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Introduction

The recycling of computer printed circuit boards is one of the main recycling activities carried out in Guiyu, a traditionally rice growing community that has been the focus of international interest in recent years because of the sheer volume of e-waste that is being processed ('recycled') by primitive and crude methods. In small family-run workshops, printed circuit boards are heated over makeshift grills fuelled by coal blocks to melt solder and to remove reusable electrical components which are then sold. During the heating process, pungent and potentially toxic fumes are released. Fans placed in front of the grills are the only precautionary measures used to exhaust the fumes (from inside the workshops to outdoors) and reduce exposure to the fumes. One of the pollutants of concern are brominated flame retardants such as polybrominated diphenyl ethers (PBDEs) which are commonly applied on electrical and electronic equipment. As PBDEs are additive and not chemically bound to their products, they may be leached into the environment under elevated temperatures[1]. PBDEs are available as three different types of technical mixtures, namely Penta-BDE, Octa-BDE, and Deca-BDE. Due to health risks, such as endocrine disruption, thyroid hormone imbalance and neurodevelopmental dysfunctions[2], Penta-BDE and Octa-BDE have been banned within the EU since August 2004 and are being phased out in several states of the United States since January 1, 2006[3,4]. The EU Directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) (Directive 2002/95/EC) prohibits the use of Penta-BDE and Octa-BDE which exceed set maximum concentration values in new electrical and electronic products that enter the EU market after July 1, 2006[5]. Deca-BDE is currently the most widely used commercial PBDE flame retardant[6]. A Swiss study reported that printed circuit boards contain Penta-BDE, Octa-BDE and Deca-BDE[7]. To date, there is very little information about PBDE levels in dust, particularly at an e-waste hotspot. Henceforth, the objectives of this study were to conduct a reconnaissance survey of the PBDE levels of surface dust collected from a printed circuit board recycling workshop and nearby roads in the e-waste recycling centre of Guiyu, China, and also to investigate the dust PBDE congener profiles.

Materials and methods

Study area

Guiyu, a village located about 250 km northeast of Hong Kong, in Guangdong Province, China, has a population of 150,000 and has been involved in e-waste 'recycling' for approximately ten years. The extraction of electrical components and solder recovery from printed circuit boards are mainly conducted in the Beilin district of Guiyu. Residential neighbourhoods have been transformed into rows of printed circuit board recycling workshops.

Sample collection and preparation

Sampling was conducted in 2004 in Beilin, Guiyu using plastic brushes and dustpans. Dust samples were collected from 1) the floor of a printed circuit board recycling workshop, 2) sections of a road directly underneath exhaust fans of recycling workshops (the fans were located approximately 0.5 m from the ground), 3) the middle of a road near an intersection and about 10 m from a workshop exhaust fan, 4) a primary trunk road with relatively heavy traffic and few printed circuit board workshops (this road is located 3 streets away from location 2), and from 5) Shantou University campus located 30 km east of Guiyu. The latter site was used as control. All samples were stored and sealed in polyethylene bags (Ziploc®) for transport to the laboratory. The samples were sieved to <2 mm prior to chemical analyses.

Analyses of PBDEs in dust

Each sample was precisely weighed (3.0 g) and Soxhlet extracted according to EPA Standard Method 3450C[8] with a solvent mixture of acetone and dichloromethane (1:1, v/v) for 18 h at 65°C. The concentrated extract was cleaned up using two glass chromatography columns placed in series, each packed with 1g of florisil and a top layer of anhydrous sodium sulfate (Method 3620B)[7]. The cleaned-up extracts were analysed by GC/MS (Hewlett Packard Model HP6890 Series, DB-1 fused silica capillary column and a HP5973 Mass Selective Detector). Ultra high purity helium was used as the carrier gas at a flow rate of 1.0 ml/min. The mass spectrometer was operated in electron impact with selected ion monitoring (EI/SIM) mode. The BDE congeners were quantified using isotope dilution method with addition of ^{13}C labeled BDEs. Concentrations of BDEs were measured by using a ^{13}C labeled BDE internal standard mixture. In total, 27 BDE congeners were investigated (BDE-3, -7, -15, -17, -28, -49, -71, -47, -66, -77, -100, -119, -99, -85, -126, -154, -153, -138, -156, -184, -183, -191) which included -196, -197, -206, -207, and -209 (using a shorter column). Absolute recoveries of PBDEs were calculated and QA/QC was conducted by performing method blanks, standard spiked recoveries and GC/MS detection limits. The relative standard deviation was below 10% for BDE congeners.

