HUMAN EXPOSURE TO BROMINATED FLAME RETARDANTS AND DIOXIN-RELATED COMPOUNDS IN VIETNAMESE E-WASTE RECYCLING SITES

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1. INTRODUCTION

E-waste recycling sites (EWRSs) in Asian developing countries have been identified as hotspots of contamination by persistent organic pollutants including polychlorinated biphenyls (PCBs) (1), brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) (2, 3), and may also be a source of various dioxin-related compounds (DRCs). DRCs are known to bind to the aryl hydrocarbon receptor (AhR) and induce the expression of related genes (4), causing a multitude of adverse effects including reproductive and developmental abnormalities, immune deficiency, tumor promotion and endocrine disruption (5). Therefore, it is critical to assess the exposure of EWRS residents to these contaminants.

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 in combination with chemical analysis in order to elucidate the overall dioxin-like activities, occurrence and profiles of PCDD/Fs, DL-PCBs, PBDD/Fs, monobromo PCDD/Fs (MoBPCDD/Fs) as well as their potencies relative to the overall values in persistent (sulfuric acid-treated) extracts of settled house dust. Human exposure to DRCs from dust ingestion was also estimated.

2. MATERIALS AND METHODS

2.1. Sample collection

The samples were collected in September 2008 in three locations in the Red River Delta, northern Vietnam: one EWRS in Hai Phong city (TrangMinh, EW1, n = 10), another in Hung Yen province (Bui Dau, EW2, n = 10), and an urban control site (Hanoi, UB, n = 11). Both EWRSs were small rural communes with 80 households or less, about 30% of which involved in recycling of metals and plastics from e-waste such as disposed computers, TVs, video players, phones and printers since the early 2000s. Metals were recovered by manual dismantling as well as burning of wires and circuit boards, whereas plastic casings were shredded into saleable pellets. Recycling operations were family-based and took place in the backyard of the house, often within 20 m of the living area. Settled dust samples were collected in the living rooms of the houses from the surface of furniture and fan blades using a straw broom. After collection the samples were stored at -25^{o}C until analysis.

2.2. Sample preparation

Before extraction, large pieces of matter in the dust samples including hair, textile fibers, paint fragments, etc. were manually removed 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^{-1} first with an acetone/hexane mixture (1/1 v/v) at 35^{o}C for 1 h and then with toluene at 80^{o}C for another 1 h. The combined extract was solvent-exchanged into hexane and treated with hexane-washed sulfuric acid (98%), passed through a glass column packed with sulfuric acid-impregnated silica (Wako, 44% sulfuric acid, 1.5 g and 22% sulfuric acid, 1 g, in bottom-up order) with hexane (100 ml) as eluant and then subjected to gel-permeable chromatography (packed Bio-Bead S-X 3, BioRad Laboratories). Non-persistent compounds such as polyaromatic hydrocarbons (PAHs) were removed by this clean-up procedure. The extract was then concentrated, solvent-exchanged into 0.1 ml biochemical-grade dimethyl sulfoxide and stored at 4^{0}C for subsequent analyses. Every set of seven samples was accompanied with a procedural blank.

2.3. DR-CALUX assay

Dioxin-like activity was measured as AhR-mediated luciferase using DR-CALUX assay with a rat hepatoma cell line with an AhR-regulated luciferase gene construct (H4IIE-luc, BioDetection Systems B.V.). The culture

conditions, assay procedures and data analysis followed the protocol described elsewhere (6). Throughout the study, the calculated EC50 of the 2,3,7,8-CDD (TCDD) standard was 7.4 ± 1.0 pM (n = 27) and the maximum induction ranged from 6.6 to 13.1 (9.2 ± 1.8), satisfying the quality levels indicated in the standard operating procedure (7). The limit of quantification ranged from 0.07 to 0.80 pM TCDD in well. Results were expressed in picogram CALUX TCDD-equivalent (CALUX-TEQ) per gram dust.

