

Environmental Chemistry

DECHLORANE PLUS IN HOUSE DUST FROM E-WASTE RECYCLING AND URBAN AREAS IN SOUTH CHINA: SOURCES, DEGRADATION, AND HUMAN EXPOSURE

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Abstract—Dechlorane Plus (DP) was measured in house dust from e-waste recycling and from urban and rural areas of South China, with geometric mean concentrations of 604, 14.5, and 2.89 ng/g, respectively. Dechlorane Plus in house dust in the e-waste area originated from e-waste recycling activities, whereas household appliances served as a major source of DP in urban house dust. The isomer ratios (f_{anti}) of DP in most dust samples from the e-waste area were significantly lower than those in the urban and rural dust samples and the commercial mixture. Several [−1Cl + H] and [−2Cl + 2H] dechloro-DPs were identified in house dust from the e-waste area, and an a-Cl₁₁ DP was qualified with concentrations of <55.1 ng/g. Photolytic degradation experiments were conducted by exposing anti-DP, syn-DP, and commercial DP solutions to ultraviolet (UV) light. The slight difference in isomeric half-life derived by photodegradation, as well as the lower f_{anti} values in the e-waste combusted residue, suggest a significant influence of isomer-specific thermal degradation of DP during e-waste burning on isomer composition in house dust in the e-waste area. The average estimated daily intakes (EDIs) of DP via house dust ranged from 0.06 to 30.2 ng/d for adults and 0.14 to 121 ng/d for toddlers in the studied area. The average EDIs of a-Cl₁₁ DP for adults and toddlers in the e-waste area were 0.07 and 0.18 ng/d, respectively. Environ. Toxicol. Chem. 2011;30:1965–1972. © 2011 SETAC

Keywords—Dechlorane Plus House dust Isomer composition Dechlorination Estimated daily intake

INTRODUCTION

Dechlorane Plus (DP), an additive halogenated flame retardant (HFR), has been used in commercial polymer products including cable and wire coatings, connectors in computers and televisions, and plastic roofing materials for buildings for more than 40 years [1]. However, environmental concerns about DP use have arisen only recently. After its first identification in environmental samples from the Great Lakes region in 2006 [1], DP has been found in a wide range of environmental samples from North America [2–5], Europe [3], and Asia [6–9]. There is also growing evidence over recent years demonstrating its bioavailability and bioaccumulation potential [4,10–14].

Dechlorane Plus emissions can occur during the production, use, disposal, and recycling of products treated with DP. Although published data on the biological toxicology of DP are limited, the Robust Summaries and Test Plans provided by the DP manufacturer (Oxychem; <http://www.epa.gov/HPV/pubs/summaries/dechlorp/c15635tc.htm>) reported that DP has biomagnification effects in fish and may affect sediment-bearing organisms because of its adsorptive characteristics. House dust serves as a repository and concentrates many environmental contaminants that accumulate from various pathways, including volatilization and deterioration from household products and deposition of particulates transferred from the outdoors [15,16]. Thus, house dust plays an important role in human exposure to contaminants in the indoor environment. This is particularly important for HFRs because of their widespread use in many household products. For example, a causal

link between the concentrations of polybrominated diphenyl ethers (PBDEs; a major group of HFRs) in house dust and human milk was reported [17]. Furthermore, strong correlations between dust and serum concentrations of PBDEs were also observed in a recent study [18]. However, most of the previous studies on HFRs in house dust have focused on brominated flame retardants (BFRs), especially PBDEs [19–22], but little attention has been paid to the potential health risk of exposure to chlorinated flame retardants including DP [23].

Currently, there is a debate over the dehalogenation of highly halogenated HFRs to potentially more toxic and bioaccumulative constituents in the environment [24]. For example, fully brominated diphenyl ether (BDE) 209 was thought to have a low bioavailability and bioaccumulation potential because of its high molecular mass and, therefore, was thought to be a low environmental risk. However, increasing laboratory and field studies have demonstrated its capability to debrominate to light BDE congeners [25–27]. Dechlorane Plus may also have the potential to behave similarly in the environment and to degrade to lower chlorinated products. In fact, two previous studies have mentioned the possibility of DP dechlorination in the environment and the human body. For example, Sverko et al. [5] identified several dechlorinated DP products in sediments from Lake Ontario, Canada. In addition, Ren et al. [28] detected a dechlorination DP tentatively identified as a [−Cl + H] product in serum from electronics-dismantling workers. However, these studies did not provide quantitative data because of a lack of authentic standards for dechlorination DP products.

In our previous study, several BFRs were detected in house dust collected from e-waste recycling and urban areas in Guangdong Province, South China [29]. More recently, we examined the correlation between DP in human hair and house dust from the same areas and suggested that the ingestion of dust was one of the major routes for DP human exposure [30].

All Supplemental Data may be found in the online version of this article.

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However, the source and behaviors of DP in the house dust as well as the pathway, mechanisms, and kinetics of DP degradation are poorly understood.

Human exposure to DP by house dust has never been assessed in South China. Therefore, in the present study, DP isomers were determined in house dust samples from the e-waste and urban areas, as well as those collected from rural areas in South China. In addition, the relationships between DP and BFRs were examined. The primary objective of the present study was thus to understand the sources and environmental processes of DP in house dust. Photodegradation experiments were conducted by exposing DP solutions to UV light in the laboratory to understand the products and kinetics of DP photodegradation and to identify the dechlorination products of DP in house dust. In addition, the present study also provides data on human exposure to DP and dechlorination products by household dust in South China.

MATERIALS AND METHODS

Sample collection

The method of sample collection was described in a previous article [29]. Twenty-seven indoor dust samples were collected between November, 2008, and April, 2009, from Guangzhou City, the capital of Guangdong province and the largest urban center in South China. Thirty-nine dust samples, including indoor ($n=23$) and yard ($n=16$) dust, were collected from an e-waste recycling area located approximately 50 km north of Guangzhou in October, 2007. A detailed description of the e-waste area is given elsewhere [31]. In addition, 20 samples were collected from rural areas outside Guangdong province in 2008.

House dust was collected using a standardized sampling technique recommended by VDI (Verein Deutscher Ingenieure, Association of German Engineers) 4300 Part 8 guideline ([http://www.vdi.eu/index.php?id=44061&no_cache=1&tx_vdirili_pi2\[showUID\]=91310](http://www.vdi.eu/index.php?id=44061&no_cache=1&tx_vdirili_pi2[showUID]=91310)). The house dust samples were obtained from the surface of furniture, tables, windowsills, and floors of the bedroom and living room using woolen brushes cleaned with ethyl alcohol. Likewise, the yard dust samples were obtained from the surface of objects in the yards, such as tables and stools. The samples were wrapped in aluminum foil and sealed in polyethylene zip bags before being transported to the laboratory, where the samples were kept at -20°C until chemical analysis.

