DIOXIN-RELATED COMPOUNDS IN HOUSE DUST FROM VIETNAMESE E-WASTE RECYCLING SITES: COMPARISON OF IN VITRO BIOASSAY- AND CHEMICAL ANALYSIS-DERIVED TOXIC EQUIVALENTS

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Introduction

Large scale of uncontrolled recycling of electrical and electronic waste (e-waste) in developing countries have been perceived as a source of contamination by a wide range of toxic substances[1], including many dioxin-related compounds (DRCs). Crude thermal processing of e-waste has been reported to cause elevated levels of polychlorinated dibenzo-*p*-dioxin/furans (PCDD/Fs) in the surrounding environment[2]. The abundance of brominated flame retardants such as polybrominated diphenyl ethers (PBDEs) in e-waste may lead to a release of polybrominated dibenzo-*p*-dioxin/furans (PBDD/Fs), which exist as impurities in technical PBDEs[3] or can be generated from PBDE by thermal or photolytic degradation[4,5]. Moreover, mixed halogenated dioxins/furans (PXDD/Fs) can also be formed in low temperature combustion[4].

It is critical to assess the DRC exposure of EWRS residents, on account of many adverse effects of these contaminants[6]. However, data on PBDD/Fs and PXDD/Fs released from e-waste recycling are scarce[7,8] and virtually non-existent outside China, partly due to the difficulties in analyzing the large number of chemicals involved. Human risk assessment based on available data is also incomplete, considering the lack of toxicological data for many compounds.

This study investigated house dust as potential human exposure medium of DRCs in two EWRSs in Vietnam. The Dioxin-Responsive Chemically Activated LUciferase gene eXpression (DR-CALUX) *in vitro* bioassay was used to determine the overall dioxin-like activities, combined with chemical analysis to elucidate the composition as well as dioxin-like potencies of PCDD/Fs, dioxin-like PCBs (DL-PCBs), PBDD/Fs and monobromo PCDD/Fs (MBPCDD/Fs). Human exposure of DRCs via dust ingestion was also estimated.

Materials and methods

Samples: The samples were collected in September 2008 in three locations in the Red River Delta, northern Vietnam: two e-waste recycling sites, in Hai Phong city (EW1, n = 10) and Hung Yen province (EW2, n = 10), as well as an urban control site (Hanoi, UB, n = 11). House dust samples were collected from the surface of furniture and fan blades into zip-locked polyethylene bags and covered with aluminum foil. After collection the samples were stored at –25 °C until analysis.

Sample preparation: After manual removal of large pieces of matter using tweezers, 1–4 g dust was extracted using a rapid solvent extractor (SE100, Mitsubishi Chemical Analytech) at a flow rate of 6 ml/min with an acetone/hexane mixture (1:1 v/v) and then toluene for 1 h each. The combined extract was solvent-exchanged into hexane and treated with hexane-washed sulfuric acid (98%), passed through a sulfuric acid-impregnated silica gel column and then subjected to gel-permeable chromatography (packed Bio-Bead S-X 3, Bio-Rad Laboratories). The extract was finally solvent-exchanged into 100 µl biochemical grade DMSO and stored at 4 °C until subsequent analysis.

DR-CALUX assay: Dioxin-like activity was measured as AhR-mediated luciferase activity using DR-CALUX assay

with a H4IIE-*luc* rat hepatoma cell line (BioDetection Systems B.V.). The culture conditions, assay procedures and data analysis were as per the protocol described elsewhere[9]. Results were expressed in picogram CALUX TCDD-equivalent (CALUX-TEQ) per gram dust.

Analysis of PCDD/Fs, DL-PCBs, PBDD/Fs and MBPCDD/Fs: Based on the CALUX-TEQ levels and sample volumes, a selected number of extracts were analyzed for DRCs. Each extract was divided into two portions. The first was spiked with $^{13}C_{12}$-labeled PCB standard surrogates then cleaned-up with a multilayer silica gel column with copper chips. The second was spiked with $^{13}C_{12}$-labeled PCDD/Fs, PBDD/Fs, MBPCDD/Fs and cleaned-up with a multilayer silica gel column with copper chips and subsequently an activated carbon-impregnated silica gel column. DRCs were determined using GC-HRMS; compounds were identified and quantified using dilution method with the corresponding $^{13}C_{12}$-labeled congeners and concentration of each homologue group was calculated from the total area of standard-assigned and potential peaks.

Theoretical CALUX-TEQs of DRCs: Assuming dose-additivity, the dioxin-like activities of the identified DRCs were evaluated as theoretical CALUX-TEQs, calculated from chemical concentrations using published CALUX relative potency factors (REP)[10,11].

