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RESEARCH ARTICLE

Legacies and health risks of heavy metals, polybrominated diphenyl ethers, and polychlorinated dibenzo-dioxins/furans at e-waste recycling sites in South China

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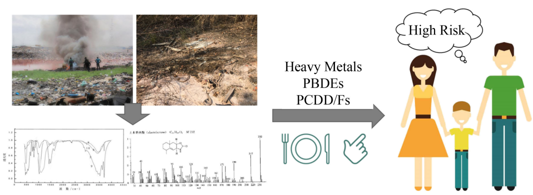
HIGHLIGHTS

- Heavy metals and organic toxins may persist in legacy sites for a long time.
- Contaminants pose potential harms to the nearby community (HI > 1).
- PCDD/Fs had the risk of endocrine disruption and reproductive risk.
- Further intervention is needed to reduce pollution and related risks.

GRAPHIC ABSTRACT



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ABSTRACT

Informal electronic-waste (e-waste) recycling sites pose substantial health risks to surrounding environments and populations, yet they are not properly regulated. In this study, the soil levels of copper, lead, cadmium, eight polybrominated diphenyl ethers (PBDEs), and 18 polychlorinated dibenzo-dioxins/furans (PCDD/Fs) were measured at two e-waste recycling sites in South China between 2014 and 2019. Both sites have been abandoned for natural restoration. Our results indicate that the mean Cd and PCDD/F levels at Site A in 2019 were higher than those recommended by current safety guidelines. Meanwhile, the highest exposure among children was 1.36×10^{-2} mg/(kg·d) for Cu, followed by 5.05×10^{-3} mg/(kg·d) for Pb, 9.71 ng/(kg·d) for PBDEs, and 6.82 ng TEQ/(kg·d) for PCDD/Fs. Children were at elevated risk for health problem posed by Pb and Cu exposure at both sites (hazard quotient > 1) and by PCDD/Fs at Site A. Further risk assessment was conducted on the target organs and endpoints of heavy metals and PCDD/Fs. The hazard index (HI) for the target organ mixed-risk of heavy metals was high (HI = 1.27), as was that of PCDD/Fs (HI = 1.66), which can disrupt endocrine function and pose a risk of reproductive toxicity in children. Owing to incomplete cleaning, contaminants persist in soils over long periods and may harm nearby environments and communities. Our study demonstrates that heavy metal, PBDE, and PCDD/F contamination have not yet been remediated, and intervention is needed to reduce pollution and associated risks in areas affected by e-waste.

1 Introduction

Electronic and electrical technologies have transformed our societies and interactions with the environment. Electrical and electronic equipment (EEE) is a large class of commercial "products with circuity or electrical components with a power or battery supply" (Chen et al., 2021); this includes cell phones, laptops, washing machines, refrigerators, and many other items. EEEs are often discarded, becoming either waste of electrical and electronic equipment (WEEE) or electronic waste (e-waste). In 2019, 5.36×10^{10} kg —an estimated equivalent of 7.3 kg per capita—of e-waste was generated worldwide, according to the Global E-Waste Monitor 2020 (Forti et al., 2020). This amount is expected to double, reaching 7.47×10^{10} kg, by the end of 2030. Sites of WEEE have been termed "urban mines" owing to their high concentrations of valuable metals and metalloids

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(Awasthi et al., 2016; Ackah, 2017). High percentages of Fe, Al, and Cu can be found in raw waste materials; for example, Cu (~16%), Sn (~4%), Fe (~3%), Ni (~2%), Zn (~1%), and Au (~0.03%) are valuable metals in waste printed circuit boards. Consequently, e-waste recycling activities have been promoted since 1990, particularly in developing countries such as China (Balde et al., 2017; Forti et al., 2020).

Polybrominated diphenyl ethers (PBDEs) and other organic chemicals are used as raw materials in EEE, while polychlorinated dibenzo-dioxins/furans (PCDD/Fs) occur as by-products following inadequate combustion. Consequently, the informal recycling of e-waste causes serious environmental contamination (Fujimori and Takigami, 2014; Dos Santos et al., 2017; Liu et al., 2021). An increasing number of studies have reported a wide range of metal pollution levels at e-waste recycling and disposal sites. Xue et al. (2012) detected Cu, Pb, Cr, and Cd in printed circuit board automatic line workshops, with Pb (1.40 μg/m^3) and Cu (1.22 μg/m^3) being the most abundant metals in total suspended particles. Zinc contamination (5200 μg/g) has been reported in the soils of e-waste sites in Ghana, along with Cr (490 μg/g), Cu (360 μg/g), and Pb (300 μg/g) (Moeckel et al., 2020). Additionally, contamination by polychlorinated biphenyls (PCBs), PBDEs, polyaromatic hydrocarbons (PAHs), and polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) has been widely reported from e-waste recycling areas (Sepúlveda et al., 2010; Chan and Wong, 2013). The environmental impact of e-waste varies among regions and is influenced by the composition and treatment of e-waste, as well as environmental conditions, social awareness, and policy interventions (Zhang et al., 2017). For example, the availability of recycling technologies for disassembly, upgrading, comminution, and separation affects the amount of metals that can be recovered or left in the recycling process (Chan and Wong, 2013).

