

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/47716829>

Evaluation of Dioxin-Like Activities in Settled House Dust from Vietnamese E-Waste Recycling Sites: Relevance of Polychlorinated/Brominated Dibenzo-p-Dioxin/Furans and Dioxin-Like...

ARTICLE in ENVIRONMENTAL SCIENCE & TECHNOLOGY · NOVEMBER 2010

Impact Factor: 5.33 · DOI: 10.1021/es102505j · Source: PubMed

CITATIONS

28

READS

26

7 AUTHORS, INCLUDING:



Nguyen Minh Tue

Ehime University

32 PUBLICATIONS 267 CITATIONS

SEE PROFILE



Go Suzuki

National Institute for Environmental Studies

72 PUBLICATIONS 729 CITATIONS

SEE PROFILE



Shin Takahashi

Ehime University

217 PUBLICATIONS 4,181 CITATIONS

SEE PROFILE



Tomohiko Isobe

National Institute for Environmental Studies

131 PUBLICATIONS 2,619 CITATIONS

SEE PROFILE

Evaluation of Dioxin-Like Activities in Settled House Dust from Vietnamese E-Waste Recycling Sites: Relevance of Polychlorinated/Brominated Dibenzo-*p*-Dioxin/Furans and Dioxin-Like PCBs

NGUYEN M. TUE,[†] GO SUZUKI,[‡] SHIN TAKAHASHI,[†] TOMOHIKO ISOBE,[§] PHAM T. K. TRANG,[⊥] PHAM H. VIET,[⊥] AND SHINSUKE TANABE^{*,†}

Center for Marine Environmental Studies, Ehime University, 2-5 Bunkyo-cho, Matsuyama 790-8577, Japan, Research Center for Material Cycles and Waste Management, National Institute for Environmental Studies, Onogawa 16-2, Tsukuba 305-8506, Japan, Senior Research Fellow Center, Ehime University, 2-5 Bunkyo-cho, Matsuyama 790-8577, Japan, and Centre for Environmental Technology and Sustainable Development, Hanoi University of Science, 334 Nguyen Trai, Hanoi, Vietnam

Received July 23, 2010. Revised manuscript received October 14, 2010. Accepted October 21, 2010.

Few studies have investigated the human exposure to the ensemble of dioxin-related compounds (DRCs) released from uncontrolled e-waste recycling, especially from a toxic effect standpoint. This study evaluated the TCDD toxic equivalents (TEQs) in persistent extracts of settled house dust from two Vietnamese e-waste recycling sites (EWRs) using the Dioxin-Responsive Chemically Activated Luciferase gene eXpression assay (DR-CALUX), combined with chemical analysis of PCDD/Fs, DL-PCBs, PBDD/Fs, and monobromo PCDD/Fs to determine their TEQ contribution. The CALUX-TEQ levels in house dust ranged from 370 to 1000 pg g⁻¹ in the EWRs, approximately 3.5-fold higher than in the urban control site. In EWRs house dust, the concentrations of the unregulated PBDFs were 7.7–63 ng g⁻¹, an order of magnitude higher than those of regulated DRCs (PCDD/Fs and DL-PCBs), and PBDFs were also principal CALUX-TEQ contributors (4.2–22%), comparable to PCDD/Fs (8.1–29%). The CALUX-TEQ contribution of DRCs varied, possibly depending on thermal processing activities (higher PCDD/F-TEQs) and PBDE content in the waste (higher PBDF-TEQs). However, the percentage of unknown dioxin-like activities was high in all dust samples, indicating large contribution from unidentified DRCs and/or synergy among contaminants. Estimates of TEQ intake from dust ingestion suggest that children in the EWRs may be adversely affected by DRCs from dust.

Introduction

The increasing activities of electrical and electronic waste (e-waste) recycling in developing countries received global attention because of the emission of a wide range of toxic chemicals resulting from the uncontrolled and often hazardous recycling methods and the large volume of the waste, both domestically generated and imported from developed nations (1, 2). E-waste recycling sites (EWRs) in Asian developing countries have been identified as hotspots of contamination by persistent organic pollutants including polychlorinated biphenyls (PCBs) (3), brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) (4, 5), and may also be a source of various dioxin-related compounds (DRCs). Polychlorinated dibenzo-*p*-dioxin/furans (PCDD/Fs) can be formed as secondary contaminants during crude thermal processes in e-waste recycling (6, 7). Polybrominated dibenzo-*p*-dioxin/furans (PBDD/Fs) may occur as impurities in technical PBDEs (8) and products of PBDE degradation during production, recycling or weathering of the flame-retarded plastics (9–11). Both PBDD/Fs and their mixed halogenated homologues (PXDD/Fs) can also be generated in low temperature combustion (9, 10).

