Title
Emission characteristics and exposure assessment of particulate matter and polybrominated diphenyl ethers (PBDEs) from waste printed circuit boards de-soldering

Authors
Guo, Jie
Ji, Ang
Wang, Jianbo
et al.

Publication Date
2019-04-01

DOI
10.1016/j.scitotenv.2019.01.176

Peer reviewed

Science of the Total Environment 662 (2019) 530–536

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Emission characteristics and exposure assessment of particulate matter and polybrominated diphenyl ethers (PBDEs) from waste printed circuit boards de-soldering

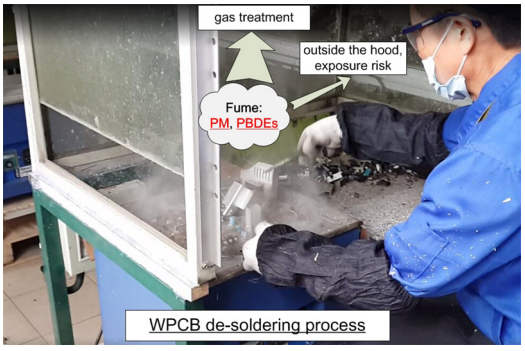
Jie Guo [a,b], Ang Ji [a], Jianbo Wang [a], Oladele A. Ogunseitan [b], Zhenming Xu [a,*]

[a] School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China
[b] Department of Population Health and Disease Prevention & School of Social Ecology, University of California, Irvine, CA 92697-3957, USA

HIGHLIGHTS

- Toxic fumes were generated during waste printed circuit board heating process.
- Particulate matter and PBDEs were two key pollutants during de-soldering process.
- The deposition flux for coarse particles in the head airways was the largest.
- PM in fumes can be effectively removed by the negative pressure hood.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 November 2018
Received in revised form 14 January 2019
Accepted 14 January 2019
Available online 15 January 2019

Editor: Adrian Covaci

Keywords:
Electronic waste
Recycling
Fumes
Particulate matter
Risk assessment

ABSTRACT

Heating processes for the removal of electronic components from waste printed circuit boards (WPCBs) is an important step in the chain of electronic waste recycling, and toxic fumes are generated during the de-soldering process, causing environmental pollution and posing health risks for the workers. This study is aimed to characterize emission and deposition fluxes of respirable particulate matter (PM), and assess exposure of workers to particle-bound polybrominated diphenyl ethers (PBDEs). An electrical low-pressure impactor was used to measure the real-time PM concentrations inside and outside the hood during the WPCBs de-soldering process. The results show that PM mass concentration inside the hood (204 mg/m^3) was significantly higher than outside the hood (9.4 mg/m^3), representing 95.4% PM removal by the hood. According to the International Commission on Radiological Protection model, the total deposition fluxes of PM in head airways region, tracheobronchial region, and alveolar region were determined as 1930, 74.0, and 123 μg/h, respectively. The deposition flux for coarse particles (2.5–10 μm) in the head airways was the largest (1830 μg/h), accounting for 86.1% of total PM deposited in respiratory system. The $\sum_8$PBDEs concentration in PM_{10} inside the WPCBs de-soldering workshop was 20,300 pg/m^3, and the $\sum_8$PBDEs inhalation exposure for the worker was 1.46 ng/kg/day. This study improves understanding of PM emission mechanisms and provides fundamental data for health assessments during WPCBs de-soldering process.

* Corresponding author.
E-mail address: zmxu@sjtu.edu.cn (Z. Xu).

https://doi.org/10.1016/j.scitotenv.2019.01.176
0048-9697/

1. Introduction

The generation of waste electrical and electronic equipment (WEEE) in all parts of the world continues to increase rapidly. For example, data show that 633 million tonnes of WEEE were generated in China, in 2014, accounting of about 13.2% of global generation of WEEE (Baldé et al., 2015; Ogunseitan et al., 2009; Chen et al., 2011). Waste printed circuit boards (WPCBs) form the base component of WEEE, consisting of the electronic components and the base board. Generally, electronic components are attached on the base board through the adhesion of solder. Therefore, heat treatment is needed to melt this solder for removal of the electronic components during disassembly in the recycling process.

Previously in Guiyu (Guangdong Province, China) primitive recycling methods were used without environmental protection. These included first placing the WPCBs on the coal-heated grills to melt solder, and then removing the various components with pliers (Puckett et al., 2002). During the de-soldering process, substantial quantities of harmful fumes were emitted intermittently, resulting in severe toxic pollution in the workshop and nearby environment (Leung et al., 2011; Ren et al., 2014; Bi et al., 2010).

Various toxic compounds were emitted during WPCBs recycling processes, such as volatile organic compounds (VOCs) (An et al., 2014; Chen et al., 2016a, 2016b; He et al., 2015; Liu et al., 2017), semi-volatile organic compounds (Ortuño et al., 2014; Li et al., 2018), and heavy metals (Bi et al., 2010; Duan et al., 2012; Fang et al., 2013). Many researchers (Ren et al., 2014; Bi et al., 2010; An et al., 2011) studied the airborne and floor pollution caused by WPCBs de-soldering processes in WEEE recycling areas in China, and found that particulate matter (PM) and polybrominated diphenyl ethers (PBDEs) are two key pollutants contained in emitted fumes during WPCBs de-soldering process. Bi et al. (2010) found that organic matter comprised 46.7–51.6% of the PM collected from WPCBs recycling workshop, and metal elements (Pb, Zn, Sn, Cu, and Mn) were found in PM. However, research on the PM emission mechanism during WPCBs de-soldering process is not extensive. PBDEs, a group of brominated flame retardants, were widely used in the base board of WPCBs in old home appliances. The data show that 25% of Flame Resistant 2-type WPCBs used in old home appliances were treated with penta-BDE mixtures (UNEP, Stockholm Convention on Persistent Organic Pollutants (POPs), 2009). Due to the semi-volatile properties of PBDEs, PBDE congeners contained in WPCBs are typically emitted to the environmental medium, especially during heating process, thus posing exposure risk and resulting adverse effects for workers due to the inhalation of polluted air (Ma et al., 2009; Zeng et al., 2016).

The fumes emitted from WPCBs de-soldering, including PM and particle-bound PBDEs, has many negative effects on environmental quality and human health (Zheng et al., 2017; Chen et al., 2011). The Chinese government has banned the crude method for WPCBs de-soldering without pollution control; instead, policies and guidelines allow WPCBs de-soldering processes equipped with a negative pressure platform and gas treatment mechanisms (Li et al., 2015; MEE, China. Ministry of Ecology and Environment of the People's Republic of China, 2014). Thus, the majority of the fumes can be withdrawn by the hood and treated by gas control facilities. However, some fumes are inevitably leaked out of the hood, polluting the air quality in the workshop and posing an occupational exposure risk for the workers.