Standards and chemicals

Individual standard solutions of the syn- and anti-DP isomers ($50\ \mu\text{g}/\text{ml}$, in toluene), two dechlorination products of anti-DP (1,6,7,8,9,14,15,16,17,17,18-octadeca-7,15-diene, termed *a-Cl₁₁ DP*; and 1,6,7,8,9,14,15,16,17,17-octadeca-7,15-diene, termed *a-Cl₁₀ DP*) were obtained from Wellington Laboratories. Solutions of ^{13}C -PCB 208 and ^{13}C -BDE 209 were purchased from Cambridge Isotope Laboratories. Brominated diphenyl ethers 77, 181, 118, and 128 were purchased from Accustandards. A commercial DP product was purchased from Anpon Electrochemistry Company. All organic solvents (purity $>99.9\%$) were redistilled using a glass system.

Sample preparation

The extraction method and instrument analysis procedures in the present study were reported in detail in our previous article on BFRs [29]. Briefly, the dust samples were sieved through a stainless-steel sieve ($500\ \mu\text{m}$) to remove large debris

before analysis. The samples ($0.5\text{--}2\ \text{g}$) were spiked with ^{13}C -BDE 209, -BDE 77, and -BDE 181 and then Soxhlet-extracted with a mixture of acetone and hexane (1:1 v:v) for 48 h. The extracts were further cleaned by passing through a multi-layer silica/alumina column. The final extract was condensed to 1 ml, and known amounts of ^{13}C -PCB 208, -BDE 118, and -BDE 128 were added as internal standards before instrumental analysis.

Photodegradation experiments

Photodegradation experiments were designed to identify the degradation products of individual DP and to examine the degradation kinetics of two DP isomers. The experiments were performed with a GGZ-125 125 W high-pressure mercury lamp (Yaming Lighting) housed on the top of the reactor to serve as an irradiation source ($360\text{--}420\ \text{nm}$) and a quartz immersion well with circulating water. The quartz photoreactor was positioned in a water bath with constant water circulation to keep the temperature at a constant 20°C . A substrate solution ($20\ \mu\text{g}/\text{ml}$ DP) was prepared by dissolving commercial DP into isooctane. Two solutions of individual isomers ($2\ \mu\text{g}/\text{ml}$) were also prepared by diluting the syn- and anti-DP standard solutions ($50\ \mu\text{g}/\text{ml}$) into isooctane. Commercial DP sample aliquots were removed from the photoreactor to glass vials at different time points (1, 2, 4, 8, 15, 30 min), kept in the dark, and analyzed with a gas chromatograph-mass spectrometer (GC-MS). Dark control experiments were performed during the irradiation period, and no degradation occurred.

Instrument analysis

The samples were analyzed with a Shimadzu 2010 GC-MS and an Agilent 6890-GC coupled to an Agilent 5975B-MS operated in electron-capture negative-ionization (ECNI) mode. A DB-5HT ($15\ \text{m long} \times 0.25\ \text{mm inner diameter}$ [i.d.], $0.10\ \mu\text{m}$ film thickness) capillary column was used to determine DP isomers. The oven temperature was held at 110°C for 2 min, followed by a temperature ramp of $20^{\circ}\text{C}/\text{min}$ to 280°C (held for 3 min), which was then followed by a final temperature ramp of $30^{\circ}\text{C}/\text{min}$ to 310°C (held for 15 min). A DB-XLB ($30\ \text{m long} \times 0.25\ \text{mm i.d.}$, $0.25\ \mu\text{m}$ film thickness) column was used for the separation of dechlorinated products of DP. The column temperature was initiated at 110°C (held for 1 min) and increased to 180°C at $8^{\circ}\text{C}/\text{min}$ (held for 1 min), 240°C at $2^{\circ}\text{C}/\text{min}$ (held for 5 min), 280°C at $2^{\circ}\text{C}/\text{min}$ (held for 25 min), and 310°C at $10^{\circ}\text{C}/\text{min}$ (held for 15 min). Methane was used as a chemical ionization moderating gas at an ion source pressure of $2.4 \times 10^3\ \text{Pa}$ and helium as the carrier gas at a flow rate of $1\ \text{ml}/\text{min}$. Injection was performed in pressure-pulsed splitless mode with an injection port temperature of 280°C . The transfer line and ion source temperatures were maintained at 290 and 200°C , respectively. The syn- and anti-DP isomers were quantified by monitoring the two dominant ion fragments of the molecular ion cluster (m/z 653.8 and 651.8). Ion clusters monitored for the dechlorinated products included m/z 618.0/620.0 for Cl_{11} -DP and 584.0/586.0 for Cl_{10} -DP. Brominated diphenyl ethers 77, 118, 128, and 181 were monitored through m/z 79 and 81. Ions used to monitor ^{13}C -BDE 209 were m/z 494.6 and 496.6. The solutions from the photolytic degradation experiments and the extraction of selected dust samples were also analyzed in the full-scan mode (m/z 50–1,000) to record the full scan mass spectra of the dechlorinated products.

Quality assurance/quality control

A procedural blank was run with each batch of samples (11 samples in each). No target compound was detected in the blank samples. The recovery of BDE 77, BDE 181, and ¹³C-BDE 209 averaged 99.9, 80.6, and 84.3%, with standard deviations of 7.3, 8.1, and 23.2%, respectively. Three spiked blanks were also analyzed alongside the dust samples to examine the percentage recovery of the target compounds. The average recoveries of syn-DP, anti-DP, a-Cl₁₀ DP, and a-Cl₁₁ DP were 84.6 ± 6.4, 98.6 ± 12.8, 88.0 ± 5.9, and 88.8 ± 4.0%, respectively. The relative standard deviations among triplicate house dust samples were <10% for target compounds. The limit of detection (LOD) was defined as a signal of five times the noise level; the LODs were found to be 0.55, 0.61, 0.14, and 0.32 ng/g for syn-DP, anti-DP, a-Cl₁₀ DP, and a-Cl₁₁ DP, respectively, based on a 1-g sample. Reported concentrations were not corrected for the recoveries.

RESULTS AND DISCUSSION

DP in house dust

Table 1 summarizes the DP concentrations in house dust in different sampling areas. Dechlorane Plus was found in more than 85% of the samples, indicating the wide presence of DP in indoor environments in South China. Dechlorane Plus concentrations in house dust in the e-waste area demonstrated a log-normal distribution ($p > 0.05$, one-sample Kolmogorov-Smirnov test), ranging from nondetectable (ND) to 21,000 ng/g (with a geometric mean of 604 ng/g). The levels were one to two orders of magnitude higher than the concentrations of DP in house dust in the urban (2.78–70.4 ng/g, with a geometric mean of 14.5 ng/g) and rural (ND–27.1 ng/g, with a geometric mean of 2.89 ng/g) areas. Data from urban and rural areas followed normal distributions and showed no significant difference. The DP concentrations between the indoor and yard dust samples in the e-waste area were also not significantly different (Mann-Whitney rank sum test, $p = 0.806$), suggesting an outdoor origin for DP in the indoor dust.

