LEVELS OF POLYCHLORINATED BIPHENYLS, BROMINATED FLAME RETARDANTS AND DIOXIN-LIKE ACTIVITES ASSOCIATED WITH E-WASTE RECYCLING IN VIETNAMESE HOUSE DUST

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Abstract

PCBs, brominated flame retardants (BFRs) and dioxin-like activities were investigated in house dust collected from two Vietnamese e-waste recycling sites (EWRS) and an urban control site. Levels of PBDEs and HBCDs in the EWRS were 110–10000 and 5.4–400 ng/g, respectively; median levels were higher than in the urban control site by a factor of 3 to 7 for both groups of contaminants. PCB levels, 5–320 ng/g, were not statistically higher than control levels but higher percentages of *tri-* and *tetra*-CBs were observed. Dioxin-like activities ranged from 370 to 1000 pg CALUX-TEQ/g with the median level (500 pg CALUX-TEQ/g) higher than the median control level by a factor of 2.5. These results indicate that e-waste recycling activities play a role as significant sources of BFRs and dioxin-like compounds and suggest dust ingestion as an important intake pathway for these contaminants particularly in case of e-waste recyclers.

Introduction

E-waste, obsolete electrical and electronic products, has become a subject of growing environmental concern in Asian developing countries due to a large volume of illegal import from developed nations[1]. The e-waste hazard is associated with the high content of many toxic substances including brominated flame retardants (BFRs), polychlorinated biphenyls (PCBs), and heavy metals which can be released into the environment during disposal and recycling. Moreover, the uncontrolled combustion processes widely employed by recyclers in developing countries to retrieve rare metals have been known to generate unintentional contaminants such as polychlorinated dioxins/furans (PCDD/Fs)[2] and potentially their brominated homologues[3]. The environmental impacts in Chinese e-waste recycling sites (EWRS) have been well documented in terms of PCBs, BFRs and PCDD/Fs[2,4,5]. However the contamination status in EWRS in other Asian countries has been almost unknown. Information on other dioxin-like compounds are also scarce in general, possibly due to the technical difficulties in analysing the large number of chemicals involved.

House dust has recently been identified as an important human exposure pathway for BFRs including polybrominated diphenylethers (PBDEs)[6,7] and hexabromocyclododecanes (HBCDs)[8]. As particulate matter is generated during uncontrolled recycling activities[4], dust in EWRS is a potential carrier of e-waste related contaminants to human via accidental ingestion and inhalation. This study investigates the levels of PCBs, PBDEs, HBCDs (using chemical analysis) as well as dioxin-like activities (using Dioxin-Responsive Chemical-Activated LUciferase gene eXpression assay – DR-CALUX) in house dust collected from two EWRS in northern Vietnam.

Materials and Methods

The study locations were two e-waste recycling areas in the Red River Delta, one in Hai Phong city (Trang Minh, EW1) and the other in Hung Yen province (Bui Dau, EW2), as well as a typical urban area (Hanoi, UB) for reference. Dust samples were collected from surfaces such as fans, air conditioning units and furniture during September 2008. The samples were kept in ice during transport and ultimately stored at –20 °C until analysis.

Seven samples from each location were analysed for 62 PCB congeners, 14 PBDE congeners (BDE-3, -15, -28, -47, -99, -100, -153, -154, -183, -196, -197, -206, -207 and -209), 3 HBCD isomers (α, β, γ) and dioxin-like activity. Before extraction, large pieces of matter were manually removed from the samples. Approximately 4 g dust was extracted with an acetone/hexane mixture (1:1 v/v) and then with toluene using a rapid solvent extractor

(SE-100, Mitsubishi Chemical Analytech, Japan). The combined extract was solvent-exchanged into hexane and divided into two portions. The portion for chemical analysis, with a volume equivalent to 0.5 g sample, was spiked with ^{13}C-labelled surrogates, treated with sulphuric acid (98%), cleaned-up with multi-layer silica-gel column and then subjected to gel permeation chromatography (GPC). An activated silica-gel column was then used for fractionation. PCBs and PBDEs were eluted with 5% dichloromethane in hexane, concentrated and solvent-exchanged into isooctane. HBCDs were eluted with 25% dichloromethane in hexane, concentrated to dryness then dissolved in methanol. ^{13}C-BDE-139 and D-HBCDs were finally added as internal standards, respectively. PCBs and PBDEs were quantified by GC-MS and HBCDs by LC-MS-MS according to the method described previously[9]. The remaining portion of the extract was treated with sulfuric acid (98%), cleaned-up with sulphuric acid-impregnated silica-gel, subjected to GPC, concentrated and solvent-exchanged into dimethyl sulfoxide. AhR-mediated luciferase activity as dioxin-like activity was measured using DR-CALUX assay with a rat hepatoma cell line with an AhR-regulated luciferase gene construct (H4IIE-luc, BioDetection Systems B.V., The Netherlands) according to culture conditions and assay procedures described elsewhere[10].

