

Detection of Dechlorane Plus in Residential Indoor Dust in the City of Ottawa, Canada

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Dechlorane plus (DP), a flame retardant recently identified in the air and sediment of the Great Lakes region, has been detected in residential indoor dust in the city of Ottawa, Canada using gas chromatography–mass spectrometry under negative chemical ionization mode. DP was detected in all dust samples with a concentration range of 2.3 to 182 ng g⁻¹, except for one dust sample (5683 ng g⁻¹) which was much higher. The levels of DP in indoor dust were several times higher than those in the sediment of the Great Lakes. The presence of DP in indoor environments could have implications for potential human exposure to this chemical. The daily human intake of DP from dust was estimated using dust ingestion data from the U.S. Environmental Protection Agency. The large variation of the ratio of syn- and anti-DP isomers in the dust samples also suggests a complex degradation process of DP in the environment.

Introduction

While flame retardants (FRs) are playing a significant role in reducing human fatality and property damage related to fires in modern society, some of the FRs exhibit toxicities and potential health risks to the human population. So far, investigation of halogenated FRs has been focused on brominated compounds, mainly the polybrominated diphenyl ethers (PBDEs) (1–3). PBDEs are two brominated benzene rings linked through an oxygen atom. Like the polychlorinated biphenyls (PCBs), PBDEs are persistent in the environment and some are also bioaccumulative. Human exposure to PBDEs through inhalation and dust and food intake has been reported (4–6). PBDEs have also been detected in human body fluids such as breast milk and blood (7, 8). With increasing evidence of the potential risks of PBDEs to the environment and humans, measures are being introduced to restrict the use of PBDEs, particularly in Europe and North America (9). In Canada, PBDEs have been added to the List of Toxic Substances under the Canadian Environmental Protection Act (10).

The presence of two other brominated FRs, hexabromocyclododecane and tetrabromobisphenol A, in the environment and in ecosystems has also been reported (11–13). The latter has the basic structure of bisphenol A whereas the

former has the basic structure of an aliphatic cyclic hydrocarbon. These two brominated FRs have structures very different from that of PBDEs. Hexabromocyclododecanes in the environment and humans has been critically reviewed (14).

Recently, a chlorinated FR commonly known as Dechlorane plus (DP) (CAS No. 13560-89-9) has been identified in the ambient air, lake sediment, and fish of the Great lakes region (15). Structurally, DP is created by the reaction of two units of hexachlorocyclopentadiene and one unit of 1,5-cyclooctadiene (see Scheme 1). Detection of DP in environmental media, particularly air from remote sites and sediment cores away from sources, in the region around the Great Lakes has attracted interest in this compound. DP was introduced as a substitute for Dechlorane or Mirex (C₁₀Cl₁₂, CAS No. 2385-85-5) by Hooker Chemical in the mid-1960s. Although the annual production of DP was not reported, it was categorized as a High Production Volume (HPV) substance by the United States Environmental Protection Agency (USEPA)'s high production volume challenge program, where annual production of a HPV typically exceeds 1 million pounds in the United States (16). The major applications of DP are in industrial polymers used for coating electrical wires and cables, connectors used in computers, and plastic roofing material (17). Three types of DP products are available (DP-25, DP-35, and DP-515). These products differ in their particle sizes, but they all have the same chemical composition (C₁₈H₁₂Cl₁₂). In commercial DP products, there are two stereoisomers, syn-DP and anti-DP, which are the products of the Diels–Alder reaction of 2 mol of hexachlorocyclopentadiene with 1 mol of 1,5-cyclooctadiene (16) (Scheme 1).

