

## A Recently Discovered Flame Retardant in the Environment, Dechlorane Plus®: Fate and Levels in the Lower Great Lakes

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### Introduction

In the last few years flame retardants have received considerable attention from environmental scientists, and more recently regulators, as the physical-chemical properties that make such compounds very useful as flame retardants also give rise to environmental concern.

Polybrominated diphenylethers, especially the penta and octa formulations, now face regulation worldwide. Although focus has been on the brominated flame retardant chemicals, a *chlorinated* flame retardant, called Dechlorane Plus (DP), was recently measured in air and sediment samples for the first time in the Great Lakes region where it has been produced since the 1970s (Hoh *et al.* 2006). This compound has not been commonly identified in the environment before.

An earlier chlorinated flame retardant developed by Hooker Chemical (now Oxychem, Niagara Falls, NY, USA), called Dechlorane or Mirex, was banned because of its toxicity to marine invertebrates. In 1972, DP was developed to replace Mirex with production volumes reported to be one million pounds annually (Betts K.S. 2006). DP is an additive flame retardant that is compatible with a range of polymers, and is used in wire coatings and plastic roofing materials (Occidental Chemical Corp., DP Manual). While DP is on the Domestic Substances List (DSL) it does not rank highly in terms of risk for bioaccumulation because of its high molecular weight and high log Kow (9.3). However, the data in the Hoh *et al.* (2006) article tend to support the DSL categorization ranking in terms of persistence and bioaccumulation.

The technical DP formulation, although primarily comprised of *syn* and *anti* isomers (Fig. 1), includes other by-products and therefore accurate quantitative analysis was not possible. A newly purified DP standard (Wellington Laboratories, Guelph, ON, Canada) was used to accurately quantify concentration levels. Further investigation into the by-products in the technical mixture resulted in the discovery of other possible minor isomers and dechlorinated moieties. An analytical method has been developed to measure the *syn*- and *anti*-DP isomers to determine their fate in the lower Great Lake sediments. Furthermore, tentative identification of a number of the technical mixture by-products is presented and their occurrence in the lower Great Lakes. This is the first study in which DP levels, and their related by-products, are reported in Lakes Erie and Ontario surficial sediment.

### Methods and Materials

*Sampling:* Surficial sediment samples were collected aboard the *CCGS Limnos* via the mini box coring procedure. Samples were freeze dried, transferred to a Teflon-lined, capped glass jar and frozen (-20°C) until analysis.

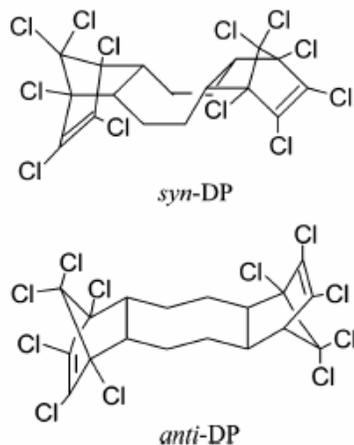
*Extraction and Analysis:* After the addition of surrogates (CB30 and CB204), samples (5 g) were extracted using pressurized fluid extraction with acetone:hexane (1:1, v/v). Extracts were purified using modified silica gel and fractionated into A and B with hexane and DCM:hexane (1:1, v/v), respectively. Fraction B was injected onto an Agilent (Mississauga, ON, Canada)

5980 GC, fitted with a 30 m DB-5 capillary column (0.25  $\mu\text{m}$  film thickness x 0.25 mm i.d; J&W Scientific, Folsom, CA, USA), coupled to a 5973 mass selective detector. Splitless injections of 2  $\mu\text{L}$  were made onto an injector set isothermally at 265°C. The initial oven temperature was set at 80°C with a 2 min hold time, ramped at 10°C/min to 295°C, and held for 5 min. The MS analysis was performed in the electron capture negative ion (ECNI) mode using methane as the buffer gas. Source and quadrupole temperatures were set to 150°C and 106°C, respectively. The dominant peak in the molecular ion cluster of the *syn* and *anti* isomers ( $m/z$  651.8; spectra were identical) was used for quantitation while the second most abundant peak ( $m/z$  653.8) was used for confirmation. Measurement of the dechlorinated isomers,  $\text{C}_{18}\text{H}_{13}\text{Cl}_{11}$  and  $\text{C}_{18}\text{H}_{14}\text{Cl}_{10}$  was conducted by monitoring  $m/z$  ions 617.7/619.7 and 583.8/585.8, respectively. Extraction efficiencies of the chlorinated biphenyl surrogates were measured during OC analyses by GC/ECD. All recoveries were within 75% - 118%.