There are two main pathways of human exposure to e-waste contaminants at disassembly sites—ingestion and dermal exposure. Ingestion exposure is the exposure of people around a site through the unconscious swallowing of soil particles or ingestion of contaminated food or water. Dermal exposure is caused by soil particles suspended in the air falling on the skin through sedimentation and contaminants penetrating the human body. People who live, work, and play around informal e-waste recycling sites experience elevated exposure to toxic substances (Song and Li, 2014), especially workers and children (Xue et al., 2012). Infants and children can be exposed by ingesting indoor dust on surfaces and playing with dismantled electronics, as well as via breastfeeding (Song and Li, 2014). Previous studies have shown that the ingestion of PCDD/Fs from dust in recycling regions ranges from 10 to 32 pg toxic equivalency (TEQ)/(kg·d), exceeding the tolerable daily intake limit of 1–4 pg TEQ/(kg·d). Heavy metals can also accumulate in the soil–vegetable system. Liu et al. (2021) measured 11 types of vegetables around a historical e-waste site and found higher metal accumulation in leafy and solanaceous vegetables (lettuce and eggplant). It has been suggested that exposure to toxic substances is orders of magnitude higher in the villages surrounding e-waste sites than in other areas (Ngo et al., 2021). Moreover, e-waste recycling has been associated with increased adverse health effects, including birth defects (Zhang et al., 2017), development delays (Soetrisno and Delgado-Saborit, 2020), immune dysfunction (Huo et al., 2019a; 2019b), and endocrine disruption (Grant et al., 2013). However, limited biomonitoring data (placenta, umbilical cord blood, blood and serum, hair, urine, etc.) are available on the physiologic burden or daily intake of e-waste contaminants, which hampers further restrictions on e-waste recycling activities.

E-waste management infrastructure and regulations were first developed in China after 2010. In the 1990s, e-waste was primarily managed by families and small businesses. Under inferior techniques and awareness, e-waste was openly burned, washed with acid, and dumped without further control (Yu et al., 2006), resulting in serious heavy metal, PCDD/F, PCB, and PAH contamination in e-waste regions (Zhang et al., 2017; Huang et al., 2021). South China has suffered from long-term illegal e-waste recycling activities (Yu et al., 2006). It is known for its heavy metal recycling industries, which produce 1.2 t of solid waste annually. In 2013, under strict regulations on e-waste recycling in Guangdong Province, China, a few cities established centralized industrial parks and abolished the family-operated recycling sector to reduce environmental impacts. The open burning and disposal of e-waste were abolished, and advanced techniques and management methods were adopted. In 2014, some cities in South China initiated a restoration project for abandoned e-waste sites. However, only conventional restoration methods have been employed. In this study (Fig. 1), we selected two e-waste sites (denoted as A and B) and evaluated the levels of heavy metals, PBDEs, and PCDD/Fs in the soil between 2014 and 2019. Exposures to these contaminants were also calculated among children (aged 9–12) and adults based on the Exposure Factors Handbook of Chinese Population (Ministry of Ecology and Environment, 2016), and potential hazards near the two sites were evaluated using a total risk assessment and target organ and endpoint risk assessments.

2 Materials and methods

2.1 Study area

The study areas (A and B) were located in South China. In 2014, a preliminary site investigation was conducted.

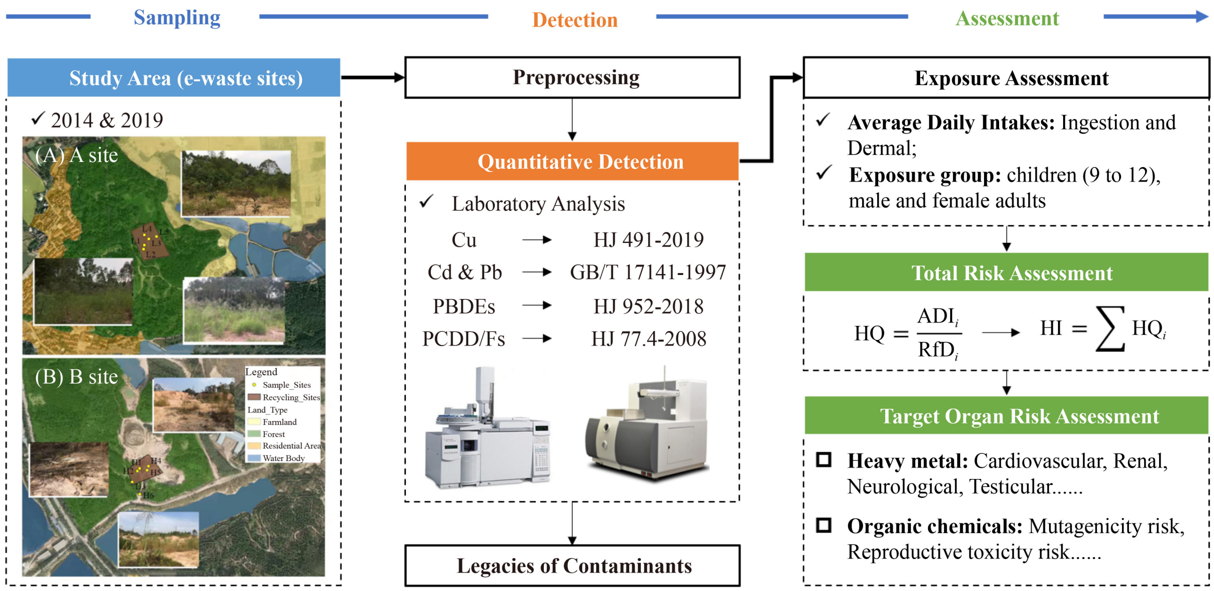

Fig. 1 Workflow of exploring the human health risks of heavy metals, polybrominated diphenyl ethers and polychlorinated dibenzodioxins/furans at e-waste recycling sites in South China.