Emission of DP from e-waste recycling activities was the source of DP in the residential environment in the e-waste area. The concentrations of dust DP in the e-waste area in the present study were intermediate between those in the residential dust (geometric mean of 187 ng/g) and the e-waste workshop dust (geometric mean of 1,140 ng/g) in our previous study [30]. In

the urban area, DP in house dust may be derived mainly from industrial sources and/or household appliances [1]. The DP levels in the urban house dust in our study were similar to the values (geometric mean of 18 ng/g in 2002–2003 and 28 ng/g in 2007) in house dust reported from Ottawa, Ontario, Canada [23]. For the rural house dust, levels might have been influenced by DP via atmospheric transport from urban or e-waste sources.

In our earlier work, we measured the concentrations of BFRs in the same set of dust samples from the e-waste and urban areas [29]. The correlations between DP and BFRs will then provide insights into the sources of these chemicals in house dust in South China. Correlation analysis (Pearson product moment correlation) showed that DP in the e-waste area was positively correlated with the BFRs that we measured ($r > 0.62$, $p < 0.01$), except for 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE; see Supplemental Data, Table S1). This finding suggested common sources (e-waste recycling) of these HFRs in house dust in the e-waste area. In the urban area, however, there were no significant correlations between DP and most of the BFRs. Brominated flame retardants in the urban house dust were thus derived largely from extensive industrial activities, especially electronics manufacturing [29]. These results indicated that DP in the urban house dust may have different sources or transport pathways from the BFRs.

It was interesting that DP showed a significantly positive correlation with polybrominated biphenyls (PBBs; $r = 0.504$, $p = 0.007$), which were banned in the United States in the 1970s and likely were never produced in China. The correlation between DP and PBBs thus suggests that DP and PBBs in the urban area probably originated from old household appliances. The HFR profiles present in the house dust also revealed their different sources in the two areas (Supplemental Data, Fig. S1). In addition, DP was the second most important HFR in the e-waste area, comprising 26.7% (on average) of the total HFR concentrations, whereas, in the urban area, DP had a minor contribution of only 0.24% on average. The different HFR profiles between e-waste and urban dusts also suggest that e-waste recycling was a more significant source of DP in the environment in South China than urban industry.

The isomer ratios can be used to trace the sources of DP and to explore the difference in environmental behaviors between two isomers [1,6]. The isomer ratio f_{anti} , defined as the concentration of anti-DP divided by total DP concentration, in the house dust samples from different sampling areas was calculated and shown in Figure 1. In each sampling area, there were

Table 1. Summary of Dechlorane Plus (DP) levels in house dust (ng/g) from different areas of South China

	Range	Median	Arithmetic mean	Geometric mean	5th percentile	95th percentile	DF ^a (%)
Syn-DP							
e-Waste area	ND ^b –8,810	212	839	242	9.72	6,360	97
Guangzhou	ND–21.6	2.98	4.62	3.9	NC ^c	18.7	74
Rural area	ND–7.97	0.971	1.75	0.765	NC	7.89	75
Anti-DP							
e-Waste area	ND–12,200	325	1,040	338	7.62	4,090	97
Guangzhou	1.83–62.1	12.4	14.3	11.1	1.97	51.5	100
Rural area	ND–20.7	2.49	4.24	1.94	NC	20.4	85
ΣDP							
e-Waste area	ND–21,000	541	1,880	604	17.3	9,070	97
Guangzhou	2.78–70.4	13.8	18.9	14.5	2.92	62.2	100
Rural area	ND–27.1	3.95	5.99	2.89	NC	26.8	85

^a Detection frequency.

^b Not detectable.

^c Not calculated because fifth percentile is below limits of detection.

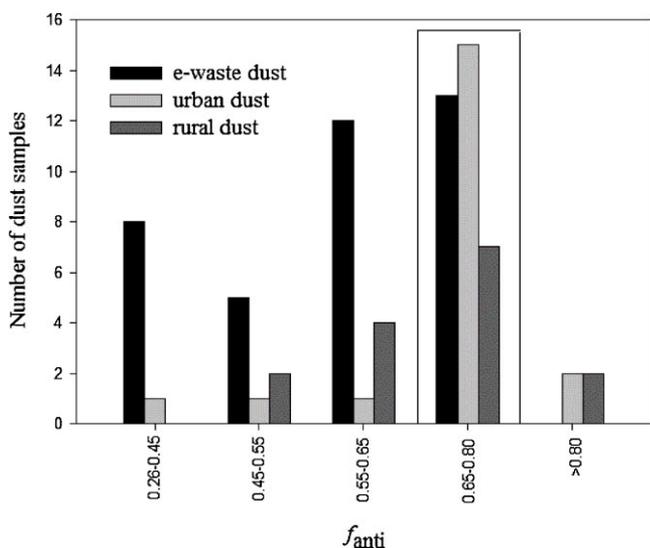


Fig. 1. Distribution of f_{anti} values in house dust from e-waste, urban, and rural areas (data were excluded if only one isomer was detected). The box represents the range of f_{anti} reported for commercial products.

samples with f_{anti} values deviating from the range measured in the commercial mixtures (0.65–0.80) in the literature [1,10,14]. In the urban area, most samples (75%) showed f_{anti} values similar to those of the commercial mixture. However, in the e-waste area, more than 65% of dust samples had f_{anti} values lower than those of the commercial DP, with a large variation from 0.26 to 0.79. Furthermore, there was no significant difference in f_{anti} values between the indoor and yard dusts.

In the rural areas, approximately 50% of the samples had f_{anti} values within the range of 0.65 to 0.80. The f_{anti} values in the e-waste area were significantly lower ($p < 0.01$) than those from the urban and rural areas. In addition, no significant difference in f_{anti} values was found between urban and rural dust. The similarity of f_{anti} values in the urban dust to the commercial products indicates the emission of DP from household appliances and a similar persistence in the indoor environment for the two isomers. The deviation of f_{anti} values in the rural dust might have been due to different environmental behaviors (such as gas–particle partitioning) of the two isomers during long-range atmospheric transport. For example, decreased f_{anti} values have been reported in the air from the Great Lakes (United States and Canada) and Arctic regions [1,32]. A possible explanation for the notable depletion of anti-DP in many dust samples from the e-waste area was an isomer-specific degradation of DP during e-waste recycling, which is discussed further below.

Dechlorination products in house dust

The chromatograms of most dust samples from the e-waste area exhibited several apparent unknown peaks with predominant ion fragments of m/z 618.0/620.0 or 584.0/586.0, which are not present in the commercial mixture and DP standard solution (Fig. 2). Many of the full mass spectra of the unknown peaks recorded by GC–ECNI–MS matched the spectra of the two available authentic standards (a-Cl₁₁ and a-Cl₁₀ DP in Supplemental Data Fig. S2), showing that they were [–Cl + H] + H and [–2Cl + 2H] degradation products (marked as n^{-x} , where n signifies the order of peaks and $-x$ signifies [–Cl + H] or [–2Cl + 2H] dechloro-DPs; Fig. 2 and Supplemental Data, Fig. S3). One peak had the same retention time as the a-Cl₁₁ DP

standard, whereas no peaks for [–2Cl + 2H] degradation products matched the a-Cl₁₀ DP.