Method detection limits (MDLs) were estimated from the procedural blanks which consisted of Ottawa sand. No amount of both isomers were detected in the blanks. Using an average sample mass of 5 g, MDLs of 0.9 pg/g and 4.5 pg/g for *syn*- and *anti*-isomers were determined. The linear dynamic range of the instruments was 10 pg to 2500 pg on column ( $r^2 > 0.995$ ) for both isomers. The ratio of the quantitation and confirmation ions in samples was within 15% of measured standard values in all cases.

*Identification of DP By-products:* Identified suspect peaks were analysed for exact mass using the Agilent 5890 GC coupled to a Micromass (Mississauga, ON, Canada) TOFMS in both negative ion chemical ionization and electron ionization modes (resolution @5000). Elemental compositions of the unknown compounds were determined within 3.5 ppm error.

**Figure 1.** Molecular structures of the major isomers in technical DP ( $\text{C}_{18}\text{H}_{12}\text{Cl}_{12}$ ).

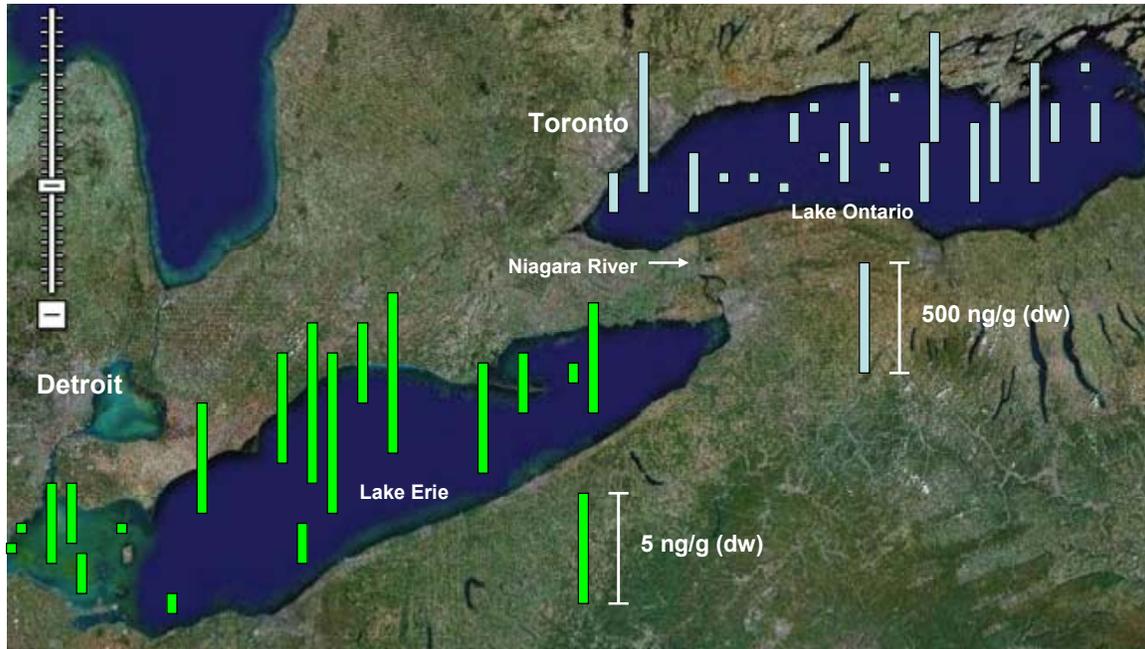


## Results and Discussions

*Levels of syn- and anti-DP:* The total dry-weight DP concentration ranges for Lakes Erie and Ontario were 0.061 ng/g – 8.62 ng/g and 2.23 ng/g – 586 ng/g, respectively (Fig. 2). The non-depositional zones showed the lowest levels because of continual redistribution into the water column. The central basin in Lake Erie exhibited the highest concentrations throughout the lake and, although Lake Ontario's central basin did follow a similar trend, the highest level was measured near the city of Toronto. This is somewhat puzzling if one was to consider the Niagara River as the point source and the counter clock-wise flow pattern of the lake. A possible contribution to the lake's DP burden would be the cable manufacturers who include DP in their

cable formulation. This may suggest a possible secondary source into the lake. However, the significant difference DP concentrations between lakes, strongly points to the Niagara River as a main DP contributor to Lake Ontario.

Figure 2. Levels of total *syn* and *anti*-DP isomers in surficial sediment in Lakes Erie and Ontario.



Note scale difference between lakes.

*Syn- and anti-DP ratios:* The main isomer ratios can be described as fractional abundance, where  $f_{syn}$  would be the amount of *syn*-DP divided by the total *syn*- and *anti*-DP concentration. Table 1 shows the summary of these calculations for the Lakes and the technical DP. We also were able to compare these data to fractional abundances measured in the Niagara River suspended sediment (Reiner E., Study by the Ontario Ministry of the Environment). The table obviously shows the stereo selective enrichment of the *anti* isomer when compared