Results and Discussion

PCBs PCBs were detected in house dust with total concentration ranging from 5 to 320 ng/g but mostly below 100 ng/g (Figure 1). These levels were not significantly different among locations, indicating that e-waste recycling is not a major source of PCBs with respect to the urban environment. However dust in EWRS contained higher proportion of *tri* and *tetra* congeners, notably PCB-28, -33 and -77 (Figure 2). The source of these congeners may be old electrical capacitors and transformers which are known to contain commercial PCB mixtures with low degrees of chlorination, and lower chlorinated PCB congeners evaporate more readily than higher chlorinated homologues.

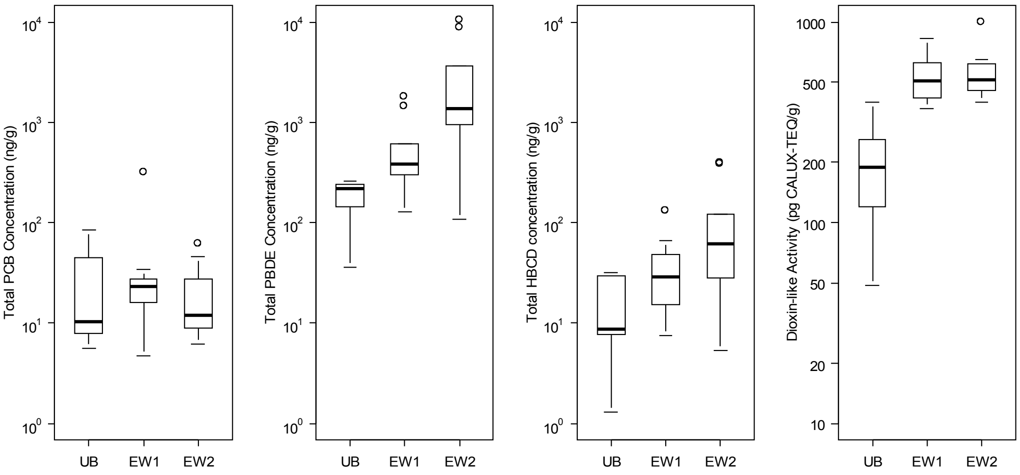

Figure 1. Levels of PCBs, PBDEs, HBCDs and dioxin-like activity in house dust from Vietnamese e-waste recycling and control sites.

BFRs PBDEs were the most abundant among target compounds (Figure 1). Total PBDE levels in the control site were from 36 to 260 ng/g (median 220 n/g), significantly lower than in EW1 (130–1800, median 390 ng/g) and EW2 (110–10000, median 1400 ng/g). HBCD levels were also higher in EWRS (median 29 and 62 ng/g in EW1 and EW2, respectively) than in control site (median 8.7 ng/g) although the difference was statistically significant only for EW2 ($p = 0.015$). Furthermore, levels of HBCDs and PBDEs were strongly correlated (Spearman's $\rho = 0.6$, $p < 0.0001$). These results indicate that e-waste recycling activities may be a source of both PBDEs and HBCDs in Vietnamese EWRS.

Levels of BFRs in Vietnamese house dust were comparably lower than those reported elsewhere in the literature. Median PBDE levels in EW2, highly contaminated area in the present study, were similar to those in common houses from Singapore (1200 ng/g)[11], Australia (1200 ng/g)[12] and Canada (950 ng/g)[13] but lower than those in USA (3500 ng/g)[13] and UK (2900 ng/g)[13]. However it is noteworthy that the samples for the present study were dust collected from high places in contrast to the floor dust used in most other studies and the latter may contain larger quantities of particle-bound contaminants such as BFRs. The Vietnamese HBCD levels, including in EWRS, were also lower than those reported elsewhere[8], almost by one order of magnitude. The reasons, besides the above-mentioned, may be the low content of HBCDs in electronics and the limited presence of HBCD-containing products in Vietnam.

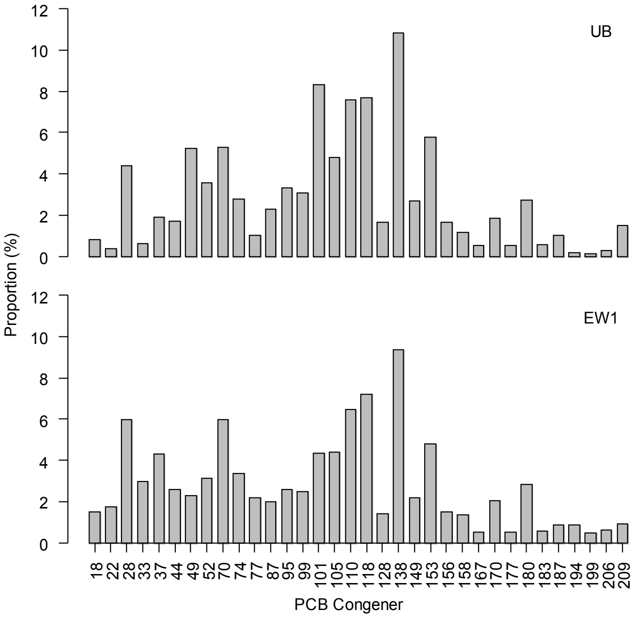

Figure 2. Profiles of PCB congeners.