Because of the lack of standards of the other dechlorination products, only the a-Cl₁₁ DP in dust samples was quantified. The a-Cl₁₁ DP was detected in 38 of the 39 samples from the e-waste area, but in only one of 27 samples from the urban area. The concentration of a-Cl₁₁ DP in dust samples from the e-waste area ranged from ND to 55.1 ng/g, with a geometric mean value of 3.56 ng/g. There was a significantly positive correlation between a-Cl₁₁ DP and anti-DP ($r = 0.738$, $p < 0.001$; Supplemental Data, Fig. S4), which provided a reliable indication of the coexistence of these two compounds in the indoor environment.

Although many dechlorination products could not be quantified, we calculated the ratios of the GC peak areas of these compounds versus DP, which effectively may reflect the degradation potential of DP in house dust. The presence of BDE 202 and elevated proportions of nona-BDEs in house dust were thought to be indications of the degradation of BDE 209 [27,29], and thus the ratios of BDE 202/BDE 209 and nona-BDEs/deca-BDE were reflections of the degradation degree of BDE 209. Correlation analysis was also conducted between the ratios for dechlorinated DPs/DP and BDE 202/BDE 209, and nona-BDEs/BDE 209 and f_{anti} values of house dust in the e-waste area (Supplemental Data, Fig. S5). The results showed that the ratios of dechloro-DPs/DP negatively correlated with f_{anti} values ($p = 0.033$), demonstrating a clear preferential degradation of anti-DP. It was interesting to find that the ratios for dechloro-DPs/DP positively correlated with both nona-BDEs/deca-BDE ($p = 0.003$) and BDE 202/BDE 209 ratios, although the latter correlation was not statistically significant. This observation indicated a similar degradation pathway for both DP and BDE 209 in house dust, because degradation products of BDE 209, BDE 202, and nona-BDEs were present in higher proportions in house dust in the e-waste area than the urban dust [29].

Degradation of DP and its implication

To understand better the DP degradation in house dust, we conducted three photolytic degradation experiments by exposing anti-DP, syn-DP, and commercial DP solutions to UV light. Dechlorane Plus was reduced to approximately 3% of the original concentration after 15 min of irradiation of the commercial DP solution under UV light. The degradation was mainly by [–Cl + H] and [–2Cl + 2H] processes. Besides a-Cl₁₁ DP, at least five unknown dechlorinated degradation products (peaks 5⁻¹, 7⁻¹, 8⁻², 9⁻¹, 11⁻¹ in Fig. 2) were identified in both the chromatograms of the exposed DP solution and the dust samples. Surprisingly, however, the two predominant compounds (peaks 6⁻¹ and 10⁻¹ in Figure 2, which were derived from anti-DP and syn-DP, respectively) produced in the photodegradation experiments were not present in the dust extracts. This suggests that the degradation mechanism and pathway of DP in house dust may be different from those in the UV experiments.

The DP degradation products present in the house dust therefore might not be derived primarily from photolytic pathways. Recently, the findings of Raff and Hites [33] suggested that particle-bound organic compounds are not susceptible to photodegradation because of the shielding effects of carbonaceous aerosols.

The commercial DP products for the degradation experiment data were analyzed for their fitness in the first-order and second-order reaction models. The pseudofirst-order kinetic model well