to the technical DP. This holds true for all data except in the Lake Erie non-depositional zones, where  $f_{anti}$  is close to the technical DP abundance. While the non-depositional zones tended to exhibit lower  $f_{anti}$  values than depositional areas of the lake, the opposite occurs in Lake Ontario where  $f_{anti}$  values increase in the non-depositional zones. The overall mean  $f_{anti}$  abundance in Lake Ontario is greater than that of Erie's and may reflect the similar fractional abundance profile exhibited in the Niagara River suspended sediments, which flows into Ontario.

Table 1. Comparison of mean fractional abundances.

Location	$f_{syn}$	$f_{anti}$	n
Lake Erie (Depositional)	0.220	0.780	14
Lake Erie (Non-depositional)	0.319	0.681	6
Lake Ontario (Depositional)	0.167	0.833	19
Lake Ontario (Non-depositional)	0.069	0.931	7
Niagara River	0.099	0.901	12
Technical DP	0.355	0.645	3

*Identification of DP By-products:* The chromatogram of technical mixture exhibited some minor peaks in and around the retention time of major *syn*- and *anti*-DP isomers. Successive single ion monitoring analyses using the GC-ECNIMSD showed what looked like possible -Cl and -2Cl isomers. However, the Oxychem Material Safety Data Sheet indicates that DP begins to thermally breakdown at 300°C, therefore an investigation was conducted to determine whether dechlorination was possibly occurring in the instrument and giving rise to these extra peaks. GC injector temperature studies (220°C – 300°C) did not change the overall chromatographic profile of any of the compounds and therefore no breakdown is likely occurring. In fact, no peaks were evident at an injector temperature of 220°C indicating that the compounds did not evaporative off of the liner. As a precaution, all other MS components were kept at 290°C or less during sample analysis.

GC-TOFMS analysis and elemental composition determinations indicated two -Cl compounds and two -2Cl compounds which were related to molecular formulae  $C_{18}H_{13}Cl_{11}$ , and  $C_{18}H_{14}Cl_{10}$ , respectively (error <3.5 ppm). GC-ECNIMSD semi-quantitative analyses of select Lake Ontario sediment measured these compounds near, or above, the *syn*- and *anti*-DP levels (i.e. measured at similar chromatographic peak intensity). If these chemicals are in fact related to the DP formulation, toxicity implications need to be addressed because the Log  $K_{ow}$  generally decreases with decreasing chlorination. If any of the Log  $K_{ow}$  of these compounds are below 8.0, bioaccumulation could become an important environmental pathway, as suggested by the UN Environmental Commission.

## References

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