Results and discussion

Dioxin-like activities

As shown in Fig. 1, dioxin-like activities in house dust collected from the EWRSs (median 490 and 520 pg CALUX-TEQ/g in EW1 and EW2, respectively) were significantly higher than those from the urban control site (median 140 pg CALUX-TEQ/g), and also higher compared with those observed in the previous study on dust from Japanese common house and office (median 110 and 220 pg CALUX-TEQ/g, respectively[9]). These data clearly indicate that houses in Vietnamese EWRSs are considerably contaminated with DRCs released from uncontrolled recycling activities.

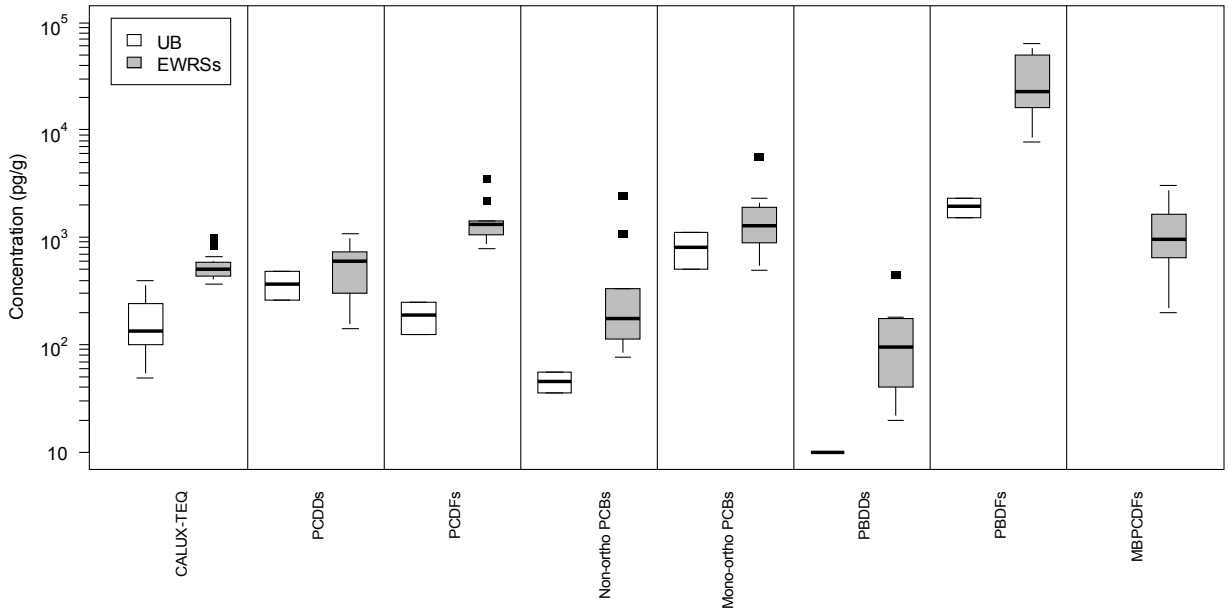

Fig. 1. Dioxin-like activities (pg CALUX-TEQ/g) and concentrations (pg/g) of DRCs in Vietnamese house dust.

PCDD/Fs, DL-PCBs, PBDD/Fs and MBPCDD/Fs

Consistent with the difference in DR-CALUX results, halogenated dibenzofurans (PCDFs, PBDFs and MBPCDFs) as well as non-*ortho* PCBs and PBDDs were detected at higher levels in house dust from the EWRSs than from UB (Fig. 1). While it is clear that uncontrolled e-waste recycling in Vietnam leads to a significant release of these DRCs, their specific sources may be different. In terms of abundance, PBDFs were the predominant compounds among DRCs in all samples, up to tens of nanogram per gram. The predominance over PBDDs reflects the favorable formation of PBDFs from precursor PBDEs by mild thermal stress[4] or photolysis[5]. Moreover, the ratios of PBDFs/PBDEs, calculated from PBDE data previously reported for the same sample set[12], were not significantly different in house dust from the EWRSs (3% in average) and from the urban site (2.5% in average), suggesting that a large portion of PBDFs in house dust may have been formed during production or weathering of polymers containing PBDEs rather than during recycling. PCDFs were the second most abundant detected in EWRS house dust (790–3500 pg/g), but less abundant than mono-*ortho* PCBs and PCDDs in urban house dust. The elevated levels of PCDFs observed in the EWRSs, especially relative to PCDDs, suggest that their main source is low temperature thermal processing of e-waste. MBPCDFs can be generated together with PCDFs in such thermal processes by parallel bromine and chlorine substitution, as evidenced by a significant positive correlation between their levels (Pearson's $r > 0.7$, $p < 0.01$) but not between MBPCDFs and PBDFs. Regarding non-*ortho* PCBs, their elevated levels in EWRS dust, notably CB-77, may be associated with another source, possibly old electrical capacitors and transformers. These may contain technical PCBs as dielectric and heat transfer fluid, and less substituted congeners such as CB-77 can be more readily released and dispersed from e-waste into the surrounding environments because of their volatility.

