

Dechlorane Plus, a Chlorinated Flame Retardant, in the Great Lakes

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A highly chlorinated flame retardant, Dechlorane Plus (DP), was detected and identified in ambient air, fish, and sediment samples from the Great Lakes region. The identity of this compound was confirmed by comparing its gas chromatographic retention times and mass spectra with those of authentic material. This compound exists as two gas chromatographically separable stereoisomers (syn and anti), the structures of which were characterized by one- and two-dimensional proton nuclear magnetic resonance. DP was detected in most air samples, even at remote sites. The atmospheric DP concentrations were higher at the eastern Great Lakes sites (Sturgeon Point, NY, and Cleveland, OH) than those at the western Great Lakes sites (Eagle Harbor, MI, Chicago, IL, and Sleeping Bear Dunes, MI). At the Sturgeon Point site, DP concentrations once reached 490 pg/m³. DP atmospheric concentrations were comparable to those of BDE-209 at the eastern Great Lakes sites. DP was also found in sediment cores from Lakes Michigan and Erie. The peak DP concentrations were comparable to BDE-209 concentrations in the sediment core from Lake Erie but were about 30 times lower than BDE-209 concentrations in the core from Lake Michigan. In the sediment cores, the DP concentrations peaked around 1975–1980, and the surficial concentrations were 10–80% of peak concentrations. Higher DP concentrations in air samples from Sturgeon Point, NY, and in the sediment core from Lake Erie suggest that DP's manufacturing facility in Niagara Falls, NY, may be a source. DP was also detected in archived fish (walleye) from Lake Erie, suggesting that this compound is, at least partially, bioavailable.

Introduction

The market for flame retardants has been growing rapidly due to stringent fire safety regulations, but because of the potential toxicity and frequent environmental detection of some of these compounds (1), some flame retardants have faced governmental regulations. For example, an early chlorinated flame retardant developed by Hooker Chemical, called Dechlorane or Mirex, was banned because of its toxicity to marine invertebrates (2). More recently, penta- and octabromodiphenyl ethers (the so-called penta- and octa-BDE products) have been banned in Europe and in some of the United States as a result of the persistence and bioaccumulation of these compounds (3). Perhaps motivated by this regulatory pressure, the only producer of these two products, Great Lakes Chemical Corp., stopped producing them at the end of 2004 (4).

Flame retardants taken off the market are likely to be replaced by nonregulated flame retardants (5). For example,

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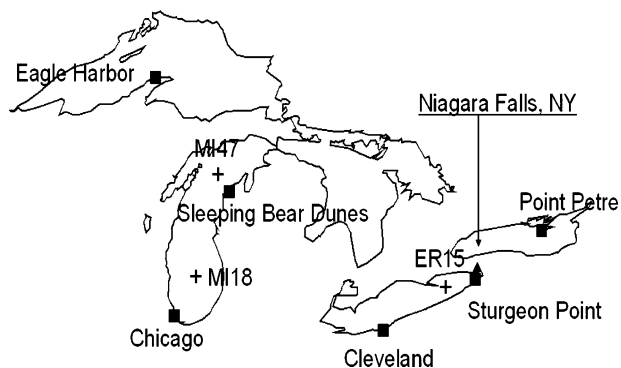


FIGURE 1. Map of the Great Lakes region. Squares represent each air sampling site; crosses represent each sediment core site; and the triangle represents OxyChem's DP manufacturing plant site in Niagara Falls, NY.

current data show that the worldwide sales of the decabromodiphenyl ether product (deca-BDE) and other brominated flame retardants (BFRs) were higher in 2002 and 2003 than in 2001 (6). Thus, it is prudent to monitor the environment for the presence of unexpected flame retardants that may enter the marketplace as other, regulated compounds leave.

In this paper, we report on two significant, unknown, chlorine-containing gas chromatographic peaks noticed during the course of analyzing for BFRs in particle-phase atmosphere samples collected near the Great Lakes. We have identified and quantitated these compounds in several Great Lakes environmental compartments. This is an example of a relatively old compound that has apparently slipped under the regulatory radar and that is still currently being used without attracting public attention. This compound has not been identified in the environment before.

Experimental Section

Sample Information. Full details about the sampling sites are available at the Integrated Atmospheric Deposition Network (IADN) website (http://www.msc-smc.ec.gc.ca/iadn/Stations/station_master_e.html), but a brief summary is presented here. Air samples are collected at five U.S.-only IADN stations (Eagle Harbor in Michigan, Chicago in Illinois, Sleeping Bear Dunes in Michigan, Cleveland in Ohio, and Sturgeon Point in New York) and at one joint U.S.–Canadian station (Point Petre in Ontario). These sites are located near the lake shores, and the locations are shown in Figure 1. The Chicago and Cleveland sites are in urban areas; the Sturgeon Point site is in a town with a population of ~10 000; the Point Petre site is in a lightly populated rural area; and the Sleeping Bear Dunes and the Eagle Harbor sites are in remote areas.