The profiles of PBDE congeners and HBCD isomers (Figure 3) reveals distinct patterns in EW2. First, while DecaBDE seemed to be the most common PBDE formulation in home environment as indicated by a very high percentage of BDE-209 (60–87%), samples from EW2 contained notably higher proportions of congeners of the PentaBDE formulation (BDE-47, -99 and -153), suggesting that the sources were more diverse in term of PBDE composition. Second, dust in EW2 contained high percentage of α-HBCD (median 80%). This profile is markedly different than in the technical mixtures in which the γ isomer is accounted for 70% content. HBCD isomer profile is known to change through γ-to-α rearrangement during thermal processes; at 160 °C the steady-state composition is reported to be 81.3% α and 8.7% γ[14]. Depending on the method of applying HBCD on polymers, the final products may contain more α isomer and less γ isomer than in the technical mixtures. In Vietnamese house dust, α-HBCD was more abundant than γ-HBCD. The percentages observed in EW2 is similar to the high-temperature profile mentioned above, suggesting that local sources of HBCDs in the EWRS might involve high temperature processes such as burning, moulding, melting, etc.

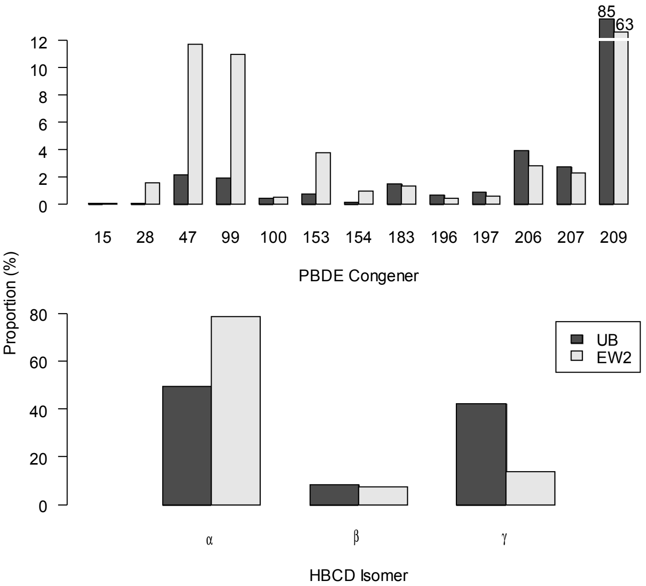

Figure 3. Profiles of PBDE congeners and HBCD isomers.

Dioxin-like activities were detected in a range of 50–1000 pg CALUX-TEQ/g (Figure 1). Levels in the EWRS (median 500 pg CALUX-TEQ/g) were significantly higher than in the urban site (median 190 pg CALUX-TEQ/g). Thus e-waste recycling activities may be a source of dioxin-like compounds. Contamination by polychlorinated dioxins and furans (PCDD/Fs) generated by uncontrolled burning of plastics in e-waste has been reported in soil samples from Chinese EWRS[2,4]. Polybrominated dioxins and furans as well as their mixed halogenated homologues are known to be generated from BFRs under similar conditions[3]. To our knowledge this is the first report on possible contamination of the home environment by dioxin-like compounds related to the recycling of e-waste. The CALUX-TEQ levels in house dust from Vietnamese EWRS reported here were in the upper range of the levels in Japanese dust (38–1400, median 220 pg CALUX-TEQ/g)[10].

Implications for human exposure Dietary intake has been considered as the dominant human exposure pathway for POPs such as PCBs. However recent studies[12,15,16] have found correlations between PBDE levels in human matrices and house dust. Other studies[6,7,8] also estimated that the intake via house dust to impart sizeable contributions to total human intake of BFRs. Considering an ingestion rate of 20 mg dust/day for an average adult[17] and the median exposure levels reported here, the estimated daily intake values for UB, EW1 and EW2 are 4.4, 12 and 28 ng PBDEs/day and 0.174, 0.58 and 1.24 ng HBCDs/day, respectively. Compared with the dietary intake of an average Vietnamese person via freshwater and marine fish consumption estimated by our research group (3.0 ng/day for both PBDEs and HBCDs, details not shown) the *via*-dust intake figures are comparable or higher for PBDEs but not for HBCDs. For dioxin-like compounds, the CALUX-TEQ levels in house dust from the EWRS were higher than those in food reported from Belgium[18] by 3–5 orders of magnitude. Coupled with a dust ingestion rate of 3–4 order lower than food consumption, these levels suggest house dust as an important exposure source of dioxin-like compounds in Vietnamese EWRS.

Acknowledgements

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