

PROFILES OF DECHLORANE PLUS AND NEW RELATED COMPOUNDS IN A LAKE ONTARIO SEDIMENT CORE

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Abstract

Although the highly chlorinated flame retardant, Dechlorane Plus (DP), has been manufactured for over 40 years, its occurrence in the environment has only recently been reported. To better understand its historical occurrence in the environment, a sediment core near the manufacturing plant was analysed for DP. DP was first detected in a core depth representing 1971 (74 ng g⁻¹). The concentration range was 23 – 3100 ng g⁻¹, the maximum occurred during 1976-1980. New compounds with similar *m/z* ion ratios to DP and similar peak intensities to *syn*-DP were identified in core samples related to 1974-1978. These compounds were ascribed to impurities in DP's starting material. Synthesized products of these impurities exhibited the same retention times as peaks in question suggesting that these compounds were previously manufactured together with DP. These compounds also exist in shallower, more recent cores, but at lower intensities.

Introduction

Environmental levels of brominated flame retardants (BFRs) have been a primary focus for environmental scientists during the last decade. Polybrominated diphenyl ethers (PBDEs), used extensively in various commercial products, have come under worldwide scrutiny. Notably, the pentabromo and octabromo PBDE formulations have been discontinued either through legislative restrictions or voluntary withdrawals by manufacturers due to concerns related to their toxicity and bioaccumulative properties. While policy makers consider further restrictions on these currently used BFRs, Dechlorane Plus (DP, C₁₈H₁₂Cl₁₂) manufactured since the early 1970s has been measured in the biotic, sediment and atmospheric environmental compartments¹. Few reports currently exist on its occurrence in the environment even though DP is sold worldwide, including Europe and the Far East. In a European Union report, annual importation of DP into the EU was estimated to be 1.1 million pounds². This formulation is used primarily in products such as cable coatings, plastic roofing materials and hard connectors in computers and televisions. The United States Environmental Protection Agency has classified this flame retardant additive as a High Production Volume (HPV) chemical. DP is also on the Canadian Domestic Substances List but not ranked highly in terms of risk for bioaccumulation because of its high molecular mass (684 Da) and high log *K*_{ow} (9.3). However, recent research by Tomy et al. demonstrated the biomagnification properties of DP for certain trophic relationships in food webs within Lake Winnipeg and Lake Ontario, Canada³. Furthermore, the two isomers in the technical DP mixture (*syn* and *anti*) exhibit different biomagnification properties. 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 properties⁴.

To further investigate DP's historical occurrence in the environment and the determination of possible new related compounds, an analysis of a Lake Ontario sediment core, near the manufacturing plant, was conducted.

Materials and Methods

The benthos gravity core sample was collected in Lake Ontario's Niagara River Bar in 2007. Sediment core slices, divided into 1 cm portions from core section 1 – 10 cm, beyond which 2 cm portions were collected. Sediment samples were freeze-dried and stored at -20 °C until extraction. The ²¹⁰Pb profile of the sediment core was used to determine the sedimentation rate (0.80 g cm⁻² yr⁻¹). After the addition of performance recovery standards (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 contained the DP and related compounds, was injected onto an Agilent (Mississauga, ON, Canada) 5980 GC, fitted with a 30 m DB-5 capillary column (0.25 μm film thickness x 0.25 mm i.d), 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 μL 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. 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. All concentrations are reported on a dry weight basis.

Results and Discussions

Core Profile

The Niagara River Bar is located 16 km from the mouth of the Niagara River and is the first area of sedimentation down stream of the river (LO1, Figure 1). Our core taken within the Bar would therefore primarily represent an historical profile for chemicals stemming from the Niagara River. Our previous research showed that the river was the main, if not only, contributor to Lake Ontario's DP burden; likely due to the manufacturer's location upstream⁵. DP was first detected in the core extracts in 1970. The sample concentration of DP was 23 ng g^{-1} in the surficial sediment with a maximum concentration of 3100 ng g^{-1} occurring between 1976-1980. This maximum is 10-fold higher than that reported by Qui et al. in a central Lake Ontario core⁶. This is likely attributed to the propensity for DP to be entirely particle bound which are largely deposited nearest the river's mouth. Resuspension and distribution throughout the lake causes a dilution effect with resuspended sediment from other "clean" locations within the lake. The suspension and resuspension of DP laden sediment is a process which may take years to lay its footprint throughout the entire lake bottom. This is consistent with the DP core maximum (1994) reported by Qui et al. located in Lake Ontario's central basin⁶. Furthermore, Hoh et al. measured core maxima in Lakes Michigan and Erie between 1975-1980¹. Their suggestion that DP in the lakes is a result from atmospheric deposition released during manufacturing coincides with our maximum measured DP concentration in Niagara River Bar core.