Since some DP-containing materials and products are primarily used indoors, there is a high likelihood that DP might be present in the indoor environment, where people in modern society spend the majority of their time, leading to potential human exposure to this chemical. During our survey of the levels of several selected volatile organic compounds (VOCs) in residential homes in the winter of 2002–2003 in the city of Ottawa, Canada (18), dust samples from vacuuming devices were collected for the determination of several semivolatile organic compounds including phthalates (19), PBDEs (5), and a number of fluorinated chemicals (20, 21). We have recently measured DP in these archived dust samples. In this paper, we are reporting the levels of DP found in these archived dust samples, as well as seven new dust samples collected in 2007 from residential homes, and the estimation of potential human exposure to DP through ingestion of indoor dust.

Experimental Section

Standards and Chemicals. 2,2',3,3',4,4',5,5'-octachlorodiphenyl-ether-¹³C₁₂ (¹³C-OctaCDE) used as internal standard and dechlorane plus (DP) were both purchased from Cambridge Isotope Laboratories Inc. (Andover, MA). Dichloromethane (DCM) (GC Resolv Grade) and hexane were obtained from Omnisolv (EMD Chemical Inc., Gibbstown, NJ). N-octane was purchased from Caledon laboratories Ltd. (Georgetown, ON.) Deionized (DI) water (18.3 Ω) was generated in-house using a Super-Q water generation system (Fisher Scientific, Ottawa, Canada). Sodium sulfate was purchased from Fisher Scientific (Ottawa, Canada).

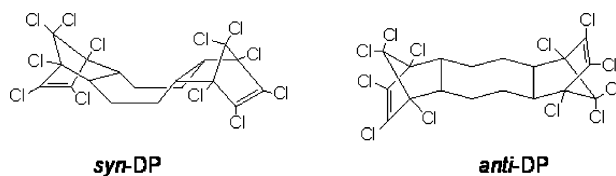
Dust Samples. Residential homes for the 2002–2003 dust samples, collected during November 2002 to March 2003, were selected randomly according to the procedures described elsewhere (18). Dust samples of year 2007 were

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SCHEME 1



collected in the spring from several volunteer's homes. To collect the dust sample, a whole vacuum cleaner bag with the dust content in it was detached from the floor model vacuum cleaners and placed in a polyethylene zip-seal plastic bag (Fisher Scientific, Nepean, Ontario). In the case of central vacuum systems, dust in the bins was transferred to polyethylene bags (to be brought to the lab) while wearing a powder-free nitrile glove (Tec Choice Nitrile, DiaMed Lab Supplies, Mississauga, Canada). Upon arrival at the laboratory, dust samples were immediately stored at -20°C . Fine dust for the analysis was obtained by sieving the vacuum dust using an all stainless steel testing sieve VWR 100 mesh for a $150\ \mu\text{m}$ cutoff (VWR International, Montreal, Quebec). The sieved fine dust was stored at -20°C in a glass jar with a Teflon-lined lid (VWR International, Montreal, Quebec).

Sample Preparation. One gram of dust and ten g of sodium sulfate were weighed into a 50-mL centrifuge tube (CanadaWide, Ottawa, Canada), and the sample was then spiked with ^{13}C -OctaCDE at a level of 5 ng per sample. The tube was tightly closed, vortexed, and left in the dark overnight at room temperature. The samples were then extracted 4 times each with 15 mL of 1:1 hexane/DCM. Between each extraction, the tubes were centrifuged at a speed of 3000 rpm for 5 min using a Heraeus Multifuge Centrifuge (VWR international, Montréal, Québec) to better separate the solvents and dust. The extracts were then combined and concentrated to 1–2 mL on the rotavapor R110 (Brinkman, Rexdale, Ontario, instruments) for further cleanup on an aluminum oxide (neutral, 150 mesh size, (Sigma-Aldrich, Oakville, Ontario)) open column (1.0 i.d.). The aluminum oxide (45 g) was deactivated with 6% Super Q water at least 24 h prior to use and wet packed with hexane. After the extract was introduced onto the top of the aluminum oxide, hexane containing 7% DCM was used to elute the analyte. The first 15 mL of eluate was discarded and the next 80 mL was collected. The volume of the eluate was reduced to 1–2 mL on a rotavapor machine, and the content was transferred to a 5-mL graduated tube. The volume in the tube was reduced to about 0.5 mL under gentle nitrogen stream followed by the addition of 500 μL of n-octane, and the volume was further reduced to 500 μL for instrument analysis.