The deposition of PM in the respiratory systems is important for evaluating the potential risk of inhaled particles. The human respiratory system has three regions: head airways region (HA), tracheobronchial region (TB), and alveolar region (AR) (Hinds, 1999). Those three respiratory regions are markedly different in structure, function, and sensitivity to particles, thus influencing the aerodynamic behavior and deposition location of PM with particle size and shape on the respiratory system. Based on the particle distribution of PM and International Commission on Radiological Protection (ICRP) exposure model, the health effects of size-dependent PM after fume inhalation can be assessed.

This study aimed to investigate hazards associated with WPCBs de-soldering through PM emission characteristics and health risk assessment related to PM and particle-bound PBDEs, with particular emphasis on the effectiveness of the extraction hood. We also sought to evaluate the inhalation exposure risk for e-waste workers and the potential for environmental pollution from e-waste management practices.

2. Methods

2.1. Sampling information

The WPCBs samples were dismantled from waste cathode ray tube TV sets, before processing in the WPCBs de-soldering workshop of a WEEE recycling plant in Shanghai, China. The platform was equipped with negative pressure ventilation and hood, and a furnace for heating tin ingot was fixed inside the hood. The WPCBs de-soldering procedures were as follows as shown in Fig. S1 in the Supplementary Data (SD): (1) Tin ingot was melted to liquid state in the heating furnace at 300 °C; (2) WPCBs samples with solder-tin side were immersed into the liquid tin. After 20–30 s, the solder-tin on the WPCBs melted; (3) the worker removed the electronic components from the base board with pliers.

2.2. PM sampling

An electrical low-pressure impactor (ELPI, Dekati Co. Ltd., Finland) and a PM_{10} sampler (100 L/min, Lao Ying 2030, Qingdao Laoshan electronic instrument factory Co. Ltd., China) were placed in the workshop. The ELPI was fixed about 1 m away from the hood in one side, while the PM_{10} sampler was fixed about 2 m away from the hood in the other side.

Real-time detection of PM: The ELPI was used to detect the particle size distribution of the fumes generated during the WPCBs de-soldering process. ELPI is a real-time airborne particle size spectrometer, measuring particle size distribution in the size range of 0.03–10 μm with 12 channels. The particle size ranges and geometric mean of aerodynamic diameter (D_i) of 12 channels are shown in Table 1. The ELPI operating principle is based on particle charging, inertial classification in a cascade impactor, and electrical detection of the aerosol particles. The PM particles were collected on the aluminum substrate with grease-coated, and 3 kinds of particles range in 1.0–1.6, 2.5–4.4, and 6.8–9.97 μm were used for Scanning Electron Microscopy (SEM) coupled with Energy-Dispersive X-ray (EDX) analysis. The air samples were withdrawn to the inlet of ELPI machine by a vacuum pump, and a 1.5-m vacuum hose was connected to the inlet of ELPI machine. When turning on the vacuum pump, the air samples were collected from the inlet of the hose, and then entered into the inlet of ELPI machine. The inlet of the hose was fixed at 3 different sites: (1) from 0 to 100 s: gas samples (about 1 m away from the hood) in the workshop were withdrawn; (2) from 100 to 370 s: gas samples outside the hood (close to the nose of the worker) were sampled, and the data can be used for occupational exposure assessment; (3) from 370 to

Table 1
Particle size ranges and geometric mean of aerodynamic diameter (D_i) of 12 channels of ELPI.

Channel	Particle size range		D_i (μm)
	Lower limit (μm)	Upper limit (μm)	
1	0.03	0.081	0.039
2	0.081	0.108	0.071
3	0.108	0.17	0.12
4	0.17	0.26	0.20
5	0.26	0.4	0.31
6	0.4	0.65	0.48
7	0.65	1.0	0.76
8	1.0	1.6	1.22
9	1.6	2.5	1.94
10	2.5	4.4	3.06
11	4.4	6.8	5.12
12	6.8	9.97	8.08

520 s: gas samples inside the hood (on top of the heating furnace) were withdrawn. The particles were divided to 3 categories according to the aerodynamic diameter (D_i): coarse particles ($PM_{2.5-10}$, $2.5 < D_i < 10$ μm, channel 10–12), fine particles ($PM_{2.5}$, $D_i < 2.5$ μm, channel 1–9), and ultrafine particles ($PM_{0.1}$, $D_i < 0.1$ μm, channel 1–2).

PM_{10} sampling: PM_{10} samples in the workshop were collected on glass fiber filters (diameter = 90 mm, pore size = 0.1 μm). The sampling duration for each sample was 4 h during the working time near the worker. Concentrations of PM_{10} were determined by weighing filters before and after sampling.

2.3. Deposition of PM in the respiratory system

The deposition characteristics of PM in the respiratory system of the worker for WPCBs de-soldering were estimated with an ICRP model. The deposition efficiencies of inhaled PM in three regions (HA, TB, and AR) in the respiratory system for male worker at the sitting level of exercise (breathing rate of 0.54 m^3/h) were calculated based on the ICRP model. More details about the ICRP are shown in the SD.

2.4. PBDEs measurement

The particles in PM_{10} were collected for particle-bound PBDEs tests. Firstly, the weighed glass fiber filters were cut into chips using stainless scissors. Then chopped PM_{10} filters were extracted by soxhlet extraction using and a dichloroethane/hexane solvent mixture (1:3 v/v) for 12 h. Samples were concentrated to a small volume and transferred into hexane. Further cleanup using a multilayer silica gel column was carried out, and samples were eluted with dichloromethane/hexane mixture (1:1 v/v). The sample extracts were analyzed by an Agilent 7890A gas chromatograph coupled with a 5975C mass spectrometer using negative chemical ionization (GC-NCI-MS) in the selected ion monitoring (SIM) mode. More details on the extraction procedure were illustrated in the SD. The 8 BDE congeners (BDE-28, -47, -100, -99, -154, -153, -183, and -209) in PM_{10} samples were tested.

3. Results

3.1. PM emission characteristics

Fig. 1 shows the current values of the 12 channels in the ELPI during the WPCBs de-soldering process.