The detailed descriptions of the sampling and analytical procedures have been given elsewhere but are summarized here (7, 8). Modified Anderson high-volume air samplers (General Metal Works, model GS2310) fitted with XAD-2 (Sigma, Amberlite, 20–60 mesh) resin and with a Whatman quartz fiber filter (QM-A) were used to collect air. These samplers draw air through the filter to collect the particle-phase compounds and then through the XAD-2 resin to collect the gas-phase compounds. Sampling took place for 24 h every 12 days except at Point Petre, where the frequency was once every 24 days. Sample volumes were ~800 m³. Samples collected from April to December 2004 were used in this study.

Two sediment cores were taken from northern and southern Lake Michigan at the end of April, 2004. At the

northern site (MI-47), the water depth was 197 m, and at the southern site (MI-18), the water depth was 161 m. A sediment core was also taken from the eastern basin of Lake Erie at site ER-15 in August, 2003, where the water depth was 62 m. In all cases, a 30 cm × 30 cm × 52 cm box corer was deployed from the U.S. Environmental Protection Agency's research vessel, the *Lake Guardian*. Once the box core was back on the deck, three subcores were taken by carefully inserting subcore tubes (10 cm i.d. × 60 cm) into the sediment box in such a way as to avoid distortion of the sediment. These sediment cores were 51 cm in length. For Lake Michigan, the cores were cut into 0.5-cm intervals down to 10 cm and in 1-cm intervals afterward. For Lake Erie, the cores were cut into 1-cm intervals down to 30 cm and in 2-cm intervals afterward. The samples were immediately frozen, returned to our laboratory, and stored at -30 °C. Archived fish samples (walleye), taken from Lake Erie in 1980, 1984, 1990, 1992, 1994, 1996, and 2000 were obtained from the U.S. Geological Survey. Except for 1980 and 1984, there were three samples in each sampling year, and the reported concentrations of the brominated diphenyl ethers (PBDEs) and of DP in each year were the average of these three samples.

Materials. DP was obtained from OxyChem (Dallas, TX). Decabromodiphenyl ether (BDE-209) was purchased from AccuStandard (New Haven, CT), and the other PBDE congeners used in this study were purchased from Cambridge Isotope Laboratories (Andover, MA). All of the solvents used for the extraction and cleanup procedures were residue-analysis grade.

Sample Preparation. For air sampling, precleaned XAD-2 resin and baked filters were used; details on cleaning these materials are available elsewhere (8). After being collected, the XAD-2 samples and the filters were prepared separately. Each sample was spiked with known amounts of 3,3',4,4'-tetrabromodiphenyl ether (BDE-77) and ¹³C-decabromodiphenyl ether (¹³C-BDE-209) and then Soxhlet-extracted for 24 h with 400 mL of 1:1 acetone-hexane. After extraction, the solvent was exchanged to hexane, reduced by rotary evaporation, and fractionated on 3.5% water deactivated silica with hexane and 1:1 hexane-dichloromethane. Each fraction was reduced by rotary evaporation and concentrated further by N₂ blowdown. Prior to gas chromatographic mass spectrometric analysis, each extract was spiked with the quantitation standards, 2,3,3',4,4',5,6-heptabromodiphenyl ether (BDE-190) and decabromobiphenyl (BB-209, purchased from Dr. Ehrenstorfer, GmbH, Augsburg, Germany). PBDEs were eluted in both fractions, but DP was eluted only in the second fraction. Each fraction was analyzed separately.

For the sediment samples, about 15 g of wet sediment was mixed with ~100 g of precleaned, anhydrous sodium sulfate (Na₂SO₄) and ~20 g of precleaned granular copper (20-30 mesh; J. T. Baker, NJ), which was used to remove elemental sulfur. After being spiked with a known amount of the internal standards, ¹³C₁₂-2,3,3',4,4',5-hexachlorodiphenyl ether (CDE-156) and ¹³C₁₂-2,2',3,3',4,4',5,5'-octachlorodiphenyl ether (CDE-194) (Cambridge Isotope Laboratories), the samples were Soxhlet-extracted for 24 h with 300 mL of 1:1 acetone-hexane. Throughout the extraction and analysis procedure, the analytes were protected from light by wrapping the containers with aluminum foil or by using amber glassware.

After evaporating most of the solvent, approximately 4 mL of concentrated sulfuric acid (H₂SO₄) (EM Science, Gibbstown, NJ) was added to remove any lipids present in the sediment samples. After centrifugation for 10 min, the hexane layer was recovered and combined with 5 mL of hexane used to wash the sulfuric acid residue. The solvent was evaporated to 500 μL, and the samples were fractionated on an alumina (ICN Biomedicals GmbH, Eschwege, Germany) column (0.6 cm i.d. × 6 cm). The column was first eluted by

8 mL of hexane followed by 8 mL of 2:3 dichloromethane-hexane. The PBDEs and DP eluted in the second fraction. After solvent exchange to hexane, 2,3',4,4',5-pentabromodiphenyl ether (BDE-118) and BB-209 were added as quantitation standards, and the samples were analyzed by gas chromatography/mass spectrometry (GC/MS).

A sample preparation method similar to the sediment preparation method was used for the fish samples. After Soxhlet extraction, the lipid contents of the fish samples were determined gravimetrically. Then the samples were treated with H₂SO₄ and cleaned up as described above. The detailed procedure has been described elsewhere (9).

