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Polybrominated diphenyl ethers (PBDEs) emitted from heating machine for waste printed wiring boards disassembling

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Abstract

Polybrominated diphenyl ethers (PBDEs) contained in waste printed wiring board (PWB) matrix and surface dust can be emitted into the air during thermal process, which is widely used to detach the electronic components from the base boards of waste PWB. In this study, PBDEs concentrations in air and dust samples were detected in a PWB-heating workshop. The results showed that the mean concentrations of $\sum_8$PBDEs in PM_{10} and TSP were 479 and 1670 ng/m^3, respectively. Compared with surface dust collected from waste PWB (15600 ng/g), PBDEs concentrations in dust from the workshop floor (31100 ng/g), heating machine inside (84700 ng/g), and the cyclone extractor (317000 ng/g), were condensed after thermal process. All the results showed that recycling of waste PWB was an important source of PBDEs emission.

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Keywords: electronic waste; recycling; PBDEs;

1. Introduction

Disassembling electronic components from waste printed wiring board (PWB) is an important step in the PWB recycling chain. In order to simplify the subsequent recovery of materials, electronic components attached on base boards of PWB, such as cell batteries, capacitors, resistors, should be removed and separately disposed in an appropriate way. Although the Chinese government has banned the primitive methods for recycling PWB, such as open burning and acid washing, there are still convert family run workshops, where PWB are heated over coal-heated grills to melt solder and to remove reusable electrical components by artisanal tools in e-waste dismantling

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region. Many studies showed that persistent organic pollutants were released to the surrounding environment during the primitive recycling of electronic waste[1,2], especially from PWB baking[3, 4].

Polybrominated diphenyl ethers (PBDEs), a class of widely used brominated flame retardants, are commercially produced in three forms: penta-BDE, octa-BDE and deca-BDE. Due to the low price and excellent flame-retardant effect, generous penta-BDE products were widely used in old electrical appliances. A report showed that 25% of FR2-type PWB in old appliances, such as TV sets, radios, washing machines, were treated with the mixture of penta-BDE[5]. Therefore, the waste PWB is an important source of PBDEs release.

In this study, PBDEs concentrations in air and dust inside a PWB-heating workshop were detected to investigate the PBDEs emission mechanism. Hence the results will help to analyze the emission rates of PBDEs under thermal process of waste PWB.

2. EXPERIMENTAL SECTION

2.1. Sampling information

The PWB samples were from waste cathode ray tube TV sets manufactured in the 1990s and early 2000s. Electronic components (CPU, power choke coil, and flyback transformer) were manually removed before PWB samples were fed into the thermal treating machine. The structure of thermal treating machine was shown in Figure 1. The heating machine consisted of rotary screen, heating apparatus, and exhaust treatment. The PWB samples were heated and rotated in the rotary screen, and the electronic components detached from the PWB when the solder melted. A cyclone extractor and a spray tower were used to collect and treat the exhaust. About 6 ton PWB samples each day were processed by thermal treating machine with the heating temperature of about 300 °C, and heating time in the rotary screen was about 10~15 minutes.

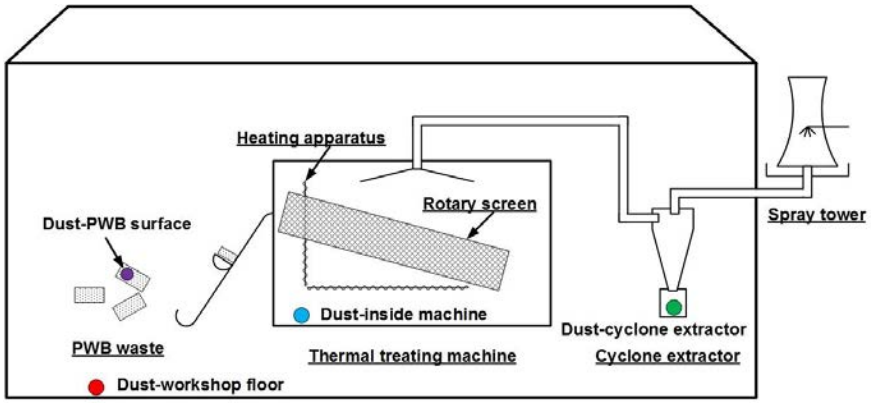

Fig. 1. Plot of PWB heating machine in the workshop.

The dust and air samples were collected in the PWB heating workshop. Dust samples from PWB surface, workshop floor, inside of the heating machine, and the dust bag of the cyclone extractor were collected (Figure 1). Then dust samples were added through 100-mesh (0.15 mm) screen.