DRCs are known to bind to the aryl hydrocarbon receptor (AhR) and induce the expression of related genes (12), causing a multitude of adverse effects including reproductive and developmental abnormalities, immune deficiency, tumor promotion and endocrine disruption (13). Therefore it is critical to assess the exposure of EWRs residents to these contaminants. However, partly due to the large number of chemicals involved, research on DRCs other than the conventional PCDD/Fs and dioxin-like PCBs (DL-PCBs) in EWRs is scarce (14, 15), and virtually absent in developing countries other than China. Furthermore, current data on DRCs provide very limited information regarding human health impacts, considering the huge toxicological data gap for many compounds and possible “mixture effects” of contaminants.

This study investigated house dust as potential human exposure medium of DRCs in two EWRs 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 (MoB-PCDD/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.

Experimental Section

Sample Collection. The samples were collected in September 2008 in three locations in the Red River Delta, northern Vietnam: one EWR in Hai Phong city (Trang Minh, EW1, *n* = 10), another in Hung Yen province (Bui Dau, EW2, *n* = 10), and an urban control site (Hanoi, UB, *n* = 11). Both EWRs 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. Other details on these

* Corresponding author phone: +81 89 927 8171; fax: +81 89 927 8171; e-mail: shinsuke@agr.ehime-u.ac.jp.

[†] Ehime University.

[‡] National Institute for Environmental Studies.

[§] Ehime University.

[⊥] Hanoi University of Science.

locations have been described elsewhere (5). Settled dust samples were collected in the living rooms of the houses from the surface of furniture and fan blades using a straw broom. The broom was washed with dishwashing detergent before sample collection and a new one was used for each sampling location. Each sample was collected into an aluminum foil pocket placed inside a zip-locked polyethylene bag. After collection the samples were stored at -25°C until analysis.

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°C for 1 h and then with toluene at 80°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, Bio-Rad Laboratories). Nonpersistent compounds such as polyaromatic hydrocarbons (PAHs) were removed by this cleanup procedure. The extract was then concentrated, solvent-exchanged into 0.1 mL biochemical-grade dimethyl sulfoxide and stored at 4°C for subsequent analyses. Every set of seven samples was accompanied with a procedural blank.

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 (16). Throughout the study, the calculated EC_{50} of the 2,3,7,8-CDD (TCDD) standard was $7.4 \pm 1.0\text{ pM}$ ($n = 27$) 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 (17). 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.

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 cleanup 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 $^{13}\text{C}_{12}$ -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 (18). 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 (19).

Results and Discussion

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 (see examples in SI, Figure S1) and the curve shapes were similar to that of TCDD. As shown in Figure 1, the activity levels in the EWRs samples

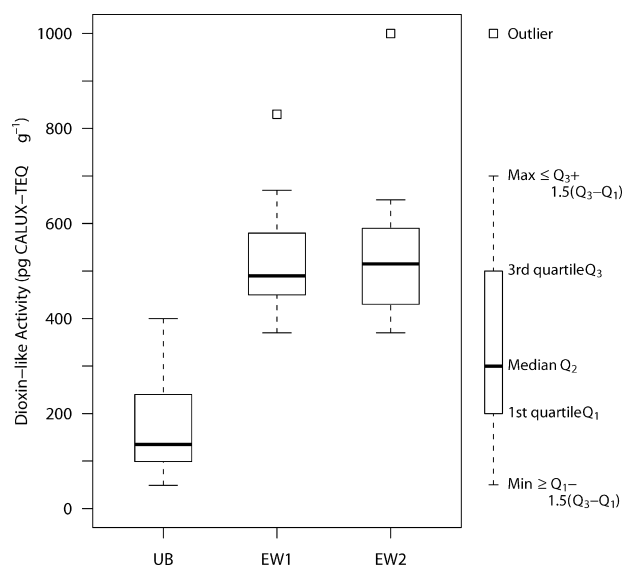


FIGURE 1. Dioxin-like activities determined using DR-CALUX in settled house dust from the urban (UB) and e-waste recycling (EW1 and EW2) sites.

were similar (EW1 370–830, median 490; EW2 370–1000, median 520 $\text{pg CALUX-TEQ g}^{-1}$) and significantly higher than in the urban control samples (49–400, median 140 $\text{pg CALUX-TEQ g}^{-1}$, 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 EWRs 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} , ref 16), whereas the levels in Vietnamese urban house dust were comparable to those in Japanese houses (median 110 pg g^{-1} , ref 16). Studies on DRCs in indoor dust are scarce, mostly reporting only TEQ levels derived from the concentrations of PCDD/Fs and DL-PCBs using toxic equivalency factors (TEFs) established by the World Health Organization (WHO-TEFs, ref 20), and these levels were often less than 50 pg WHO-TEQ g^{-1} (21, 22). However, PBDD/Fs have recently been found in indoor dusts at levels similar to those of PCDD/Fs (23), indicating that dioxin-like activities may be higher than previously thought.