Instrumental Analysis. DP in the air and sediment samples was identified using GC/MS (an Agilent 5973 system) operating in the full-scan electron impact (EI) and electron capture negative ionization (ECNI) modes. ECNI selected ion monitoring was used for quantitation, and the following ions were monitored: *m/z* 651.8 and 653.8 for DP, *m/z* 486.6 and 488.6 for BDE-209, *m/z* 79 and 81 for the other BDEs and BB-209, and *m/z* 494.6 and 496.6 for ¹³C-BDE-209. BDE-190 in the air samples and BDE-118 in the other samples were used as the quantitation standards for DP, and BB-209 was used for BDE-209. GC injections (2 μL) were made in the pulse splitless mode, with a purge time of 2.0 min. The injection port was held at 285 °C. The separation used a 15 m × 250 μm (i.d.) fused silica capillary column coated with DB-5-MS (0.25 μm film thickness; J&W Scientific, Folsom, CA). The GC oven temperature program was: 110 °C for 1 min, 15 °C/min to 300 °C, and held at 300 °C for 17 min. The GC to MS transfer line was held at 285 °C. The ion source temperatures were 230 and 150 °C for the EI and ECNI modes, respectively. Commercial DP has two gas chromatographically separable stereoisomers, the ECNI mass spectra of which are identical to each other. Because individual standards for each stereoisomer were not available, we used the sum of the responses for the two GC peaks for DP quantitation.

Thin-Layer Chromatography. Thin-layer chromatography (TLC) was used to separate the two stereoisomers in commercial DP so that we could obtain one-dimensional proton nuclear magnetic resonance (1D ¹H NMR) spectra for each individual compound. Highly purified silica gel TLC plates (Sigma-Aldrich) were used. To isolate the compound with the earlier GC retention time, 60% chloroform in hexane was used on a TLC plate spotted with the DP commercial mixture. The spot at *R_f* = 0.87 (UV detectable) was excised and extracted with dichloromethane. The extract was concentrated by N₂ blowdown, applied to another TLC plate, and eluted with 2% dichloromethane in hexane. The spot at *R_f* = 0.60 (UV detectable) was the compound with the earlier GC retention time (Figure SI-4). To isolate the second compound, 90% chloroform in hexane was used on a TLC plate spotted with the DP commercial mixture. The spot at *R_f* = 0.80 was excised, extracted with dichloromethane, and concentrated by N₂ blowdown prior to GC/MS and 1D ¹H NMR analysis (Figure SI-5). The purity of each separated isomer was >95% (as measured by GC/MS).

Quality Control. Three quality control criteria were used to ensure the correct identification and quantitation of the target compounds: (a) The GC retention times matched those of the standard compounds within ± 0.1 min. (b) The signal-to-noise ratio was greater than 5:1. (c) The isotopic ratios for selected ion pairs were within ± 15% of the theoretical values. For the air samples, the average recovery of the internal standard (BDE-77) was 102 ± 18% (mean ± one standard deviation), and the average recovery of ¹³C-BDE-209 was 77 ± 15%. Through the use of spiked samples, the recoveries for DP for the air filter, sediment samples, and fish samples were 98 ± 5%. A procedural blank was run with each batch of seven or eight samples. The DP and BDE-209 levels in the blanks were low enough so that we did not correct the