Site A (23°34.844′50.64″N, 113°02′14.16″E) was a dismantling and incineration site with an area of 1002.3 m^2. The site was operated mainly by family-owned workshops near their respective farmlands. In 2015, under the government restoration project, severely contaminated soils were transferred to hazardous waste landfill sites, and the abandoned sites were abandoned to natural restoration, with vegetation planted in potentially contaminated areas. Site B (23°31′46.56″N, 113°03′20.46″E) was an e-waste recycling and dismantling site located near a reservoir, with an estimated area of 6000 m^2. Three water ponds and one residential area were observed within a 500 m radius of this site. In 2019, we conducted a second investigation (Fig. 2). Site A had developed into a forest and no e-waste residue was observed at Site B, which was buried with clay and sand and sparsely vegetated by grass and shrubs. At nearby sites, water ponds, residential areas, and farmlands were identified as potentially affected areas.

2.2 Laboratory analyses

During our first investigation (in 2014), we collected 20 g samples of the upper (0–20 cm) and deep (20–60) soil layers at sites A and B and mixed them at a 1:1 to obtain the final samples for each site. As the representative high-concentration points differed between the sites, five and six mixed samples were collected at Site A and Site B, respectively. The collection method was modified based on the Technical Specification for Soil Environmental Monitoring (HJ/T 166-2004) of China.

During our second investigation (in 2019), a hand-held alloy analyzer (Vanta Element-S, Olympus, Japan) was employed to rapidly determine the concentrations of metals. We then collected 20-g samples from the upper (0–20 cm) soil layers at Site A ($N = 5$) and Site B ($N = 6$) in areas with positive detection results. The second sampling point is shown in Fig. 2. Samples were air-dried in the laboratory for 48 h, sieved using a 10-mesh nylon sieve, and then stored in labeled plastic bags for later analysis. Our sample preparations and analyses followed the methods reported by Li et al. (2009), Zhang et al. (2017) and Ngo et al. (2021). For heavy metals, soil samples were digested with HCl–HNO_3–HF (1:1:1). Cu concentrations were determined using a flame atomic absorption spectrophotometer (AA 600, PerkinElmer, USA) (standard HJ491-2019), and Cd and Pb were measured using a graphite furnace atomic absorption spectrometer (AA 600, PerkinElmer, USA) (standard GB/T 17141-1997). Soil samples were extracted via Soxhlet extraction and purified using silica gel column chromatography to determine the concentrations of PBDEs and PCDD/Fs. Eight PBDEs (Table S1) were measured using a gas chromatography–mass spectrometer (GCMS-7890B-5977A, Agilent, USA) (standard HJ952-2018), and 17 PCDD/F congeners (Table S2) were analyzed using high-resolution gas chromatography–mass spectrometer (Trace 1310 GC/DFS-718109180/SN03380M, ThermoFisher, USA) (standard HJ77.4-2008).

2.3 Exposure assessment

As there were no agricultural soils or potable water around either Site A or B, we considered the ingestion of and dermal contact with contaminated soils to be the major routes of human exposure. We calculated the

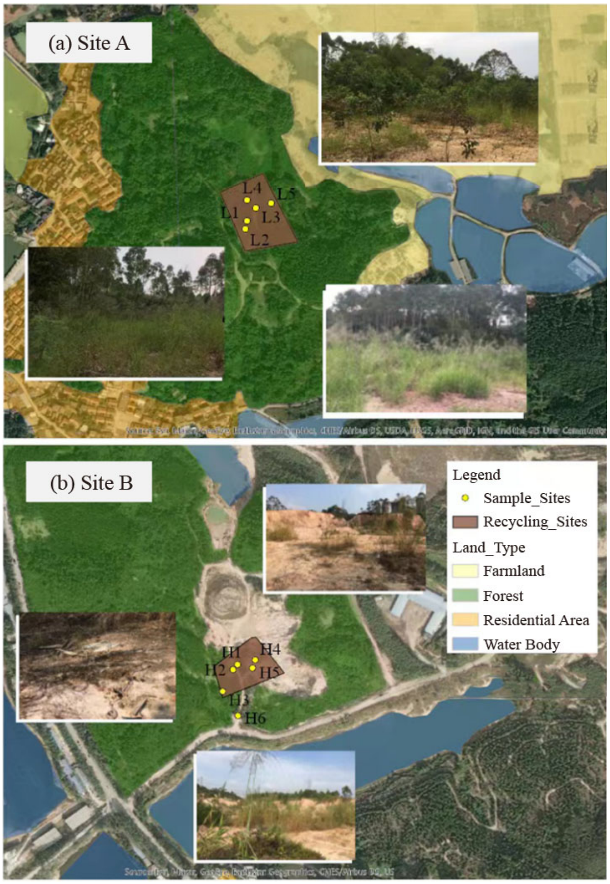

Fig. 2 Sampling locations of A (a) and B (b) e-waste sites in South China.