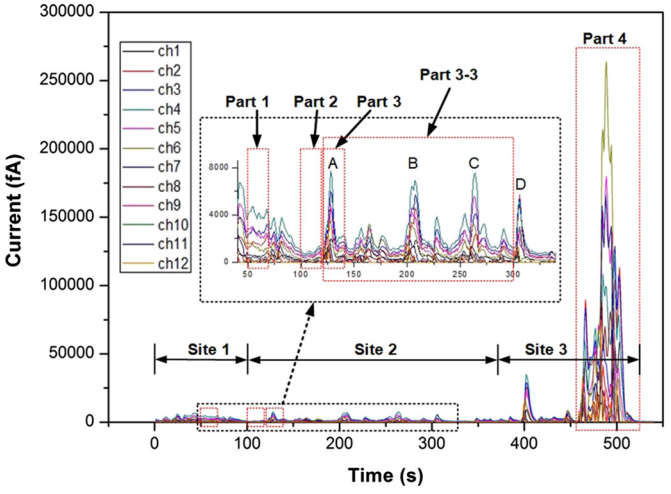


Fig. 1. Current values of 12 channels in ELPI during WPCBs de-soldering process. 3 inlet sampling sites for ELPI: Site 1 - gas samples in the workshop, and it means that the background PM in the workshop; Site 2 - the inlet sampling position was moved outside the hood, close to the nose of worker dismantling WPCBs; Site 3 - sampling inlet was moved inside the hood (on top of the heating furnace).

As mentioned, there are 3 inlet sampling sites as shown in the current values of ELPI: (1) Site 1 (0–100 s): gas samples in the workshop were withdrawn, and the current line were relatively stable, and no obvious peeks occurred. This means that the background PM in the workshop was a stable control; (2) Site 2 (100–370 s): the inlet sampling position was moved outside the hood, close to the nose of worker dismantling WPCBs. During this time period, four current value peaks (A–D) can be seen, which represented the de-soldering process for four pieces of WPCBs. The current values of the ELPI were proportional to the number and mass concentrations of collected particles, and the current peaks represented the real-time increase of particle population. The de-soldering process mainly includes two steps: the first step is the heating process for melting the solder, and the second step is to manually remove the electronic components through knocking and pulling with pliers by dismantling workers. During the heating process, the resin matrix and organic additives (PBDEs etc.) contained in the base board of WPCBs were also heated by the hot liquid tin, thus generating the fumes. After 20–30 s of heating time, the solder on the WPCB melted, and the worker started to manually remove the electrical components. Meanwhile, the fumes released from the base board were withdrawn by the negative pressure hood or diffused outside the hood due to the removal process. The knocking and pulling process for each piece of WPCBs lasted about 20 s, which was consistent with the duration of each peak. The operation of knocking and pulling by the hands of dismantling worker stirred the air fluent inside the hood, likely resulting in the leakage of fumes outside the hood. Then the fume was sampled by the ELPI, resulting in the occurrence of Peak A–D. (3) Site 3 (370–520 s): sampling inlet was moved inside the hood (on top of the heating furnace). The current peaks during this time period were obviously higher than the peaks sampled at Site 1 and Site 2.

In order to compare PM number concentration and mass concentration distribution, we chose four parts of time period as shown in Part 1 (50–70 s), Part 2 (100–120 s), Part 3 (121–141 s), and Part 4 (460–520 s). Part 1 represents the background of PM in the workshop, Part 2 and Part 3 represents the PM levels before and after WPCBs de-soldering process outside the hood, and Part 4 represents the PM emission inside the hood. Fig. 2 shows the number and mass concentration distribution of PM in the Part 1, Part 2, Part 3, and Part 4.

Generally, PM number concentrations decreased with the increase of particle size, while mass concentrations increase with the increase of particle size. However, the mass concentration distribution displays a slightly unimodal distribution, with peaks located at 0.31 μm for Part 1 and Part 2. The PM in Part 2 was affected by the negative pressure inside the hood, so PM concentration outside the hood before WPCBs de-soldering was lower than that in the workshop (Part 1). The mass concentration distribution ($dM/dlogD_p \sim D_p$) in Part 3 and Part 4 have no obvious peak (Fig. 2b), and the shapes are similar. $PM_{0.1}$ number and mass concentrations vary from 8.67×10^4 to 7.09×10^6 cm^{-3}, 2.66×10^{-3} to 1.07 mg/m^3. $PM_{2.5-10}$ number and mass concentrations vary from 10.8 to 3445 cm^{-3}, 0.25 to 679 mg/m^3. The values of PM number and mass concentrations in Part 4 were about 2–3 orders of magnitude higher than those in Part 1, 2 and 3.

3.2. Deposition characteristics of PM in the respiratory system

To evaluate exposure to PM through inhalation during WPCBs de-soldering process, we chose Part 3–3 (from 120 to 300 s) as the actual scenario for assessment when the sampling position was fixed near the nose of the worker outside the hood. Part 3–3 represents the period of treating 3 pieces of WPCBs. The peaks (A, B, C) in Fig. 1 represent the fumes leaked from the hood during the removal process of WPCBs, while some lower peaks represent the fumes leaked from the hood during heating process. So, the mass concentration of PM inhaled by the worker was taken to be the mean value of mass concentrations in the Part 3–3. Detailed data on the deposition fractions and fluxes of PM in the three regions are shown in Table 2.

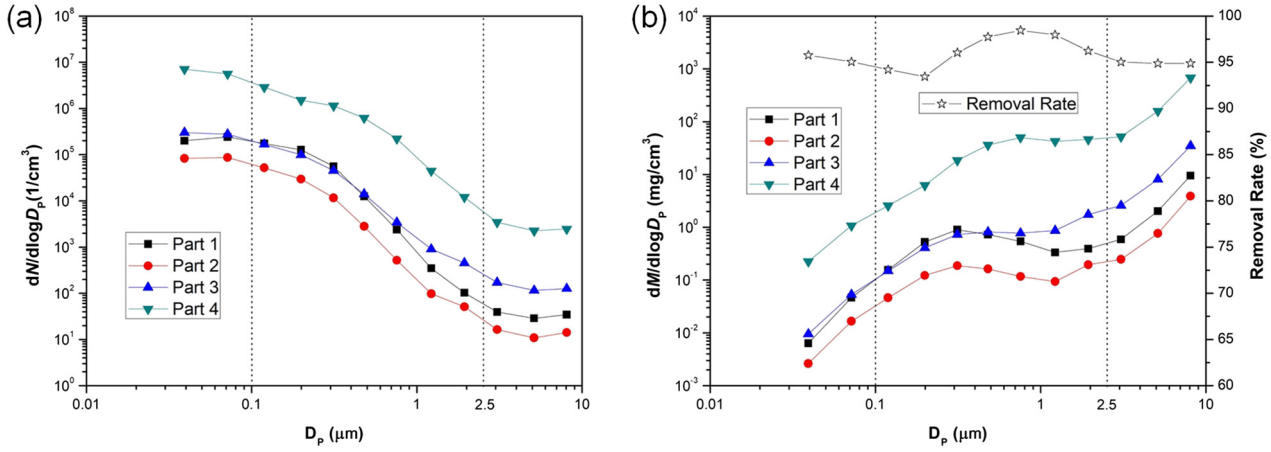


Fig. 2. Number (a) and mass (b) concentrations of PM. Part 1 represents the background of PM in the workshop, Part 2 and Part 3 represent the PM samples before and after WPCBs de-soldering process outside the hood, and Part 4 represents the PM emission inside the hood.