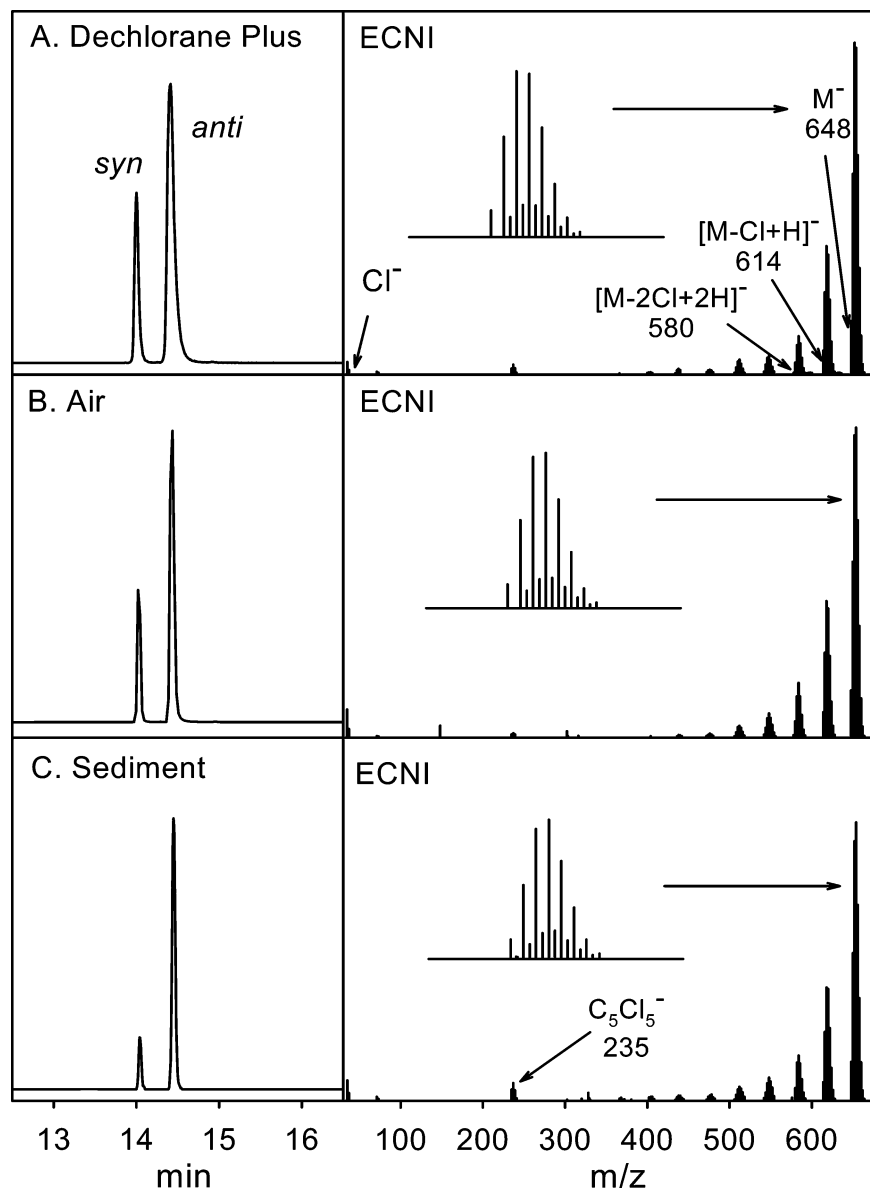


FIGURE 2. Electron capture negative ionization (ECNI) GC/MS chromatograms (monitored at m/z 652) and ECNI mass spectra for *anti*-DP from (A) Dechlorane Plus commercial compound, (B) the particle-phase atmospheric sample collected from Sturgeon Point, NY, on July 2–3, 2004, and (C) the sediment core sample taken at a depth of 39 cm from Lake Erie at ER-15. The corresponding electron impact (EI) mass spectra are given in Figure SI-1.

concentrations in the samples. Field blanks were collected at each air sampling site every season. Concentrations below these average field blank levels were treated as nondetects (Supporting Information).

Sediment Dating. The cores from MI-47 and ER-15 were dated by measuring the specific activities of ^{210}Pb as a function of depth in one of the three subcores. These samples were air-dried for 2 weeks, ground in a mortar, and sieved through a 2-mm mesh screen. Each sample was loaded into a Petri dish (50 mm o.d. \times 9 mm), and the ^{210}Pb activities were measured by gamma spectrometry at 46.54 keV, using a high-purity germanium detector (Canberra GL 2820R, Canberra Industries, Meriden, CT). The dating results for MI-47 and ER-15 have been reported previously (10). The core from MI-18 was not dated in our laboratory, but a sedimentation rate from the literature was used (11).

Results and Discussion

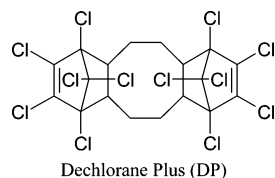
Identification of Dechlorane Plus. Using a 15-m DB-5 column and GC/MS, we noted two significant, unknown,

chlorine-containing GC peaks with retention times of 14.00 and 14.40 min. These unknown compounds eluted after BDE-190, and the intensities of these peaks were particularly high in an atmospheric sample taken at Sturgeon Point, NY, on July 2–3, 2004.

To identify these unknown compounds, full-scan mass spectra for these two peaks were obtained in both ECNI and EI modes. The mass spectra of the two peaks were identical under both ionization modes; therefore, only the mass spectra for the 14.40 min peak are shown (Figures 2 and SI-1B). The ECNI mass spectrum in Figure 2B indicated a molecular ion at m/z 648 with 12 chlorines. The two fragment ions at m/z 614 and 580 correspond to the sequential loss of 34 amu, in each case, due to loss of a chlorine atom and the addition of a hydrogen atom. This fragmentation process is widely observed in the ECNI mass spectra of highly chlorinated compounds (12, 13). In addition, the fragment ion cluster at m/z 235 indicated C_5Cl_5^- , and the chloride ion was observed at m/z 35. In the EI spectrum (Figure SI-1), the most abundant ion was at m/z 270, corresponding to C_5Cl_6^+ , suggesting the

presence of a hexachlorocyclopentadiene moiety. The EI spectrum also showed a molecular ion at m/z 648, but it was of low intensity.

On the basis of this analysis, we suspected that these GC peaks might be bis(hexachlorocyclopentadieno)cyclooctanes, which are known commercially as Dechlorane Plus, with a molecular formula of $C_{18}H_{12}Cl_{12}$. This identification was confirmed by comparison of the GC retention times and of the full-scan ECNI and EI mass spectra of the unknowns with those of authentic Dechlorane Plus obtained from OxyChem (Figures 2A and SI-1A). The retention times and the full-scan mass spectra of the GC peaks in one of the sediment core sections from Lake Erie were also confirmed to be those of Dechlorane Plus (Figures 2C and SI-1C).