exposure for children (age 9–12) and adults based on the Exposure Factors Handbook of Chinese Population (Ministry of Ecology and Environment, 2016; Table 1), which provides localized Chinese exposure parameters. The average daily intake via ingestion (ADI_{ing} (mg/(kg·d))) and dermal contact (ADI_{ds} (mg/(kg·d))) were calculated using the following equations (Eqs. (1) and (2)):

$$ADI_{ing}=\frac{C\times IR\times EF\times ED}{BW\times AT}, \tag{1}$$

$$ADI_{ds}=\frac{C\times CF\times AF\times F_{exp}\times ABS\times SA\times EV\times EF\times ED}{BW\times AT}, \tag{2}$$

where C refers to the concentration of contaminants in the soil (mg/kg), IR is the rate of ingestion of contaminated soils (mg/d), CF is the conversion factor (kg/mg), AF is the adherence factor of soil to skin (mg/cm^2 per event), ABS is the dimensionless dermal absorption fraction, F_{exp} is the dimensionless fraction of the exposed skin area, SA is the surface area of the skin exposed to contaminants (cm^2), EV refers to the frequency of exposure events (events/d), EF is the exposure frequency (d/a), ED is the exposure duration (a), AT is the average exposure time (d), and BW refers to bodyweight (kg).

2.4 Total risk assessment

We evaluated the non-carcinogenic risks posed by all studied contaminants. The hazard quotient (HQ) and hazard index (HI) were calculated using the following equations (Eqs. (3) and (4)):

$$HQ=\frac{ADI_i}{RfD_i}, \tag{3}$$

$$HI=\sum_1^i HQ, \tag{4}$$

where RfD is the oral reference dose of a contaminant i (mg/(kg·d)). An exposed child is likely to experience

Table 1 Summary of exposure factors for children aged 9–12 years and both male and female adults

Exposure factors	Values			References
	Adult (male)	Adult (female)	Children (aged 9–12)	
ABS	Pb (0.01); Cd (0.01); PBDEs (0.03); PCDD/Fs (0.10)			Wu et al., 2015; US EPA, 2015
AF (mg/cm^2 per event)	0.07	0.07	0.2	Zhao et al., 2012
AT (d)	ED × 365	ED × 365	ED × 365	Zhao et al., 2012
BW (kg)	62.9	54.4	23.8	Ministry of Ecology and Environment, 2016
CF (kg/mg)	1.00×10^{-6}	1.00×10^{-6}	1.00×10^{-6}	–
ED (a)	24	24	6	Zhao et al., 2012
EF (d/a)	365	365	365	Zhao et al., 2012
EV (events/d)	1	1	1	–
F_{exp}	0.33	0.33	0.338	US EPA, 2015
IR (mg/d)	50	50	66	Ministry of Ecology and Environment, 2016
SA (cm^2)	17000	15000	9300	Ministry of Ecology and Environment, 2016

Notes: ABS, dermal absorption factor; AF, adherence factor (soil to skin); AT, average exposure time; BW, bodyweight; CF, conversion factor; ED, exposure duration; EF, exposure frequency; EV, exposure event frequency; F_{exp}, fraction of exposed skin area; IR, ingestion rate; SA, surface area; PBDEs, polybrominated diphenyl ethers; PCDD/Fs, polychlorinated dibenzo-dioxins/furans.

adverse health effects if HQ (HI) > 1. The reference doses used in this study were based on oral ingestion (Table S3). The RfDs for each target substance were as follows: Pb = 0.00015 mg/(kg·d), Cu = 0.003 mg/(kg·d), Cd = 0.0005 mg/(kg·d), BDE-47 = 0.0001 mg/(kg·d), BDE-99 = 0.0001 mg/(kg·d), BDE-153 = 0.002 mg/(kg·d), BDE-209 = 0.007 mg/(kg·d), and PCDD/Fs = 7×10^{-10} mg/(kg·d) (Table S3).

2.5 Target organ and endpoint risk assessments

The target organ toxicity dose (TTD) model proposed by the Agency for Toxic Substances and Disease Registry (ATSDR, USA) was used for target organ risk assessments of heavy metal mixtures. The TTD method represents an improvement over traditional hazard indices. By exploring the target organ toxicity of a mixture, collecting the critical thresholds for the effects of contaminants on target organs, and calculating the corresponding risks posed to target organs, the risk of mixed pollutants can be more accurately reflected. TTD is determined from toxicological data and should be based on the highest no-observed-adverse-effect level (NOAEL) that does not exceed the lowest-observed-adverse-effect level (LOAEL) for the specified endpoint. The main target organs of heavy metals include the nervous system, kidneys, cardiovascular system, blood and liver. The hazard indices of different target organs (HI_{organ}) are calculated as follows (Eq. (5)):

$$HI_{organ} = \sum_{0}^{i} \frac{E_i}{TTD_i}, \tag{5}$$

where HI_{organ} is the hazard index of different target organs (nerve, kidney, cardiovascular, blood, testis, or liver), E_i is the exposure of the i^{th} heavy metal and TTD_i is the target organ toxicity dose of the i^{th} heavy metal.

Target endpoint risk assessments were conducted for organic contaminants using extrapolated values for specific toxicological endpoints. Similarly, the highest NOAEL value that did not exceed the LOAEL of a specific endpoint was selected as the basis for extrapolation and 100 was selected as the uncertainty factor (UF) of the extrapolation. Toxicity thresholds were derived from the PubChem (NIH) and QSARToolBox (OECD and ECHA) databases, and the minimum value among all data was selected for evaluation. The main toxicological endpoints of the selected organic pollutants included acute toxicity, mutagenicity, reproductive toxicity, carcinogenicity, and repeated-dose toxicity. The calculation of risk quotient was Eqs. (3) and (4) in Section 2.4.

