

## ISOMERS OF DECHLORANE PLUS® AND NEWLY IDENTIFIED COMPOUNDS IN SEDIMENT OF THE LOWER GREAT LAKES

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### Abstract

A recently discovered chlorinated flame retardant, Dechlorane Plus (DP), was reported in air and a sediment core within the North American Great Lakes region. To further reveal the fate of DP in the Great Lakes, 40 surficial sediments from Lakes Erie and Ontario were analyzed. The maximum total concentration in Lake Ontario was over 60-fold higher than Lake Erie, 586 ng/g and 8.62 ng/g, respectively. Additionally, analysis of archived suspended sediments collected from the Niagara River (1980 – 2002) showed a declining total DP concentration of 89 ng/g to 7.0 ng/g, suggesting a possible decrease in production or the reduction of free DP released into the environment during manufacturing. The average *syn*-DP fractional abundance ( $f_{syn}$ ) in our study was less than the commercial DP composition indicating a stereo selective enrichment of *anti*-DP in the environment. During the course of the analysis, apparent DP related degradates were also detected in sediments from the Niagara River and Lake Ontario; identified as [-Cl+H] and [-2Cl+2H] by high resolution mass spectrometry (< 3.7ppm error). To our knowledge, this is the first report of DP degradates in the environment.

### Introduction

Dechlorane Plus® is an additive chlorinated flame retardant used primarily in wire cable coatings and plastic roofing material. The United States EPA has categorized this chemical as a High Production Volume Chemical (HPVC) with estimated production volumes at more than one million pounds annually.<sup>1</sup> Although focus has been on the brominated flame retardant chemicals, the chlorinated flame retardant, Dechlorane Plus® (DP, CAS #13560-89-9), was recently measured in air and sediment samples in the Great Lakes region where it has been produced for over 40 years.<sup>2</sup> An earlier chlorinated flame retardant developed by Hooker Chemical (now OxyChem, Niagara Falls, NY, USA), called Dechlorane or Mirex (C<sub>10</sub>Cl<sub>12</sub>), was banned because of its toxicity to marine invertebrates. The DP (C<sub>18</sub>H<sub>12</sub>Cl<sub>12</sub>) formulation replaced the banned flame retardant with subsequent production volumes estimated to be one million pounds annually and potentially as high as 10 million<sup>1,3</sup>. While DP is on the Canadian Domestic Substances List it does not rank highly in terms of risk for bioaccumulation because of its high molecular weight and log K<sub>ow</sub>, 9.3, however data reported by Tomy *et al.* show bioaccumulation for certain organisms in food webs of Lakes Winnipeg and Ontario.<sup>4,5</sup> Additionally, Oxychem's submission to the voluntary EPA HPV Challenge Program indicates that DP has ecotoxicological effects in fish and may affect sediment bearing organisms due to its adsorptive properties.<sup>4</sup> Sediments in the Great Lakes are the main repository for hydrophobic and persistent organic pollutants such as polychlorinated biphenyls (PCBs) and decabromodiphenyl ether (BDE209).<sup>6,7</sup> In this paper we present spatial DP distribution in surficial sediments for Lakes Erie and Ontario, its temporal trend in Niagara River suspended sediment and new dechlorinated compounds likely relating to DP.

### Materials and Methods

Surficial sediment samples for Lake Erie and Lake Ontario were collected in 1997/1998 and 1998, respectively, aboard the *CCGS Limnos* via the mini box coring technique. Samples comprised of the top three centimeters of lake-bottom sediment were freeze dried, transferred to a Teflon-lined, capped glass jar and frozen (-20°C) until analysis. Niagara River suspended sediments were collected by centrifuging large volumes (~8000 L) of Niagara River water at Environment Canada's Niagara-on-the-Lake monitoring station, near the mouth of the river. For this study, samples collected mid-March (1980 – 2002) were analyzed to capture spring runoff with higher particulate loads. Bottom sediment samples were processed at Environment Canada's National Water Research Institute in Burlington, ON. After the addition of

