

# HISTORICAL TRENDS OF NON-BDE HALOGENATED FLAME RETARDANTS IN SEDIMENT OF LAKES IN THE GREAT LAKES REGION

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## Introduction

Numerous halogenated flame retardants (HFRs) have been used as additive flame retardants in electronics, building materials, carpeting, and textiles, and can subsequently be detected in environmental matrices. Dechlorane Plus (DP) is an example of an in-use chlorinated flame retardant recently found in the environment (1), and decabromodiphenylethane (DBDPE), 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE) are brominated flame retardants that are in-use and present in the environment (2). Dechlorane (Dec) 602, 603, and 604 are other chlorinated and chloro/bromo flame retardants that also have been recently detected in the Great Lakes basin, and Dec 602 are more bioaccumulated/or bioavailable than those BDE 47 and total PCBs(3-5).

The establishment of an accurate record of the historic trends of current and past-use chemicals of concern in the Great Lakes region is critical for evaluating current policies for virtually eliminating priority pollutants, and for establishing a baseline of information for which to assess new regulatory actions within the basin and around the world. In this study, we report concentrations and temporal trends of several in-use and past-use HFRs in sediment from Lake Ontario of the Laurentian Great Lakes, Lake Simcoe, a large inland lake with urban development and recreational populations within its watershed, and remote lakes within the Great Lakes region. The in-use and past-use HFRs include the dechlorane series flame retardants (DP, Dec 602, 603 and 604) and some other halogenated flame retardants such as 2,2',4,4',5,5'-hexabromobiphenyl (BB153), pentabromoethylbenzene (PBEB), hexabromo-benzene (HBB), 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE), 2-ethylhexyl-2,3,4,5-tetrabromo- benzoate (EHTeBB), and bis(2-ethyl-1-hexyl)tetrabromophthalate (BEHTBP), and octabromotrimethylphenyl-indane (OBIND), decabromodiphenylethane (DBDPE). For comparative purposes, Mirex and polybrominated diphenylethers (PBDEs) are also reported.

## Materials and methods

Analytical standards of Dec 602 (95%), Dec 603 (98%), and Dec 604 (98%) were purchased from Toronto Research Chemical Inc. (Toronto, ON, Canada) and Mirex from Cambridge Isotope Laboratories Inc. (Andover, MA, USA). DP was purchased as *syn*-DP and *anti*-DP standards from Wellington Laboratories Inc. (Guelph, ON, Canada). The non-BDE HRFs and PBDEs standards were also obtained from Wellington Laboratories Inc.

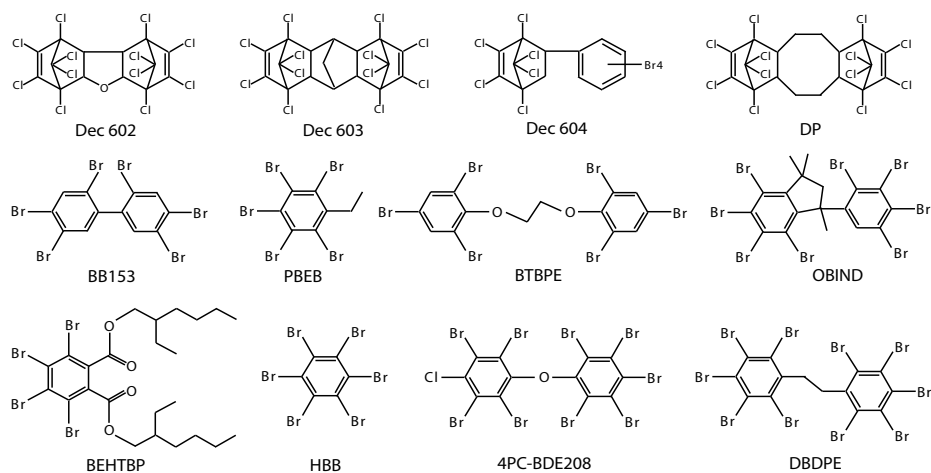


Figure 1. Chemical structures of target HFR analytes

Remote sediment cores were obtained from Siskiwit Lake on Isle Royale in Lake Superior in 2005 and from Plastic Lake near Dorset, Ontario in 2009. Lake Simcoe cores were collected in 2008. In Lake Ontario, sediment cores from station 1004, 1034, and 1046 were collected in 2007. Cores were sectioned into 0.5 or 1 cm slices, with duplicate cores sent for dating and determination of sedimentation rates. Air-dried sections were extracted as described previously.