A dramatic decrease in DP levels occurred during 1980-1982 following the core's maximum. In the late 1970's, a community in Love Canal, Niagara Falls, New York, was severely contaminated with industrial chemicals. Subsequently, new state and federal clean water acts were conceived to control free release of these chemicals into the environment. This may help explain the steep decrease in DP concentration during this period. A second, but less dramatic decrease in DP occurred between 1986- 1990. In 1985, a wastewater treatment facility located along the Niagara River attained USEPA approval to receive and process industrial wastewater. To maintain its federal government Water Discharge Permits, the discharge point into the river is monitored annually for certain chemicals including DP. This would be consistent with the prospect that OxyChem began submitting its DP process wastewater to the treatment facility. However, this supposition is complicated by the fact that OxyChem also possesses discharge points for which DP is monitored by the USEPA; suggesting several entry points into the Niagara River may exist.

Identification of New Compounds

Certain chromatograms in our core exhibited five peaks eluting near the DP isomers with similar m/z ion ratios and similar peak intensities to *syn*-DP. This occurred in the deeper core depths relating to 1974-1978. During the course of our research we noted that one of DP's starting material, 1,5 cyclooctadiene (1,5-COD), may also contain 1,3-cyclooctadiene (1,3-COD) and 4-vinyl cyclohex-1-ene (VCH) as impurities^{7,8}. Furthermore, the Diels-Alder reaction of these impurities together with DP's other starting material, hexachlorocyclopentadiene (HCCPD), would result in products possessing the same molecular weight as DP (Figure 3). Wellington Laboratories (Guelph, Ontario) synthesized and provided the Diels-Alder products using purified solutions of these impurities in the presence of HCCPD. Of the five extra peaks in our deeper core samples, retention times for two matched to those in the VCH solution. GC/HRMS analysis confirmed their presence. The existence of these DP related compounds can ostensibly be explained perhaps by the lower grade purity of the 1,5-COD available during the late 1970's. Closer

analysis of the shallower, and more recent cores, also revealed the presence of these extra peaks although in diminished peak intensity. This suggests to us that if these chemicals are related to the manufacturing of DP, products from these impurities in the bulk 1,5-COD starting material are still being produced today. Further investigation is required to better understand their occurrence and source(s) in the environment.

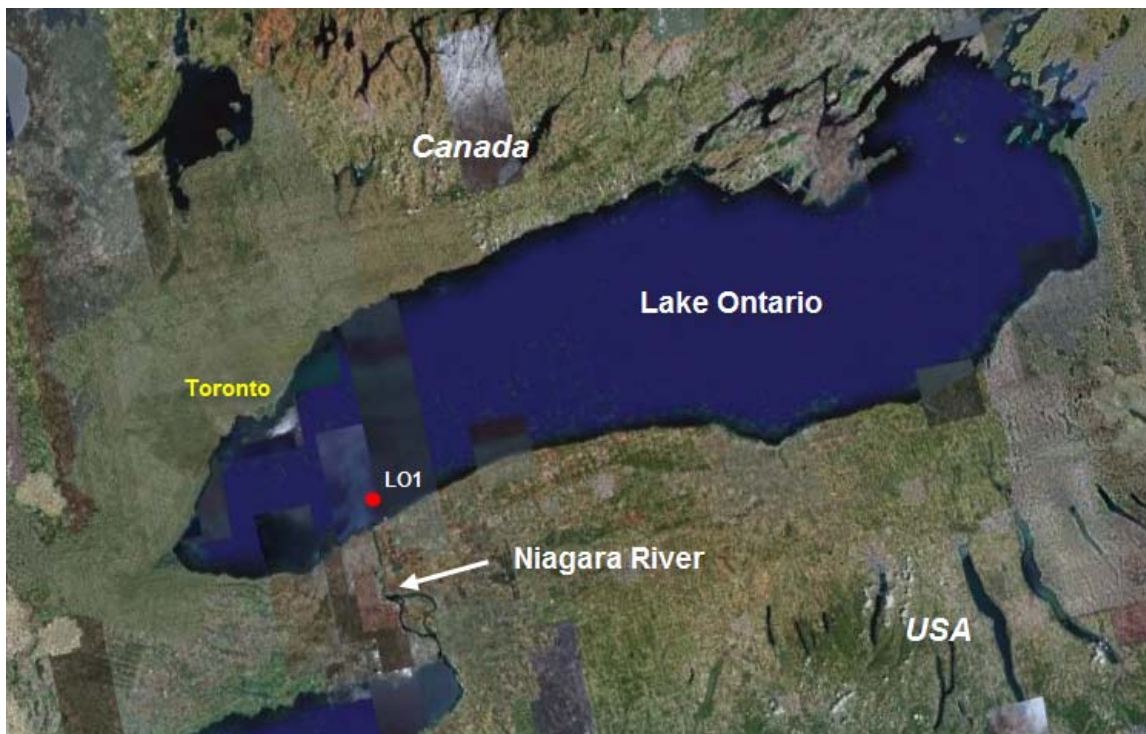


Figure 1. Core sampling site location (red dot) in the Niagara River Bar.