Results and discussion

The average concentrations of PBDEs for the sum of total 27 congeners are shown in Table 1. The highest average concentration was found in dust collected underneath exhaust fans followed by dust from workshop, road near intersection, primary trunk road and control site. Minimum and maximum concentrations ranged from exhaust fan (6150-61400 ng/g) > workshop (15400-23800 ng/g) > primary trunk road (1990-3370 ng/g) > road near intersection (2040-2420 ng/g) > control (231-405 ng/g) with the largest range in PBDE concentration in dust collected from underneath exhaust fan (maximum being ten times higher than the minimum). The reason may be attributed to plastic computer scraps found on the road outside the workshop which also contain PBDEs. The concentrations of BDE-28 in workshop dust was found to be significantly higher (p<0.05, by Duncan's multiple range test) than the other sampling locations. BDE-209 levels in workshop and exhaust fan dust were also found to be significantly higher (p<0.05) than dust from the other sites. No significant differences were found with respect to BDE-47, - 99, -100, - 153, -154 and -183 due to wide variability in the concentrations, in particular exhaust fan dust. BDE-47, -99, -183 and -209 constituted the most to the average total concentration. For workshop dust, the highest percentages were attributed to BDE-47 (18-26%), -99 (16-17%) and -183 (6.0-23%). For exhaust fan dust, the highest percentages were attributed to BDE-99 (26-39%), -47 (17-21%) and -209 (2.3-16%). Highest percentages of BDE-209 were found in dust at primary trunk road (9.2-27%) and at the control site (26-30%). From the congener profiles, it was obvious that the source of PBDEs in the dust at Guiyu was not the same as that for the control site because the percentage of BDE-209 was comparatively higher at the latter site. In fact, it was not surprising to detect a higher percentage of BDE-209 at the control site because the commercial product Deca-BDE is still commonly used whereas Penta-BDE and Octa-BDE are globally phasing out. The source of

PBDEs at the four sampling locations in Guiyu appeared to be the same due to similarities in their congener profiles. It is possible that PBDEs generated from the printed circuit board recycling workshops may have been atmospherically transported (i.e. by wind) to the surrounding area (i.e. primary trunk road). Furthermore, due to the heat generated from circuit board recycling, BDE-209 may have debrominated into lower brominated congeners, however, this requires further investigation. In general, the average concentrations of the eight PBDE congeners (see Table 1) in dust from workshop were higher than dust from the other sampling sites in Guiyu. The eight congeners found in PBDE commercial formulations (i.e. BDE-28, -47, -99, -100, -153, -154, -183, -209) contributed to an average of 74% for workshop, 84% for exhaust fan dust and 44% for the control site. For the control site, the dust was dominated by high brominated compounds (BDE-206, -207 and -209) which accounted for 55-63% of the total concentration. From the homologue profiles (Figure 1), tetra-BDE, penta-BDE were prominent in the workshop and exhaust fan dust whereas nona-BDE and deca-BDE were prominent in dust at the control site.

Although there are an increasing number of studies regarding PBDE levels in indoor dust[9-11], there are very few studies on PBDE levels in outdoor dust, such as road dust. BDE-47 concentrations at all the study sites were at least 4-76 times higher than that of bulk dust collected at Ground Zero, New York World Trade Center (WTC) and BDE-99 concentrations were approximately 2-82 times higher[12]. The range of BDE-154 concentrations from workshop and exhaust fans was fairly similar to those of WTC. Dust collected inside homes in Singapore, UK, Finland, Denmark and US consisted predominantly of BDE-209 since Deca-BDE is widely used as an additive to carpet textiles[8-10].

