NEW HALOGENATED NORBORNENE FLAME RETARDANTS IN THE LAURENTIAN GREAT LAKES: DECHLORANES 602, 603 AND 604

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Abstract

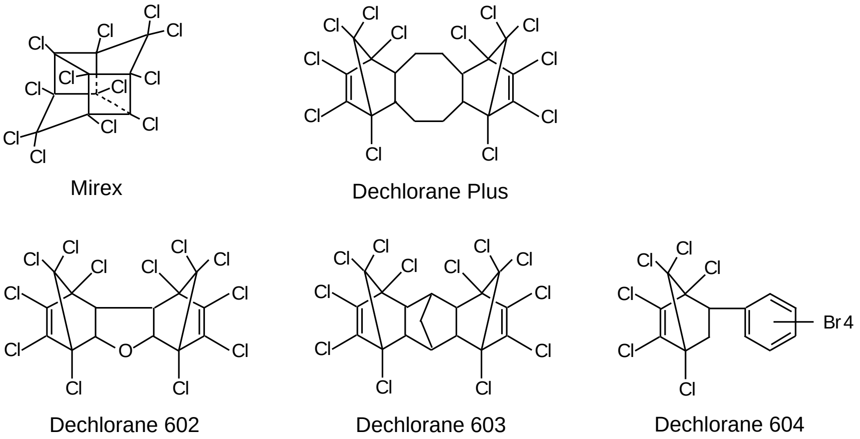
Dechlorane 602 (Dec 602), Dechlorane 603 (Dec 603), and Dechlorane 604 (Dec 604) have been identified in sediment and fish samples from the Laurentian Great Lakes. The identification of these target compounds were confirmed by comparing their gas chromatographic retention times with synthesized standards and monitoring the two most abundant ions and ratios of the molecular ion cluster. Dec 602, 603 and 604 were detected in all surficial sediment samples, while only Dec 602 was detected in all of the fish samples Analysis of sediment cores from Lake Ontario showed that peak concentrations of Dec 602, 603 and 604 occurred in early 1980s. Concentrations of Dec 602, 603 and 604 in sediment and fish samples were compared to those of mirex and dechlorane Plus (DP). The spatial distribution pattern of Dec 602 and 604 in sediment is similar to mirex and DP, but different from that of Dec 603, indicating the main source of Dec 603 to the Great Lakes might be different. This work is the first report of Dec 602, 603, and 604 in the Laurentian Great Lakes basin. The widespread detection of these legacy flame retardant compounds implies the importance of identifying and monitoring halogenated norbornene flame retardants in the environment.

Introduction

Flame retardants have been routinely used in polymeric and textile materials to enhance the flame retardancy of consumer products. A number of brominated and chlorinated compounds have commercial significance as flame retardants (http://www.inchem.org/documents/ehc/ehc192.htm). Although flame retardants can provide protection from fires, environmental concern for some of flame retardants has risen because of their widespread detection in the environment, bioaccumulation in biota, and persistence in sediment. Flame retardants that are persistent, bioaccumulative or toxic such as the brominated diphenyl ethers (PBDEs) have been restricted and regulated. Recently, tetra-, penta-, hexa- and hepta-BDEs were added to Annex A (Elimination of production and use of all intentionally produced POPs) at the 4th Meeting of the Parties to the Stockholm Convention on Persistent Organic Pollutants (POPs) (May 4–8, 2009) (http://www.chemsec.org/news/226-new-pops-suggested-for-the-stockholm-convention). Mirex is a legacy organochlorine pesticide, also used as a flame retardant, under the name Dechlorane, in plastics, rubbers, paints, etc[1]. Mirex was banned in the 1970s because of its toxicity and non-agricultural mirex was replaced partially by Dechlorane Plus (DP), Dechlorane 602 (Dec 602), Dechlorane 603 (Dec 603), and Dechlorane 604 (Dec 604) (Figure 1). Similar to mirex, DP, Dec 602, 603, and 604 are also hexachlorocyclopentadiene Diels-Alder adducts and these dechloranes are norbornene derivatives containing a basic structure of biocyclo [2,2,1]-heptene. Fire retardant properties of DP, Dec 602, 603, and 604 are similar to mirex (http://www.inchem.org/documents/ehc/ehc44.htm). These legacy dechlorane substitutes of mirex have most likely been used since 1970s. For example, DP manufactured before 1970 was first reported in air, sediment, and biota samples from the Laurentian Great Lakes in 2006[2], and DP was also found to have biomagnification potential for certain trophic relationships within food webs from Lake Ontario[3]. However, very little information is available on environmental occurrence of Dec 602, 603, and 604 in the Laurentian Great Lakes. In this study, we report concentrations and spatial distribution of Dec 602, 603, and 604 in sediment and fish samples collected from the Laurentian Great Lakes. Concentrations of mirex and DP were also determined for comparison purposes.