Occurrence and Profiles of Dioxin-Related Compounds. Concentrations of DRCs determined in 12 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 \approx 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 EWRs 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 EWRs were respectively 3–5 times and 20–50 times higher than in vacuum cleaner dust from Japanese houses (23), but lower than in e-waste workshop floor dust in China (14) by a factor of 17–28 and 2–5, respectively.

The profiles of PCDD/F homologues in dust from the EWRs showed a preponderance of furans, especially Pe- and HxCDFs (SI Figure S2). In contrast, OCDD was the most abundant in the samples from UB, in agreement with a

TABLE 1. Concentrations (pg g⁻¹) of PCDD/Fs, DL-PCBs, PBDD/Fs and MoBPCDD/Fs in Selected Indoor Settled Dust Samples^a

compound	UB (n = 2)		EW1 (n = 5)		EW2 (n = 5)	
	range	median	range	median	range	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	590–100	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
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	2800–11 000	4500
PeBDFs	300–340	320	2000–10 000	5000	2600–20 000	8300
HxBDFs	300–500	400	2000–9200	4100	2500–16 000	12 000
HpBDFs	210–500	360	1000–4700	2100	2200–13 000	6800
OBDF	250–900	580	1500–5800	3200	310–24 000	3500
Total PBDFs	1500–2300	1900	7700–33 000	23 000	12 000–63 000	49 000
Total PBDD/Fs	1500–2300	1900	7700–33 000	23 000	12 000–63 000	49 000
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

^a ND, not detected.

previous report on urban house dust from Japan (21). Compared with the profiles of different soils described in (24), the first pattern resembles the profile of combustion sources, whereas the second is similar to that of background soils. PCDFs have also been detected at higher levels than PCDDs in dust and soil of areas with low temperature combustion sources such as Chinese EWRSs (7) or open dumping sites in Asian developing countries (25). Therefore 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 (25), suggesting that PCDD/Fs in Vietnamese urban house dust may be from soil particles.

As shown in Table 1, PBDFs were more abundant than PBDDs by more than 2 orders of magnitude in all samples. The predominance of furans compared with dioxins is in agreement with the results of other studies on dust (14, 23) and air (26), and consistent with the lower energetic requirement of their formation from BFR precursors, notably PBDEs (10). PBDFs, rather than PBDDs, have been reported as products of PBDE degradation by mild thermal stress (10) or photolysis under natural light (11), and as byproduct in

technical PBDEs (8). Thus, PBDEs in flame-retarded polymers may be the source of PBDFs in both urban and EWRS house dust. Origin from PBDEs can also explain the higher PBDF levels in dusts from EW2 compared with those from EW1, as a previous report of the same sample set has shown significantly higher PBDE levels in EW2 samples (27). The PBDFs/PBDEs ratios in all dust samples of this study (0.5–14%, details not shown) were higher than those in Japanese TV cases (0.02–0.05%, refs 11, 28) which in turn were substantially higher than in technical PBDEs (<0.005%, ref 8), indicating the formation of PBDFs during not only the production and operation but also during weathering of electronic devices. The PBDFs/PBDEs ratios in EWRS house dust (0.5–14%, median 3%) were not significantly different from those in UB house dust (1–4%), suggesting that the higher levels of PBDFs in EWRS house dust might have been caused mainly by their release from e-waste together with PBDEs rather than by secondary generation during e-waste recycling activities. The recycling processes, however, may alter the composition of PBDFs. SI Figure S2 shows that PBDF homologues in both urban and EWRS settled house dust had a balanced profile rather than the one biased toward OBDF, the major homologue in the most ubiquitous DecaBDE technical mixture (8). This suggests debromination of the highly substituted PBDFs, in agreement with the results

in Japanese indoor dust (23). Even though not significant, the lower proportion of OBDF in EWRS house dust compared with urban house dust could be considered as due to a more aggressive debromination during thermal processing of e-waste. The shift to homologues of lower molecular weights is also a possible reason for the reduced PBDFs/PBDEs ratio observed.

MoBPCDFs were detected only in the EWRSs, and MoBPCDDs only in EW1 (Table 1). A significant positive correlation was observed between the levels of MoBPCDFs and PCDFs (Pearson's $r = 0.72$, $p < 0.01$ with log-transformed concentrations) but not between MoBPCDFs and PBDFs ($r = -0.27$, $p = 0.46$). These results suggest that MoBPCDFs are generated together with PCDFs during crude thermal processes employed in e-waste recycling, possibly by parallel bromine and chlorine substitution (10), rather than by bromine-chlorine exchange of PBDFs.