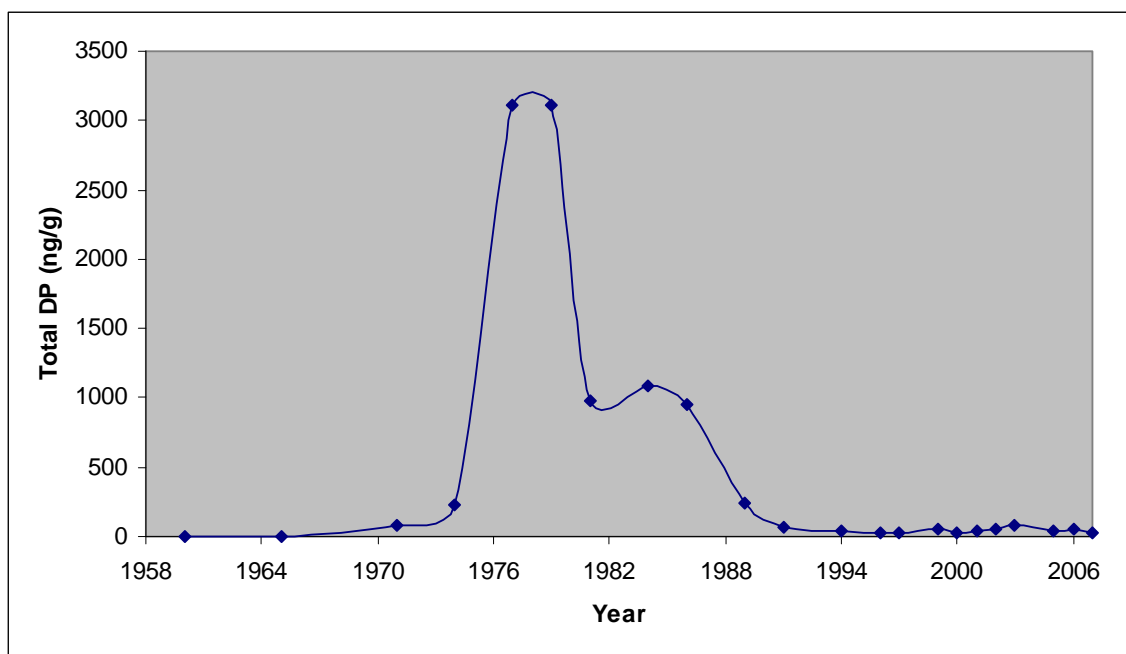


Figure 2. Total DP concentration profile in the Niagara River Bar core.

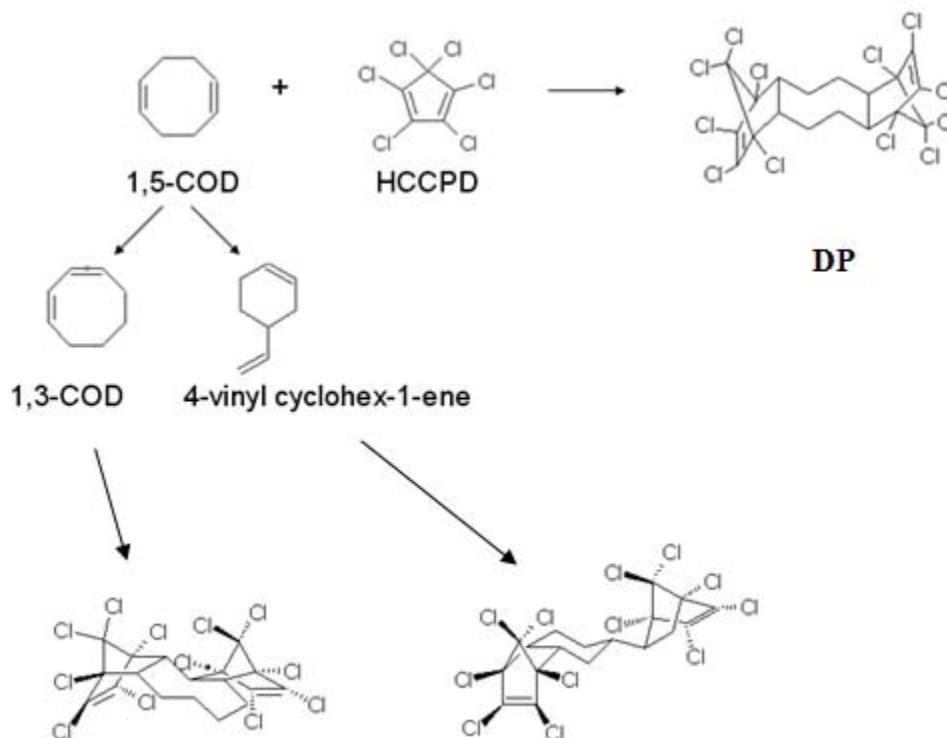


Figure 3. Possible Diels-Alder products from 1,5-cyclooctadiene (1,5-COD) impurities and hexachloro cyclopentadiene (HCCPD).

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