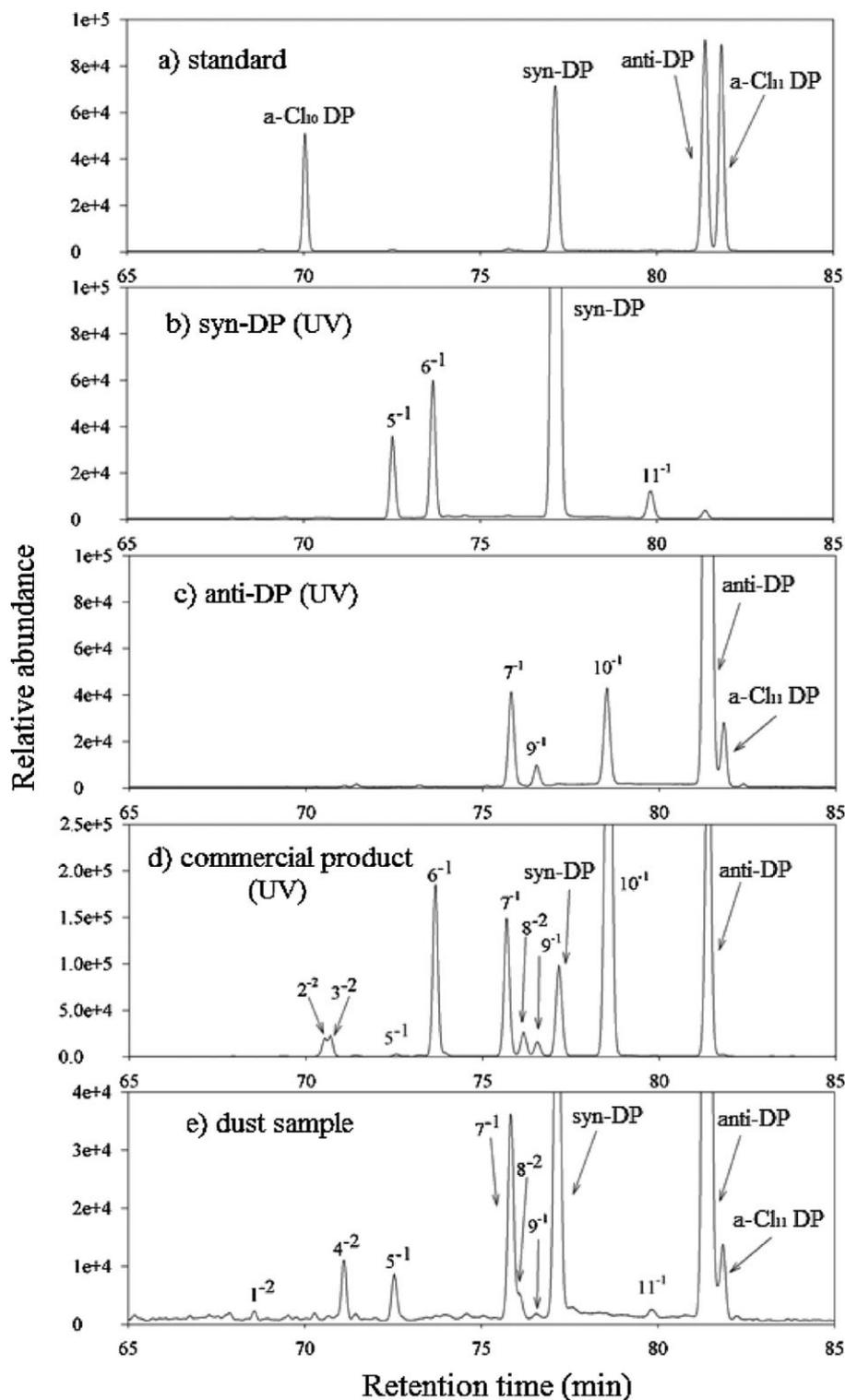


Fig. 2. Gas chromatograph (GC)–electron capture negative ionization (ECNI)–mass spectrometer (MS) chromatogram (m/z 653.8/651.8, 618.0/620.0, and 584.0/586.0) of Dechlorane Plus (DP) isomers and $a\text{-Cl}_{10}$ and Cl_{11} dechlorinated products in standards (a), degradation products of syn-DP under ultraviolet (UV) light (b), degradation products of anti-DP under ultraviolet (UV) light (c), degradation products of commercial DP (d), and a dust sample from the e-waste area (e). The identified degradation products were numbered consecutively by their retention time; superscripts 1 and 2 signify $[-\text{Cl} + \text{H}]$ and $[-2\text{Cl} + 2\text{H}]$ dechlorinated DP products, respectively. The separation was performed on a DB-XLB column (30 m long \times 0.25 mm inner diameter, 0.25 μm film thickness).

described the degradation kinetics (Fig. 3). The degradation rate constants (k) were determined by $C = C_0 e^{-kt}$, where C is the concentration of individual DP, C_0 is the initial concentration of an individual DP, and t is the reaction time. The $k_{\text{syn-DP}}$ was 0.235, and the $k_{\text{anti-DP}}$ was 0.246. Furthermore, the half-lives for DP were calculated by $t_{1/2} = \text{Ln } 2/(k)$. The results showed that

the half-life of anti-DP (2.82 min) was only slightly less than that of syn-DP (2.94 min). In a 30-d UV exposure experiment in isooctane solution for each DP isomer, initiated by Sverko et al. [5], anti-DP was found to degrade more readily than syn-DP, but no half-life data for each DP isomer were reported from their study. The slight difference in the half-lives of the two isomers

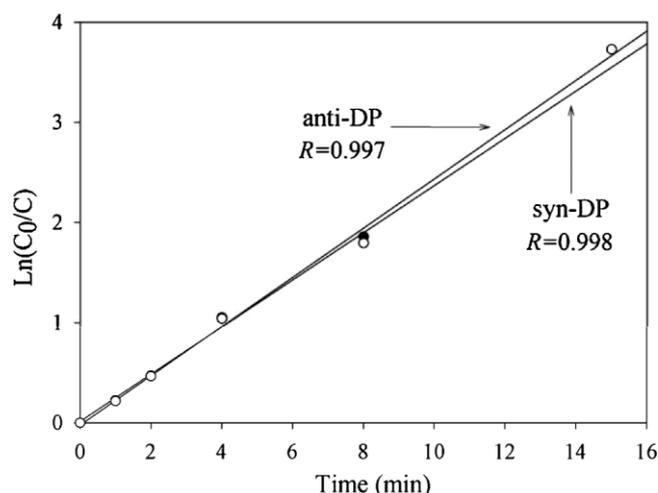


Fig. 3. Photochemical degradation of syn-Dechlorane Plus (DP) and anti-DP. C_0 = initial concentration of DP.

under light might help to explain why many f_{anti} values in the urban house dust were not significantly different from the commercial mixture. This observation was, however, not in agreement with the low f_{anti} values and their negative correlation with the ratios of dechloro-DPs/DP in house dust in the e-waste area, which indicated different degradation pathways leading to dechloro-DPs in house dust in the e-waste area.

The e-waste in this area is processed using technologically primary methods, such as mechanical shredding, acid processing, and open burning. Therefore, it is very likely that the isomer-specific degradation of DP in house dust samples from the e-waste area could originate from pyrolytic reactions, which occur during the e-waste burning processes. To help understand whether pyrolysis may play a significant role, we collected four combusted residue samples dumped in a field near the e-waste recycling workshops. The DP concentrations in these samples varied from 410 to 4,200 ng/g, with f_{anti} values (0.28, 0.28, 0.52, and 0.57) lower than those in the commercial mixture, indicating the significant influence of e-waste burning on the isomeric composition of DP in the environment in this area. It was reported that pyrolytic degradation of DP can occur on the

GC injection liner induced by elevated injector temperatures ($\geq 285^\circ\text{C}$) [5]. Degradation during instrument analysis was checked by regular injection of a commercial DP solution in the present study. Trace amount of dechlorination degradation products were found in the checking solutions, but the decomposition rates, which were calculated by the sum of all peak areas of the identified dechlorination degradation product divided by the sum of peak areas of anti-DP and syn-DP, were much lower ($<1.5\%$) in all calibration standards than those in dust samples ($17.3 \pm 15.3\%$) from the e-waste area.

In addition, thermal degradation may occur during the process of incorporating the DP flame retardant into consumer products, which was partially supported by the f_{anti} values in a small number of urban house dust samples that deviated from the range of technical DP mixtures. However, it is possible that slight difference in degradation rate could still alter the isomer composition if house dust stayed indoors for a long time. Further studies are therefore needed to understand DP degradation in natural particles.

Human exposure

House dust is a significant pathway for human exposure to environment chemicals, because it can be incidentally ingested directly or indirectly on a daily basis and because people spend most of their time indoors. We assumed 100% absorption of intake due to the lack of data on human absorption efficiency. Mean dust ingestion of 20 and 50 mg/d and high dust ingestion of 50 and 200 mg/d for adults and toddlers, respectively, were used in the assessment [34]. The estimated daily intakes (EDIs) of DP and a- C_{11} DP for residents from different areas in the present study were calculated based on the 5th percentile, median, geometric mean, and 95th percentile of DP concentrations and are listed in Table 2. No data are available on the daily intake of DP via other indoor exposure pathways (inhalation and diet), so a comparison was impossible. The EDIs of DP for average adults and toddlers living in the e-waste area were 12.1 and 30.2 ng/d, respectively, as a result of the high concentration of DP in house dust. In the e-waste area, EDIs were much higher than those from the urban and rural areas for adults and toddlers. If the higher estimated dust ingestion and the 95th percentile concentration (9,100 ng/g) were used, the

Table 2. Summary of the estimates of exposure (ng/d) to Dechlorane Plus (DP) by dust ingestion for adults and toddlers from different areas of South China

	Adult				Toddler			
	Median	GM ^a	5th percentile	95th percentile	Median	GM	5th percentile	95th percentile
Mean dust ingestion, 20 mg/d for adult and 50 mg/d for toddler								
ΣDP								
e-Waste area	10.8	12.1	0.35	181	27.1	30.2	0.87	454
Guangzhou	0.28	0.29	0.06	1.24	0.69	0.73	0.15	3.11
Rural area	0.08	0.06	NC ^b	0.54	0.20	0.14	NC	1.34
a- C_{11} DP								
e-Waste area	0.07	0.07	0.01	0.82	0.19	0.18	0.03	2.06
High dust ingestion, 50 mg/d for adult and 200 mg/d for toddler								
ΣDP								
e-Waste area	27.1	30.2	0.87	454	108	121	3.46	1810
Guangzhou	0.69	0.73	0.15	3.11	2.76	29.0	0.58	12.4
Rural area	0.20	0.14	NC	1.34	0.79	0.58	NC	5.36
a- C_{11} DP								
e-Waste area	0.19	0.18	0.03	2.06	0.74	0.71	0.13	8.24

^a Geometric mean.