2.4. Chemical analyses of DRCs

Based on the amount of CALUX-TEQ in the samples, two extracts of dust from UB and five each from EW1 and EW2 were analyzed for DRCs. The extracts were subjected to an additional clean-up procedure as described in the supporting information (SI). DL-PCBs, 2,3,7,8-substituted PCDD/Fs, PBDD/Fs, MoBPCDD/Fs and four non-2,3,7,8-TeBDDs (1,3,6,8-, 1,3,7,9-, 1,2,3,4- and 1,3,7,8-BDDs) were identified and quantified by gas chromatography/high resolution mass spectrometry (GC-HRMS) using isotope dilution method with the corresponding $^{13}C_{12}$-labeled congeners (see SI for details on the instruments). Concentrations of each homologue group were calculated from the total area of standard-assigned and potential peaks. Recoveries of DRCs were between 64% and 110%. Calculation of limits of detection followed the Japanese Industrial Standards for measurements of PCDD/Fs and coplanar PCBs (8). Quality assurance and quality control for our analytical method have been confirmed in an intercalibration study on DRCs and PBDEs using an air-dried sediment sample (9).

3. RESULTS AND DISCUSSION

3.1. Dioxin-like activities

All sulfuric acid-treated extracts of settled house dust exhibited dioxin-like activities in the DR-CALUX assay. Near full dose-response curves could be achieved for a number of samples and the curve shapes were similar to that of TCDD.

As shown in Figure 1, the activity levels in the EWRS samples were similar (EW1 370–830, median 490; EW2 370–1000, median 520 pg CALUX-TEQ g^{-1}) and significantly higher than in the urban control samples (49–400, median 140 pg CALUX-TEQ g^{-1}, Wilcoxon rank sum test $p < 0.01$), indicating that uncontrolled e-waste recycling may be an important source of DRCs contaminating the surrounding home environments. The CALUX-TEQ levels in the EWRSs were high compared with those reported in the previous study on Japanese house and office dust, in the upper quartile (360–1400 pg g^{-1}; 6) whereas the levels in Vietnamese urban house dust were comparable to those in Japanese houses (median 110 pg g^{-1}; 16).

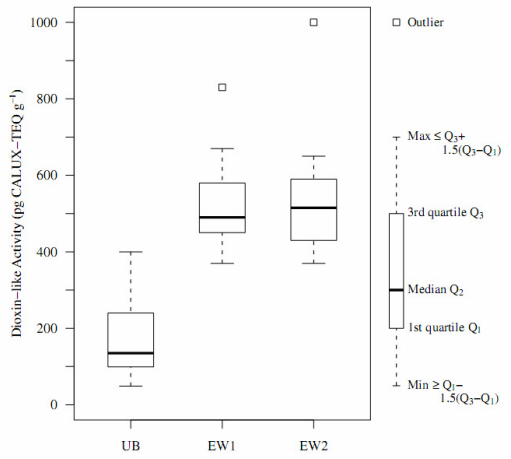

Figure 1. Dioxin-like activities determined using DR-CALUX in settled house dust from the urban (UB) and e-waste recycling (EW1 and EW2) sites

3.2. Occurrence and profiles of dioxin-related compounds

Concentrations of DRCs determined in twelve selected dust samples are summarized in Table 1. The results showed a clear predominance of PBDFs in terms of abundance, in the low ppb range in urban house dust and up to tens of ppb in EWRS house dust. PCDFs were detected in the latter at relatively high levels in the ppb range, comparable to those of mono-ortho PCBs, followed by PCDDs > MoBPCDFs > non-ortho PCBs > PBDDs >MoBPCDDs. In dust from UB, mono-ortho PCBs were the second most abundant, followed by PCDDs > PCDFs > non-ortho PCBs whereas PBDDs and MoBPCDD/Fs were not detected. Levels of dibenzofurans, including chlorinated, brominated and mixed halogenated compounds, as well as non-ortho PCBs and PBDDs were significantly higher in the EWRSs than in UB ($p < 0.05$), indicating a substantial release of these contaminants by recycling activities. The levels of PCDD/Fs and PBDD/Fs in settled dust from Vietnamese EWRSs were respectively 3–5 times and 20–50 times higher than in vacuum cleaner dust from Japanese houses (10), but lower than in e-waste workshop indoor dust in China (11) by a factor of 17–28 and 2–5, respectively.