The number and mass cumulative distribution in PM_{10} are shown in Fig. 3, and similar distribution patterns were observed in Parts 1, 2, 3, and 4. The number cumulative values of ultrafine particles ($PM_{0.1}$) in Part 1, Part 2, Part 3, and Part 4 (Fig. 3a) were 59.0%, 68.1%, 68.3%, and 71.4%, respectively.

Based on the ICRP equations (in the SD) and the mass concentrations of PM detected from the ELPI machine, the total deposition fluxes of PM in the HA, TB, and AR were 1930, 74.0, and 123 μg/h, respectively. The deposition flux for coarse particles in 2.5–10 μm in the HA was the largest (1830 μg/h), accounting for 86.1% of the total PM deposited in respiratory system. Conversely, the deposition fluxes for the ultrafine particles (Di < 0.1 μm, channel 1 and 2) in the HA, TB, and AR were 0.16, 0.27, and 1.30 μg/h, respectively. It indicated that ultrafine PM were dominant in the AR, accounting for 75.1% of the ultrafine particles in the respiratory system.

3.3. SEM morphology of PM

SEM coupled with EDX was used to characterize the size, morphology and chemistry of particles collected from aluminum substrates.

Fig. 4a shows the morphology of particles in 1.0–1.6 μm. The upper-left and upper-right figures are the EDX spectrum and mapping distribution of Sn for Fig. 4a. Some individual fine particles circled in red dashed line circles are for ~1 μm particle size. However, some fine and coarse particles with irregular shapes agglomerated loosely in the center position, and the relatively coarse particles in Fig. 4a were mainly captured inside the hood from tin melting process. During both the solder melting and manual removing process, tiny fractions affiliated with liquid metals-droplets were withdrawn by the pump of ELPI. From the upper-left spectrum of three repeat EDX analysis, the dominated element is Al (88.04%), but also includes several other metal elements, including Mn (2.07%), Fe (0.59%), Zn (0.36%), Sn (0.81%), and Au (2.18%). The collection substrate consisted of aluminum, so the weight percentage of Al was up to 88.04%. According to the mapping of Sn spatial distribution in the upper-right figure, the Sn distribution is consistent with the SEM morphology, and the 0.81% Sn element dispersed over the whole zone, especially affiliated on the surface of coarse particles. During the WPCBs de-soldering process, the fixed temperature of furnace was 300 °C, while the melting point of Sn element is 232 °C. Therefore, the tin ingot and the solder on the WPCBs can melt to liquid state and generate Sn vapor. It is likely that the Sn vapor can float to the fumes in the condition of negative pressure of the hood. As the fumes were withdrawn into the ELPI, the Sn vapor cooled and adsorbed on the surface of particles. Fig. 4b shows that fine particles with particle size of 2.5 μm are mainly in the form of individually spherical particles. The spherical shape is indicative of a high-temperature process, which may originate from the melting process (Zhao et al., 2016). In Fig. 4c, coarse particles with irregular shapes in 6.8–10 μm range can be seen, and the fractions of WPCBs base board are the likely source.

3.4. Exposure and health assessment of PM and PBDEs

The PM_{10} concentration (detected by PM_{10} sampler) in the workshop was 397 μg/m^3, which was about 8 times higher than WHO guidelines for PM_{10} (50 μg/m^3, 24-hour mean) (WHO (World Health Organization), 2006), and over 2 times higher than 2nd grade for PM_{10} (150 μg/m^3, 24-hour mean) from Chinese Ambient Air Quality Standards (GB3095-2012). High-level PM_{10} inside the workshop, consisting of a complex

Table 2
Mean mass concentrations (μg/m^3), inhalation fraction (IF), deposition fractions (DF, %), and deposition fluxes (F, μg/h) of PM outside the hood.

Channel	D_i	Mean mass concentration	IF	DF-HA	DF-TB	DF-AR	DF	F-HA	F-TB	F-AR	F
	μm	μg/m^3		%				μg/h			
1	0.039	1.70	1	4.79	8.91	37.0	50.7	0.04	0.08	0.34	0.47
2	0.071	8.23	1	2.64	4.30	21.5	28.4	0.12	0.19	0.96	1.26
3	0.12	22.6	1	2.02	2.02	11.2	15.2	0.25	0.25	1.37	1.87
4	0.20	72.9	1	2.58	0.86	6.25	9.69	1.02	0.34	2.46	3.81
5	0.31	98.8	1	4.68	0.48	5.93	11.0	2.50	0.26	3.16	5.92
6	0.48	136	1	9.31	0.66	7.94	17.9	6.85	0.49	5.84	13.1
7	0.76	122	1	19.1	1.65	10.8	31.5	12.6	1.09	7.13	20.8
8	1.22	138	1	36.8	3.64	12.7	53.1	27.5	2.72	9.49	39.7
9	1.94	150	0.998	58.0	5.57	12.1	75.6	46.9	4.51	9.80	61.2
10	3.06	256	0.991	76.0	6.03	9.40	91.4	105	8.35	13.0	126
11	5.12	829	0.966	86.6	4.39	5.58	96.5	387	19.6	24.9	432
12	8.08	2900	0.896	85.4	2.31	2.84	90.5	1340	36.1	44.4	1420
total	–	4730	–	–	–	–	–	1930	74.0	123	2120