^b Not calculated because fifth percentile is below limits of detection.

intake via house dust could be as much as 450 ng/d for adults and 1,810 ng/d for toddlers in the e-waste area. Moreover, the EDIs of a-C₁₁ DP were 0.18 ng/d for adults and 0.71 ng/d for toddlers in the e-waste area. Although few data exist on the toxicity of these compounds, great concern should be given to exposure to DP, considering the sensitivity of children to toxic chemicals during development.

CONCLUSIONS

Dechlorane Plus is widely present in house dust in South China. Dechlorane Plus concentrations in house dust in the studied area varied spatially, with obviously higher levels in the e-waste area than in the urban and rural areas. E-waste recycling was thus a significant source of DP to the surrounding communities. Dechlorane Plus in urban house dust was likely to be derived from household appliances, and rural house dust DP might have been influenced by atmospheric transport. The results suggest that the dechlorination DP products in house dust in the e-waste area in the present study may be the result of pyrolytic degradation. Therefore, photodegradation is not likely the major factor influencing the isomer compositions of DP in house dust. Toddlers in the e-waste area could be exposed to high doses of DP from the house dust alone. The present study highlights the need of further studies on the degradation of DP in the environment and the evaluation of the risk of human exposure to DP and dechlorination products.

SUPPLEMENTAL DATA

Table S1. Correlations between Dechlorane Plus (DP) and brominated flame retardants in house dust from the e-waste and urban areas.

Fig. S1. Halogenated flame retardant profiles in house dust from the e-waste and urban areas of South China.

Fig. S2. Full-scan mass spectra of a-Cl₁₁ Dechlorane Plus (DP) (A) and a-Cl₁₀ DP (B) in authentic standards, and Cl₁₁ and Cl₁₀ dechlorinated DP (C,D) in dust samples recorded by electron capture negative ionization-mass spectra (ECNI-MS).

Fig. S3. Gas chromatograph-mass spectrometer (GC-MS) chromatogram (m/z 653.8/651.8, 618.0/620.0, and 584.0/586.0) of Dechlorane Plus (DP) isomers and dechloro-DPs in dust samples from the e-waste area (a), commercial DP (b) and standard solution (c).

Fig. S4. Relationship between the concentration of anti-Dechlorane Plus (DP) and a-Cl₁₁ DP in dust samples from the e-waste area.

Fig. S5. Correlation between logarithmic normalized ratios of dechlorinated Dechlorane Plus (DP) to DP and f_{anti} values, nona-brominated diphenyl ethers (BDEs)/deca-BDE, and BDE 202/BDE 209 in house dust in the e-waste area (717 KB DOC).

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SUPPLEMENTAL DATA

Dechlorane Plus in House Dust From E-Waste Recycling and Urban Areas in South China: Levels, Dechlorinated Products, and Human Exposure

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The Supplemental Data section contains 1 table and 5 figures.

Table S1. Correlations between dechlorane plus (DP) and brominated flame retardants in house dust from the e-waste and urban areas.

	e-waste area		Urban area	
	<i>r</i>	<i>p</i>	<i>r</i>	<i>p</i>
PBDE ^a	0.902	0	-0.027	0.893
BTBPE ^b	0.289	0.074	0.271	0.172
PBT ^c	0.785	0	-0.016	0.937
PBEB ^d	0.897	0	0.15	0.455
HBB ^e	0.621	0	-0.043	0.832
DBDPE ^f	0.677	0	-0.161	0.422
PBBs ^g	0.744	0	0.504	0.007

^a Polybrominated diphenyl ethers.

^b 1,2-bis(2,4,6-tribromophenoxy)ethane.

^c Pentabromotoluene.

^d Pentabromoethylbenzene.

^e Hexabromobenzene.

^f Decabromodiphenyl ethane.

^g Polybrominated biphenyls.

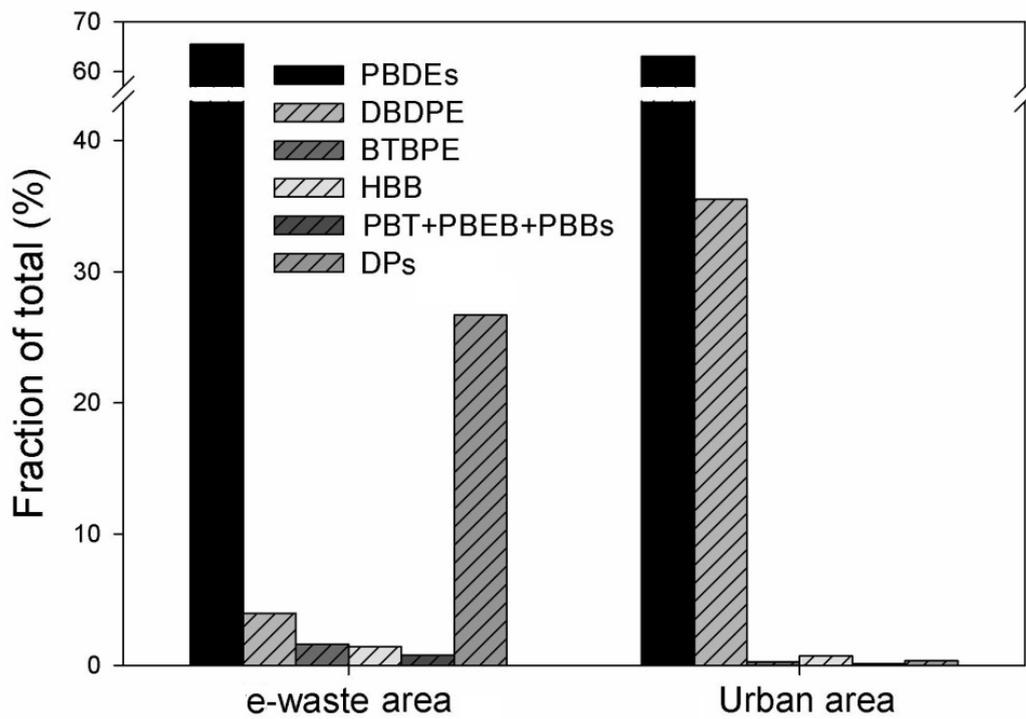


Fig. S1. Halogenated flame retardant profiles in house dust from the e-waste and urban areas of South China.