3 Results and discussion

3.1 Contaminant legacies

Our study provides new insights into the legacies of raw material pollution, including those of heavy metals and PBDEs, caused by the informal dismantling of electronics (Table 2). In 2014, we detected averages of 5.5 mg/kg of Cd, 1520 mg/kg of Cu, 760 mg/kg of Pb, and 424 TEQ ng/kg of PCDD/Fs at Site B. After the first investigation, private (family-owned and small business) e-waste workshops were closed in response to new regulations,

Table 2 Concentrations of heavy metals (Cd, Cu and Pb, mg/kg), PBDEs (ng/kg), and PCDD/Fs (ng/kg) in soil samples from Site A and Site B

Chemicals	Site A				Site B				
	2014		2019: L1–L5		2014		2019: H1–H5		2019: H6
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	
Cd (mg/kg)	2.36	0.28–5.46	18.9	4.84–33.5	5.5	0.28–24.2	57.2	0.03–194	0.03
Cu (mg/kg)	560	51.9–1450	4478	1708–6271	1520	113–8490	2826	7–9660	5
Pb (mg/kg)	295	21.7–664	1664	417–2959	760	50.9–3970	505	198–847	120
PBDEs (ng/kg)	–	–	2722013	1058072–4657745	–	–	27127	266–63411	824
BDE-209	–	–	87.09%	938486–4336507	–	–	60.90%	169–38144	86.85%
BDE-100	–	–	0.58%	4486–30913	–	–	13.00%	36.3–9455	1.91%
BDE-154	–	–	0.98%	6371–55012	–	–	9.70%	26.7–7347	1.66%
PCDD/Fs (ng/kg)	–	–	247653	33828–514256	–	–	682	333–974	2328
1,2,3,4,6,7,8-HpCDF	–	–	26.64%	8281–136487	–	–	11.50%	3.52–200	0.53%
OCDF	–	–	11.08%	3571–57857	–	–	14.10%	1.5–283	0.30%
1,2,3,4,6,7,8-HpCDD	–	–	12.04%	4192–62463	–	–	3.90%	2.94–54	0.62%%
OCDD	–	–	20.87%	8081–107995	–	–	54.10%	136–2278	97.83%
I-TEQ (ng/kg)	1382	677–2458	12640	1654–26855	424	68–956	17.6	1.41–47.7	5.13

Notes: I-TEQ, International Toxic Equivalence Quantity.

vegetation was planted at these former e-waste sites, and centralized parks were created for formal recycling activities. However, after five years of natural restoration, the sites remained contaminated. The Cu and Cd levels at Site B in 2019 were approximately 10× and 2× higher, respectively, than those in 2014, and this pattern was even more severe at site A. Moreover, we found various PBDE contaminants in both areas, although no direct comparison was made between 2014 and 2019 owing to a lack of data. In general, contamination was more severe at Site A than at Site B, possibly owing to differences between the original workloads at these two sites.

Zhang et al. (2017) reported significantly reduced PCDD/F levels (0.271 pg I-TEQ/m^3) in the ambient air of a region where informal incineration dismantling methods were employed when compared to data from 2009 (8.48 pg I-TEQ/m^3) (Liu et al., 2021). However, following a 5-year study period at two e-waste sites, we found the opposite (Table 2). This may be because e-waste residues were not properly handled, resulting in the continued leaching of contaminants, even after workshops were closed. According to the scope of the renovation project, soil that was severely contaminated by e-waste was excavated for treatment and vegetation was planted for on-site remediation. However, it is possible that the pollution source was not fully identified and therefore remained. The PCDD/F levels were 1000 orders of magnitude higher at Site A than at Site B, possibly owing to different incineration volumes between the sites.

3.2 Human exposure

In this study, we only calculated the potential exposure to contaminated soils from dermal contact and ingestion using the 2019 data (Fig. 3). It should be noted that other routes, including inhalation and the ingestion of contaminated water, food, and dust, are also likely to have occurred. However, because there was no agricultural land or drinking water around the sites, these other routes were not considered.

Total heavy metal exposures at Site A through the ingestion of soils and skin contact (dermal route) were approximately 10^{-2} to 10^{-5} mg/(kg·d) and ~10^{-3} to 10^{-6} mg/(kg·d), respectively, and the intakes of PBDEs and PCDD/Fs via both routes were 10^{-6} mg/(kg·d) and 10^{-7} mg/(kg·d). Heavy metal exposure at Site B was ~10^{-2} to 10^{-4} mg/(kg·d) (ingestion) and approximately 10^{-3} to 10^{-5} mg/(kg·d) (dermal route), and the intakes of PBDEs and PCDD/Fs via both routes were 10^{-8} mg/(kg·d) and 10^{-9} mg/(kg·d), respectively. These findings indicate that the heavy metal exposure through the dermal route was 1–2 orders of magnitude less than via ingestion, although