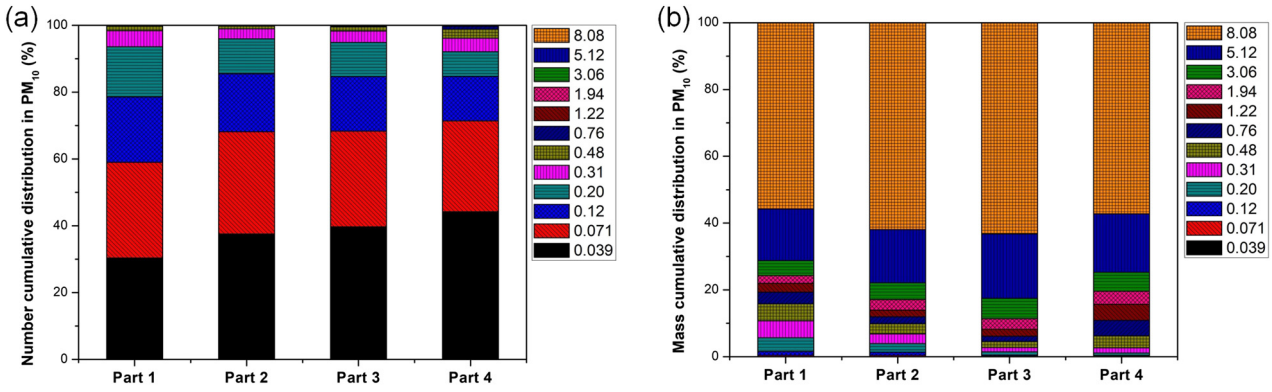


Fig. 3. Number (a) and mass (b) cumulative distribution in PM. Part 1 represents the background of PM in the workshop, Part 2 and Part 3 represent the PM samples before and after WPCBs de-soldering process outside the hood, and Part 4 represents the PM emission inside the hood.

mixture of organic and inorganic substances, can enter the respiratory system and potentially cause adverse effects on workers' health.

In order to investigate the inhalation exposure of particle-bound PBDEs in the workshop, the PBDEs concentration in PM_{10} were measured. The congener concentrations of BDE-28, -47, -100, -99, -154, -153, -183, and -209 in PM_{10} were 677, 9470, 910, 6480, 228, 541, 20.2, and 1990 pg/m^3, respectively (Table 3). From Table 3, showing comparison in various sampling workshops for e-waste recycling, we discovered that the indoor air concentrations of PBDEs were in order of WPCBs heating process > WPCBs/plastic shredding process > TV dismantling process > e-waste storage facility. In Ren et al.'s (2014) and Guo et al.'s (2015b) studies, the concentrations of BDE-47 and -99 were in range of 139,000–236,000 pg/m^3, 2–4 orders magnitude higher than those in other workshops.

4. Discussion

Since China's Guiyu e-waste recycling region shifted away from primitive processes by the start of 2016, the e-waste recycling activity in Guiyu has moved from dispersed home-workshops to industrial parks equipped with chimney systems for reducing the gaseous emissions. Currently, WPCBs de-soldering processes still exist in the industrial park workshops, and pollution caused by WPCBs de-soldering remains a grave problem in e-waste dismantling zones. The hood was used to withdraw the fumes emitted from the WPCBs de-soldering process, and PM in Part 3 (Fig. 1) was the leakage of PM out of the hood. So, the PM removal rate of the hood can be calculated by comparing the Part 3 and Part 4. Compared with PM in Part 4, the total PM (from channel 1 to 12) mass concentrations in Part 3 decreased from 203.6 mg/m^3 to 9.4 mg/m^3, equating to a total removal rate of 95.4%. The detailed removal rates for different size particles were shown in Fig. 2b. The removal rate of different size particles can reach 93.4–98.5%, and the hood has the strongest and weakest faculty to remove the particles with D_i of 0.76 and 0.20 μm, respectively. The particles have various dynamic behaviors when the worker stirred the air flow and the removal process can be influenced by many factors, such as inertial impaction, interception, diffusion collision, and gravity, etc. (Zhao et al., 2016). The fumes in Part 4 inside the hood had the highest percentage of

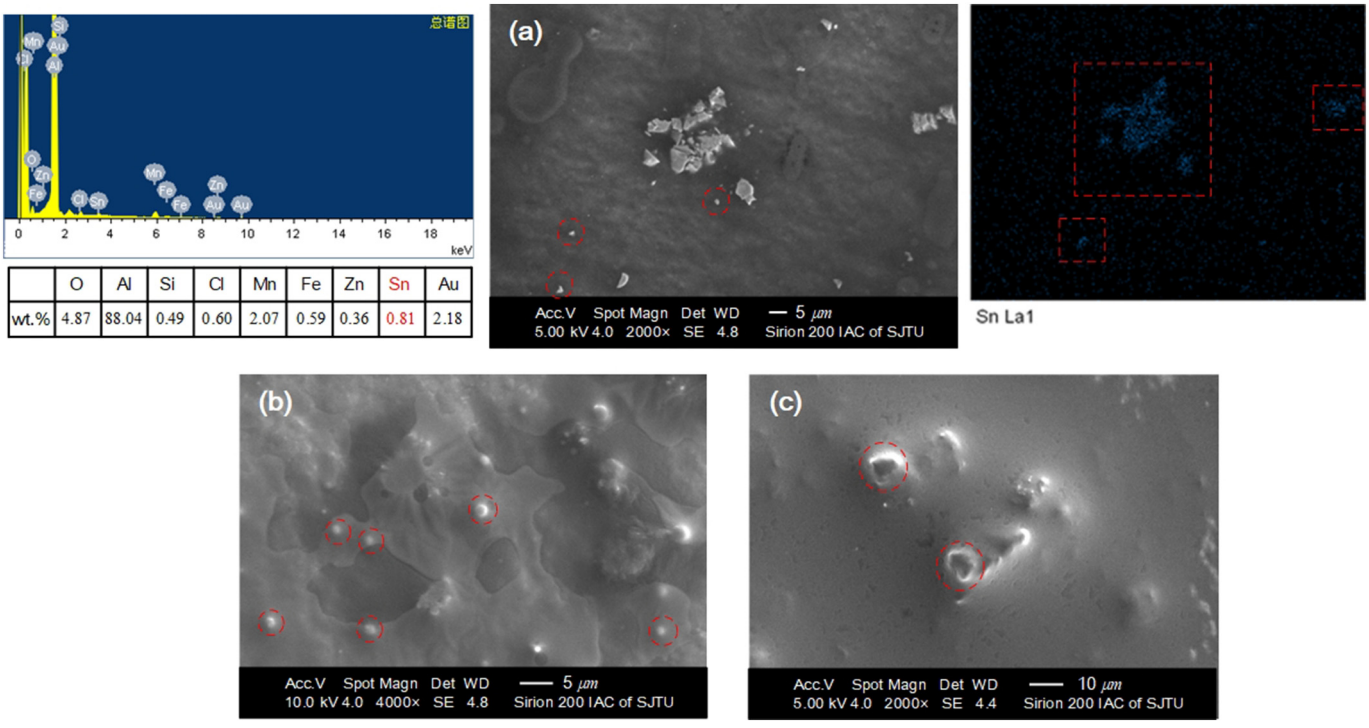


Fig. 4. SEM of PM at different collection substrates. (a) 1.0 < D_i < 1.6 μm; (b) 2.5 < D_i < 4.4 μm; (c) 6.8 < D_i < 9.97 μm. The upper-left and upper-right are the spectrum and Sn element mapping for the Fig. 4a.