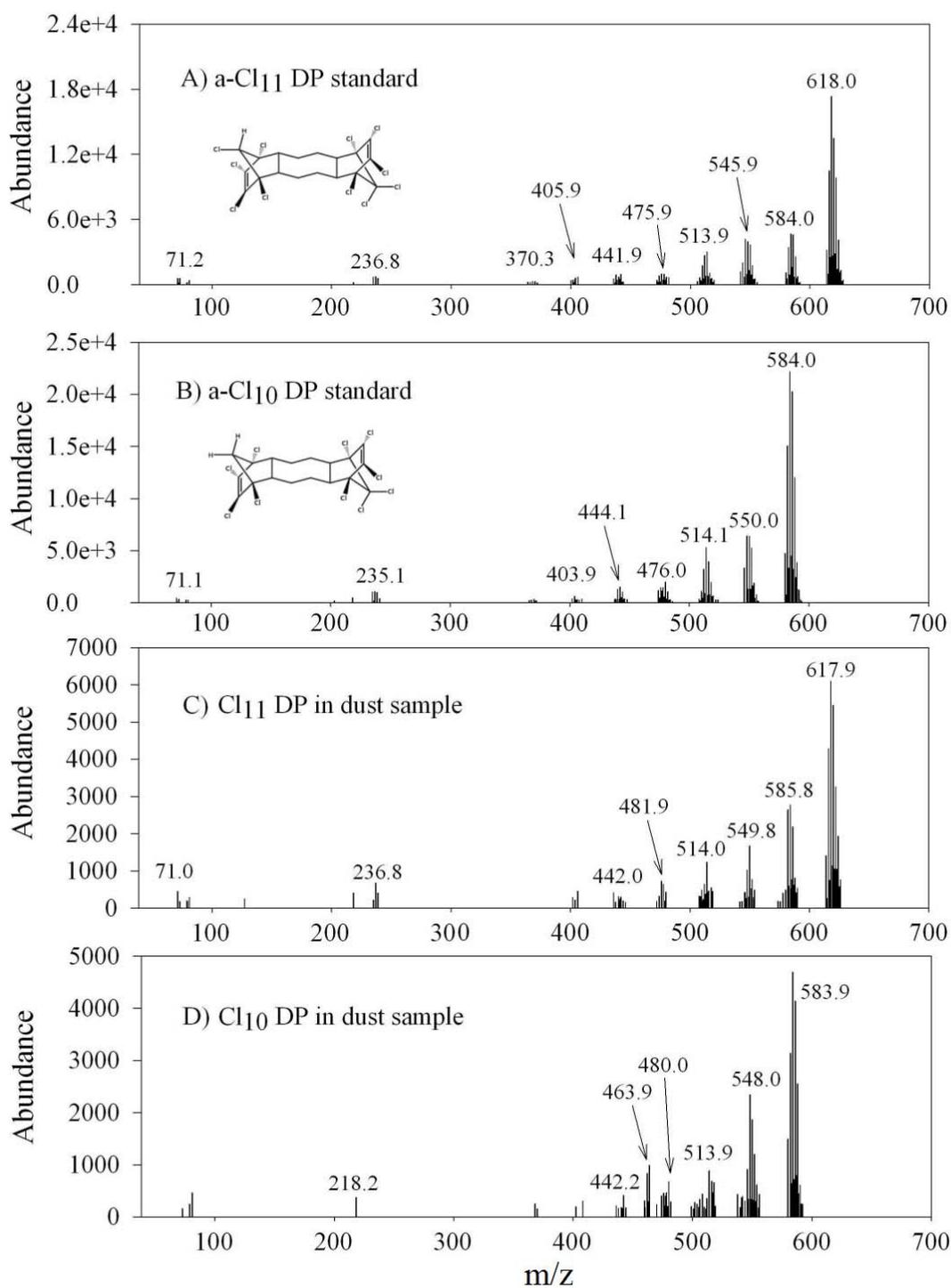


Fig. S2. Full- scan mass spectra of a-Cl₁₁ dechlorane plus (DP) (A) and a-Cl₁₀ DP (B) in authentic standards, and Cl₁₁ and Cl₁₀ dechlorinated DP (C and D) in dust samples recorded by electron capture negative ionization-mass spectra (ECNI-MS).

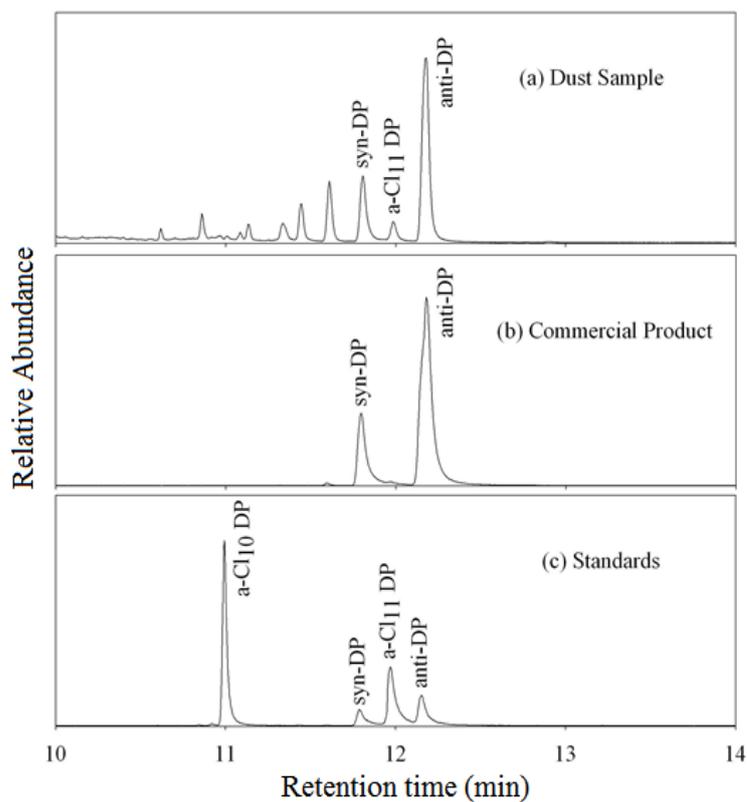


Figure S3. Gas chromatograph-mass spectrometer (GC-MS) chromatogram (m/z 653.8/651.8, 618.0/620.0, and 584.0/586.0) of dechlorane plus (DP) isomers and dechloro-DPs in dust samples from the e-waste area (a), commercial DP (b) and standard solution (c). The separation was done by a DB-5HT column (15 m long \times 0.25 mm inner diameter, 0.10 μm film thickness).