Therefore, in addition to high heavy metal concentrations[13], this study shows that the recycling of printed circuit boards is a significant contributor of PBDEs in dust to the local environment. In particular, tetra-, penta- and decabrominated congeners were found to be elevated. The elevated levels may pose adverse health impacts to children playing outdoors and there is also a concern that the contaminated outdoor dust may migrate indoors to homes whereby the potential for human exposure by ingestion, inhalation and dermal contact may be greater.

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Table 1: Average concentrations of PBDEs in dust (<2 mm)(ng/g, dry wt)

	Workshop	Road at exhaust fan	Road near intersection	Primary trunk road	Control
No. of samples	3	3	3	3	2
BDE-28	1700 ± 383	696 ± 901	76.4 ± 32.9	97.7 ± 39.8	9.26 ± 7.26
BDE-47	3990 ± 245	5180 ± 6940	418 ± 152	479 ± 163	10.4 ± 6.40
BDE-99	2960 ± 880	9290 ± 12900	478 ± 106	457 ± 116	17.6 ± 22.9
BDE-100	227 ± 47	1080 ± 1510	39.5 ± 8.25	44.3 ± 12.8	3.97 ± 2.87
BDE-153	941 ± 757	1290 ± 1740	61.6 ± 28.0	112 ± 73.6	4.75 ± 5.04
BDE-154	214 ± 138	386 ± 515	25.8 ± 3.93	34.2 ± 19.6	3.82 ± 0.68
BDE-183	2500 ± 2550	1750 ± 1440	135 ± 58.7	297 ± 295	7.57 ± 2.09
BDE-209	1100 ± 53	1100 ± 278	271 ± 182	456 ± 395	87.1 ± 25.6
Σ8 PBDE congeners*	13600 ± 4200	20800 ± 26200	1510 ± 487	1980 ± 558	144 ± 72.8
Σ27 PBDE congeners	18200 ± 4830	24900 ± 31600	2270 ± 203	2630 ± 693	318 ± 122

*BDE-28, -47. -99, -100, -153, -154, -183. -209

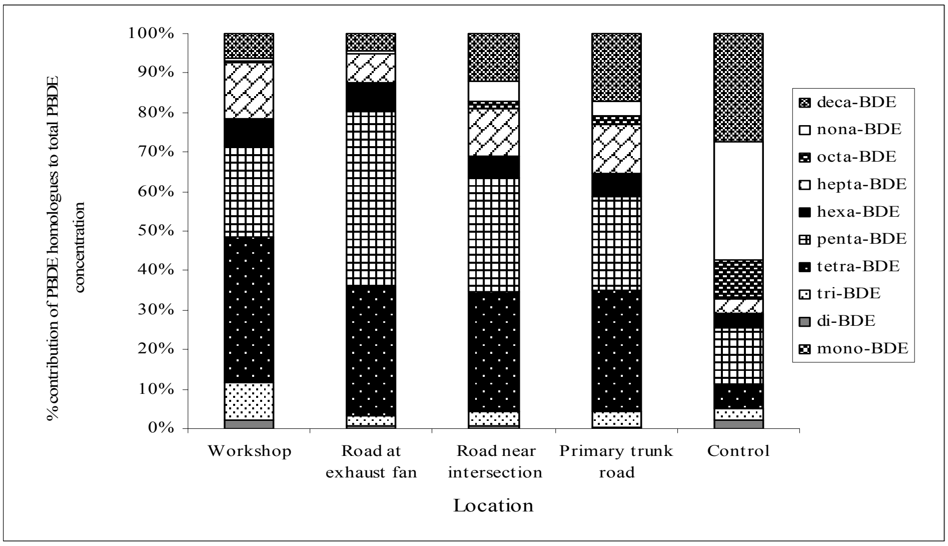

Figure 1: Average percentage contribution of PBDE homologues to total PBDE concentration in dust