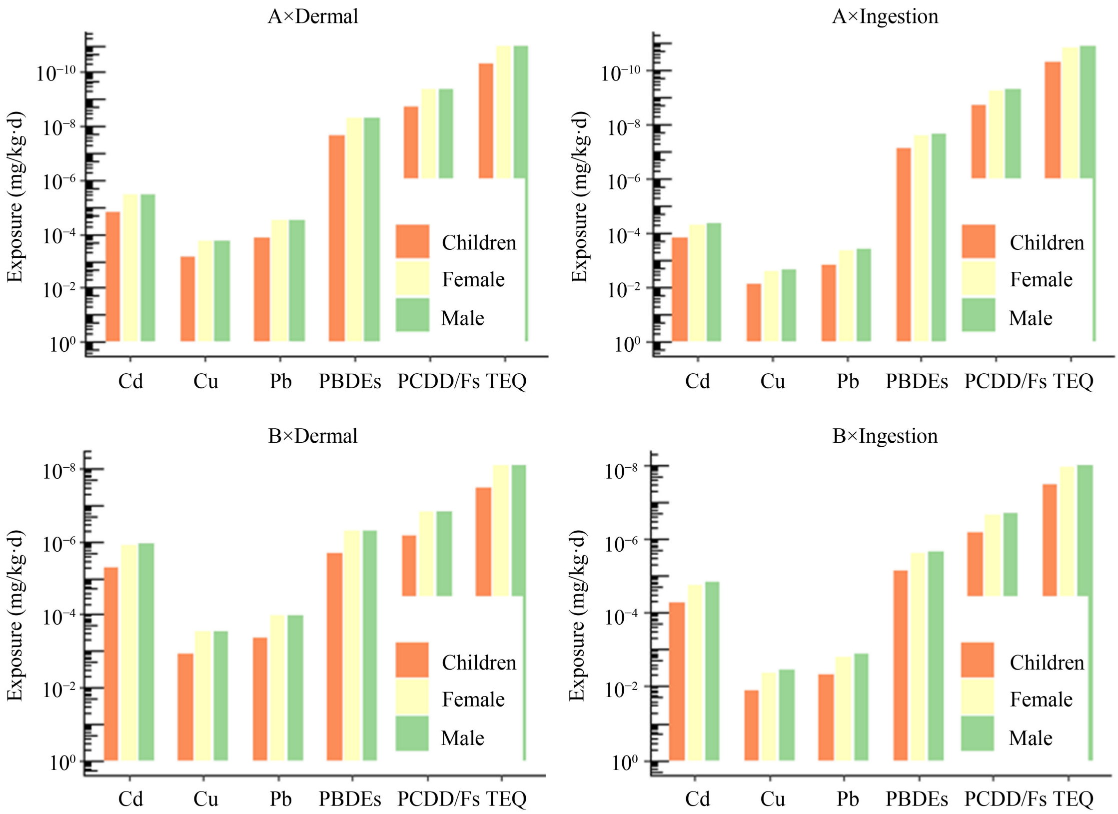

Fig. 3 Estimated average daily intake (ADI, mg/(kg·d)) of heavy metals (Cd, Cu and Pb), PBDEs and PCDD/Fs via dermal contact and ingestion of soil for children, male and female adults at A and B e-waste sites in 2019.

there was little difference between the routes for organic pollutant exposure. This is because it is difficult for intact skin to absorb heavy metals; however, it can absorb organic pollutants; these results are consistent with those of previous studies (Soetrisno and Delgado-Saborit, 2020). Additionally, the level of exposure at Site A was generally higher than that at Site B, which is also consistent with the detection results presented in Section 3.1, and may have been caused by different amounts of disassembly and incineration between the two sites. Exposure to heavy metals (Cu, Cd, and Pb) was approximately four orders of magnitude higher than exposure to PBDEs and PCDD/Fs. Cu and Pb exposures were especially high, reaching 10^{-3} mg/(kg·d), which may be explained by their high concentrations in electronic products.

Estimated levels of contaminant exposure were higher in e-waste recycling sites than in areas free of e-waste, where the average intake doses of PCDD/Fs are 0.72 pg TEQ/(kg·d) for adults and 1.08 pg TEQ/(kg·d) for children (Chan et al., 2007). Likewise, people living around Site A were exposed to higher levels of contaminants, especially PBDEs and PCDD/Fs, than those near Site B. For example, PBDE exposure via ingestion among children at Site A (7.55×10^{-6} mg/(kg·d)) was 100 times higher than that at Site B (7.52×10^{-8} mg/kg). It is important to note that children are the population most susceptible to environmental pollution. One reason for this is that children spend more time playing on the ground, have a higher chance of ingesting contaminated soils and dust, and often put their hands into their mouths before washing. Another reason is that children have a higher physiologic burden owing to a larger bodyweight-to-surface area ratio, resulting in higher exposure levels per bodyweight. For example, the daily intake of Pb among children (1.53 mg/(kg·d)) was four times higher than that among male (4.33 mg/(kg·d)) and female adults (4.96 mg/(kg·d)). Moreover, as childhood is a critical stage of developmental, contaminants can be especially harmful to children. An increasing number of studies have indicated an association between contaminant exposure in early life with later health consequences, including adverse developmental effects (Xue et al., 2012).

