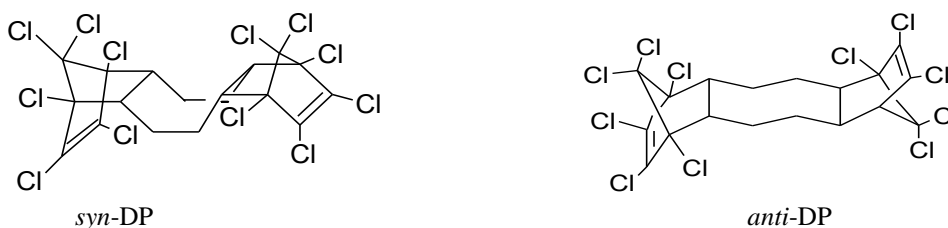


DECHLORANE PLUS: A REVIEW WITH NEW DATA

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Introduction. Dechlorane Plus (DP) is a chlorinated flame retardant, which was introduced as a substitute for Dechlorane (also called Mirex) by Hooker Chemical (now a part of Occidental Chemical Corporation and known as OxyChem) in the mid-1960s. The commercial product consists of two conformers, *syn* and *anti*, in a ratio of about 1:3. The structures are shown below. Dechlorane Plus is still being used. Major applications of DP are industrial polymers used for coating electrical wires and cables, connectors used in computers, and plastic roofing material¹. 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). Otherwise, there was no scientific literature about the fate of this compound in the environment or about its toxicity.



DP in the Great Lakes regional atmosphere. Work in our laboratory found that Dechlorane Plus was present in the gas and particle phases of the atmosphere² and in precipitation samples³ collected at six sites on the North American Great Lakes; for a map, see Figure 1. These atmospheric and precipitation total DP concentrations are summarized in Figure 2 as box plots. The mean DP atmospheric concentration was highest at Sturgeon Point, where the average concentration was 20 ± 6 pg/m³ (mean \pm one standard error) and second highest at Cleveland. Point Petre showed the highest average DP concentration in precipitation (950 ± 190 pg/L) followed by Cleveland and Sturgeon Point. In general, much higher DP concentrations were observed at the three eastern Great Lakes sites (Cleveland, Sturgeon, and Point Petre) in both air and in precipitation, suggesting a local source for this compound.

The single highest DP atmospheric concentration (490 pg/m³) occurred at Sturgeon Point on July 2-3, 2004. This is clearly not an urban effect; 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 the city of Niagara Falls, New York. This plant is operated by OxyChem, the only producer of DP in the United States (see 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. We suggest that the higher DP concentrations observed at the three eastern Great Lake sites, compared to the western sites, might be explained by "leakage" of DP from its manufacturing facility.

While not atmospheric samples in the strictest sense, Zhu et al.⁴ measured DP concentrations in 76 residential indoor dust samples collected from homes in Ottawa, Canada, in 2002-2007 and found median concentrations of 15 ng/g of dust. For comparison, the median concentration of BDE-209 in these samples was 630 ng/g of dust. From these levels Zhu et al. calculate an average annual exposure of 20 ng for an adult and 300 ng for a child and a maximum exposure of 400,000 ng for a child. It is not clear if these are toxicologically significant levels.

DP in Great Lakes sediment. Our laboratory also found DP in sediment cores from Lakes Michigan, Erie, and Ontario^{2,5}. The surficial concentrations of total DP were are 5 ng/g dry wgt in Lake Michigan, 2.5-40 ng/g dry wgt in Lake Erie (higher in the east), and 150 ng/g dry wgt in Lake Ontario. These concentrations suggest a DP source between Lakes Erie and Ontario. It is interesting to note that DP is the single most abundant flame retardant in Lake Ontario's sediment and that the total load (burden) of DP in this lake is ~25,000 kg⁵. Subsequently, Tomy et al.⁶ analyzed sediment from Lakes Ontario and Winnipeg and measured DP concentrations of 210 and 0.03 ng/g dry wgt, respectively. While this DP concentration in Lake Ontario is similar to those reported elsewhere, the level in Lake Winnipeg is very low. The region around Lake Winnipeg is remote (it is well north of Minnesota, and only 23,000 people live on its shore), and thus, it is likely that the small amount of DP in this lake arrives there by atmospheric transport.

Recently, Sverko et al.⁷ reported DP concentrations in 0.06-8.6 ng/g dry wgt in Lake Erie and 2.2-590 ng/g dry wgt in Lake Ontario in 40 surficial sediments from these two lakes. In general, the DP concentration was ~50 times higher in Lake Ontario compared to Lake Erie. These authors also measured DP in two undated sediment cores from Lake Erie and noted much higher concentrations in the central basin compared to the western basin. They also analyzed some archived suspended sediments collected from the Niagara River; these results showed a declining trend in total DP concentration over the period 1980 to 2002, which roughly agrees with the sediment core data and which suggests a possible decrease in DP production or a reduction DP release into the environment. These authors also noticed the presence of DP-like products with one and two fewer chlorine atoms in their samples; it is not clear if these dechlorinated products are impurities in the technical DP material or are environmental degradation products. Taken together these authors' data suggests a source of DP between Lakes Erie and Ontario, probably the DP manufacturing facility on the Niagara River.