Material and Methods

Dec 602 (95%, CAS# 31107-44-5), Dec 603 (98%, CAS# 13560-92-4), and Dec 604 (98%, CAS# 34571-16-9) were synthesized by Toronto Research Chemical Inc. The identity of these dechlorane compounds was confirmed by ^{1}H NMR spectroscopic and mass spectrometric analysis. Syn-DP and anti-DP standards were purchased from Wellington Laboratories Inc and mirex from Cambridge Isotope Laboratories Inc.


Mirex

Dechlorane Plus

Dechlorane 602

Dechlorane 603

Dechlorane 604

Figure 1. Structures of Mirex, Dechlorane Plus, Dechloranes 602, 603, and 604.

Surficial sediment samples (top 3 cm) were collected from Lake Superior in 2001, Lakes Huron and Michigan in 2002, and Lake Erie in 2004. A sediment core from Lake Ontario was sampled in 2006 (Figure 2). The core was sliced into 1 cm intervals to 15 cm and 2 cm intervals afterward to 25 cm. The core intervals were dated by determining the ^{210}Pb activity as function of depth. Lake trout was collected from Lake Superior in 2002, Lake Huron in 2001, and Lake Ontario in 1998 and 1999. Whitefish was collected from Lake Erie in 2002. For each fish, a skinless, boneless fillet of the dorsal muscle was used for chemical analysis. Identification and determination of Dec 602, Dec 603, and Dec 604 in sediment and fish were performed on extracts previously prepared for determination of mono-ortho dioxin-like polychlorinated biphenyls (DLPCBs). The extraction and cleanup procedure for sediment and fish samples are described elsewhere[4]. The sample extracts were analyzed on a high resolution Micromass Autospec (HRMS) equipped with a Hewlett-Packard HP 6890 gas chromatograph (GC) using a 20 m Rtx-PCB column (0.18 mm i.d, 0.18 μm film thickness, Restek). The temperature program was: 140°C for 1 min; 140°C to 300°C at 20°C/min; 300°C for 15 min. The HRMS system was operated in EI positive mode with electron energy of 42 eV and was tuned to greater than 10,000 RP (10% valley definition). The concentrations of Dec 602, Dec 603, and Dec 604, as well as mirex and DP, in sediment and fish samples were determined by monitoring the two most abundant ions of the fragment cluster at m/z 271.8102/273.8072 for mirex, syn- and anti-DP and Dec 602, 262.8570/264.8540 for Dec 603, and 417.7026/419.7006 for Dec 604.

The identification and quantification of the target compounds are based on the following criteria: (1) Sample peaks have an approximately Gaussian shape and their GC retention times match those of the standard compounds within ± 0.1 min. (2) All peaks have a signal-to-noise ratio of greater than 5:1. (3) Peak areas are within 15% of the corresponding theoretical isotopic ratios. (4) If the target compounds are detected in the procedural blank processed with samples, the samples must have more than five times the value of the blank to be positively identified. Low levels of Mirex, DP, and Dec 602 were detected in the procedural blanks for sediment samples, and mirex and Dec 602 in blanks for the fish samples. Neither Dec 603 nor Dec 604 was detected in procedural blanks. Levels in the blanks were low enough in all samples so that the concentrations of the target compounds in the samples were not blank-corrected. For the sediment and fish samples, no recoveries of the target compounds were available due to lack of $^{13}C_{12}$-labelled standards. This work is still considered screening analysis using the extracts prepared for DLPCB. The recoveries of $^{13}C_{12}$-PCB169 and $^{13}C_{12}$-PCB189 in the sediment and fish samples were in the range of 70 ~ 100%.