Instrument Analysis. An Agilent gas chromatograph (GC)–mass spectrometer (MS) system (6890 GC/5973 MSD) (Agilent Technologies, Palo Alto, CA) fitted with a DB-1MS column (30 m long \times 0.25 mm i.d. \times 0.10 μm film thickness, J&W Scientific, Folsom, CA) was used. The oven temperature started at 70°C for 1.5 min, then increased to 210°C at a rate of $15^{\circ}\text{C}/\text{min}$, and further to 250°C at $2^{\circ}\text{C}/\text{min}$, to 290°C at $15^{\circ}\text{C}/\text{min}$, and kept at 290°C for 15 min. The carrier gas for the column was helium. The MS system was operated in methane negative chemical ionization (NCI) mode. Selected ion monitoring mode (m/z 455.8 (quantifying ion) and 457.9 for ^{13}C -OctaCDE; and m/z 617.9 (quantifying ion), 653.8, 619.8, and 651.8 for DP) was used for MS operation.

QA/QC. All calibration standards and spiking solutions were prepared by serial dilution in octane using volumetric flasks. All GC–MS peaks were normalized with the peak area of ^{13}C -OctaCDE (m/z 455.8) before data reduction. Peaks of syn- and anti-isomers of DP were combined for quantification purposes. Daily multi-level (0.001–1.0 ng/ μL) calibration was conducted and the calibration curve was fitted with power

law equation, and a regression coefficient (r^2) value of 0.998 or greater was achieved for all calibration curves. The positive identification of DP peaks was assured by both retention times and their mass ratios referenced to the standards. All laboratory glassware used in sample preparation was soaked in sulfuric acid (Fisher Scientific, Ottawa, Canada) and Chromerge (Fisher Scientific, Ottawa, Canada) mixture, cleaned with hot tap water, then rinsed with DI water and DCM, and air-dried. Although field blanks were not employed, the sample jars, gloves, and polyethylene bags used in the field were checked to be free of DP. One laboratory control sample, containing 1 g of solvent-washed dust spiked with 50 ng of DP, and one laboratory blank were included in each analytical batch of six samples. The mean recovery (standard deviation) of DP was 102 ± 12 . The average residual level of 14 blanks was $0.13\ \text{ng g}^{-1}$ with a standard deviation of $0.14\ \text{ng g}^{-1}$, which resulted in a method detection limit (MDL) of $0.59\ \text{ng g}^{-1}$ based on 1 g of dust sample. One duplicate sample analysis was performed every second batch (about 10% of all dust samples in total). The relative percent difference (RPD) between the duplicate samples ranged from 2 to 64, depending on the levels of DP in the duplicate samples, with an average RPD of 25.

Results and Discussion

Identification and Measurement of DP in Indoor Dust. Dust in vacuum cleaner bags is a readily available matrix for the determination of environmental contaminants indoors. Unlike the dust being collected on the filter, the large quantity of dust accumulated in the bags over time would allow for the measurements of many types of chemicals in it. Depending on the time period in which dust was accumulated in the bag, the levels of contaminants could be a reflection of time-averaged levels of contaminants in the indoor environment. The presence of two peaks eluting late in the GC–MS chromatogram with similar mass spectra was first observed when pooled dust extracts that had been analyzed for phthalates and polycyclic aromatic hydrocarbons (19) were screened for the presence of other environmental contaminants using NCI GC–MS in full scan mode. The spectra of these two peaks in indoor dust were similar to those of DP that have been reported by Hoh et al. (15), except that the chlorine fragment m/z 35 and m/z 37 in our case was more abundant, which is likely due to the different ion source conditions of the two studies. The identities of the two peaks were subsequently confirmed by comparing them to the retention times and NCI–MS spectra of the commercially available DP standard (Figure 1). The assignment of syn-DP and anti-DP peaks on the GC–MS chromatogram was based on the order determined by Hoh et al. (15). Since the same type of GC column was used and there was a sufficiently large difference in their respective retention times on the GC–MS chromatogram (Figure 1), a reverse of the elution orders was very unlikely. The ratio of syn-DP to anti-DP in the standard (about 1:3 in peak areas) we purchased seemed quite different from that (2:3) reported by Hoh et al., which was obtained from a different source (15). This could well be an indication that the ratio of syn-DP to anti-DP is dependent upon the manufacturing source.