Toxic equivalents of DRCs compared with DR-CALUX results

The principal contributors of dioxin-like activities in the dust samples were PCDD/Fs and PBDFs. The chemically derived theoretical CALUX-TEQs of PCDD/Fs were 88–220, 50–89 and 18–25 pg/g dust in EW1, EW2 and UB, respectively. PBDD/F-CALUX-TEQs were 26–110 pg/g in EW1, 44–200 pg/g in EW2, but very low in urban dust because the more potent 2,3,7,8-brominated furans were at non-detectable levels. DL-PCBs contributed only a small portion of CALUX-TEQs due to their weak REPs[11]. Among MBPCDFs, CALUX-TEQs were calculated only for 3-B-2,7,8-CDF (ND–3 pg CALUX-TEQ/g in EW1 house dust) due to the limited number of congeners identified and the lack of data on potency of these compounds. The theoretical contribution of each contaminant group to the DR-CALUX-derived dioxin-like activities is shown in Fig. 2. EW1 had higher PCDD/F-TEQs whereas EW2 had higher PBDF-TEQs, possibly related to higher crude thermal processing activity in EW1 and higher amount of e-waste containing PBDEs in EW2. It is apparent that the identified DRCs could explain only a small portion of the DR-CALUX activities in the sulfuric acid-treated dust extracts (Fig. 2), suggesting the presence of other persistent AhR agonists or a synergistic effect of the matrix.

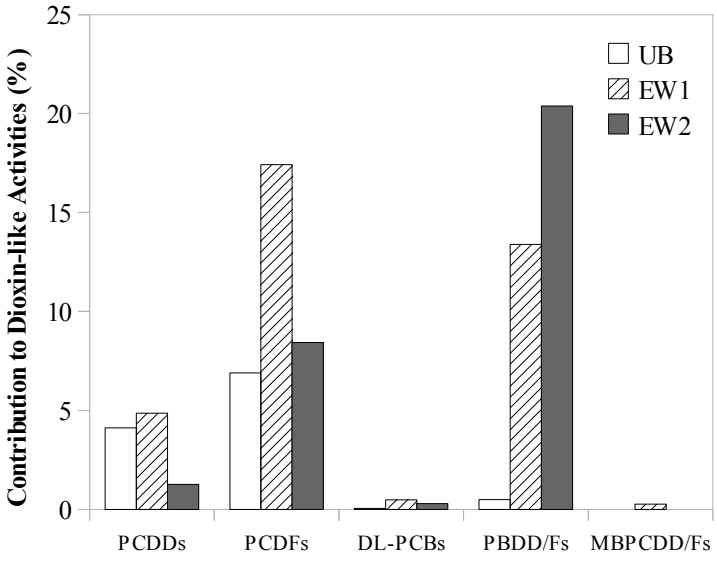

Fig. 2. Contribution of DRCs to the dioxin-like activities in house dust determined using DR-CALUX.

Human exposure

Human daily TEQ intakes were estimated assuming an average dust ingestion rate of 20 mg/day for adults, 50 mg/day for children[13] and a complete assimilation of DRCs. The median daily intake estimates for EWRS residents were 10 and 25 pg CALUX-TEQ/day for adults and children, respectively and 2.7 and 6.8 pg CALUX-TEQ/g respectively for urban residents. Compared with the recent exposure levels estimated for dietary intake, which are in the range of tens of picogram WHO-TEQ per day in Europe[14] and the USA[15], the TEQ intakes from dust are substantial for EWRS residents, especially for children. The daily intake doses (DIs) of these children by dust ingestion are estimated between 1.2 and 3.3 pg CALUX-TEQ/kg bw/day, assuming an average body weight of 15 kg[16]. Although it is difficult to compare these estimates to the WHO tolerable daily intake dose (TDI, of 1–4 pg WHO-TEQ/kg bw/day[6]), the potential risk for children exposed to such high doses of DRCs in dust should be considered, because the dust ingestion rate of EWRS residents is likely greater than the general population due to higher air concentrations of particulate matters.

In conclusion, PBDD/Fs need to be considered in monitoring studies of indoor environments, especially in e-waste recycling sites, because their contribution to dioxin-like activities is comparable to that of PCDD/Fs. Considering the high levels of unknown CALUX-TEQs in house dust and the associated potential risk for children, future research need to identify unknown DRCs or other factors responsible for these levels.

Acknowledgment

This study was partly supported by Grants-in-Aid for Scientific Research (S) (No. 20221003) from Japan Society for the Promotion of Science (JSPS), the Waste Management Research Grants (K2062, K2129 and K2121) from the Ministry of the Environment, Japan, and grants from Global COE Program of the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT).

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