DP is a chlorinated flame retardant. This compound was introduced as a substitute for Dechlorane (also called Mirex, $C_{10}Cl_{12}$) by Hooker Chemical (now a part of Occidental Chemical Corporation and now known as OxyChem) in the mid-1960s. Dechlorane Plus is still being used (1, 14). Major applications of DP are industrial polymers used for coating electrical wires and cables, connectors used in computers, and plastic roofing material. Three types of DP are available (DP-25, DP-35, and DP-515). These products differ in their particle sizes, but they all have the same chemical composition (15). DP falls under the EPA's high production volume challenge program. An environmental test plan for DP was generated by OxyChem in 2005. According to this plan, DP has the typical characteristics of a persistent organic pollutant: high lipophilicity (its estimated K_{ow} is $10^{9.3}$), resistance to photo- and biodegradation, and accumulation in fish. DP appears to have ecotoxicological effects in fish, and a dermal study with rabbits showed potential effects on reproduction. However, the studies presented in this test plan were limited in terms of DP's environmental fate (only laboratory tests were performed) and in terms of DP's toxicity (no chronic studies were performed) (16). Otherwise, there is no scientific literature about the fate or toxicity of this compound in the environment.

In the commercial DP product, two GC peaks were also observed (Figure 2A). These two peaks represent two stereoisomers, syn and anti, produced from the Diels–Alder reaction of 2 mol of hexachlorocyclopentadiene with 1 mol of 1,5-cyclooctadiene (14). Comparing the areas of these two peaks in the commercial product, we note that the higher GC retention time peak was 75–80% of the total mass. Garcia et al. synthesized these compounds and verified the structures of the two stereoisomers using 1D 1H NMR and X-ray crystallography (Figure 3) (17). In their study, the anti stereoisomer was 80% of the total (18). We measured both the 1D 1H NMR and 2D 1H – 1H NMR spectra of the commercial DP mixture. Also, we were able to separate the individual stereoisomers by TLC and obtain 1D 1H NMR spectra of each isomer. By comparing our NMR data with those reported by Garcia et al. (17), we were able to conclude that the lower GC retention time peak was the syn isomer and the other, more intense peak was the anti isomer. (The NMR data are available in Figures SI-2–5.)

Dechlorane Plus in the Great Lakes. After identifying this compound, we analyzed gas- and particle-phase atmospheric samples collected at the six IADN sites from April to December, 2004, using the commercial DP mixture as a standard. The two DP peaks were detected in these samples

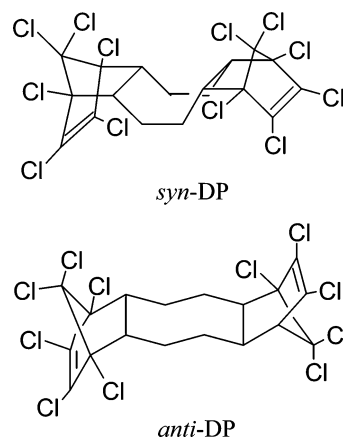


FIGURE 3. Molecular structures of the two Dechlorane Plus stereoisomers (17).

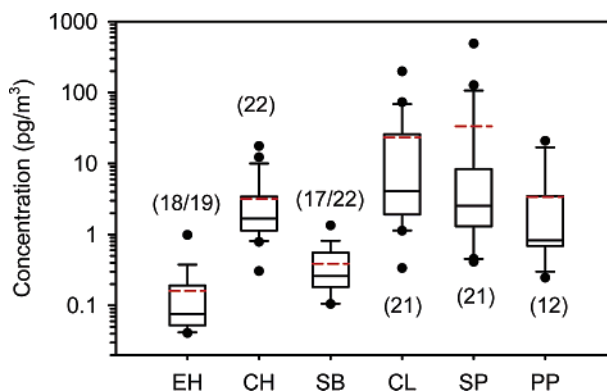


FIGURE 4. Total DP concentrations (pg/m^3) at each sampling site. The horizontal lines represent the 10th, 50th, and 90th percentiles; the boxes represent the 25–75th percentiles; the dashed red lines represent the means; samples outside of 90th and 10th percentiles are given individually. Samples below the average field blanks were treated as nondetects. (The number of samples detectable and the total number of samples are given in parentheses.) The sampling locations are sequenced from west to east. Abbreviations for the sampling sites are: EH, Eagle Harbor in Michigan; CH, Chicago in Illinois; SB, Sleeping Bear Dunes in Michigan; CL, Cleveland in Ohio; SP, Sturgeon Point in New York; and PP, Point Petre in Ontario.

at all sites, including at the very remote site at Eagle Harbor, MI. Given that <1% of the total DP (syn plus anti) was detected in the gas-phase samples, we have not reported these concentrations here.