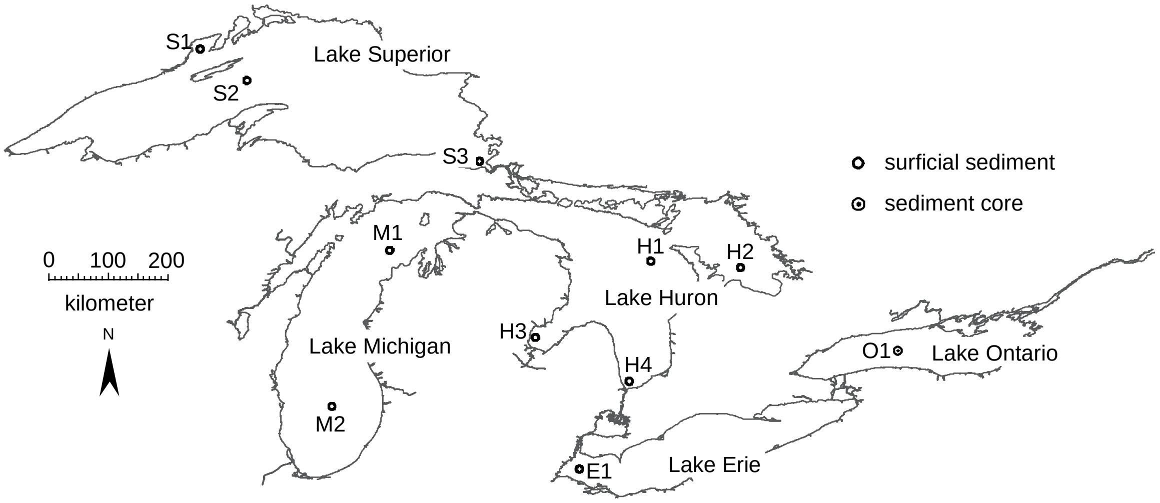


Figure 2. Sampling sites of surficial sediment and sediment core.

Results and Discussion

Identification of Dechloranes 602, 603 and 604. DP has been detected in air, sediment, and fish samples from the Great Lakes[2,5]. Sverko et al also observed some unknown peaks suspected to be DP's degradation products and other DP isomers[5]. During the process of identifying DP's breakdown products and additional isomers in sediment samples by monitoring m/z 271.8102 and 273.8072 with GC/HRMS, many unknown peaks were observed in the chromatograms. All of these peaks had isotopic ratios of 271.8102/273.8072 close to the theoretical value. The peak at m/z 272, corresponding to $C_5Cl_6^+$, is a common fragment of molecules containing a hexachlorocyclohexene unit upon electron ionization formed by a retro-Diels-Alder (RDA) reaction[6]. Based on comparison with the standards, the majority of these unknown peaks were identified as chlorinated pesticides such as chlordane, heptachlor, dieldrin, endosulfan and mirex etc, but there were still several remaining peaks which were not identified. Most of these had higher peak areas in Lake Ontario sediments than in the other lake samples. Through information from the scientific literature, Dec 602, 603, and 604 were assumed to be responsible for some of remaining unknown peaks. To confirm the presence of Dec 602, 603 and 604, sediment samples from Lake Ontario were analyzed by GC/HRMS monitoring molecular ions at m/z 611.6465/613.6436/615.6406, 635.6829/637.6800/639.6770, and 689.5128/691.5107/693.5078 for Dec 602, 603, and 604, respectively. The molecular-ion peaks were observed in all samples with isotopic ratios close to their theoretical values, and their retention times were identical to those of three unknown peaks observed in the m/z 271.8102/273.8072 mass chromatograms. The identification was further confirmed by comparing GC retention times and mass spectra of unknowns with those of Dec 602, 603, and 604 synthesized by Toronto Research Chemical Inc.