The subsequent quantitative measurements of DP in individual dust samples were performed using the selected ion monitoring (SIM) mode of the MS under the same instrumental conditions. DP concentrations reported are the sum of both peaks identified as syn-DP and anti-DP. Table 1 summarizes the levels found in indoor dust samples collected in 2002–2003 ($n = 69$) and 2007 ($n = 7$). DP was detected in all indoor dust samples. The concentrations of DP in the 2003–2003 dust samples varied from 2.3 to $182\ \text{ng g}^{-1}$, except for one dust sample ($5683\ \text{ng g}^{-1}$), while the concentrations of DP in the 2007 dust samples varied from

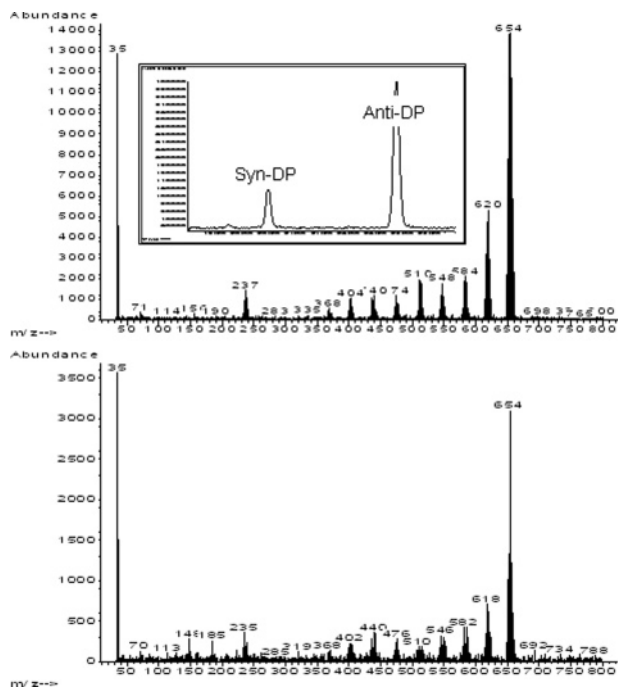


FIGURE 1. NCI mass spectrum of anti-DP standard (above) and peak from pooled dust samples (bottom). Syn-DP has very similar NCI-MS as anti-DP (spectrum not shown here). The inserted picture is the TIC chromatogram of two DP peaks with their identity.

TABLE 1. Concentrations (ng g^{-1}) of DP and PBDEs in Residential Indoor Dust

year	DP level		predominant PBDE level ^a	
	2002–2003 (<i>n</i> = 69)	2007 (<i>n</i> = 7) ^b	BDE-99 (<i>N</i> = 64)	BDE-209 (<i>N</i> = 64)
arithmetic mean	110	32	1800	1100
median	14	22	430	630
geometric mean	18	28		
min	2.3	14	19	74
max	5683	61	60000	10000
5th percentile	4.1	15	35	90
95th percentile	121	60	4700	4100

^a Values extracted from ref 5. ^b Small sample size, data not representative of city of Ottawa.

14 to 61 ng g^{-1} , well above the method detection limit (MDL) of 0.59 ng g^{-1} .