The possible source of the significantly higher levels of non-*ortho* PCBs in EWRS house dust is technical PCBs used as heat transfer and dielectric fluids in old capacitors and transformers. DL-PCBs have been detected in technical PCBs as well as transformer oils (29). The abundance of CB77, the main non-*ortho* PCB detected (SI Table S1), may be explained by the low molecular weight facilitating its release and dispersal from e-waste into the surrounding environments by volatilization. This is also consistent with the specific accumulation of tri- and tetraCBs in breast milk of women living in these EWRSs reported previously (5). The higher levels of mono-*ortho* PCBs, the less volatile congeners, in EW1 (Table 1) may indicate a greater occurrence of electrical waste containing PCBs in this location.

Toxic Equivalents of DRCs Compared with DR-CALUX Results. Dioxin-like toxicity has been commonly evaluated as TEQ calculated from the concentrations of 2,3,7,8-substituted PCDD/Fs and DL-PCBs using the WHO-TEF scheme (20). However, TEFs of PBDD/Fs and PXDD/Fs are still unavailable. This study used DR-CALUX to determine directly the TEQs of the mixture of persistent (acid resistant) compounds in settled dust. The contribution of the identified DRCs to dioxin-like activities was evaluated through their theoretical CALUX-TEQs calculated using CALUX relative potency (REP) factors (30, 31, see SI Table S1 for details). Assuming dose-additivity, the theoretical CALUX-TEQ levels were summed up for different groups of compounds and plotted against the corresponding experimental value of each sample in Figure 2. PCDD/Fs theoretically accounted for 77–200, 45–81, and 14–22 pg CALUX-TEQ g⁻¹ in dust from EW1, EW2, and UB, corresponding to 9.4–29%, 8.1–15% and 3.6–16% of the experimental levels, respectively. DL-PCBs had low theoretical CALUX-TEQ levels (few picogram per gram) due to their weak REPs. The theoretical CALUX-TEQ levels of PBDD/Fs were in the same range with those of PCDD/Fs but lower in EW1 (16–66 pg g⁻¹) and higher in EW2 (26–120 pg g⁻¹), accounting for 4.2–8.2% and 6.6–22% of the experimental levels, respectively. 2,3,7,8-BDF (REP = 0.57) was the biggest theoretical CALUX-TEQ contributor among PBDD/Fs in EWRS house dust. In urban house dust, the more potent 2,3,7,8-PBDFs were at nondetectable levels. If the proportions of these undetected congeners relative to their respective homologue groups are assumed to be the same as in EWRS house dust (approximately 1% for Te- and PeBDFs, 10% for HxBDFs, see Table 1 and SI Table S1), their theoretical CALUX-TEQ levels will range from 2.7 to 3.7 pg g⁻¹, corresponding to 0.7–2.7% of the bioassay results. Among MoBPCDFs, only a few congeners could be identified and TEQs were calculated solely for 3-B-2,7,8-CDF (ND–3 pg CALUX-TEQ g⁻¹ in EW1 dust) due to the unavailability of REP values. Comparing the theoretical CALUX-TEQ levels of different DRC groups, it is clear that in terms of dioxin-like toxicity, the contamination in EWRSs is not limited to

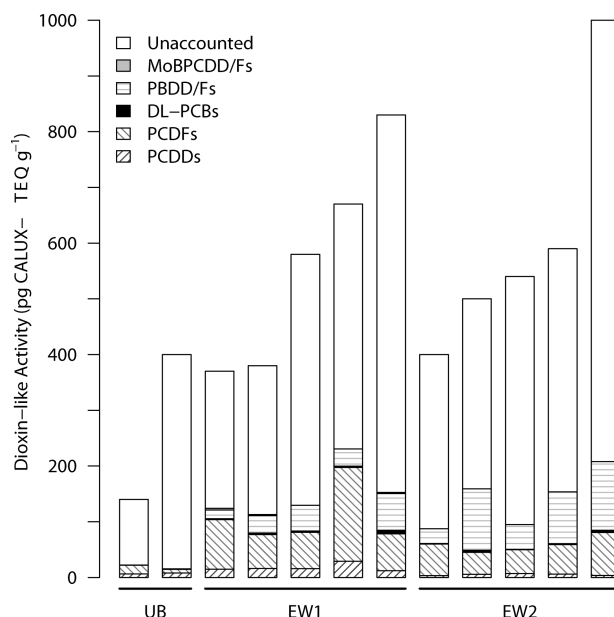


FIGURE 2. Experimental CALUX-TEQs and theoretical contribution of PCDD/Fs, DL-PCBs, PBDD/Fs and MoBPCDD/Fs in settled house dust samples from the urban (UB) and e-waste recycling (EW1 and EW2) sites.

conventional compounds such as PCDD/Fs but also include the unregulated PBDFs.