Dechloranes in sediment of the Great Lakes. Figure 3 shows concentrations of Dec 602, 603, 604, mirex and total DP in 11 surfacial sediment samples from the Great Lakes. Dec 602, 603, and 604 were detected in all surficial sediment samples, and concentrations of Dec 602 and 603 were generally higher than those of Dec 604. The highest concentration of Dec 602 was observed in Lake Ontario (O1), and Dec 604 in Lakes Erie (E1) and Ontario (O1). Typically, the lower Great Lakes (Lakes Erie and Ontario) are more contaminated with toxic substances such as Mercury, PCBs, and chlorinated pesticides compared to the upper Great Lakes (Lakes Superior, Huron, and Michigan)[7]. Interestingly, surficial sediment samples from depositional zones of Lakes Superior (S2), Michigan (M2), and Ontario (O1) had similar concentrations of Dec 603. Of the 11 surficial sediment samples, concentrations of DP were much higher than those of mirex, Dec 602, 603, and 604. The relative pattern of concentrations for mirex, Dec 602, 603, and 604 are: Dec 602 and 603 > mirex > dec 604 in Lakes Superior, Huron, and Michigan; Dec 602, 603, and 604 > mirex in Lake Erie; and mirex > Dec 602, 603, and 604 in Lake Ontario. Mirex, DP, Dec 602, 603, and 604 were developed by Hooker Chemicals (now OxyChem, Niagara Falls, NY), and the Niagara River is considered as a major source of DP to the Lake Ontario. Compared to Lakes Superior, Huron, Michigan, and Erie, Lake Ontario had relatively high concentrations of Dec 602 and 604 in sediment of Lake Ontario, as well as the similar spatial distribution pattern to DP, suggesting that the Niagara River might be also a major source of Dec 602 and 604 to the Lake Ontario.