recovery surrogates (CB30 and CB204, Accustandard, New Haven, CT, USA), the samples (5 g) were extracted using pressurized fluid extraction (Dionex Corp., Mississauga, ON, Canada) with acetone:hexane, 1:1 (v/v). Extracts were purified with modified silica gel, fractionated into A and B with hexane and DCM:hexane, 1:1 (v/v), respectively. Fraction-B, which contains the DP isomers, was injected onto an Agilent (Mississauga, ON, Canada) 5980 GC, fitted with a 30 m DB-5 capillary column (0.25  $\mu$ m film thickness x 0.25 mm i.d.; J&W Scientific, Folsom, CA, USA), coupled to an Agilent 5973 mass selective detector in negative ion chemical ionization mode using methane as the reagent gas. Split/splitless injections of 1  $\mu$ 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 285°C, and held for 5 min. 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. Measurements of the dechlorinated Cl<sub>11</sub> and Cl<sub>10</sub> moieties were conducted by monitoring  $m/z$  ions 617.7/619.7 and 583.8/585.8, respectively. Niagara River suspended sediments were processed by Soxhlet extraction for 18 hours using toluene. The raw extracts were cleaned by silica column chromatography eluted with 50:50 DCM:hexane. The DP stereoisomers were detected and quantified using the same procedures as described above. All concentrations are given on a dry weight of sediment basis. All recoveries for CB30 and CB204 were  $78 \pm 12\%$  and  $97 \pm 14\%$ , respectively ( $\pm 1$  SD).

### Results and Discussion

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 (Figure 1). The lake-wide average in Lake Ontario was more than 60 times greater than Lake Erie. In comparison, Li *et al.* (2005) reported Lake Ontario surficial sediment total PBDE levels of only four fold over Lake Erie.<sup>9</sup> This strongly suggests that the Niagara River is a likely source, being an area in which DP is manufactured. The central basin in Lake Erie exhibited the highest concentrations throughout the lake, however these concentrations were approximately five times lower than for BDE209 surficial concentrations reported by Song *et al.*<sup>7</sup>

The spatial distribution of DP in Lake Ontario was generally related to bathymetry, with the highest concentrations associated with fine grained sediments in the three major deep-water depositional basins (Figure 1), while the non-depositional sill zones exhibited the lowest levels. These sill zones are characterized by coarse sand that adsorb hydrophobic contaminants less effectively than fine silts and clays in depositional areas. In contrast to the lower comparative Lake Erie DP levels to the BDE209 concentrations reported by Song *et al.*, Lake Ontario DP values were approximately twice the BDE209 concentrations.

As a means of elucidating temporal trends in DP accumulation in Lake Ontario sediments, archived samples from the Niagara River Upstream/Downstream program were analyzed. The maximum and minimum values for total DP in Niagara River suspended sediments (1980 – 2002) ranged from 89 ng/g (1980) to 7 ng/g (1999). A slight but significant ( $p < 0.05$ ) decline in total DP concentration with time was observed with a half-life of approximately 17 years, corresponding to a 1 ng/g decline per year. Song *et al.* measured a doubling time for PBDEs of 5.3 years in Lake Erie attributable to increasing usage and manufacturing patterns. The DP half-life suggests that usage/production may be decreasing or that modern manufacturing processes release less free DP into the environment.

The main stereoisomer ratios in sediment as measured in the environment can be described as fractional abundance, given by:

$$f_{syn} = [syn-DP]/([syn-DP] + [anti-DP])$$

The fractional abundance of DP for Lakes Erie and Ontario, the Niagara River and commercial DP are shown in Table 1. These data show stereo-selective enrichment of the *anti* isomer when compared to the technical DP profile. This holds true for all data except in Lake Erie where the  $f_{syn}$  is more similar to the technical mixture. In this study, only Lake Erie is upstream of the Oxychem plant which Hoh *et al.* suggested atmospheric deposition as a possible source to the lake. It is interesting to note that the fractional abundance of the Niagara River sediments is significantly different from the commercial mixture. This is somewhat surprising when considering the proximity of the sampling site to the manufacturing plant.