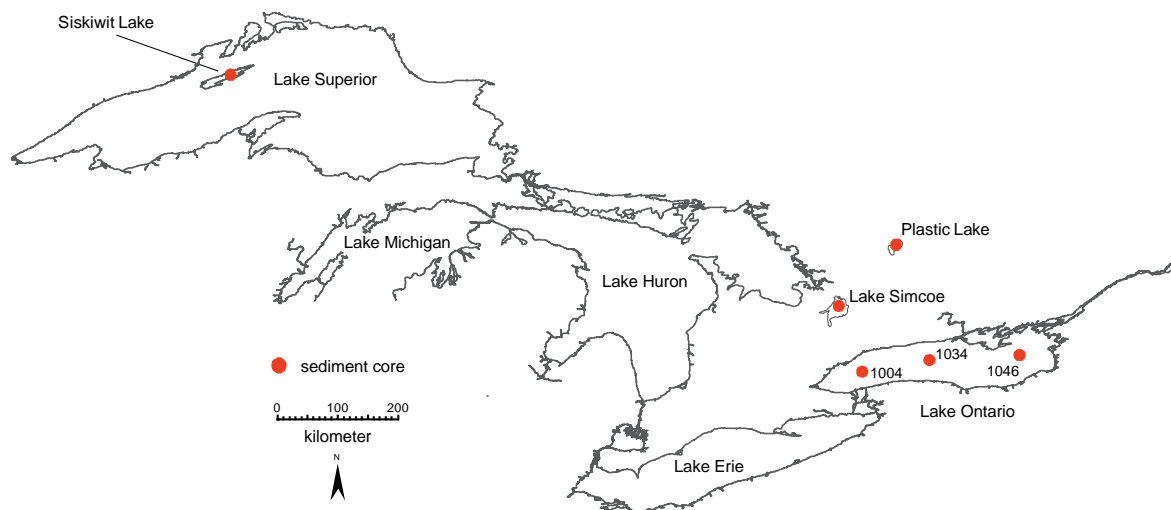


Figure 2. Sampling sites of sediment cores in the Great Lakes region

Determination of Dec 602, Dec 603, Dec 604, and DP in sediments was performed on extracts previously prepared for determination of mono-ortho dioxin-like polychlorinated biphenyls (DLPCBs) according to protocols described previously (6), and the remaining HFRs were measured using extracts for determination of PBDEs (7). All HFRs were analyzed on Agilent Technologies 6890 Plus gas chromatograph (GC) (15 m DB-5HT column, 0.25 mm i.d, 0.10  $\mu\text{m}$  film thickness, J&W Scientific, USA) interfaced to a Waters Autospec-Premier High Resolution Mass Spectrometer (Waters, Manchester, UK) in EI positive with an electron energy of 40 eV and was tuned up to 10,000 resolving power (RP). Quantification was achieved using selected ion monitoring of the two most abundant ions in the fragment clusters.