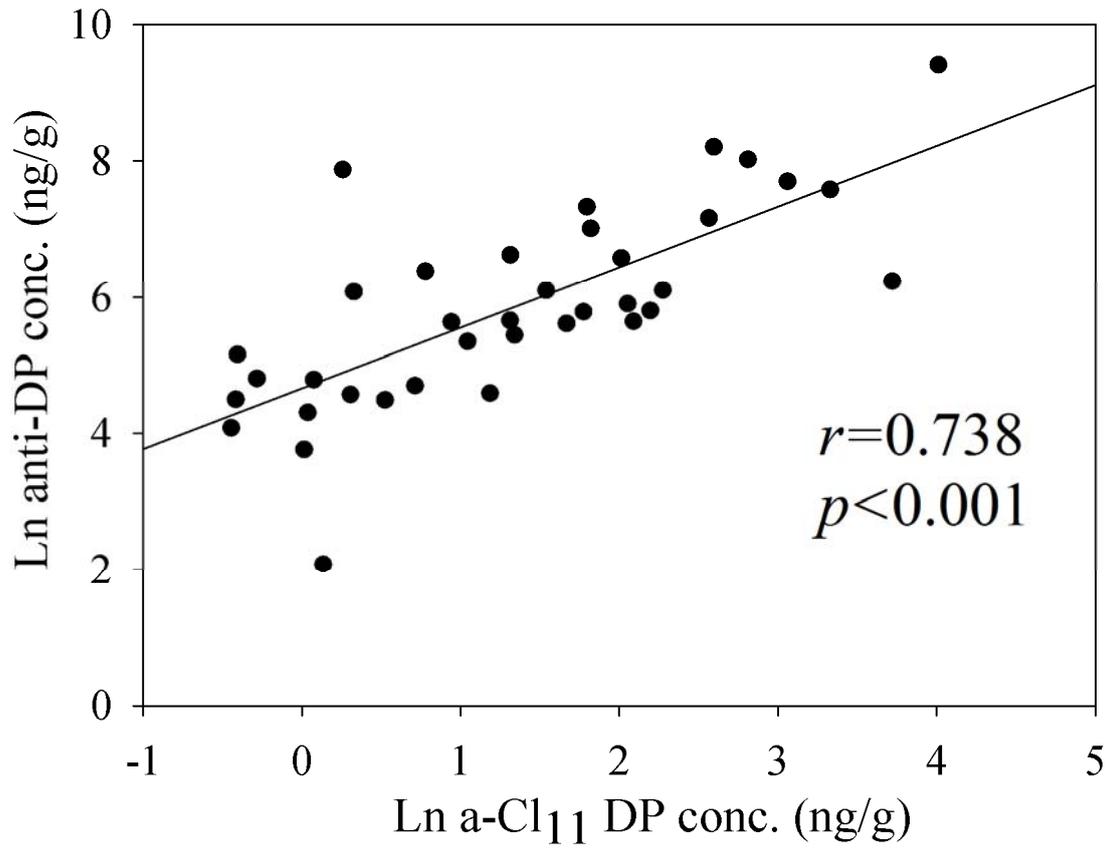


Fig. S4. Relationship between the concentration of anti-dechlorane plus (DP) and a-Cl₁₁ DP in dust samples from the e-waste area.

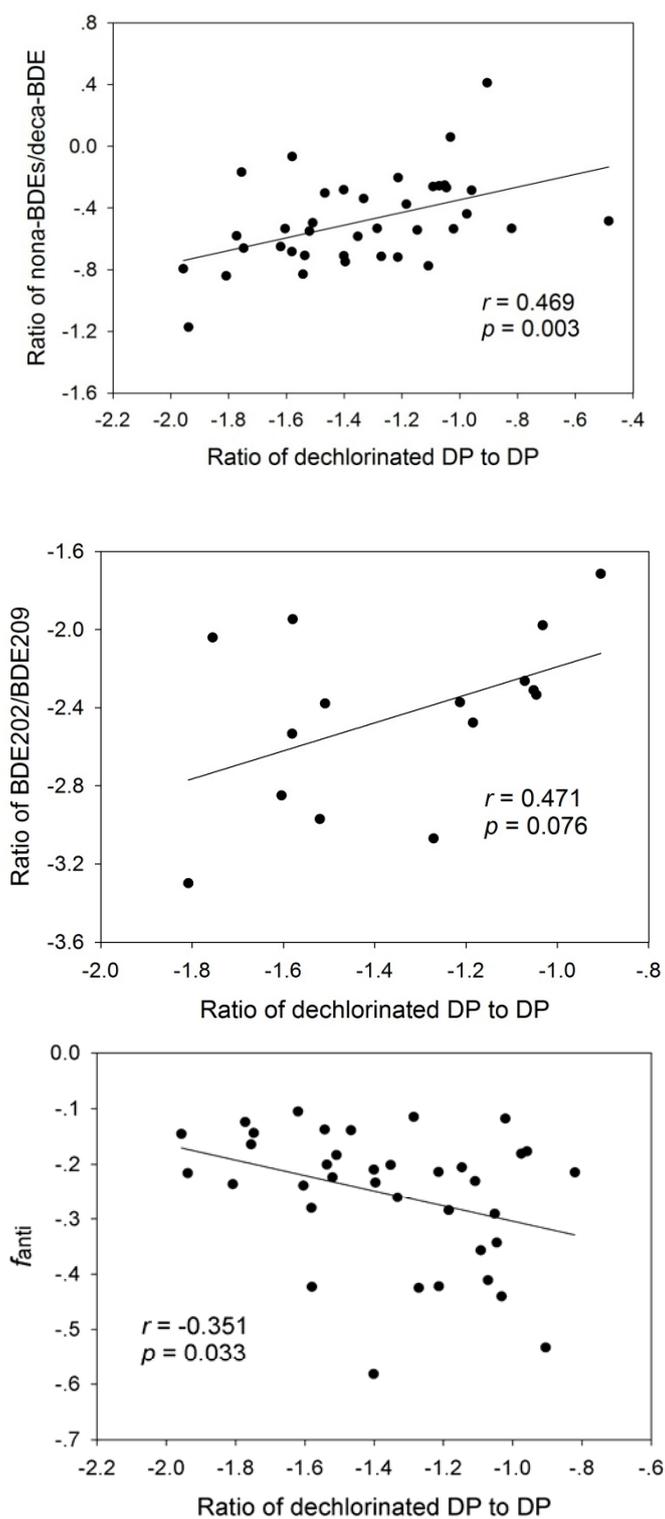


Fig. S5. Correlation between logarithmic normalized ratios of dechlorinated dechlorane plus (DP) to DP and f_{anti} values, nona-brominated diphenyl ethers (BDEs)/deca-BDE, and BDE 202/BDE 209 in house dust in the e-waste area. One

outlier was not included in the correlation analysis for f_{anti} values. Data were log-normalized to follow a normal distribution.