Particulate matter (PM) samples, including PM_{10} and total suspended particle (TSP), were collected on glass fiber filters using middle volume samplers (100 L/min, Lao Ying 2030, Qingdao Laoshan electronic instrument factory Co. Ltd., China). The sampling duration for each sample was 3 h during the working time near the PWB-heating machine. Concentrations of PM_{10} and TSP were determined by weighting filters before and after sampling. The weighted glass fiber filters were cut into chips using stainless scissors for PBDEs testing.

2.2. Sample extraction, cleanup and analysis for PBDEs

Filters (PM_{10} and TSP) and dust samples were separately extracted using microwave assisted extraction with 20 mL acetone/hexane solvent mixture (1:1 v/v). Samples were concentrated to a small volume and transferred into hexane. Further clean up using multi layer 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. Gas chromatographic separation was performed on a DB-5HT capillary column. The 8 BDE congeners investigated in this study were BDE-28, -47, -100, -99, -154, -153, -183, and -209 (in order of retention times).

3. Results and discussion

3.1. PBDEs in PM

The mass concentrations of PM_{10} and TSP in the workshop were 884 μg/m^3 and 1790 μg/m^3, respectively. TSP mass concentration in this study was lower than those in other e-waste dismantling halls in Sweden (3300 μg/m^3)[6] and in Guiyu (2210 μg/m^3), China[1].

The concentrations of $\sum_8$PBDEs in the PM_{10} and TSP as shown in Table 1 were 479 and 1670 ng/m^3, respectively. Those results were comparable to other reports in e-waste recycling plant. Cahill et al.,[7] obtained average concentration of total PBDEs in air samples collected inside the dismantling hall of an electronics recycling facility in USA was 650 ng/m^3. Ren et al.,[4] collected PM samples in a PWB recycling workshop of Guiyu, China, and the average concentration of selected 8 BDE congeners in PM was 682 ng/m^3 (Table 1).

Table 1. PBDEs Concentrations in PM10 and TSP (ng/m^3)

BDE congener	PM10	TSP	TSP[4]
BDE-28	56.5	214	17.3
BDE-47	234	746	236
BDE-100	12.0	41.6	20.4
BDE-99	139	487	228
BDE-154	6.23	22.3	8.61
BDE-153	16.8	66.6	19.1
BDE-183	4.88	20.5	6.41
BDE-209	9.49	70.6	146
Σ8PBDEs	479	1670	682

It can be obtained that BDE-47 and -99 were the main congeners in PM_{10} and TSP from this study. The concentrations for BDE congeners (Table 1) in TSP were 746 ng/m^3 for BDE-47, 487 ng/m^3 for BDE-99, and 70.6 ng/m^3 for BDE-209. The results are higher than those in a dismantling hall in Sweden, where air concentrations of PBDEs were 0.35-2.1 ng/m^3 for BDE-47, 0.54-5.5 ng/m^3 for BDE-99, and 12-70 ng/m^3 for BDE-209[6]. While the concentrations for BDE-47 (236 ng/m^3) and BDE-99 (228 ng/m^3) studied by Ren et al.,[4] were lower than those in this study, and the concentration for BDE-209 (146 ng/m^3) was higher than that in this study.

3.2. PBDEs in dust

Dust is an important media for PBDEs pollution, and it is evident that PBDEs concentrations in dust from e-waste dismantling areas are among the most contaminated in the world[3]. The general trend for the mean concentrations of $\sum_8$PBDEs in dust was cyclone extractor (317000 ng/g) > machine inside (84700 ng/g) > workshop floor (31100 ng/g) > PWB surface (15600 ng/g). The mean concentration of $\sum_8$PBDEs in cyclone

extractor (317000 ng/g) was about 20 times higher than surface dust of PWB, indicating the PBDEs concentrations in dust would be condensed after heating. As expected, the penta-BDE and deca-BDE were the major formulas contained in PWB and surface dust of PWB waste. Since PBDEs are used as additive flame retardants in PWB, they could be emitted into the environment under elevated temperature during the heating process[4,8]. In contrast, the average concentrations in dust from the underneath exhaust fans and workshop-floor of PWB heating workshops in Guiyu were 20800 ng/g and 9990 ng/g[3]. Ma et al.,[9] found that the PBDEs concentration range of dust from the floor of e-waste dismantling workshops in Taizhou, was 6300-82200 ng/g.