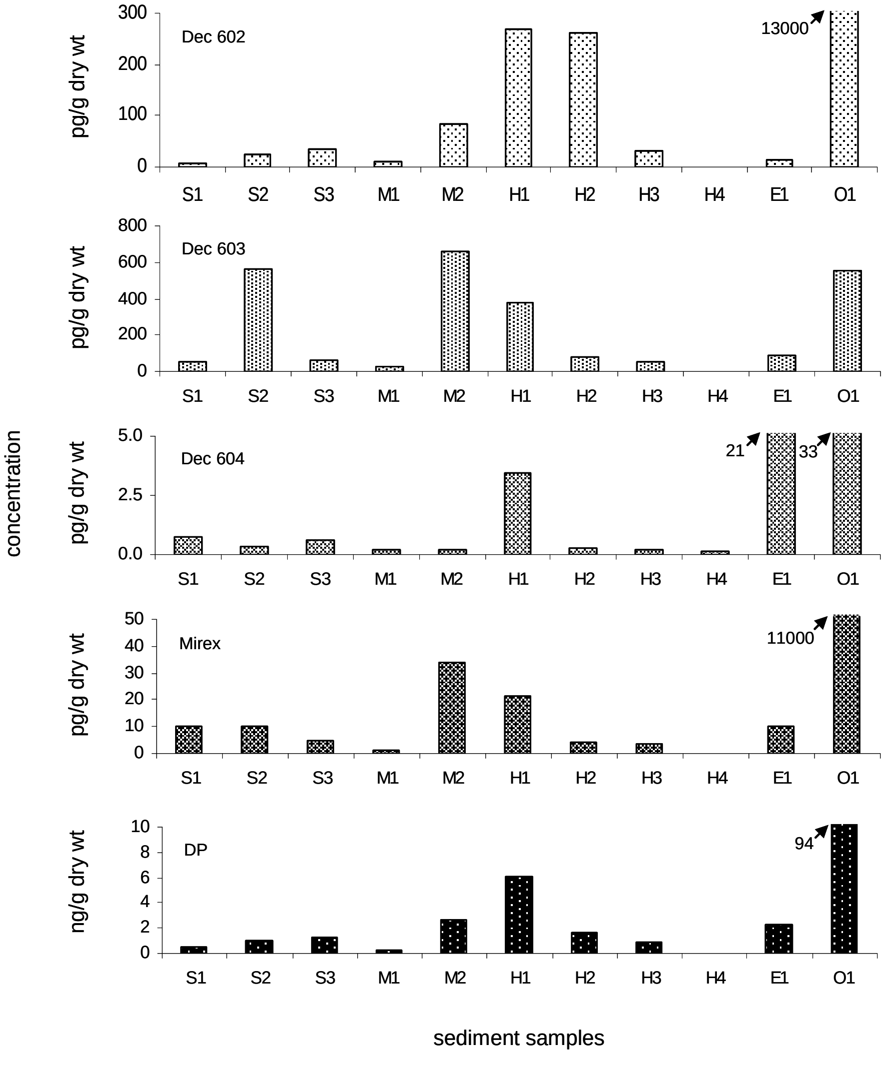


Figure 3. Concentrations of Dec 602, 603, 604, mirex, and DP in surficial sediment from the Great Lakes.

The temporal trends of Dec 602, 603 and 604, mirex, and DP are shown in Figure 3. Dec 602, 603, and DP had similar trends, taking off in early 1970s, which is proximately 10 years later than mirex. High concentrations of Dec 602, 603, and DP in sediment cores were observed in early 1980s, and have fluctuated since then. Dec 604 also peaked in early 1980s but has dramatically decreased since early 1990s.

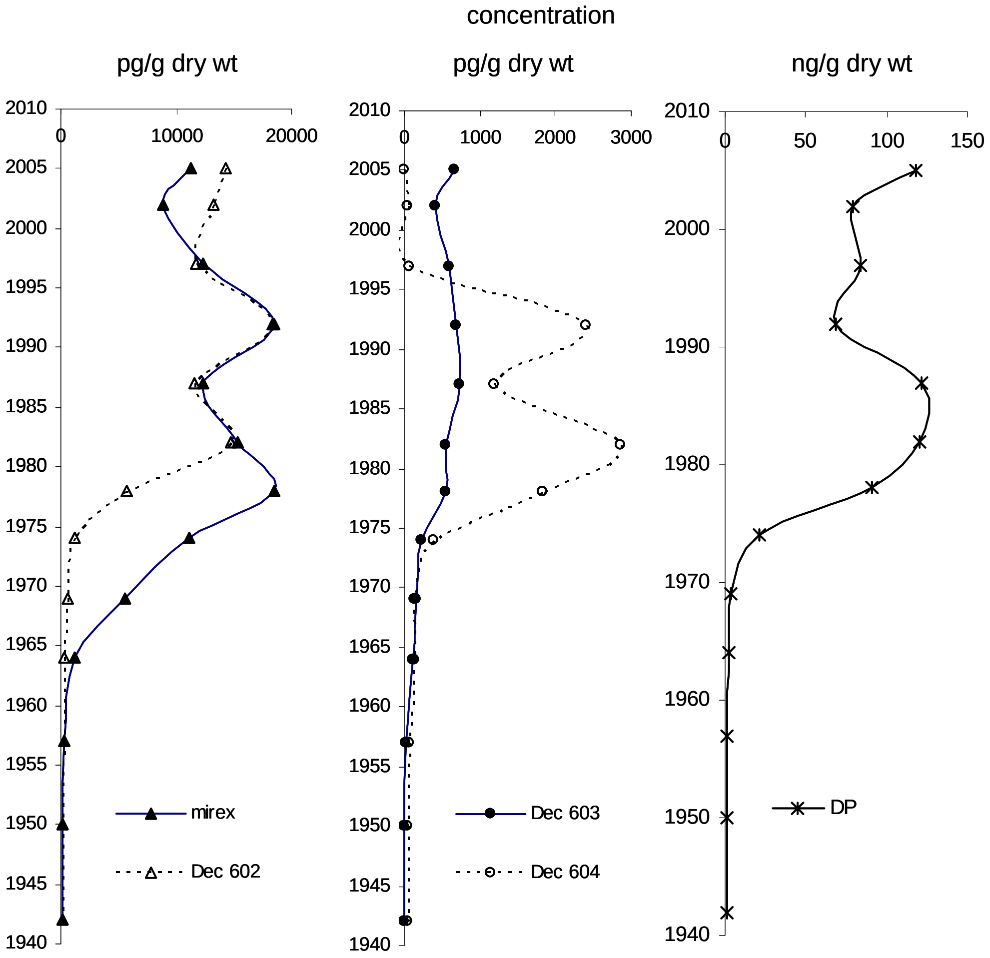


Figure 3. Concentrations of Dec 602, 603, 604, mirex, and DP in a Lake Ontario core vs. year of deposition.