DP in biota. Our laboratory detected DP in archived fish (walleye) samples from Lake Erie at levels in the range of 0.14-0.91 ng/g lipid wgt². DP has also been found in herring gull eggs at levels of 1.5-4.4 ng/g wet wgt, with the maximum concentrations in a colony near the Niagara River⁸. For comparison, the concentrations of total PBDEs in these egg samples ranged from 290-660 ng/g wet wgt, and there was no correlation by location between these two concentrations. Tomy et al.⁶ reported total DP concentrations in food web biota samples ranging from 0.02-4.4 ng/g lipid in Lake Ontario and from 0.04-0.8 pg/g lipid in Lake Winnipeg and concluded that DP in sediment is "bioavailable".

DP in tree bark from the northeastern U.S. To investigate the spatial distribution of DP in a broad geographical region, it would be helpful to have several atmospheric samples taken over the entire area to be studied. Rather than set up active (pump and trap) samplers at a few selected sites, we have used samples collected passively. Although polyurethane foam (PUF) passive samplers have been shown to be effective⁹, they have the disadvantage of requiring deployment for several months. Tree bark, on the other hand, is an easy and inexpensive monitor of persistent organic pollutants. Previous work has shown that tree bark is a good passive sampler for semi-volatile organic compounds with high K_{oa} values. Such analytes include organochlorine pesticides^{10,11}, polychlorinated biphenyls (PCBs)¹², PBDEs¹³, and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs)¹⁴.

The DP concentrations we measured in tree bark collected from the northeastern United States of DP are shown in Figure 3. These reported average concentrations are from the triplicate bark samples collected at each site. Given that DP was never directly applied to trees, it seems likely it has accumulated in the tree bark by way of atmospheric transport. In general, the higher concentrations (>4 ng/g bark) were found in or around the Niagara Falls and Buffalo areas of New York state. The highest concentration (115 ng/g bark) was found in the Hyde Park neighborhood, a location which is ~2 km away from OxyChem's DP manufacturing facility. With increasing distance from this potential source location, the concentrations of DP in tree bark decreased rapidly, but DP was still detected at low levels (0.03-0.04 ng/g bark) in samples from Virginia, Maryland, and Indiana.

It has been shown that concentrations of persistent organic pollutants in tree bark decreased rapidly with increasing distance a source and that tree bark concentrations could be used to locate these sources¹⁵. Previously, we have used a simple radial diffusion model to pinpoint source locations^{11,13}; however, this model neglected the

advective transport process of a pollutant as it moves through the atmosphere. Thus, we have improved on this simple dilution model by including advective transport in a Gaussian diffusion model¹⁵. This simplified Gaussian diffusion model is represented by $\log(C_{\text{bark},i}) = -(a_1 + a_2) \log(d_i) + K'$, where $C_{\text{bark},i}$ is the concentration of DP in tree bark at location i , d_i is the spherical distance of location i from the source, and a_1 and a_2 and K' are fitted constants. Using Pasquill's stability classes, a_1 ranges from 0.59 (moderately stable conditions) to 0.90 (extremely unstable conditions), and a_2 ranges from 0.50 (moderately stable conditions) to 1.38 (extremely unstable condition)¹⁶. Thus, the term $(a_1 + a_2)$ could range from 1.1 to 2.3, but for the most typical case (neutral conditions), $(a_1 + a_2)$ would be ~ 1.5 .

We have implemented this calculation by assuming that we did not know the location of the source, and we let the latitude and longitude of the source vary to calculate the various values of d_i . For each sample, we had measured C_i values, and we had calculated d_i . We then minimized $\xi_d = \sum_i [K' d_i^{-(a_1+a_2)} - C_{\text{bark},i}]^2$. With the assistance of the Solver feature of Excel, the fitted variables for the DP data set were obtained. The results were $K' = 10^{2.7}$, $(a_1 + a_2) = 1.42$, and the source location was calculated to be at 43.124, -78.953, with an r^2 between the observed and expected values of 0.872. This fitted source location is less than 7 km northeast of the OxyChem plant (see Figure 3). Despite the uncertainties of this approach, we conclude that DP's source is located in Niagara Falls, New York.

DP in tree bark from Europe and Asia. To evaluate the global impact of DP and BFRs, we obtained and analyzed tree bark samples from other countries. DP was not detected in tree bark from the southern Northwest Territories in Canada; however, DP was detected in all the other samples from Europe and Asia. In Germany and Italy, DP concentrations were similar to the lowest concentrations we measured in bark from the northeastern U.S.; in China and Korea, DP concentrations were nearly one order of magnitude higher than the lowest concentrations in the northeastern U.S. This latter observation suggests that there may be Asia-specific sources of DP to the environment.