Table 3
PBDEs concentration (pg/m^3) in air samples from relevant e-waste recycling environment.

	Sampling date	Sampling country	Sampling site	Air sample	BDE-47	BDE-99	BDE-153	BDE-209	Reference
Indoor	Before 2001	Sweden	Dismantling hall near plastic shredder	Gas + particles	1200	2600	3900	36,000	Sjödin et al., 2001
Indoor	Jun. 2004	USA	Dismantling hall near WPCBs shredder	Gas + particles	2400	2500	7800	600,000	Cahill et al., 2007
Indoor	Sep. 2007	Guiyu, China	WPCBs de-soldering by heating stoves	Particles	236,000	228,000	19,100	146,000	Ren et al., 2014
Indoor	Dec. 2007 – Feb. 2008	Thailand	e-waste storage facilities	Gas	23	28	7.3	–	Muenhor et al., 2010
Indoor	Oct. 2012	Korea	TV-dismantling workshop	Gas + particles	26.6	247	133	13,700	Park et al., 2014
Indoor	Dec. 2013	Jiangsu province, China	WPCBs de-soldering by heating machine	Particles	234,000	139,000	16,800	479,000	Guo et al., 2015b
Indoor	Apr. 2015	Shanghai, China	WPCBs de-soldering by furnace with hood	Particles	9470	6480	541	1990	This study
Outdoor	Sep.2004	Guiyu, China	Roof of a 3-story building near open burning operations	Particles	486	5519	811	–	Deng et al., 2007
Outdoor	Sep. 2005	Guiyu, China	Roof of a bungalow	Gas + particles	4105	2491	315	2164	Chen et al., 2009

particles in the environment as a whole. It is likely that the ultrafine particles in the fumes released from the heating pool grew bigger and bigger due to the coagulation process, resulting in the decrease of number cumulative percentage of ultrafine particles outside the hood. The mass cumulative values of coarse particles ($PM_{2.5-10}/PM_{10}$) in Part 1, Part 2, Part 3, and Part 4 (Fig. 3b) were 75.7%, 82.9%, 88.6%, and 80.4%, respectively. The PM samples in Part 3 outside the hood have the highest amount and cumulative percentage of coarse particles. It can be explained that the coarse particles are easily influenced by the turbulent air, resulting in more coarse particles leaking from the hood. In addition, the aggregation process of fine particles to coarse particles may be another reason. However, the higher percentage of coarse particles escaping from the fume hood is offset by the fact that they can be more efficiently removed by protective masks when compared to fine particles.

PM particles may deposit in the different regions of the respiratory system by impaction, sedimentation or diffusion (Hinds, 1999). Large particles ($D_i > 5$ μm) are more efficiently removed from the airstream in the HA due to inertial impaction and sedimentation (gravitational forces) after the inhalation of airstream. For the TB, impaction remains a significant deposition mechanism for particles larger than 2.5 μm. In addition, the airway volume increases and the air velocity decreases after the inhaled airstream enters the TB, providing more time for sedimentation to deposit the particles. However, the main deposition mechanism for smaller particles ($D_i < 0.5$ μm) is diffusion as gravitational forces become negligible. For the AR where the distances between the particles and airway epithelium are small, diffusion deposition is important in the small airways (USEPA, 1994).

Air concentrations of PBDEs in the workshop were related with the items of e-waste and process activity, and the BDE-47 and -99 were the main congeners in the penta-PBDEs mixture widely used as additive flame retardant in old printed circuit boards (Guo et al., 2015b; UNEP, Stockholm Convention on Persistent Organic Pollutants (POPs), 2009). During the heating process large quantities of these PBDE congeners were emitted to the surrounding microenvironment, resulting in high levels of PBDE pollution. Ren et al. (2014) studied the PBDE pollution in a workshop with 24 stoves for WPCBs de-soldering process in Guiyu, China. The government had not yet banned the primitive recycling methods without exhaust gas treatment, and the PBDE levels in air were much higher than those reported in elsewhere, comparable with WPCBs de-soldering processes using a heating machine (Guo et al., 2015a, 2015b). In our previous study (Guo et al., 2015b), the high PBDE levels in air from inside a workshop equipped with a heating machine for removing electronic components of WPCBs was caused by the leakage of fumes from the heating machine. In addition, the high volumes of waste treated and poor ventilation in the workshop were also reasons for the severe PBDE pollution. After installation of negative pressure and fume hoods, the indoor air concentration of PBDEs in the WPCBs de-soldering workshop decreased, with BDE-47 at 9470 pg/m^3 and BDE-99 at 6480 pg/m^3 (in this study), which were slightly higher than those in former studies involving outdoor air in Guiyu (Deng et al., 2007; Chen et al., 2009). For the WPCBs/plastic shredding process or e-waste dismantling workshop, the concentrations of 4 BDE congeners in indoor air (gas + particles) were 1200–36,000 pg/m^3 in Sweden (Sjödin et al., 2001), 2400–600,000 pg/m^3 in USA (Cahill et al., 2007), and 26.6–13,700 pg/m^3 in Korea (Park et al., 2014), respectively. BDE-209 and -153 were the main congeners detected in the indoor air, which originated from the crushed fractions caused by mechanical activity. The source of BDE-209 was from the plastic components of e-waste or WPCBs. The gas PBDEs concentrations in indoor air of a Thai e-waste storage facility were 23, 28, and 7.3 pg/m^3 for BDE-47, −99, and − 153, respectively (Muenhor et al., 2010). The PBDE emission velocity from e-waste items was slow, and the PBDE pollution in the e-waste storage facility was slight.