The levels of DP, sorted from low to high, in the 2002–2003 dust samples are presented in Figure 2. The distributions of the DP levels in the seven 2007 dust samples are also presented in the upper-left corner of Figure 2. The concentrations of DP in dust did not exhibit a normal distribution. It failed the Kolmogorov–Smirnov normal distribution test ($p < 0.001$) with a skewness of 8.273. The log-transformed dataset failed the test too ($p = 0.003$), but with a lesser skewness of 1.684. A normal distribution dataset would have a skewness of 1.000. The skewed dataset was also evident by the much higher arithmetic mean (AM) value (110 ng g^{-1}) compared to the geometric mean (GM) (18 ng g^{-1}) or median (14 ng g^{-1}) values (Table 1). Because the measurement of DP was not planned when the dust samples were collected during our 2002–2003 study on selected volatile organic compounds in Ottawa residences (18), the questionnaire extracting information on house characteristics and occupant activities administered at the time of sample collection was not specifically designed for the source identification of DP. Therefore, source identification for the presence of DP in

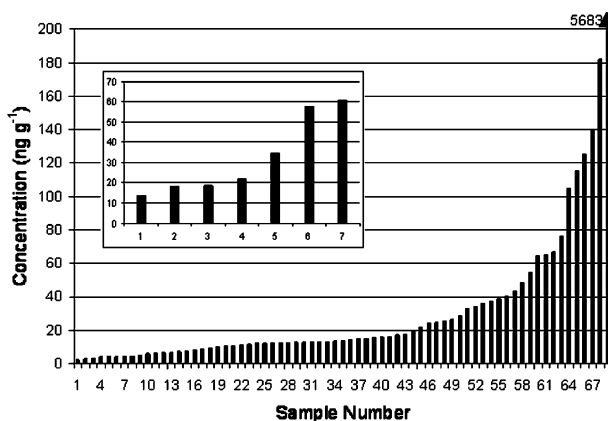


FIGURE 2. Levels of DP in sieved fine indoor dust ($<150 \mu\text{m}$) samples that were collected from 69 residential homes in 2002–2003. Note that the highest value (5683 ng g^{-1}) was off the scale. The concentration distribution of seven 2007 dust samples is illustrated in the inserted picture.

indoor environments could not be conducted, nor would it be possible to explain the extremely high level of DP (5683 ng g^{-1}) in one particular house dust sample.

To our knowledge this is the first measurement of DP in the indoor environment, therefore comparison with other studies for this medium is not possible. Since PBDEs, another group of flame retardants widely used in the past 20 years had been measured in the same 2002–2003 dust samples (5), and DP has a high lipophilicity similar to other typical persistent organic pollutants such as PBDEs (22), a comparison of DP and PBDE levels in dust could provide information on the relative levels of these substances in the same indoor dust samples. Out of a number of PBDE congeners detected in indoor dust, we selected two predominant congeners, BDE-99 and BDE-209 for the comparison. The DP levels were about 10 to 20 times lower than those of the selected PBDE congeners in terms of the GM values and 30 to 40 times lower than those of the selected PBDE congeners in terms of the median values (Table 1). The lower levels of DP in indoor dust compared to the selected PBDE congeners may reflect the amount of usage of these two types of flame retardants. Although the actual sales of DP were not reported, the global annual sales of PBDEs have been reported as approximately 70 000 tons (about 160 million pounds) in recent years (23). In the ambient air in the Great Lakes area, DP levels were reported as either similar or lower than those of BDE-209, but no comparison to other BDE congeners was reported (15).

There seems no clear correlation between levels of DP and PBDEs in indoor dust of the same samples. Using the Pearson Product Moment Correlation model, DP had significant correlation ($p < 0.05$) with BDE-209 ($r = 0.698$), but not with BDE-99 ($r = 0.002$) when all data were included. However, when the highest DP value (5683 ng g^{-1}) was excluded, the situation was reversed with BDE-99 ($r = 0.569$), not BDE-209 ($r = 0.06$), having significant correlation with DP values. Therefore, the results did not provide reliable indication of the coexisting sources for PBDEs and DP in the indoor environment.

Dechlorane Plus in Indoor and Outdoor Environments.

