroment, pp 353–362

Leung AO, Luksemburg WJ, Wong AS, Wong MH (2007) Spatial distribution of polybrominated diphenyl ethers and polychlorinated dibenzo-*p*-dioxins and dibenzofurans in soil and combusted residue at Guiyu, an electronic waste recycling site in southeast China. Environ Sci Technol 41(8):2730–2737

Li H, Yu L, Sheng G, Fu J, Pa P (2007a) Severe PCDD/F and PBDD/F pollution in air around an electronic waste dismantling area in China. Environ Sci Technol 41(16):5641–5646

Li J, Duan H, Shi P (2011) Heavy metal contamination of surface soil in electronic waste dismantling area: site investigation and source-apportionment analysis. Waste Manag Res 29(7):727–738

Li J, Lu H, Guo J, Xu Z, Zhou Y (2007b) Recycle technology for recovering resources and products from waste printed circuit boards. Environ Sci Technol 41(6):1995–2000

Liu J, Zhang XH, Tran H, Wang DQ, Zhu YN (2011) Heavy metal contamination and risk assessment in water, paddy soil, and rice around an electroplating plant. Environ Sci Pollut Res 18(9):1623–1632

Liu M, Huang B, Bi X, Ren Z, Sheng G, Fu J (2013) Heavy metals and organic compounds contamination in soil from an e-waste region in South China. Environ Sci Process Impacts 15(5):919–929

Luo CL, Liu CP, Wang Y, Liu XA, Li FB, Zhang G, Li XD (2011) Heavy metal contamination in soils and vegetables near an e-waste processing site, south China. J Hazard Mater 186(1):481–490

Luo Y, Yu XH, Yang ZY, Yuan JG, Mai BX (2008) Studies on heavy metal contamination by improper handling of e-waste and its environmental risk evaluation. I: heavy metal contamination in e-waste open burning sites. Asian J Ecotoxicol 3(1):34–41

Muller G (1969) Index of geoaccumulation in sediments of the Rhine River. Geophys J R Astron Soc 2(3):108–118

Nan Z, Zhao C, Li J, Chen F, Sun W (2002) Relations between soil properties and selected heavy metal concentrations in spring wheat (*Triticum aestivum* L.) grown in contaminated soils. Water Air Soil Pollut 133:205–213

Pant D, Joshi D, Upreti MK, Kotnala RK (2012) Chemical and biological extraction of metals present in E waste: a hybrid technology. Waste Manag 32(5):979–990

Peng PA, Sheng GY, Fu JM (2009) The pollution by electronic and electric wastes. Prog Chem 21(2/3):550–557 (in Chinese)

Rath SS, Nayak P, Mukherjee PS, Chaudhury GR, Mishra BK (2012) Treatment of electronic waste to recover metal values using thermal plasma coupled with acid leaching - a response surface modeling approach. Waste Manag 32(3):575–583

Robinson BH (2009) E-waste: an assessment of global production and environmental impacts. Sci Total Environ 408(2):183–191

SEPA (State Environmental Protection Administration) (1995) Environmental quality standard for soils (GB15618-1995), Standards Press of China, Beijing

Shen CF, Huang SB, Wang ZJ, Qiao M, Tang XJ, Yu CN, Shi DZ, Zhu YF, Shi JY, Chen XC, Setty K, Chen YX (2007) Identification of Ah receptor agonists in soil of E-waste recycling sites from Taizhou area in China. Environ Sci Technol 42(1):49–55

Silva CR, Oliveira MBN, Melo SF, Dantas FJS, De Mattos JCP, Bezerra RJCA, Caldeira-de-Araujo A, Duatti A, Bernardo-Filho M (2002) Biological effects of stannous chloride, a substance that can produce stimulation or depression of the central nervous system. Brain Res Bull 59(3):213–216

Tang X, Shen C, Chen L, Xiao X, Wu J, Khan MI, Dou C, Chen Y (2010a) Inorganic and organic pollution in agricultural soil from an emerging e-waste recycling town in Taizhou area, China. J Soils Sediments 10(5):895–906

Tang XJ, Shen CF, Shi DZ, Cheema SA, Khan MI, Zhang CK, Chen YX (2010b) Heavy metal and persistent organic compound contamination in soil from Wenling: an emerging e-waste recycling city in Taizhou area, China. J Hazard Mater 173(1–3):653–660

Terazono A, Murakami S, Abe N, Inanc B, Moriguchi Y, S-i S, Kojima M, Yoshida A, Li J, Yang J (2006) Current status and research on E-waste issues in Asia. J Mater Cycles Waste Manag 8(1):1–12

Tschan M, Robinson BH, Schulin R (2009) Antimony in the soil–plant system—a review. Environ Chem 6(2):106–115

VROM (2000) Intervention values and target values; soil quality standards, Ministry of Housing, Spatial Planning and Environment, Department of Soil Protection, The Hague, Netherlands

Wei FS, Chen JS, Wu YY, Zheng CJ (1991) Research on background values of soils in China. J Environ Sci China 12(4):12–19 (in Chinese)

Wong CS, Duzgoren-Aydin NS, Aydin A, Wong MH (2007a) Evidence of excessive releases of metals from primitive e-waste processing in Guiyu, China. Environ Pollut 148(1):62–72

Wong MH, Wu SC, Deng WJ, Yu XZ, Luo Q, Leung AO, Wong CS, Luksemburg WJ, Wong AS (2007b) Export of toxic chemicals—a review of the case of uncontrolled electronic-waste recycling. Environ Pollut 149(2):131–140

Yang RX, Luo CL, Zhang G, Li XD, Shen ZG (2012) Extraction of heavy metals from e-waste contaminated soils using EDDS. J Environ Sci China 24(11):1985–1994

Yang YC, Xue MQ, Xu ZM, Huang C (2013) Health risk assessment of heavy metals (Cr, Ni, Cu, Zn, Cd, Pb) in circumjacent soil of a factory for recycling waste electrical and electronic equipment. J Mater Cycles Waste Manag 15(4):556–563

Yu XZ, Gao Y, Wu SC, Zhang HB, Cheung KC, Wong MH (2006) Distribution of polycyclic aromatic hydrocarbons in soils at Guiyu area of China, affected by recycling of electronic waste using primitive technologies. Chemosphere 65(9):1500–1509

Zhang HB, Luo YM, Wong MH, Zhao QG, Zhang GL (2006) Distributions and concentrations of PAHs in Hong Kong soils. Environ Pollut 141(1):107–114

Zhang JH, Min H (2009) Eco-toxicity and metal contamination of paddy soil in an e-wastes recycling area. J Hazard Mater 165(1):744–750

Zhang WH, Wu YX, Simonnot MO (2012) Soil contamination due to e-waste disposal and recycling activities: a review with special focus on China. Pedosphere 22(4):434–455

Zhao G, Zhou H, Wang D, Zha J, Xu Y, Rao K, Ma M, Huang S, Wang Z (2009) PBBs, PBDEs, and PCBs in foods collected from e-waste disassembly sites and daily intake by local residents. Sci Total Environ 407(8):2565–2575