### Results and discussion:

Figure 3 shows the concentration trends for Mirex, Dec 602, 603, 604, and total DP (sum of *syn*- and *anti*-DP isomers) in the sediment core 1046 of Lake Ontario. For each dechlorane compound, the trends are similar to those found in the core 1004 (4) and 1034 (6). Sediment cores provide an indication of input trends for the target compounds prior to the 1980s when detailed monitoring programs became established. For example, Mirex concentrations gradually increased from the early 1950s, peaked in the mid-1970s, and have declined considerably since then. Dec 603 was found as an impurity in technical Aldrin and Dieldrin (5), and had a temporal trend similar to Mirex. Mirex, Aldrin, and Dieldrin were manufactured beginning in the late 1940s and/or early 1950s and their registered uses were limited by the mid-1970s in North America. Dec 602, 604, and DP concentrations increased in sediments between the mid-1960s and mid-1970s approximately 10 years after Mirex. The maximum concentration of Dec 602 and DP occurred in the early 1980s, and Dec 604 around the mid-1980s followed by decline, but concentrations have not dropped as rapidly as Mirex.

All dechlorane compounds were detected in remote lakes (Siskiwit and Plastic Lake) and Lake Simcoe except Dec 604 was not found in Siskiwit Lake. Concentrations were all lower in the remote lake cores compared to the Lake Ontario core. In comparison, declines are smaller or less apparent in the Simcoe core, and the concentration trend for DP continues to increase in Siskiwit and Plastic Lake (Figure 4). Dec 602 also had higher

concentrations near surface slices in the remote lakes. It was reported that DP had an increasing trend in air samples collected in the Great Lakes region. The source of Dec 602, 604, and DP to the Great Lakes region is mainly from manufacturing plants along the Niagara River (1, 4,5). In addition to Niagara River, Lake Ontario is mainly influenced by industrial, municipal, and other tributary inputs to the lake. The observed decreasing trends may be influenced by production changes, industrial emission abatement efforts, and remedial actions at contaminated locations along the Niagara River. However, the remote lakes mainly receive inputs from atmospheric deposition.

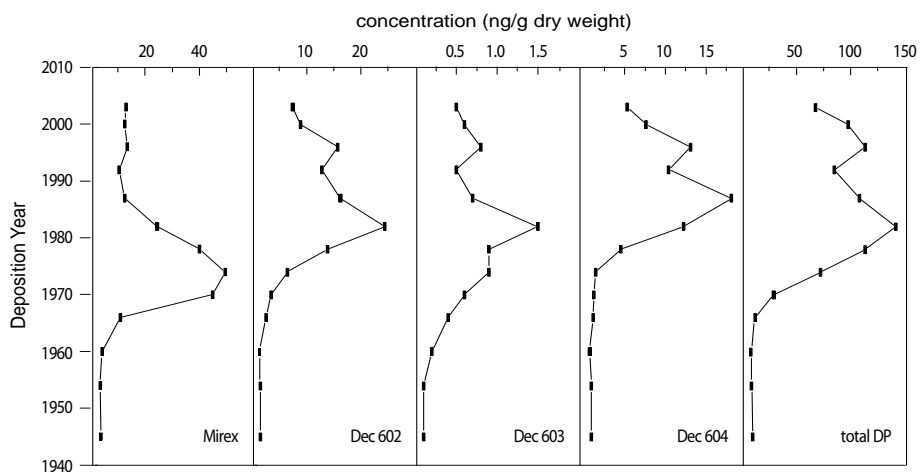


Figure 3. Temporal trends of Mirex, Dec 602, 603, 604, and total DP in Lake Ontario core 1046