It is apparent that a large portion of the DR-CALUX activity in the sulfuric acid-treated dust extracts could not be explained by the identified DRCs (Figure 2). As the dose–response curves of the samples and TCDD were similar, these unknown activities indicate dioxin-like toxicity and suggest that the toxicity levels of dust samples might have been underestimated using solely chemical analysis of currently known DRCs. It is possible that other persistent AhR agonists were responsible for such higher activities. Potential AhR agonists in indoor dust may include unidentified brominated and mixed halogenated dibenzofurans. Although non-2,3,7,8-PBDFs determined through potential peaks were up to 2 orders of magnitude more abundant than the 2,3,7,8-substituted congeners in their respective homologue groups (see Table 1 and SI Table S1), their relevance to DR-CALUX results is unknown due to the unavailability of authentic standards precluding identification and toxicological characterization. Only a few non-2,3,7,8-PBDFs have been examined in terms of dioxin-like activity and 1,2,7,8-/1,3,4,7,8-BDFs were reported as relatively potent (REP = 0.012 and 0.0064, respectively, ref 31). Based on these REPs, Hagberg et al. (32) assumed that non-2,3,7,8-PBDFs were 50-fold less potent than 2,3,7,8-PBDFs of the same homologue group and estimated that the former were important CALUX-TEQ contributors among PBDFs formed during UV-irradiation of DecaBDE. Furthermore, compounds with lower degree of substitution such as TrBDD/Fs, though not chemically analyzed in the present study, may also be potential contributors to dioxin-like activity, as suggested by the potency of 2,3,7-BDD and 2,3,8-BDF (REP = 0.081 and 0.00049, ref 31). Data on the occurrence of TrBDFs in environmental samples are even scarcer than PBDFs in general. They are minor among PBDFs photolytically generated from DecaBDE (11, 32), but have been found as the most abundant PBDF homologue in soils of a Chinese EWRS (15). Considering the abundance and potential toxicity of non-2,3,7,8-PBDFs, further identification and toxicological characterization of these compounds are necessary.

Crude combustion processes such as those employed in uncontrolled e-waste recycling are also potential sources of other persistent AhR agonists. Mixed halogenated dibenzo-

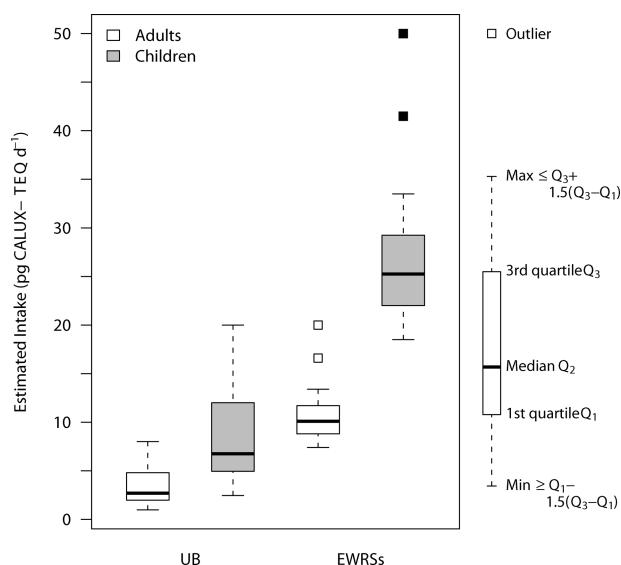


FIGURE 3. CALUX-TEQ intake from dust ingestion by residents of the urban (UB) and e-waste recycling (EWRs) sites, estimated for adults and children using dust ingestion rates of, respectively, 20 and 50 mg d⁻¹.

furans with different degrees of bromination can be generated (10), and DiBPCDFs have been reported as abundant in EWRs soils (15). Again, no toxicological data are available for DiBPCDFs but the high CALUX REP of 2,3-B-7,8-CDD (1.15, ref 30) suggests that their potency may be comparable to those of PCDFs. Chlorinated PAHs (Cl-PAHs) have also been detected in environmental samples of a Chinese EWRs at levels comparable to those of PBDFs (14). However, while some halogenated PAHs exhibit AhR agonistic activities, they are generally less potent than TCDD by 5 orders of magnitude or more (33).