Generally, WPCBs is an important PBDE pollution source, especially for lower brominated BDE congeners. Heating processes will dramatically accelerate the emission velocity of PBDEs from WPCBs. The hood can be effectively used for the PBDE pollution control inside the workshop, decreasing the exposure dose for the workers. Assuming the work time of 8 h per day, a breathing rate of 0.54 m^3/h (Hinds, 1999), and the body weight of an average adult worker of 60 kg, the inhalation dose in the workshops can be calculated. The inhalation dose of BDE-47, −99, −153, and − 209 for the workers were 0.68, 0.47, 0.039, and 0.14 ng/kg/day, respectively. The $\sum_8$PBDEs inhalation exposure for the worker is about 1.46 ng/kg/day, higher than that of $\sum_{18}$PBDEs (0.73 ng/kg/day) for residents in the e-waste recycling zone (Luo et al., 2014), but 2–4 orders magnitude lower than the draft reference dose values (100 ng/kg/day for BDE-47 and -99, 200 ng/kg/day for BDE-153, and 7000 ng/kg/day for BDE-209) (USEPA, IRIS (Integrated Risk Information System), 2008). In addition, based on the PM deposition results of the ICRP model, the majority of the PM deposition flux (90.7%) was in the HA, and only 9.3% deposited in the TB and AR. Generally, deposition in the HA can be considered to protect the deep respiratory system from toxic particles. However, there are 3 exposure routes for health assessment, including inhalation, ingestion, and dermal contact, and only inhalation of particle-bound PBDEs was considered in this study. Further studies on inhalation of gaseous PBDEs, dermal absorption and ingestion of PBDE-containing dust should be done for accurate risk assessments.

Furthermore, there are many other hazardous substances emitted during the WPCBs de-soldering process, such as VOCs, PBDD/F, PCDD/F, and heavy metals (Bi et al., 2010; Duan et al., 2012; Duan et al., 2011). For example, An et al. (2014) found that aromatic hydrocarbons and halogenated hydrocarbons were the two dominant groups of VOCs

emitted from electric heating furnaces during WPCBs dismantling processes, with total VOCs of 3.3×10^4 μg/m^3. In addition, many studies found that the incineration of WPCBs (250–400 °C) could cause the formation of polybrominated/polychlorinated dioxin and furans (Leung et al., 2011; Duan et al., 2011). Therefore, integrated exposure assessment on various toxic substances emitted from WPCBs de-soldering process is needed in further investigations.

5. Conclusion

Our results show that majority but not all PM and particle-bound PBDEs can be removed by the negative pressure hood system, thus decreasing the exposure dose of the workers. The largest deposition flux of coarse PM was in the head airways based on ICRP model. However, the leakage of fumes (including PM and PBDEs) from the hood still poses health risk for the workers. Therefore, effective personal protective equipment for the workers is essential, thus decreasing the exposure risk to the pollutants during WPCBs de-soldering process.

Declaration of competing financial interests

The authors declare they have no actual or potential competing financial interests.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (41877468, 51778360), Natural Science Foundation of Shanghai (18ZR1418200), and Shanghai Pujiang Program (18PJD022).

Appendix A. Supplementary data

Illustration of WPCBs de-soldering process, the ICRP model calculation, and detailed testing method for PBDEs were shown in the Supplementary Data on the website. Supplementary data to this article can be found online at doi: 10.1016/j.scitotenv.2019.01.176

References

An, T., Huang, Y., Li, G., He, Z., Chen, J., Zhang, C., 2014. Pollution profiles and health risk assessment of VOCs emitted during e-waste dismantling processes associated with different dismantling methods. Environ. Int. 73, 186–194.

An, T., Zhang, D., Li, G., Mai, B., Fu, J., 2011. On-site and off-site atmospheric PBDEs in an electronic dismantling workshop in South China: gas-particle partitioning and human exposure assessment. Environ. Pollut. 159, 3529–3535.

Baldé, C.P., Wang, F., Kuehr, R., Huisman, J., 2015. The Global e-Waste Monitor-2014. United Nations University, IAS - SCYCLE, Bonn, Germany.

Bi, X., Simoneit, B.R.T., Wang, Z., Wang, X., Sheng, G., Fu, J., 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 (35), 4440–4445.

Cahill, T.M., Groskova, D., Charles, M.J., Sanborn, J.R., Denison, M.S., Baker, L., 2007. Atmospheric concentrations of polybrominated diphenyl ethers at near-source sites. Environ. Sci. Technol. 41 (18), 6370–6377.

Chen, A., Dietrich, K.N., Huo, X., Ho, S., 2011. Developmental neurotoxicants in e-waste: an emerging health concern. Environ. Health Perspect. 119 (4), 431–438.

Chen, D., Bi, X., Zhao, J., Chen, L., Tan, J., Mai, B., et al., 2009. Pollution characterization and diurnal variation of PBDEs in the atmosphere of an e-waste dismantling region. Environ. Pollut. 157 (3), 1051–1057.

Chen, J., Huang, Y., Li, G., An, T., Hu, Y., Li, Y., 2016a. VOCs elimination and health risk reduction in e-waste dismantling workshop using integrated techniques of electrostatic precipitation with advanced oxidation technologies. J. Hazard. Mater. 302, 395–403.

Chen, J., Zhang, D., Li, G., An, T., Fu, J., 2016b. The health risk attenuation by simultaneous elimination of atmospheric VOCs and POPs from an e-waste dismantling workshop by an integrated de-dusting with decontamination technique. Chem. Eng. J. 301, 299–305.

Deng, W.J., Zheng, J.S., Bi, X.H., Fu, J.M., Wong, M.H., 2007. Distribution of PBDEs in air particles from an electronic waste recycling site compared with Guangzhou and Hong Kong, South China. Environ. Int. 33, 1063–1069.

Duan, H., Li, J., Liu, Y., Yamazaki, N., Jiang, W., 2011. Characterization and inventory of PCDD/Fs and PBDD/Fs emissions from the incineration of waste printed circuit board. Environ. Sci. Technol. 45 (15), 6322–6328.

Duan, H., Li, J., Liu, Y., Yamazaki, N., Jiang, W., 2012. Characterizing the emission of chlorinated/brominated dibenzo-p-dioxins and furans from low-temperature thermal processing of waste printed circuit board. Environ. Pollut. 161, 185–191.

Fang, W., Yang, Y., Xu, Z., 2013. PM_{10} and $PM_{2.5}$ and health risk assessment for heavy metals in a typical factory for cathode ray tube television recycling. Environ. Sci. Technol. 47, 12469–12476.

Guo, J., Lin, K., Deng, J., Fu, X., Xu, Z., 2015a. Polybrominated diphenyl ethers in indoor air during waste TV recycling process. J. Hazard. Mater. 283, 439–446.

