

HISTORICAL TRENDS OF HALOGENATED FLAME RETARDANTS IN AMERICAN EEL CAPTURED IN LAKE ONTARIO

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Introduction

Around the world fires are a major source of property damage, injury, and loss of life. Halogenated flame retardant chemicals are often added or applied to materials to increase the fire resistance of products such as electronics and textiles¹. Mirex (also called Dechlorane) was a first generation chlorinated flame retardant, commercialized as an insecticide, and banned in the late 1970s under the Stockholm Convention on Persistent Organic Pollutants (POPs) because of its persistence and bioaccumulation potential. Dechloranes (Dec) 602, 603, and 604, and Dechlorane Plus (DP) were produced as replacement flame retardants for mirex. Although these replacement DP-like substances have been produced for over 40 years, they were first measured in the environment in 2006, and their environmental significance first reviewed only recently².

Similarly, polybrominated diphenyl ethers (PBDEs) have been produced commercially for the last 30+ years in three technical mixtures, namely Penta-BDE, Octa-BDE, and Deca-BDE, and are used as additive flame retardants in many plastics and foams¹. Recently, the Penta-BDE and Octa-BDE commercial mixtures were amended to Annex A under the Stockholm Convention on POPs³. However, the demand for flame retardant chemicals has not diminished, and replacement BFRs are being introduced into the market place.

Production and usage information for many replacement flame retardants including Dechloranes remains largely unknown. The aim of this study was to detect and quantify selected chlorinated and brominated flame retardants in American eel (*Anguilla rostrata*) captured in Lake Ontario, and to determine concentration trends from 1988-2008. American eel migrates to Lake Ontario from the Sargasso Sea, where it grows toward maturity reaching sizes >1m in length and 2 kg in weight, before returning to the Sargasso to spawn and die. It is a benthic predator with a relatively long residency time in Lake Ontario (>15 years)⁴, and the likelihood of detecting a replacement flame retardant, if bioaccumulative, is favorable. DP-like substances have been measured in Lake Ontario Lake trout⁵, a pelagic fish; however, the bioaccumulation potential of DP is greatest in lower trophic level benthic organisms⁶. Analyses of American eel will provide a more complete depiction of the Lake Ontario food web and the bioaccumulation potential of selected flame retardants.

Materials and methods

Whole fish homogenates were prepared for eels of equivalent age (approx 20 y) captured in Lake Ontario in 1988, 1998, and 2008 (10 per year). The sample collection and chemical extraction procedures have been described previously in detail⁷. In short, chemical extracts were prepared by drying the eel tissue with anhydrous sodium sulfate, and mixing it into a free following mixture before extraction with dichloromethane (DCM). Lipid content was determined gravimetrically. Lipids were removed by gel permeation chromatography followed by a two-layered silica-alumina column eluted with 1:1 DCM:hexane (v:v). Prior to extraction, the samples were spiked with ¹³C₁₂-CB-170 to measure extraction efficiency, then additionally with ¹³C₁₂-BDE-47, -BDE-99, and -BDE-153 surrogate standards. Instrument performance standards were added prior to analysis, namely ¹³C₁₂-CB-111 and -CB-189. Analytical standards were obtained from Wellington Laboratories (Guelph, ON, Canada).

Gas chromatography-high resolution magnetic sector mass spectrometry (GC/HRMS) was carried out on a Micromass AutoSpec MS (Micromass, Manchester, UK) operated in EI mode, connected to a Hewlett-Packard 6890 GC (Hewlett Packard, Palo Alto, USA), fitted with a DB-5HT 15m x 0.25mm x 0.1µm film (J&W Scientific, USA). Each eel extract was injected twice and selectively-monitored for the chlorinated and brominated flame retardants listed below. Run 1: Dechlorane Plus (s-DP and a-DP), dechlorinated Dechlorane

Plus (aCl₁₀DP and aCl₁₁DP), 1,5-Dechlorane Plus mono-adduct (DPMA), Dechloranes 602, 603, 604 (Dec-602, Dec-603, Dec-604), Chlordene Plus (CP), and Dechlorane (Mirex); Run 2: allyl 2,4,6-tribromophenyl ether (ATE), brominated biphenyl (BB-153), 2-bromoallyl 2,4,6-tribromophenyl ether (BATE), bis(2-ethyl-1-hexyl)tetrabromophthalate (BEHTBP), 2,3-dibromopropyl-2,4,6-tribromophenylether (DPTE), decabromodiphenylethane (DBDPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB), hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), entabromotoluene (PBT), and 2,3,5,6-tetrabromo-p-xylene (p-TBX). Comparison of data among years was obtained with ANOVA.