There is no significant change or trend in the  $f_{syn}$  abundance during the 22 year sampling period.

Only one Log  $K_{ow}$  value of 9.3 was given by Oxychem's laboratory in 1979 for both *syn*- and *anti*-DP stereoisomers<sup>4</sup>. However, the same document stated that the two isomers had different aqueous solubility

at 207 ng/L and 572 ng/L, although no information was given as to which isomer exhibited which solubility. This would suggest that *syn*- and *anti*-DP possess differing physico-chemical properties and may be one of the factors contributing to the fractional abundance profile in the Niagara River suspended sediment.

The technical DP product information suggests thermal decomposition begins at 285°C<sup>4</sup> however, no indication of any identified decomposition by-products are given. Although our instrument operating temperatures were below the reported decomposition temperature, successive full scan analysis of our analytical standards resulted in the presence of new peaks within a sample sequence. The corresponding m/z ion fragment clusters of the unknown peaks related to [-Cl+H] and [-2Cl+2H] species giving rise to m/z ions of 613.7 and 579.8, respectively (Figure 2e, 2f). Once the GC liner was replaced, the dechlorinated species were no longer evident suggesting that these compounds were produced and mediated by the “dirty” glass liner via in-situ dechlorination mechanisms. Using a clean liner, certain sediment samples also showed several compounds which were tentatively identified as the same compounds produced in the “dirty liner” injections. These unknowns were particularly prevalent in the Niagara River suspended sediment from Niagara-on-the-Lake, some higher in peak area than *syn*- and *anti*-DP (Figure 2d). The chromatogram exhibits the apparent existence of several [-Cl+H] and [-2Cl+2H] species confirmed by elemental composition using GC/TOFMS to within 3.7 pmm error. Initial analysis of suspended and lake-bottom sediments reveal the predominance of these compounds resided in the Niagara River. None of these compounds were detected in Lake Erie, however were detected in Lake Ontario suggesting to us that the Niagara River was a major contributor to Lake Ontario’s DP burden.

#### Acknowledgements

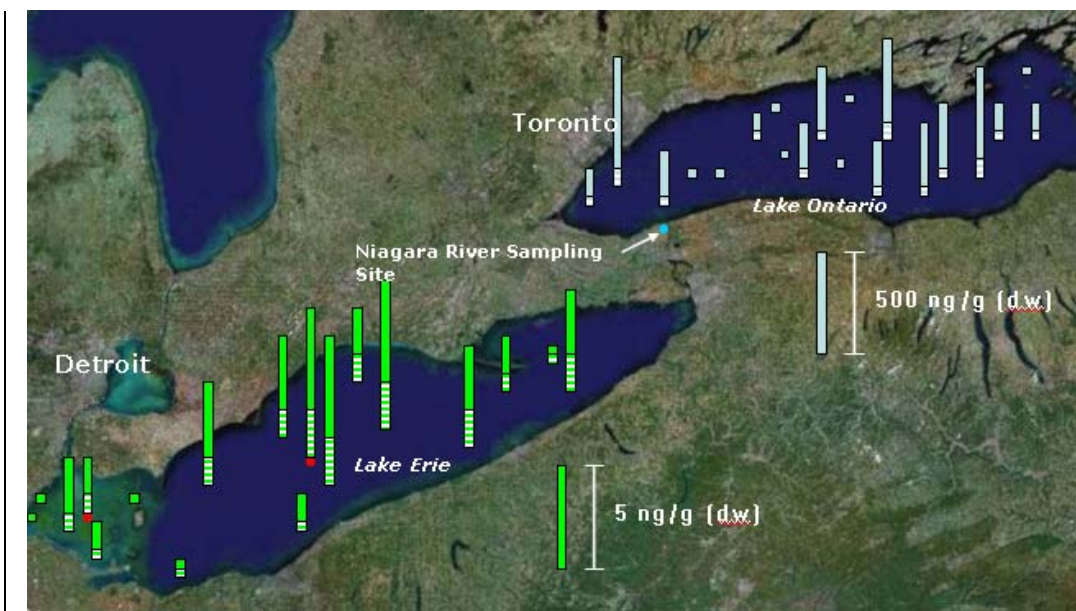
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#### References