Table 2. PBDEs Concentrations in Dust (ng/g)

BDE congener	cyclone extractor	machine inside	workshop floor	PWB surface	workshop flour[3]
BDE-28	27100	4520	1250	388	1120
BDE-47	145000	25500	6390	1640	3120
BDE-100	8350	1660	711	372	221
BDE-99	104000	22900	7250	2100	2380
BDE-154	3570	1340	748	478	178
BDE-153	9600	3690	1710	792	650
BDE-183	1700	1160	764	554	1460
BDE-209	17500	23880	12300	9290	864
Σ8PBDEs	317000	84700	31100	15600	9990

As shown in Table 2, the congener concentrations in CE-Dust were 145000 ng/g for BDE-47 (45.7%), 104000 ng/g for BDE-99 (32.8%), and 17500 ng/g for BDE-209 (5.5%), respectively. The PBDEs levels for major congeners in dust were higher than those reported of dust collected from the PWB heating workshop in Guiyu, where the concentrations in workshop-floor dust in a PWB heating workshop were 3120 ng/g for BDE-47 (31.2%), 2380 ng/g for BDE-99 (23.8%), and 864 ng/g for BDE-209 (8.6%)[3].

BDE-47, -99, and -209 were the main congeners in the 4 dust samples. The highest proportion of BDE-209 (59.6 %) was obtained in dust from PWB surface. The source of BDE-209 on PWB surface dust included: (1) volatilization from deca-BDE mixture in other materials, such as housing plastics of TV sets, during the usage life of PWB. (2) dust on PWB surface collected from the surrounding environment when the TV set was used or stored. PBDEs are semivolatile organic compounds (SVOCs), and the estimated solid phase vapor pressures (Ps) for BDE-28, -47, -99, and -209 are 9.07×10^{-4}, 5.52×10^{-5}, 3.85×10^{-6}, and 9.28×10^{-9} Pascals (at 25 °C) [10, 11]. The Ps of BDE congener represents their tendency to volatile from solid to vapor phase. As the degree of bromination decreases, the BDE congeners increasingly volatilize to the gaseous phase. When PWB samples were heated, lower brominated BDE congeners emitted from the PWB to the air inside the machine more easily, then generous amounts of lower brominated BDE congeners were absorbed by the particulates, leading to higher percentage contributions of lower brominated BDE congeners in dust from cyclone extractor.

3.3. PBDE emission from PWB heating process

PBDEs are basically flame retardant additives to materials and not bonded chemically to the matrix. This means that there exists a potential for the PBDEs to escape the matrix through the processes of volatilization to the air[11]. When the PWB samples were sent into the heating machine, PWB was heated, and then the solder was melted. The electronic components detached from base boards through the action of shocking and impact of rotary screen. Thermal process for PWB disassembling was investigated by other researchers. A heated-air (220-300 °C) disassembling equipment designed by Chen et al.,[12] was used to melt solder and to separate the components and base boards. Meanwhile, PBDEs emission was accelerated when the PWB and dust were heated inside the machine. The temperatures inside the machine varied with different parts, and the temperature of PWB ranged from 200 to 300 °C during the thermal process. The reaction inside the machine was complicated, and degradation of PBDEs

contained in PWB and dust, the formation of polybrominated dibenzo-p-dioxin and dibenzofurans (PBDD/Fs) and hydroxylated PBDEs (OH-PBDEs)[13] coexisted. Duan et al.,[14] found that the total content of twelve 2,3,7,8-substituted PBDD/Fs congeners (tetra- through octabromo-) was the largest when PWB was subjected to a heating temperature of 325 °C. Ren et al.,[13] detected five OH-PBDEs, several unidentified mono-OH-PBDE and di-OH-PBDE congeners in a PWB recycling workshop. The concentration of ΣOH-PBDEs was 1.74-4.22 ng/m^3, with 6-OH-BDE-47 (0.329 ng/m^3) as the most abundant identified congener.

The PBDEs contained in PM and dust samples originated from two sources: one was the surface dust of PWB, and the other was the base boards. When the base boards were heated, PBDEs in the resin of base boards would release gaseous PBDEs into the air, and then PBDEs in the gaseous phase would be adsorbed on the surface of PM or dust particles. In addition, the abrasion among the base boards in rotary screen would also generate scrapped fine particles, which may influence the concentration of PBDEs in PM and dust samples.

4. Conclusions

PBDEs emission from waste PWB to air environment during thermal treatment was an important source of PBDEs pollution. The indoor environment (PM and dust) in the workshop was severely contaminated by PBDEs emitted from the PWB heating machine, and the highest concentration of PBDEs occurred in the dust bag of the cyclone extractor. The detecting experiments can provide the basis data for understanding the emission mechanism of PBDEs.

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