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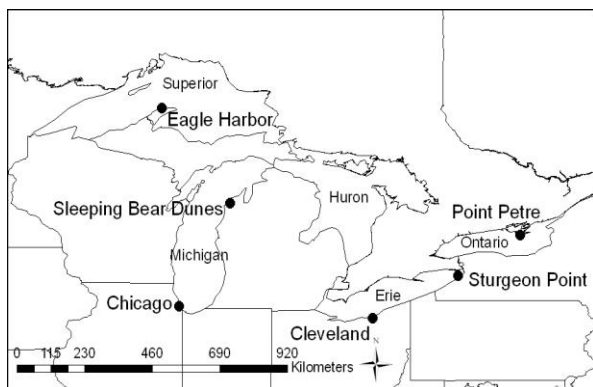


Figure 1. Map of the Great Lakes showing the six air sampling sites. OxyChem's DP manufacturing plant is in the city of Niagara Falls, New York, which is on the Niagara River, which flows north connecting Lakes Erie and Ontario. The site abbreviations are EH, Eagle Harbor; CH, Chicago; SB, Sleeping Bear Dunes; CL, Cleveland; SP, Sturgeon Point; and PP, Point Petre.

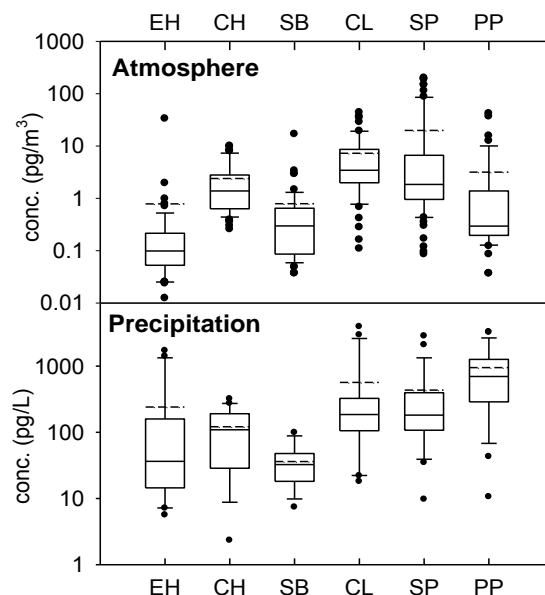


Figure 2. Total DP concentrations at each sampling site. The horizontal lines represent the 10th, 50th, and 90th percentiles; the boxes represent the 25-75th percentiles; the dashed lines represent the means; samples outside of 90th and 10th percentiles are given individually.

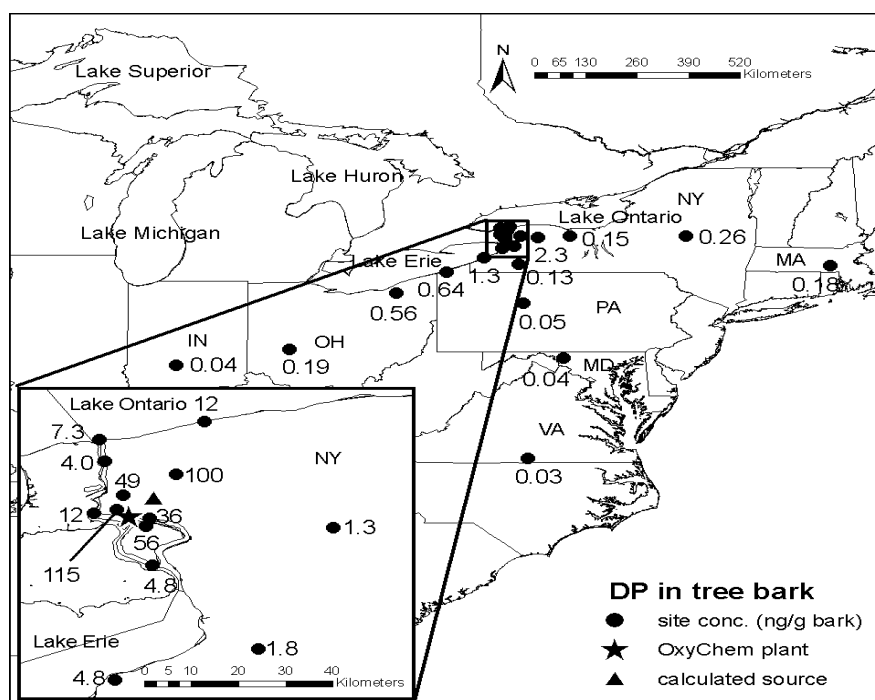


Figure 3. Map of tree bark sampling sites and the corresponding DP concentration (ng g^{-1} bark). The star represents the DP manufacturing plant located in Niagara Falls, NY. The triangle represents the calculated source location. [Reprinted from Qiu X. H. and Hites R. A. *Environ Sci Technol* 2008; 42: 31.]