The study which measured DP in the sediment of the Great Lakes reported a DP level of 40 ng g^{-1} in Lake Erie in the late 1970s to early 1980s due to possible releases of this chemical from a nearby manufacturing plant. The level has since decreased to less than 10 ng g^{-1} in recent years. In other locations of the Great Lakes area such as Lake Michigan, DP concentrations in sediment peaked at 4–6 ng g^{-1} and decreased to about 3–4 ng g^{-1} in recent years (15). The same

TABLE 2. Estimated Human Exposure (Daily Intake, ng d⁻¹) to DP through Ingestion of Indoor Dust^a

	adult		child (6–24 months)	
	average	high	average	high
dust ingestion (mg d ⁻¹)	4.16	100	55	200
DP levels in dust				
5th percentile	0.02	0.41	0.23	0.82
median	0.06	1.4	0.75	2.7
geometric mean	0.08	1.8	1.0	3.6
arithmetic mean	0.46	11	6.1	22
95th percentile	0.50	12	6.7	24
maximum	24	568	313	1137

^a The estimation was based on the DP levels in 2002–2003 dust samples, see Table 1.

study also reported ambient air concentrations around the Great lakes ranging from no detection up to 490 pg m⁻³ in the area close to the manufacturing site. Compared to the DP values in the Great Lakes sediment, residential house dust has DP concentrations which are several times higher. The city of Ottawa is located about 500 km northeast of the Great Lakes area and there are no nearby manufacturing or releasing sources of DP. The levels of DP in Ottawa homes are more likely attributed to the use of consumer products that contain DP as a flame retardant.

To further confirm the presence of DP in residential house dust and to evaluate its current levels in residential indoor dust, seven residential house dust samples collected in the year 2007 were analyzed. Although the dust samples collected in 2007 were small in number and were not considered to be representative of the city of Ottawa, the GM and median values (28 and 14 ng g⁻¹, respectively) of the 2007 dust samples were about twice the values of those collected in the 2002–2003. This observation suggests that while the levels of DP seem to be declining in the sediments of the Great Lakes, a similar declining trend was not observed for DP levels in indoor dust, at least in the period of 2002 and 2007 (Table 1).

Estimation of Human Exposure to DP in House Dust.

Because people in modern society spend the majority of their time indoors, the presence of DP in residential house dust has raised concerns over the implications of potential human exposure to this chemical. Since the dust samples of 2002–2003 were from residential homes that had been randomly selected and are representative of the residences in the city of Ottawa, the estimation of human exposure to DP in house dust was done based on the DP levels in these dust samples. The DP values from the 2007 samples were excluded from the estimation, as they are not representative of the population in the city of Ottawa. To estimate human exposure to DP in house dust, average and estimated high dust intake values for children 6–24 months old (55 and 200 mg d⁻¹, respectively) and for adults (4.16 and 100 mg d⁻¹, respectively) were assumed based on several reports (4, 24). Although the high dust intake value for children 6–24 months is only twice the amount for adults, the difference in the average dust intake values (55 vs 4.16 mg d⁻¹) between the two populations is much more significant. Children, due to their close to floor activities and hand-to-mouth habits, ingest in general a much high quantity of dust than adults. Compounded by their smaller body mass, exposure of children to contaminants in house dust on per body weight basis is much higher. The daily intake of residents based on DP levels in dust at the fifth percentile, median, GM, AM, 95th percentile, and maximum value are summarized in Table 2. The estimated central values of DP daily intake, derived from the average dust ingestion and the median level of DP in house dust, are 0.06 and 0.75 ng d⁻¹ for adults and children, respectively.