The atmospheric total DP concentrations are summarized in Figure 4 as box plots, which are sequenced from west to east. Full data for each sample are given in Table SI-1. The mean DP concentration was highest at Sturgeon Point, where the concentration was 34 ± 24 pg/m^3 (mean \pm one standard error) and second highest at Cleveland. Statistical tests (Student's t -test) were conducted to compare the DP concentrations among the sampling sites. The DP concentrations were not significantly different between Sturgeon Point and Cleveland, but the DP concentrations at these two sites were significantly higher than at the other four sites ($p < 0.107$). The DP concentrations were not significantly different between Chicago and Point Petre, but the DP concentrations at these two sites were significantly higher than those at Eagle Harbor and Sleeping Bear Dunes ($p < 0.05$). Although the DP concentrations were low at both Sleeping Bear Dunes and Eagle Harbor, a t -test showed that DP's concentration was significantly higher at Sleeping Bear Dunes than that at Eagle Harbor ($p < 0.025$). Thus, the statistically supported sequence of DP concentrations is:

Sturgeon Point \approx Cleveland > Chicago \approx Point Petre > Sleeping Bear Dunes > Eagle Harbor.

How do these DP concentrations compare to those of other flame retardants in the atmosphere? Given that DP was primarily found in the atmospheric particle phase and given that BDE-209 was also found primarily in the atmospheric particle phase (19), we thought that a comparison of these two compounds' concentrations would be pertinent. Thus, we measured BDE-209 concentrations in the air samples in which DP was found; the full data are given in Table SI-1. The BDE-209 and DP concentrations were similar to each other at the three eastern sampling sites (Cleveland, Sturgeon Point, and Point Petre), while the concentrations of DP were lower than those of BDE-209 at the other three sites ($p < 0.025$). The statistically supported sequence of BDE-209 concentrations is: Chicago \approx Cleveland > Sturgeon Point > Point Petre \approx Sleeping Bear Dunes \approx Eagle Harbor.

This spatial trend is similar to that of DP, except for Sturgeon Point, which ranks more highly for DP than for BDE-209. In fact, the single highest DP concentration (490 $\mu\text{g}/\text{m}^3$) occurred at Sturgeon Point during July 2–3, 2004. This is clearly not an urban effect (20); for example, the DP concentrations at Chicago were similar to those at Point Petre, which is a rural site compared to Chicago. The reason for this unexpected spatial trend may be the emission of DP from its manufacturing plant, which is located in Niagara Falls, NY. This plant is operated by OxyChem, the only producer of DP in the United States (Figure 1). The Sturgeon Point site is only about 50 km south of Niagara Falls, so DP emissions from this manufacturing facility may contribute to the relatively high DP atmospheric concentrations observed at this site. In general, higher DP concentrations were observed at the eastern Great Lakes sites compared to the western sites, an observation that can also be explained by the location of the DP manufacturing facility.

DP was also found in sediment cores from Lakes Michigan and Erie. The concentrations of DP as a function of year of deposition in the cores are shown in Figure 5. For both ER-15 and MI-47, DP concentrations peaked in 1976; in MI-18, the peak was around 1981. This difference could be explained by differences in the manner by which we obtained sedimentation rates for MI-47 and MI-18. The sedimentation rate for MI-47 was determined in our laboratory, but the sedimentation rate for MI-18 was taken from a report by Song et al., who dated a core taken from the same site but at a different time than ours (11). This historical deposition evidence implies that there was a relatively large input of DP into the Great Lakes starting around 1970 and peaking 5–10 years later. The surficial sediment concentrations suggest that the input of DP is now about half of what it was at its peak. According to EPA Inventory Update Rule 2002, DP's production volume has been between 1 million and 10 million pounds each year since 1986 (21). Clearly, large amounts of DP are being produced, and some of it is entering the sediment of, at least, two of the Great Lakes.

Figure 5 shows that the highest DP concentration in Lake Erie's sediment was 40 ng/g dry weight, which was around 10 times higher than the highest DP concentration in Lake Michigan sediments. For comparison, the maximum PBDE sediment concentration (almost exclusively the BDE-209 congener) was 48 ng/g dry weight in Lake Erie and 122 ng/g dry weight in Lake Michigan (10). Thus, the levels of DP and BDE-209 in Lake Erie sediment are comparable, but levels of DP in Lake Michigan sediment are ~ 30 times lower than those of BDE-209. This is still another indication that the source of DP to the Great Lakes is closer to Lake Erie than to Lake Michigan. As discussed above, DP's manufacturing facility, located in Niagara Falls, is close to the eastern basin of Lake Erie; thus, DP may be entering Lake Erie through point sources or through atmospheric deposition. The

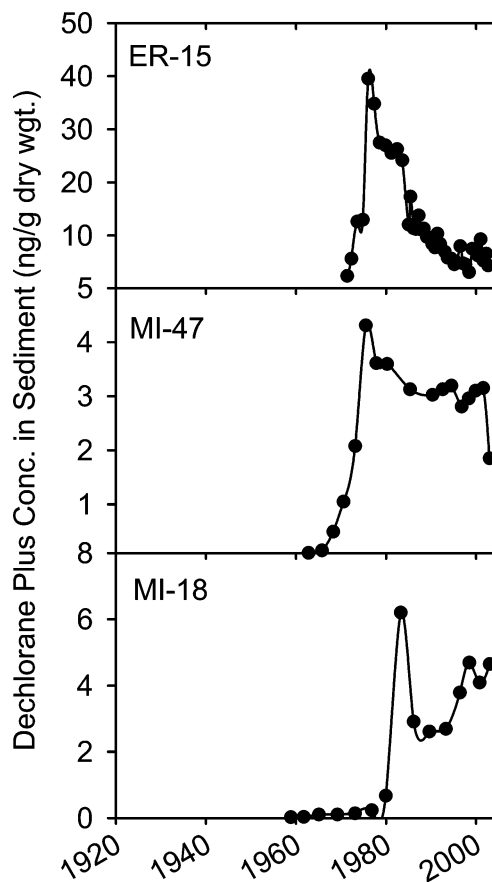


FIGURE 5. Concentrations of total DP in three sediment cores from the Great Lakes as a function of year of deposition.