Compound	UB (n = 2) Range	UB (n = 2) Median	EW1 (n = 5) Range	EW1 (n = 5) Median	EW2 (n = 5) Range	EW2 (n = 5) Median
TeCDDs	<0.7–14	7.0	31–83	36	11–25	16
PeCDDs	18–32	25	81–230	94	24–55	33
HxCDDs	64–110	87	160–360	190	31–100	57
HpCDDs	53–130	92	130–210	150	26–98	66
OCDD	100–220	160	140–520	200	19–440	110
Total PCDDs	270–470	370	590–1100	720	140–600	300
TeCDFs	23–42	33	190–570	240	93–450	240
PeCDFs	33–67	50	310–870	380	160–460	310
HxCDFs	<2–78	39	390–1100	410	190–350	280
HpCDFs	49–69	59	270–770	310	100–410	160
OCDF	<9–15	7.5	100–250	140	16–69	57
Total PCDFs	120–250	190	1300–3500	1400	790–1400	1100
Total PCDD/Fs	510–600	560	1900–4500	2400	1100–1800	1400
Non-ortho PCBs	36–56	46	150–2400	270	77–1100	110
Mono-ortho PCBs	500–1100	800	1300–5500	1800	490–2300	900
Total DL-PCBs	540–1200	850	1500–7900	2200	570–3400	1000

Compound	UB (n = 2) Range	UB (n = 2) Median	EW1 (n = 5) Range	EW1 (n = 5) Median	EW2 (n = 5) Range	EW2 (n = 5) Median
TeBDDs	<10–10	5.0	20–60	30	<7–120	50
PeBDDs	<20	<20	<10	<10	<10	<10
HxBDDs	<50	<50	<20	<20	<30	<30
HpBDDs	<40	<40	<10–20	<10	<20–40	<20
OBDD	<40	<40	<20–120	<20	<30–280	<30
Total PBDDs	ND–10	5.0	20–130	62	ND–430	100
TeBDFs	140–430	290	1200–4400	3200	2800–11000	4500
PeBDFs	300–340	320	2000–10000	5000	2600–20000	8300
HxBDFs	300–500	400	2000–9200	4100	2500–16000	12000
HpBDFs	210–500	360	1000–4700	2100	2200–13000	6800
OBDF	250–900	580	1500–5800	3200	310–24000	3500
Total PBDFs	1500–2300	1900	7700–33000	23000	12000–63000	49000
Total PBDD/Fs	1500–2300	1900	7700–33000	23000	12000–63000	49000
MoBTrCDDs	<4	<4	<1–21	<1	<2	<2
MoBTeCDDs	<4	<4	<1	<1	<2	<2
MoBPeCDDs	<5	<5	<2–12	5.0	<2	<2
MoBHxCDDs	<20	<20	<10	<10	<10	<10
MoBHpCDDs	<40	<40	<20	<20	<20	<20
Total MoBPCDDs	ND	ND	ND–34	5.0	ND	ND
MoBTrCDFs	<3	<3	33–170	51	8.0–75	45
MoBTeCDFs	<4	<4	97–210	130	4.0–89	66
MoBPeCDFs	<5	<5	120–490	200	27–220	110
MoBHxCDFs	<20	<20	62–440	180	<10–250	80
MoBHpCDF	<40	<40	70–350	160	<20–280	40
Total MoBPCDFs	ND	ND	400–1500	750	ND–820	320

ND: not detected.