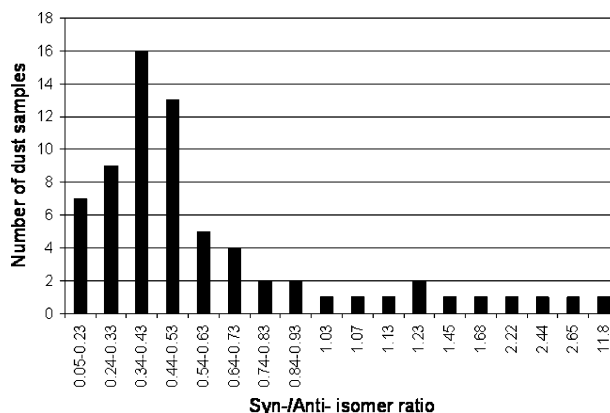


FIGURE 3. Distribution of the ratio of syn-DP and anti-DP among 69 residential indoor dust samples collected in 2002–2003.

Higher estimated daily exposures of 12 ng d⁻¹ for adults and 24 ng d⁻¹ for children could be derived using more conservative assumptions of both a higher dust ingestion and the 95th percentile level of DP in dust.

The potential human exposure to DP is a particularly concerning issue as there is presently little experimental toxicity data available for DP. In 2005, the U.S. EPA stated that both health effects and ecological effects data from the submitter for the purposes of the HPV Challenge Program were not adequate and that the submitter “needs to provide data from a combined repeated-dose/reproduction/developmental toxicity screening test”. As a result, a toxicological test plan for DP has been initiated by the submitter (16). Structurally, DP is very similar to a group of well-known organochlorine pesticides including heptachlor, chlordane, nonachlor, and aldrin, which contain one unit of hexachlorocyclopentadiene linked to another unit of cyclopentadiene with various degrees of chlorination. Due to their biopersistence and biomagnification in food chains, as well as their potential endocrine-disruptive properties or reproductive toxicity (25), these organochlorines have been either banned or restricted in their use. Further research to examine the toxicity, especially the reproductive toxicity, of DP is needed in order to better assess the risk to the environment and humans from the use of DP.

Ratio of Syn/Anti DP. DP has syn- and anti- stereoisomers. The syn-DP has both dichlorocarbon bridges of the two hexachlorocyclopentadiene moieties on the same side of the cyclooctane, whereas anti-DP has the bridges on the opposite side of the cyclooctane (Scheme 1). Stereoisomers could have different physical and chemical properties leading to variation in their persistence in the environment. The DP isomer ratios in all standards (0.31–0.36) had very little variation, over the entire calibration range of 0.001 to 1 ng. Both the laboratory blank samples and the laboratory control sample had syn- to anti- isomer ratios very similar to those of the calibration standards at 0.34 ± 0.13 (arithmetic mean ± standard deviation) and 0.41 ± 0.10, respectively. However, the syn- to anti- isomer ratio in the 69 individual 2002–2003 dust samples varied greatly from 0.05 to 11.8 with a geometric mean of 0.48 (Figure 3). Such large variation in the isomer ratios may be attributed to two factors. The first factor may be the particular manufacturing source of the products. For example, the ratio in the standard we purchased (1:3) was different from that (2:3) reported by Hoh et al. (15); the latter was obtained directly from OxyChem. However, even considering potential variation in the syn- to anti- isomer ratio from 0.3 to 0.8, there were still 12 out of 69 dust samples with a ratio greater than 0.83 and 7 dust samples with a ratio below 0.23. This might well be due to the different degradation rates of syn- and anti- isomers in the environment. Degra-

dition could occur during the production and use of the products or when DP is released into the indoor environment due to exposure to indoor air, lights, and other agents coexisting in the dust. A wide range of syn- to anti- isomer ratios was also observed in the seven 2007 dust samples (0.08, 0.11, 0.27, 0.29, 0.30, 0.92, and 2.63). Since the seven 2007 dust samples were analyzed within days of the sample collection, the possible degradation of DP isomers during sample storage at -20°C in the laboratory can be excluded. The large variation in the ratio of the two DP isomers in dust and in various environmental matrices (ambient air, sediments, and fish) reported by others (15) warrants further research to fully understand the fate of DP isomers in the environment and in biota.

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