Another possible reason for the unexplained dioxin-like activities could be a synergy between compounds in the sulfuric acid-treated dust extracts. For instance, a synergistic increase in cytochrome P450A level has been observed in mice coexposed to TCDD and CB153, a non-DL but major PCB congener (34). Such mixture effect in environmental samples has also been examined by Suzuki et al. (35), who fractionated a crude compost extract using a polarity-based scheme and found that fractions corresponding to a log octanol–water partition coefficient of more than 6 exhibited a nonadditive increase in DR-CALUX activity with TCDD. This synergy is believed to be caused by an increase of AhR-mediated expression by non-AhR-binding compounds in the presence of AhR agonists (34). The implication of these findings is that an increase in DR-CALUX response may be related to certain persistent and hydrophobic non-DRCs coexisting with DRCs in the matrix. On account of the high levels of unknown dioxin-like activities in dust samples, future studies are needed to identify unknown dioxin-related compounds or other factors affecting these levels, in both e-waste recycling and common home environment contexts.

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 (36) and a complete assimilation of DRCs, the daily TEQ intake (DI) was estimated and plotted in Figure 3. 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 EWRs.

It is generally accepted that diet is the most important human exposure pathway of persistent organic pollutants such as PCDD/Fs and DL-PCBs (37). 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 U.S. (38, 39) and up to 160 pg WHO-TEQ d⁻¹ in Japan (16). Compared with these values, it is clear that dust is a minor DRC exposure medium for Vietnamese urban residents. In the EWRs, 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 (40), 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 (13). 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 EWRs, 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. It should also be noted that the dust ingestion rate for children used in this study is rather conservative. This rate has been estimated as high as 200 mg d⁻¹, which would result in a significant TEQ-DI from dust ingestion even for children living in noncontaminated areas (16). In view of the abundance of PBDFs and in indoor environments and their dioxin-like activity, the establishment of TEFs for these contaminants is necessary for future monitoring and risk assessment related to indoor exposure. For such purposes, DR-CALUX responses may indicate only worst-case effects, and other factors important to human exposure also need to be considered. These factors include bioaccessibility of the contaminants and their persistence in the human body, both still undetermined for new DRCs such as PBDD/Fs and mixed halogenated homologues.

Acknowledgments

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), and JSPS.

Supporting Information Available

Clean-up procedure and instruments used for analyses of DRCs, examples of DR-CALUX dose–response curves of dust extracts (Figure S1), concentrations and relative potencies of individual DRC congeners (Table S1), and homologue profiles of PCDD/Fs and PBDD/Fs (Figure S2). This material is available free of charge via the Internet at <http://pubs.acs.org/>.

Literature Cited

- (1) *E-waste, the hidden side of IT equipment's manufacturing and use*, 2005. http://www.grid.unep.ch/product/publication/download/ew_ewaste.en.pdf.
- (2) Wong, M. H.; Wu, S. C.; Deng, W. J.; Yu, X. Z.; Luo, Q.; Leung, A. O. W.; Wong, C. S. C.; Luksemburg, W. J.; Wong, A. S. Export of toxic chemicals. A review of the case of uncontrolled electronic-waste recycling. *Environ. Pollut.* **2007**, *149*, 131–140.
- (3) Zhao, G.; Xu, Y.; Li, W.; Han, G.; Ling, B. PCBs and OCPs in human milk and selected foods from Luqiao and Pingqiao in Zhejiang, China. *Sci. Total Environ.* **2007**, *378*, 281–292.