Guo, J., Zhang, R., Xu, Z., 2015b. PBDEs emission from waste printed wiring boards during thermal process. Environ. Sci. Technol. 49 (5), 2716–2723.

He, Z., Li, G., Chen, J., Huang, Y., An, T., Zhang, C., 2015. Pollution characteristics and health risk assessment of volatile organic compounds emitted from different plastic solid waste recycling workshops. Environ. Int. 77, 85–94.

Hinds, W.C., 1999. Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles. John Wiley & Sons, Inc.

Leung, A.O.W., Zheng, J., Yu, C.K., Liu, W.K., Wong, C.K.C., Cai, Z., et al., 2011. Polybrominated diphenyl ethers and polychlorinated dibenzo-*p*-dioxins and dibenzofurans in surface dust at an e-waste processing site in Southeast China. Environ. Sci. Technol. 45 (13), 5775–5782.

Li, J., Zeng, X., Chen, M., Ogunseitan, O.A., Stevels, A., 2015. "Control-Alt-Delete": rebooting solutions for the e-waste problem. Environ. Sci. Technol. 49, 7095–7108.

Li, T., Zhou, J., Wu, C., Bao, L., Shi, L., Zeng, E., 2018. Characteristics of polybrominated diphenyl ethers released from thermal treatment and open burning of e-waste. Environ. Sci. Technol. 52, 4650–4657.

Liu, R., Chen, J., Li, G., An, T., 2017. Using an integrated decontamination technique to remove VOCs and attenuate health risks from an e-waste dismantling workshop. Chem. Eng. J. 318, 57–63.

Luo, P., Bao, L., Wu, F., Li, S., Zeng, E.Y., 2014. Health risk characterization for resident inhalation exposure to particle-bound halogenated flame retardants in a typical e-waste recycling zone. Environ. Sci. Technol. 48 (15), 8815–8822.

Ma, J., Addink, R., Yun, S., Cheng, J., Wang, W., Kannan, K., 2009. Polybrominated dibenzo-*p*-dioxins/dibenzofurans and polybrominated diphenyl ethers in soil, vegetation, workshop-floor dust, and electronic shredder residue from an electronic waste recycling facility and in soils from a chemical industrial complex in eastern China. Environ. Sci. Technol. 43 (19), 7350–7356.

MEE, China. Ministry of Ecology and Environment of the People's Republic of China, 2014. Announcement on Releasing the Guidelines for Disassembly Operation and Production Management of Waste Electrical and Electronic Products. 2015 edition. (in Chinese). http://www.mee.gov.cn/gkml/sthjbgw/qt/201412/t20141219_293233.htm.

Muenhor, D., Harrad, S., Ali, N., Covaci, A., 2010. Brominated flame retardants (BFRs) in air and dust from electronic waste storage facilities in Thailand. Environ. Int. 36 (7), 690–698.

Ogunseitan, O.A., Schoenung, J.M., Saphores, J.M., Shapiro, A.A., 2009. The electronics revolution: from e-wonderland to e-wasteland. Science 326, 670–671.

Ortuño, N., Conesa, J., Moltó, J., Font, R., 2014. Pollutant emissions during pyrolysis and combustion of waste printed circuit boards, before and after metal removal. Sci. Total Environ. 499, 27–35.

Park, J., Kang, Y., Kim, W., Jeon, T., Shin, S., Jeong, M., Kim, J., 2014. Emission of polybrominated diphenyl ethers (PBDEs) in use of electric/electronic equipment and recycling of e-waste in Korea. Sci. Total Environ. 470–471, 1414–1421.

Puckett, J., Byster, L., Westervelt, S., Gutierrez, R., Davis, S., Hussain, A., et al., 2002. Exporting Harm: The High-tech Trashing of Asia. BAN, SVTC, Seattle.

Ren, Z., Xiao, X., Chen, D., Bi, X., Huang, B., Liu, M., et al., 2014. Halogenated organic pollutants in particulate matters emitted during recycling of waste printed circuit boards in a typical e-waste workshop of southern China. Chemosphere 94, 143–150.

Sjödin, A., Carlsson, H., Thuresson, K., Sjölin, S., Bergamn, Å., Östman, C., 2001. Flame retardants in indoor air at an electronics recycling plant and at other work environments. Environ. Sci. Technol. 35, 448–454.

UNEP, Stockholm Convention on Persistent Organic Pollutants (POPs), 2009. The 9 New POPs Risk Management Evaluations 2005-2008 (POPRC1-POPRC4). Secretariat of the Stockholm Convention, United Nations Environment Programme, Switzerland.

USEPA, 1994. Methods for Derivation of Inhalation Reference Concentrations and Application of Inhalation Dosimetry. EPA/600/8-90/066F; North Carolina.

USEPA, IRIS (Integrated Risk Information System), 2008. (Last Updated). 2,2′,4,4′-Tetrabromodiphenyl ether (BDE-47) (CASRN 5436-43-1). https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?&substance_nmbr=1010 (accessed December 2018); 2,2′,4,4′,5-Pentabromodiphenyl ether (BDE-99) (CASRN 60348-60-9). https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?&substance_nmbr=1008 (accessed December 2018); 2,2′,4,4′,5,5'-Hexabromodiphenyl ether (BDE-153) (CASRN 68631-49-2),. https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?&substance_nmbr=1009 (accessed December 2018); 2,2′,3,3′,4,4′,5,5′,6,6′-Decabromodiphenyl ether (BDE-209) (CASRN 1163-19-5),. https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?&substance_nmbr=35 (accessed December 2018).

WHO (World Health Organization), 2006. WHO Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide. Global Update 2005. Summary of Risk Assessment. WHO/SDE/PHE/OEH/06.02, Geneva, Switzerland.

Zeng, Y., Tang, B., Luo, X., Zheng, X., Peng, P., Mai, B., 2016. Organohalogen pollutants in surface particulates from workshop floors of four major e-waste recycling sites in China and implications for emission lists. Sci. Total Environ. 569–570, 982–989.

Zhao, G., Zhao, Z., Guo, X., Du, Q., Gao, J., Dong, H., et al., 2016. Emission and morphological characteristics and elemental compositions of fine particulate matter from an industrial pulverized coal boiler equipped with a fabric filter in China. Energy Fuel 30 (5), 4307–4317.

Zheng, J., He, C., Chen, S., Yan, X., Guo, M., Wang, M., et al., 2017. Disruption of thyroid hormone (TH) levels and TH-regulated gene expression by polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and hydroxylated PCBs in e-waste recycling workers. Environ. Int. 102, 138–144.