Dechloranes in fish of the Great Lakes. Dec 602, mirex, and DP were detected in all fish samples from Lakes Superior (lake trout S9a and b), Huron (lake trout H3a and b), Erie (whitefish E1a and b, E2a and b, E4a and b), and Ontario (lake trout O4, O8, O11a and b). Dec 603 was detected in 5 of 6 whitefish samples from Lake Erie and 2 of 4 lake trout samples from Lake Ontario with low concentrations in the range of 1 ~ 4 pg/g wet wt. Dec 604 was only detected in 2 of 4 lake trout from Lake Ontario at concentrations of 2 and 12 pg/g wet wt. Figure 4 presents concentrations of Dec 602, mirex, and DP in lake trout from Lakes Superior, Huron, and Ontario and whitefish from Lake Erie. In all of the fish samples, the pattern of relative concentrations is DP < Dec 602 < mirex. In lake trout from Lakes Superior and Huron and whitefish from Lake Erie, concentrations of Dec 602 were 2 ~ 10 times higher than those of DP. In lake trout from Lake Ontario, concentrations of Dec 602 were 50 ~ 150 times higher than those of DP. The higher concentrations of Dec 602 indicate that Dec 602 is more bioavailable and/or bioaccumulated than DP. Zitko also observed that Dec 602 was bioaccumulated by fish from water[1].

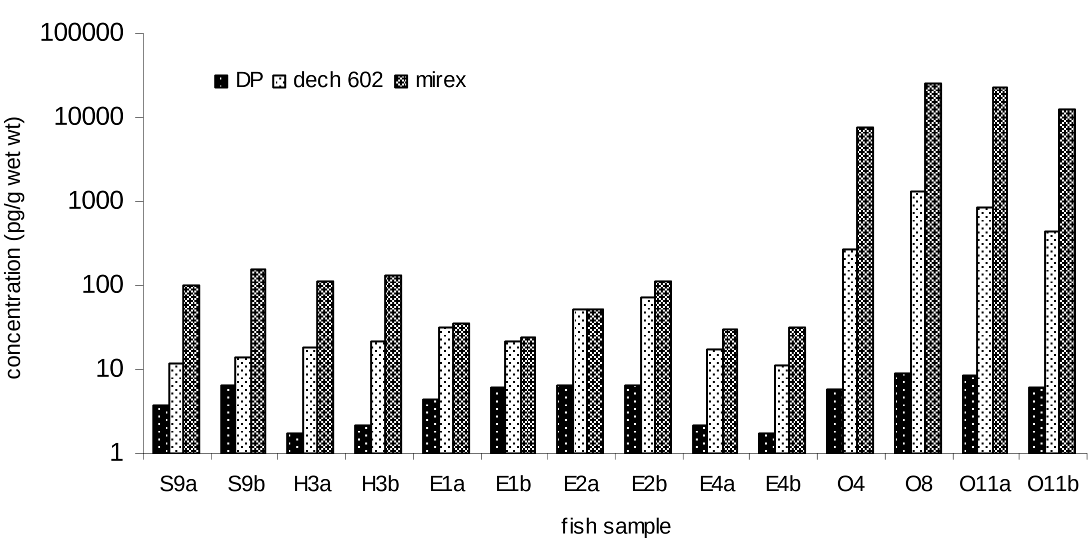


Figure 4. Concentrations of Dec 602, mirex, and DP in lake trout from Lakes Superior, Huron and Ontario and in whitefish from Lake Erie.

Information on application and use of Dec 602, 603, and 604 is very limited. Recently, Hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO), a norbornene flame retardant used in the past, was detected in residential indoor air and dust. Detection of Dec 602, 603, and 604 in sediment and fish of the Great Lakes, along with DP and HCDBCO, implies importance of monitoring occurrence of norbornene flame retardants in the environment.

Acknowledgements

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