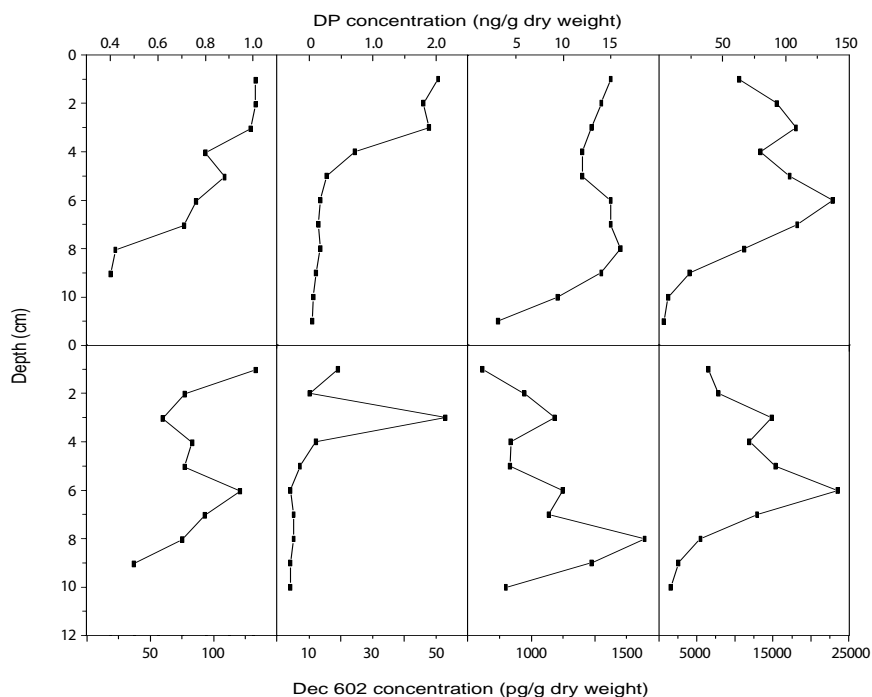


Figure 4. Temporal trends of DP and Dec602 in sediment cores in the Great Lakes region

HBB, PBEB, BB153, BTBPE, BEHTBP, OBIND, 4PC-BDE 208, and DBDPE were detected in most samples, including the core from Siskiwit Lake. Similar to dechlorane compounds, concentrations were all lower in Siskiwit Lake, Plastic Lake, and Lake Simcoe. However, they all had different temporal concentration profiles compared to dechloranes. For example, concentration trends of BTBPE, BEHTBP, OBIND, and DBDPE are presented in Figure 5. As expected, the surface or near surface slices exhibited the highest concentrations of those flame retardant as they are new emerging chemicals found in the environment. BDE 209 is a dominated congener in lake sediment, accounting for more than 90% of total PBDEs. As shown in Figure 5, BDE 209 had an increasing trends until 2000, and then levelled off. However, DBDPE increases rapidly since mid-1990s as a replacement of dec-BDE flame retardant.

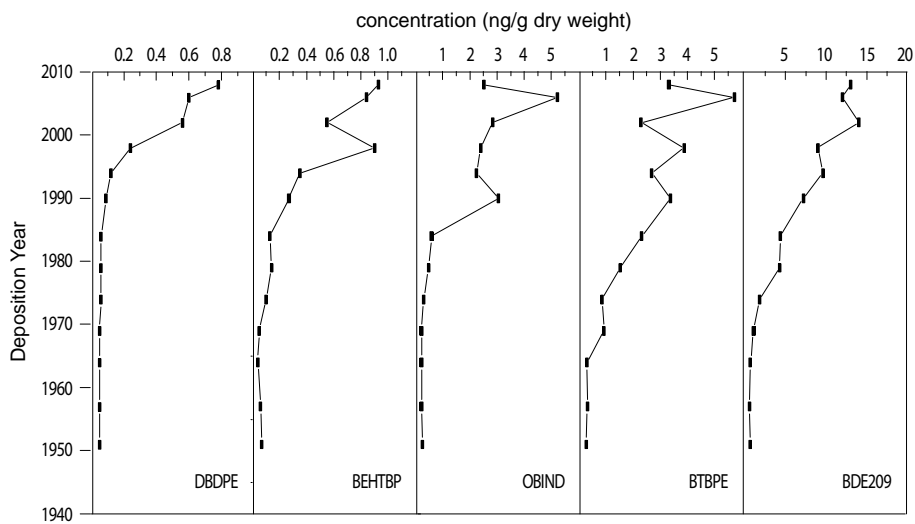


Figure 5. Temporal trends of BTBPE, BEHTBP, OBIND, DBDPE in Lake Simcoe sediment cores

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