3.3 Total risk

We quantified non-carcinogenic health risks by using HQs, which were only calculated based on ingestion exposure (not including dermal contact) because the reference doses used in this study were based on oral data. We found a potential for health risks due to Cu, Pb, and TEQ, indicated by HQ > 1 (Fig. 4). In general, compared to both male and female adults, children were at elevated health risks owing to their relatively high exposure, which is consistent with previous findings (Soetrisno and Delgado-Saborit, 2020). At both sites, heavy metals (Cu and Pb) posed potential hazards to nearby residents. It is possible that e-waste residues were not fully removed and remained in the soil. Further research and treatment are needed to reduce these risks. Additionally, PCDD/Fs posed health risks at Site A, yet they are not properly handled or are left untreated at most

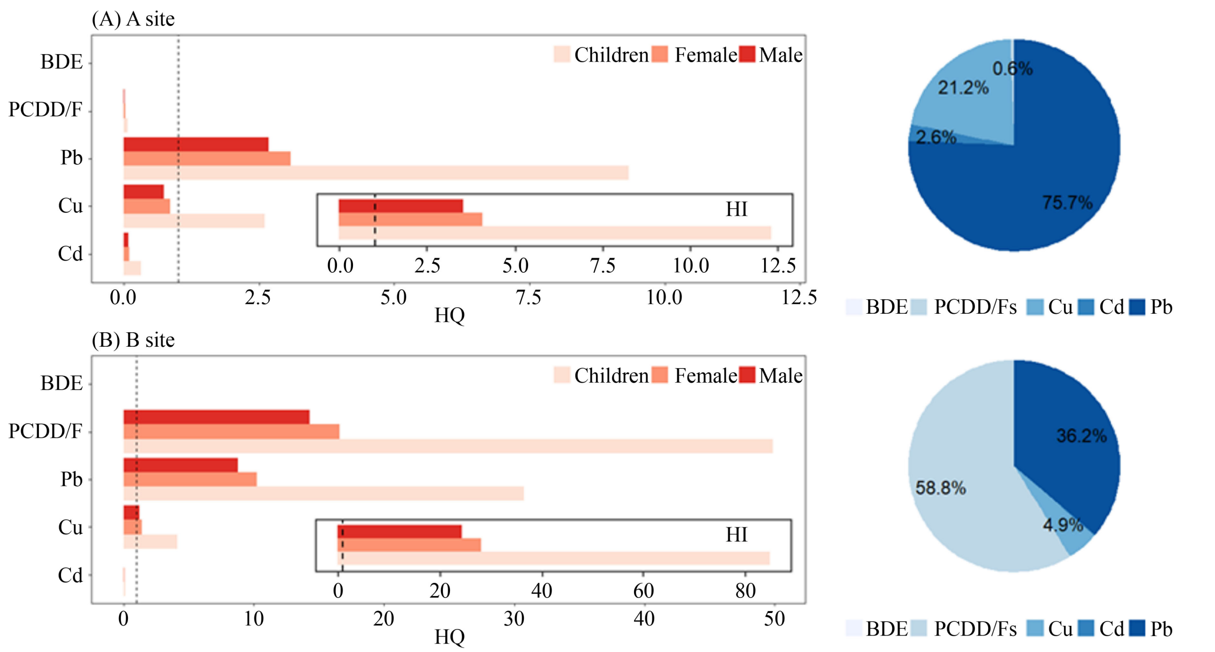

Fig. 4 Estimated hazard quotients for heavy metals (Cd, Cu and Pb), PBDEs and PCDD/Fs via ingestion of soil for children, male and female adults at A and B e-waste sites.

abandoned e-waste sites. The legacies of these contaminants may pose risks to surrounding neighborhoods without notification and awareness. Interventions are needed before adverse health effects occur.

We examined the PCDD/Fs that contributed the most to overall health risk among the 17 detected at Site A and Site B (Fig. 5). Among them, 2,3,4,7,8-PeCDF accounted for ~13.43%–40.26% of the risk at each site owing to its high toxicity, despite relatively low concentrations. This is consistent with the results of Hu et al. (2009) and indicates that concentrations alone can not be used to evaluate the risks posed by PCDD/Fs; rather, the contribution of the corresponding toxic equivalent should be considered. Additionally, because e-waste in South China is incinerated, the impacts on the atmospheric environment are also particularly large (Xiao et al., 2014), which may be due to the easier evaporation of 2,3,4,7,8-PeCDF, resulting in more of it staying in the atmosphere.

3.4 Risk to target organs and endpoints

We performed further risk assessments for target organs and endpoints for compounds with an overall HI > 1. At Site B, only Pb posed a risk to the entire population, and Cd had the risk of exposure to children. After further calculations, we found that the target organ and specific endpoint risks of Site B were all less than 1; therefore, we focused on Site A. The target organ risk assessment of the TTD model was used to assess heavy metals. The target organs for Pb to produce effects were the nervous system, kidneys, blood, cardiovascular system, and testis (Hana and Moi, 2018), for which the TTD values were 0.1, 0.34, 0.1, 0.1, and 0.4 mg/(kg·d), respectively. The TDD values for the target organs of Cd production (Hana and Moi, 2018) were 2 × 10^{-4} mg/(kg·d) (nervous system), 1 × 10^{-4} mg/(kg·d) (kidneys), 8 × 10^{-4} mg/(kg·d) (blood), and 3 × 10^{-3} mg/(kg·d) (testis). The target organs of Cu were the blood and liver (Hana and Moi, 2018), for which the TTD values were 0.3 and 0.14 mg/(kg·d), respectively. Blood was the common target organ of all three heavy metals. Considering the additive effects of heavy metals in all target organs, we found that there was little risk independently imposed by Pb, Cu, and Cd on the nervous system (HI = 0.34), kidneys (HI = 0.59), cardiovascular system (HI = 0.05), blood (HI = 0.16), testis (HI = 0.03), or liver (HI = 0.10). However, the superimposed HI value of the toxic effects was 1.27, meaning that the heavy metals pose a collective health risk.