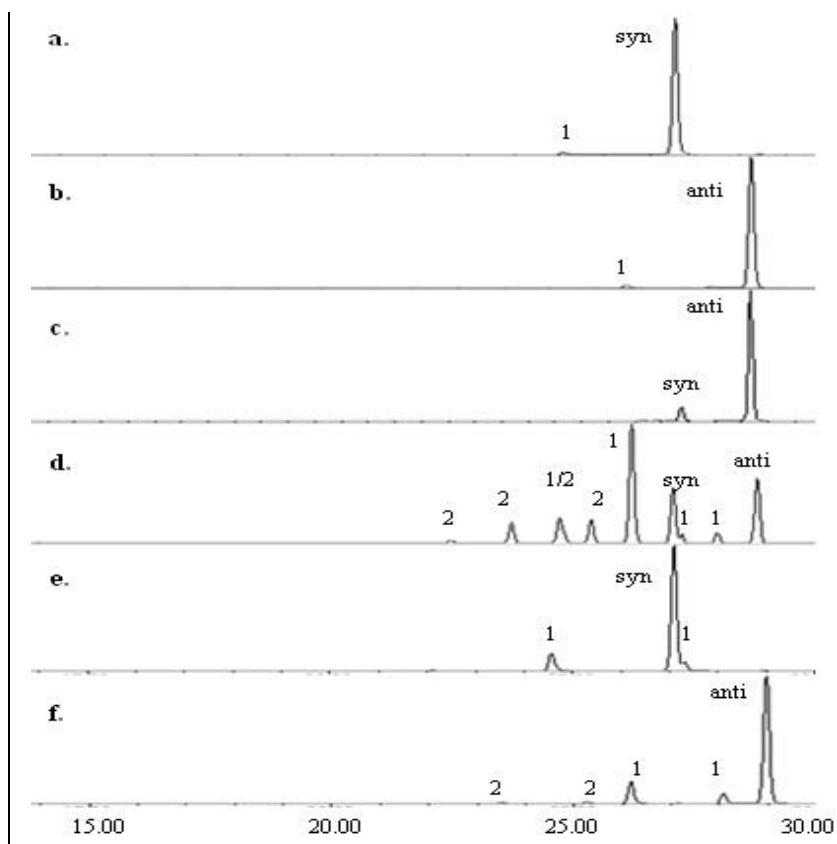
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Location (Zone)	$f_{syn}$	+/- SD	n
Technical DP	0.355	0.004	3
Niagara River	0.099	0.042	22
Lake Ontario (depositional)	0.167	0.061	14
Lake Ontario (non-depositional)	0.069	0.042	7
Lake Erie (depositional)	0.216	0.066	7
Lake Erie (non-depositional)	0.263	0.082	11

**Table 1.** Comparison of fractional abundances for *syn*-/*anti*-DP isomers between the technical mixture and lower Great Lakes sediment.



**Figure 1.** Total *syn*- and *anti*-DP levels in surficial sediment. Red dots represent core sample sites, lined and solid colors represent *syn*- and *anti*-DP, respectively.



**Figure 2.** Total ion chromatograms of: a.) *syn*-DP; clean liner, b.) *anti*-DP; clean liner, c.) Lake Ontario sediment, d.) Niagara River sediment, e.) *syn*-DP; dirty liner, f.) *anti*-DP; dirty liner. “1” and “2” signify -1Cl and -2Cl dechlorination DP species, respectively.