Table 1. Concentrations (pg g 1) of PCDD/Fs, DL-PCBs, PBDD/Fs and MoBPCDD/Fs in selected indoor settled dust samples

The profiles of PCDD/F homologues in dust from the EWRSs showed a preponderance of furans, especially Pe- and HxCDFs. In contrast, OCDD was the most abundant in the samples from UB, in agreement with a previous report on urban house dust from Japan (12). The elevated levels of PCDFs in the EWRSs, especially EW1 which had the highest levels of PCDD/Fs, are probably related to crude thermal processes such as melting and burning of e-waste for retrieval of metals. The predominance of OCDD in UB house dust is consistent with the homologue profiles in urban soil of Asian developing countries (13), suggesting that PCDD/Fs in Vietnamese urban house dust may be from soil particles.

3.3. Implication for human exposure

The DR-CALUX results of this study provided a quantitative estimate of the mixture of persistent compounds exhibiting dioxin-like activities in indoor settled dust. As these dusts are formed mainly by accumulation of fine particles deposited from indoor air over time, they can be representative of the dust ingested accidentally by human and a good matrix to assess the exposure to DRCs through this pathway. Assuming average dust ingestion rates of 20 and 50 mg d^{-1} for adults and children (14) and a complete assimilation of DRCs, the daily TEQ intake (DI) was estimated and plotted in Figure 2. The median DI estimates of urban residents were 2.7 and 6.8 pg CALUX-TEQ d^{-1} for adults and children, respectively and 10 and 25 pg CALUX-TEQ d^{-1} , respectively for residents of EWRSs.

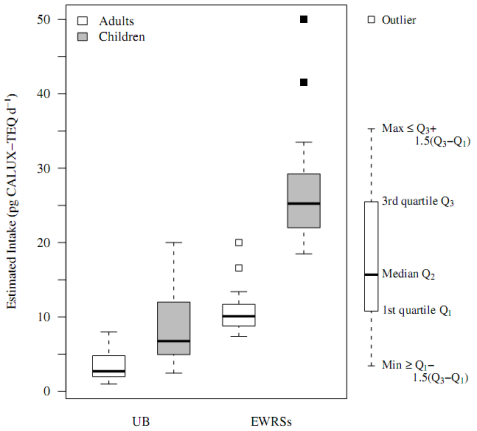

Figure 2. CALUX-TEQ intake from dust ingestion by residents of the urban (UB) and e-waste recycling (EWRSs) sites, estimated for adults and children using dust ingestion rates of respectively 20 and 50 mg d^{-1}

It is generally accepted that diet is the most important human exposure pathway of persistent organic pollutants such as PCDD/Fs and DL-PCBs (15). While no information on the background dietary exposure of DRCs in Vietnam is available, recent DI estimates are in the range of tens of picogram WHO-TEQ per day in Europe and the USA (16,17) and up to 160 pg WHO-TEQ d^{-1} in Japan (6). Compared with these values, it is clear that dust is a minor DRC exposure medium for Vietnamese urban residents. In the EWRSs, however, the estimated DIs from dust are considerable, notably for children. Assuming an average weight of 15 kg for children of 2–5 year old (18), the daily intake doses from dust ingestion estimated for EWRS children were between 1.2 and 3.3 pg CALUX-TEQ kg bw^{-1} d^{-1}. By comparison, WHO established a range of tolerable daily intake dose as 1–4 pg WHO-TEQ kg bw^{-1} d^{-1}, derived from hormonal, reproductive and developmental effects on animals (5). Although CALUX- and WHO-TEQs are not directly comparable, such high levels of exposure dose to DRCs in dust suggest potential risk for children in the EWRSs, especially when considering that EWRS residents may have a greater dust ingestion rate than the general population due to the large amount of particulate matter generated during e-waste recycling activities.

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