- (4) Bi, X. H.; Thomas, G. O.; Jones, K. C.; Qu, W. Y.; Sheng, G. Y.; Martin, F. L.; Fu, J. M. Exposure of electronics dismantling workers to polybrominated diphenyl ethers, polychlorinated biphenyls, and organochlorine pesticides in South China. *Environ. Sci. Technol.* **2007**, *41*, 5647–5653.
- (5) Tue, N. M.; Sudaryanto, A.; Minh, T. B.; Isobe, T.; Takahashi, S.; Viet, P. H.; Tanabe, S. Accumulation of polychlorinated biphenyls and brominated flame retardants in breast milk from women living in Vietnamese e-waste recycling sites. *Sci. Total Environ.* **2010**, *408*, 2155–2162.
- (6) Leung, A. O. W.; Luksemburg, W. J.; Wong, A. S.; Wong, M. H. Spatial distribution of polybrominated diphenyl ethers and polychlorinated dibenzo-*p*-dioxins and dibenzofurans in soil and combusted residue at Guiyu, an electronic waste recycling site in Southeast China. *Environ. Sci. Technol.* **2007**, *41*, 2730–2737.
- (7) Ma, J.; Kannan, K.; Cheng, J.; Horii, Y.; Wu, Q.; Wang, W. Concentrations, profiles, and estimated human exposures for polychlorinated dibenzo-*p*-dioxins and dibenzofurans from electronic waste recycling facilities and a chemical industrial complex in Eastern China. *Environ. Sci. Technol.* **2008**, *42*, 8252–8259.
- (8) Hanari, N.; Kannan, K.; Okazawa, T.; Kodavanti, P. R. S.; Aldous, K. M.; Yamashita, N. Occurrence of polybrominated biphenyls, polybrominated dibenzo-*p*-dioxins, and polybrominated dibenzofurans as impurities in commercial polybrominated diphenyl ether mixtures. *Environ. Sci. Technol.* **2006**, *40*, 4400–4405.
- (9) Watanabe, I.; Sakai, S. Environmental release and behavior of brominated flame retardants. *Environ. Int.* **2003**, *29*, 665–682.
- (10) Weber, R.; Kuch, B. Relevance of BFRs and thermal conditions on the formation pathways of brominated and brominated-chlorinated dibenzodioxins and dibenzofurans. *Environ. Int.* **2003**, *29*, 699–710.
- (11) Kajiura, N.; Noma, Y.; Takigami, H. Photolysis studies of technical decabromodiphenyl ether (DecaBDE) and ethane (DeBDethane) in plastics under natural sunlight. *Environ. Sci. Technol.* **2008**, *42*, 4404–4409.
- (12) Behnisch, P. A.; Hosoe, K.; Sakai, S. Combinatorial bio/chemical analysis of dioxin and dioxin-like compounds in waste recycling, feed/food, humans/wildlife and the environment. *Environ. Int.* **2001**, *27*, 495–519.
- (13) van Leeuwen, F. X. R.; Feeley, M.; Schrenk, D.; Larsen, J. C.; Farland, W.; Younes, M. Dioxins: WHO's tolerable daily intake (TDI) revisited. *Chemosphere* **2000**, *40*, 1095–1101.
- (14) Ma, J.; Addink, R.; Yun, S.; Cheng, J.; Wang, W.; Kannan, K. Polybrominated dibenzo-*p*-dioxins/dibenzofurans and polybrominated diphenyl ethers in soil, vegetation, workshop-floor dust, and electronic shredder residue from an electronic waste recycling facility and in soils from a chemical industrial complex in Eastern China. *Environ. Sci. Technol.* **2009**, *43*, 7350–7356.
- (15) Zennegg, M.; Yu, X.; Wong, M. H.; Weber, R. Fingerprints of chlorinated, brominated and mixed halogenated dioxins at two e-waste recycling sites in Guiyu/China. *Organohalogen Compd.* **2009**, *71*, 2248–2252.
- (16) Suzuki, G.; Takigami, H.; Nose, K.; Takahashi, S.; Asari, M.; Sakai, S. Dioxin-like and transthyretin-binding compounds in indoor dusts collected from Japan: Average daily dose and possible implications for children. *Environ. Sci. Technol.* **2007**, *41*, 1487–1493.
- (17) *Analyse, Review and Control of Results Obtained by the DR CALUX Bioassay*, Pe-BDS-007; BioDetection Systems: Amsterdam, The Netherlands, 2004.
- (18) *Method for Determination of Tetra-through Octachlorodibenzo-*p*-Dioxins, Tetra-through Octachlorodibenzofurans and Dioxin-Like Polychlorinatedbiphenyls in Industrial Water and Waste Water*, JIS K0312; Japanese Industrial Standard, 2005.
- (19) Takahashi, S.; Sakai, S.; Watanabe, I. An intercalibration study on organobromine compounds: Results on polybrominated diphenylethers and related dioxin-like compounds. *Chemosphere* **2006**, *64*, 234–244.
- (20) Van den Berg, M. et al. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicol. Sci.* **2006**, *93*, 223–241.
- (21) Saito, K.; Takekuma, M.; Ogawa, M.; Kobayashi, S.; Sugawara, Y.; Ishizuka, M.; Nakazawa, H.; Matsuki, Y. Extraction and cleanup methods of dioxins in house dust from two cities in Japan using accelerated solvent extraction and a disposable multi-layer silicagel cartridge. *Chemosphere* **2003**, *53*, 137–142.