presence of DP in Lake Michigan, which is further from the presumed source, may indicate that DP can transfer via the atmosphere for considerable distance. The sediment inventories (after correction for sediment focusing) of DP in Lakes Erie and Michigan were ~ 40 and ~ 1 ng/cm^2 , respectively. Accordingly, the burdens of DP in Lakes Erie and Michigan are ~ 10 and ~ 1 tons, respectively. It would be interesting to know the concentration and inventory of DP in the sediment of Lake Ontario, which is downstream of DP's production site in Niagara Falls, NY.

DP was detected in archived fish (walleye) samples from Lake Erie at levels in the range of 0.14–0.91 ng/g lipid weight, and these concentrations did not correlate ($r^2 = 0.0025$) with the year of fish sampling. In contrast, as shown by Zhu and Hites (9), the levels of PBDEs (mostly BDE-47, BDE-99, and BDE-100) ranged from 6.5 to 600 ng/g lipid and were significantly correlated ($r^2 = 0.942$) with the year of fish sampling, doubling every 3 years. There are two possibilities for the relatively low concentrations of DP observed in our fish samples. First, DP's very high hydrophobicity ($K_{ow} = 10^{9.3}$) would reduce its bioaccumulation potential because DP would be strongly attached to particles. In fact, several papers have shown that bioaccumulation diminishes when K_{ow} values are $> 10^7$ (22). Second, DP could be metabolized in fish in a manner similar to what has been observed for BDE-209 in juvenile carp (23). Nevertheless, it is clear that DP was detected in these fish samples, which indicates that DP is, at least partially, biologically available. Certainly, more research is needed to study the bioaccumulation and toxicity of DP.

DP Stereoisomer Profile. The *anti*-DP fraction was calculated from the peak areas. Figure SI-6 shows the *anti*-DP fraction in each atmospheric sample as a function of its total DP concentration and location. The *anti*-DP fractions

were more than 0.50 and close to that of commercial DP (0.75–0.80) for most samples, which suggests that the main source of atmospheric DP in the Great Lakes is commercial DP. Low *anti*-DP fractions (<0.50) were observed in relatively few samples with low DP concentrations from Eagle Harbor and Sleeping Bear Dunes. It is possible that this low fraction for these samples may indicate another DP source with relatively high levels of the *syn* isomer. These two sites are remote sites, which are far from DP's presumed source in Niagara Falls, NY. Thus, the DP sources to these sites may be emitting old DP, which may have had a different *anti*-DP fraction in the past compared to the material being produced now. Alternately, long-range atmospheric transport may change the *anti*-DP fraction due to differences in the physical or chemical properties of the two stereoisomers.

The *anti*-DP fractions in all the sediment cores were well above 0.5, which suggests that its source is commercial DP (Figure SI-7). The *anti*-DP fractions were compared among the sediment cores (two Lake Michigan sites and one Lake Erie site) using the *t*-test. The *anti*-DP fractions were not significantly different between the two sediment cores from Lake Michigan; however, these fractions were significantly higher for the Lake Erie sediment core compared to the Lake Michigan sediment cores ($p < 0.001$). This result parallels our observation of low *anti*-DP fractions in some Sleeping Bear Dunes air samples and suggests that atmospheric transport of DP may be a route by which this compound reaches Lake Michigan. There were no statistically significant temporal trends of the *anti*-DP fractions in the sediment cores.

The *anti*-DP fractions were above 0.5 in most archived fish samples except for one sample collected in 1990. The average fraction was 0.60 ± 0.05 (mean \pm one standard deviation), which was significantly lower than those of commercial DP or Lake Erie sediment samples ($p < 0.001$). The relatively low *anti*-DP fraction observed in Lake Erie fish suggests that the bioavailability or biodegradation (metabolism) of the two isomers could be different. The four interior carbons on the cyclooctane moiety of *anti*-DP are less blocked by chlorines than those of *syn*-DP (Figure 3), which suggests that *anti*-DP may be more reactive. Further research is needed to investigate the physical and chemical properties for each DP stereoisomer to obtain a better understanding of DP's behavior in the environment.