The target endpoint risk of PCDD/Fs was calculated from exposure to TEQ/ Tetrachlorodibenzodioxin (TCDD) and the RfD of each toxicity endpoint of TCDD. Toxicity thresholds were derived from the PubChem and QSAR-ToolBox databases and the minimum value among all data was selected for evaluation, of which the lethal dose 50 (LD_{50}) of acute toxicity was 7 × 10^{-5} mg/kg, the no-observable-effect level (NOEL) for repeated-dose toxicity was 4.5 × 10^{-3} mg/kg, the tumorigenic dose rate 50 (TD_{50}) for carcinogenicity was 1.6 × 10^{-4} mg/kg, the NOEL for endocrine disruption was 7.5 × 10^{-6} mg/kg, and the NOEL of reproductive toxicity was 1.6 × 10^{-6} mg/kg. An uncertainty factor (UF) = 100 was selected and the RfD of the corresponding endpoint was obtained by extrapolation. From the final risk (Table 3), it can be seen that exposure to this concentration of PCDD/Fs causes endocrine disruption in people of all ages and sexes, but especially in children (HI up to 3.54) who are also at risk of reproductive toxicity. This explains why children are a high-risk group that requires special attention and consideration.

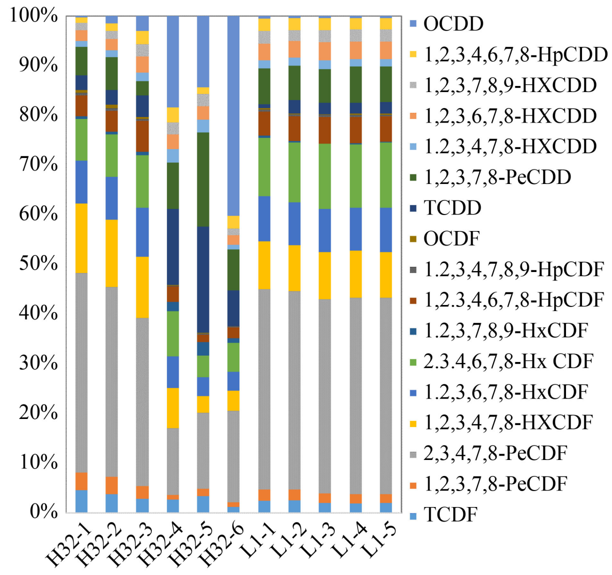

Fig. 5 Toxicity equivalent contribution ratio of 17 PCDD/Fs.

4 Conclusions

Informal e-waste activities can cause environmental contamination and potential health risks to nearby populations. This study involved 5-year site monitoring and the detection legacy of heavy metals (Cd, Cu, and Pb), PBDEs, and PCDD/Fs at two “restored” e-waste

Table 3 Risk of PCDD/Fs in male and female adults, and in children aged 9–12 for each endpoint

Endpoint	Risk (HI)		
	Adult (male)	Adult (female)	Children (aged 9–12)
Acute toxicity	0.14	0.17	0.38
Repeated-dose toxicity	0.00	0.00	0.00
Carcinogenicity	0.06	0.07	0.17
Endocrine disruption	1.34	1.55	3.54
Reproductive toxicity	0.63	0.73	1.66

sites. The concentrations and detection rates of heavy metals and PCDD/Fs were high, indicating that without proper restoration, contaminants can persist over long periods in soils, even when pollution activities have stopped.

Numerous studies have reported on the physiologic burdens of different contaminants in human specimens. It has been suggested that PCDD/F and PCB levels in hair, milk, and cord whole blood among people living around e-waste recycling sites are higher than those in reference sites. However, it should be noted that biomonitoring data only reflect the combined or total exposure. Further research on exposure pathways should be conducted to control and reduce physiologic burdens in these areas. Children are exposed to higher levels of contaminants via dermal contact with and the ingestion of contaminated soils than adults, which is especially concerning because children are more susceptible to environmental hazards.

Lead, Cu, and PCDD/Fs are more likely to have adverse health outcomes than other contaminants recorded at Site A or Site B, as indicated by HQ > 1. Our study indicates the potential for health risks (HI > 1) at both sites. Notably, the HQs in this study were calculated from external exposure and likely represent conservative estimates. Contaminants entering the human body may not be fully absorbed and may reach a target organ. With normal renal function, it is likely that they will be eliminated from urine. Abundant biomonitoring data on human placentas, blood, serum, and breast milk are available for internal exposure. These data can be used to quantify and compare health risks. Nevertheless, more studies on the mode(s) of action, adverse outcome pathways, and toxicity are needed to quantify the dose–response relationship and to inform environmental management practices.

Further attention should be paid to the stacked organ risk of heavy metal mixtures (HI = 1.27). Exposure to high concentrations of/highly toxic PCDD/Fs may cause endocrine disruption in the entire population, especially in children (HI = 3.54), who are at very high risk, including of reproductive toxicity (HI = 1.66). These results are consistent with those of previous studies that have shown that children are at greater risk than adults for adverse health effects due to contaminant exposure. Interventions are needed to control and reduce contamination and the associated health risks in e-waste-affected regions.

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