- (22) Hong, B.; Garabrant, D.; Hedgeman, E.; Demond, A.; Gillespie, B.; Chen, Q.; Chang, C.; Towey, T.; Knutson, K.; Franzblau, A.; Lepkowski, J.; Adriaens, P. Impact of WHO 2005 revised toxic equivalency factors for dioxins on the TEQs in serum, household dust and soil. *Chemosphere* **2009**, *76*, 727–733.
- (23) Takigami, H.; Suzuki, G.; Hirai, Y.; Sakai, S. Brominated flame retardants and other polyhalogenated compounds in indoor air and dust from two houses in Japan. *Chemosphere* **2009**, *76*, 270–277.
- (24) Baker, J. I.; Hites, R. A. Is combustion the major source of polychlorinated dibenzo-*p*-dioxins and dibenzofurans to the environment? A mass balance investigation. *Environ. Sci. Technol.* **2000**, *34*, 2879–2886.
- (25) Minh, N. H.; Minh, T. B.; Watanabe, M.; Kunisue, T.; Monirith, I.; Tanabe, S.; Sakai, S.; Subramanian, A.; Sasikumar, K.; Viet, P. H.; Tuyen, B. C.; Tana, T. S.; Prudente, M. S. Open dumping site in Asian developing countries: A potential source of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans. *Environ. Sci. Technol.* **2003**, *37*, 1493–1502.
- (26) Wang, L.; Chang-Chien, G. Characterizing the emissions of polybrominated dibenzo-*p*-dioxins and dibenzofurans from municipal and industrial waste incinerators. *Environ. Sci. Technol.* **2007**, *41*, 1159–1165.
- (27) Tue, N. M.; Suzuki, G.; Isobe, T.; Takahashi, S.; Viet, P. H.; Tanabe, S. Levels of polychlorinated biphenyls, brominated flame retardants and dioxin-like activities associated with e-waste recycling in Vietnamese house dust. *Organohalogen Compd.* **2009**, *71*, 368–371.
- (28) Sakai, S.; Watanabe, J.; Honda, Y.; Takatsuki, H.; Aoki, I.; Futamatsu, M.; Shiozaki, K. Combustion of brominated flame retardants and behavior of its byproducts. *Chemosphere* **2001**, *42*, 519–531.
- (29) Takasuga, T.; Senthikumar, K.; Matsumura, T.; Shiozaki, K.; Sakai, S. Isotope dilution analysis of polychlorinated biphenyls (PCBs) in transformer oil and global commercial PCB formulations by high resolution gas chromatography-high resolution mass spectrometry. *Chemosphere* **2006**, *62*, 469–484.
- (30) Behnisch, P. A.; Hosoe, K.; Sakai, S. Brominated dioxin-like compounds: in vitro assessment in comparison to classical dioxin-like compounds and other polyaromatic compounds. *Environ. Int.* **2003**, *29*, 861–877.
- (31) Olsman, H.; Engwall, M.; Kammann, U.; Klempt, M.; Otte, J.; van Bavel, B.; Hollert, H. Relative differences in aryl hydrocarbon receptor-mediated response for 18 polybrominated and mixed halogenated dibenzo-*p*-dioxins and -furans in cell lines from four different species. *Environ. Toxicol. Chem.* **2007**, *26*, 2448.
- (32) Hagberg, J.; Olsman, H.; van Bavel, B.; Engwall, M.; Lindström, G. Chemical and toxicological characterisation of PBDFs from photolytic decomposition of decaBDE in toluene. *Environ. Int.* **2006**, *32*, 851–857.
- (33) Horii, Y.; Khim, J. S.; Higley, E. B.; Giesy, J. P.; Ohura, T.; Kannan, K. Relative potencies of individual chlorinated and brominated polycyclic aromatic hydrocarbons for induction of aryl hydrocarbon receptor-mediated responses. *Environ. Sci. Technol.* **2009**, *43*, 2159–2165.
- (34) Bannister, R.; Safe, S. Synergistic interactions of 2, 3, 7, 8-TCDD and 2, 2', 4, 4', 5, 5'-hexachlorobiphenyl in C57BL/6J and DBA/2J mice: Role of the Ah receptor. *Toxicology* **1987**, *44*, 159–169.
- (35) Suzuki, G.; Takigami, H.; Kushi, Y.; Sakai, S. Evaluation of mixture effects in a crude extract of compost using the CALUX bioassay and HPLC fractionation. *Environ. Int.* **2004**, *30*, 1055–1066.
- (36) Jones-Otazo, H. A.; Clarke, J. P.; Diamond, M. L.; Archbold, J. A.; Ferguson, G.; Harner, T.; Richardson, G. M.; Ryan, J. J.; Wilford, B. Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. *Environ. Sci. Technol.* **2005**, *39*, 5121–5130.
- (37) Liem, A.; Fürst, P.; Rappe, C. Exposure of populations to dioxins and related compounds. *Food Addit. Contam.* **2000**, *17*, 241–259.
- (38) Llobet, J. M.; Martí-Cid, R.; Castell, V.; Domingo, J. L. Significant decreasing trend in human dietary exposure to PCDD/PCDFs and PCBs in Catalonia, Spain. *Toxicol. Lett.* **2008**, *178*, 117–126.
- (39) Lorber, M.; Patterson, D.; Huwe, J.; Kahn, H. Evaluation of background exposures of Americans to dioxin-like compounds in the 1990s and the 2000s. *Chemosphere* **2009**, *77*, 640–651.
- (40) CDC, Growth charts for 2–5 year old, 2002. <http://www.cdc.gov/growthcharts/>.

ES102505J