Acknowledgments

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Supporting Information Available

Concentrations of DP and BDE-209 in each atmospheric particle-phase sample; electron impact mass spectra of *anti*-Dechlorane Plus from the commercial mixture, the particle-phase atmospheric sample collected at Sturgeon Point, NY on July 2–3, 2004, and the sediment core sample taken at a depth of 39 cm from Lake Erie; 2D ^1H – ^1H NMR spectrum of a commercial Dechlorane Plus sample; 1D ^1H NMR spectrum of a commercial Dechlorane Plus sample; ECNI chromatogram for a compound extracted from the TLC plate after separation of commercial Dechlorane Plus and the 1D ^1H NMR spectrum of that compound; ECNI chromatogram for a compound extracted from the TLC plate after separation of commercial Dechlorane Plus and the 1D ^1H NMR spectrum of that compound; *anti*-DP fractions in atmospheric samples as a function of total DP concentration; and *anti*-DP fractions in sediment cores as a function of total DP concentration.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- Green, J. An overview of the fire retardant chemical industry, past–present–future. *Fire Mater.* **1995**, *19*, 197–204.
- A Historical View of Flame Retardant Research and Some Lessons Learned. http://www.sp.se/fire/Eng/Conferences/FIRESEL/summary_firesel_conference.pdf.
- BFR-Related Legislation in the United States. http://www.bsef-site.com/regulation/regulator_ov_usa/.
- PR news from Great Lakes Chemical Co. [http://www.e1.greatlakes.com/corp/news/jsp/recent_news_detail.jsp?contentfile=\(7\)01182005_FR_phase_out.htm](http://www.e1.greatlakes.com/corp/news/jsp/recent_news_detail.jsp?contentfile=(7)01182005_FR_phase_out.htm).
- Tullo, A. H. Resting easier. *Chem. Eng. News* **2003**, *81* (46), 43–44.
- Major Brominated Flame Retardants Volume Estimates. http://www.bsef-site.com/bromine/our_industry/our_industry.php.
- Basu, I. *Analysis of PCB, Pesticides, and PAHs in Air and Precipitation Samples: IADN Project Sample Procedure*; Indiana University: Bloomington, IN, 2000. http://www.msc-smc.ec.gc.ca/iadn/Resources/resources_e.html.
- Basu, I.; Lee, A. D. *Collection of Air and Precipitation Samples: IADN Project Sample Procedure*; Indiana University: Bloomington, IN, 2000. http://www.msc-smc.ec.gc.ca/iadn/Resources/resources_e.html.
- Zhu, L. Y.; Hites, R. A. Temporal trends and spatial distributions of brominated flame retardants in archived fishes from the Great Lakes. *Environ. Sci. Technol.* **2004**, *38*, 2779–2784.
- Zhu, L. Y.; Hites, R. A. Brominated flame retardants in sediment cores from Lakes Michigan and Erie. *Environ. Sci. Technol.* **2005**, *39*, 3488–3494.
- Song, W. L.; Li, A.; Ford, J. C.; Sturchio, N. C.; Rockne, K. J.; Buckley, D. R.; Mills, W. J. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 2. Lakes Michigan and Huron. *Environ. Sci. Technol.* **2005**, *39*, 3474–3479.
- Dearth, M. D.; Hites, R. A. Highly chlorinated dimethanofluorenes in technical chlordane and in human adipose tissue. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 99–103.
- Stemmler, E.; Hites, R. A. *Electron Capture Negative Ion Mass Spectra of Environmental Contaminants and Related Compounds*; VCH: New York, 1988.
- Weil, E. D.; Levchik, S. Current practice and recent commercial developments in flame retardancy of polyamides. *J. Fire Sci.* **2004**, *22*, 251–264.
- OxyChem's official website about Dechlorane Plus. http://www.oxy.com/OXYCHEM/Products/dechlorane_plus/dechlorane_plus.htm.
- High Production Volume (HPV) Challenge Program. <http://www.epa.gov/chemrtk/dechlorp/c15635tc.htm>.
- Garcia, J. G.; Fronczek, F. R.; McLaughlin, M. L. Tandem reverse-electron-demand Diels–Alder reactions of 1,5-cyclooctadiene. *Tetrahedron Lett.* **1991**, *32*, 3289–3292.
- Garcia, J. G.; McLaughlin, M. L. Reverse-electron-demand Diels–Alder dienophile π -face selectivity via conformation dependent transmission of π – σ – π electronic interactions. *Tetrahedron Lett.* **1991**, *32*, 3293–3296.
- Strandberg, B.; Dodder, N. G.; Basu, I.; Hites, R. A. Concentrations and spatial variations of polybrominated diphenyl ethers and other organohalogen compounds in Great Lakes air. *Environ. Sci. Technol.* **2001**, *35*, 1078–1083.
- Hoh, E.; Hites, R. A. Brominated flame retardants in the atmosphere of the east-central United States. *Environ. Sci. Technol.* **2005**, *39*, 7794–7802.
- United States EPA Inventory Update Rule. http://www.epa.gov/cgi-bin/iursrch3_2002.cgi.
- Meylan, W. M.; Howard, P. H.; Boethling, R. S.; Aronson, D.; Printup, H.; Gouchie, S. Improved method for estimating bioconcentration/bioaccumulation factor from octanol/water partition coefficient. *Environ. Toxicol. Chem.* **1999**, *18*, 664–672.
- Stapleton, H. M.; Alaei, M.; Letcher, R. J.; Baker, J. E. Debromination of the flame retardant decabromodiphenyl ether by juvenile carp (*Cyprinus carpio*) following dietary exposure. *Environ. Sci. Technol.* **2004**, *39*, 112–119.

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