Results and discussion:

There was an expectation to detect DP and other DP-like substances in Lake Ontario eels (1988-2008) based on a known source of DP to Lake Ontario, Oxychem, in Niagara Falls, NY, and previous reports for Lake Ontario sediment and biota^{5,8}. Concentrations of total DP and Dec 602 were greatest in the 1988 samples with mean concentrations of 106 ± 78 pg/g lw and 1895 ± 987 pg/g lw, respectively. Dec 603 and Dec 604 were statistically similar across all years (Fig. 1 and 2). DPMA was detected at low concentrations for all years with mean concentrations ranging from 0.37 – 32.7 pg/g lw, highest in 1988. DP-like compounds have been measured in Lake Ontario sediment by Shen et al.⁵. DPMA was undetectable in lake trout from Lake Ontario⁸, and appears to be less bioaccumulative than the other DP-like substances analysed in this study. We also monitored the temporal trend of mirex over the same time period as a control. Mirex concentrations were several times higher than the replacement DP-like substances, with the maximum occurring in 1988, and ranging from 5505 to 44862 pg/g lw (mean = 18192 pg/g lw).

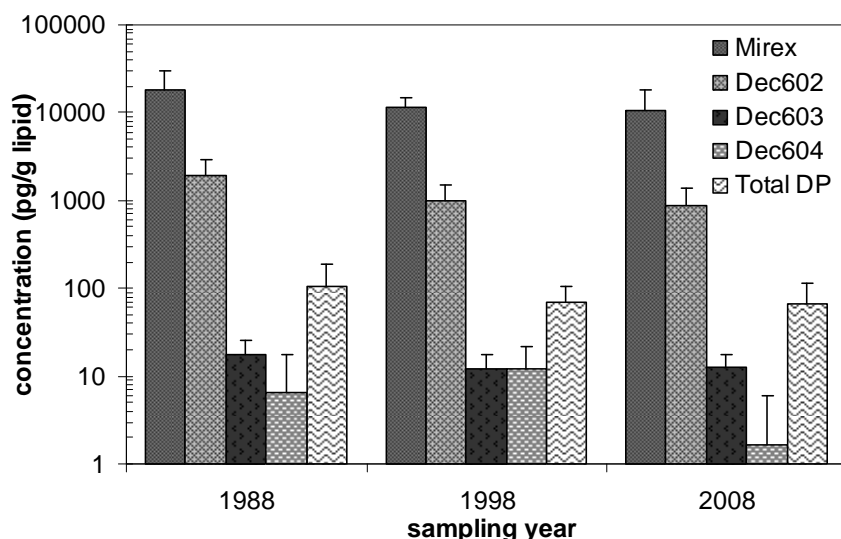


Figure 1: Concentrations of mirex, Dechloranes 602, 603, and 604, and total DP in American eel captured in Lake Ontario from 1988-2008.

Several replacement BFRs were detected in eels. We confirmed and quantified ATE, BB-153, DPTE, DBDPE, HBB, PBEB, PBT, and p-TBX. ATE was detected in every sample from 2008 and ranged from 172 to 471 pg/g lw (mean = 257 pg/g lw). PBT and p-TBX were quantified in 60% of the samples and varied from 105 to 1184 pg/g lw and 47 to 151 pg/g lw, respectively. HBB was detected in 30% of the samples ranging from 235 to 684 pg/g lw. Comparatively, BDE-47 was measured in the same samples and ranged from 11 to 162 ng/g lw, occurring orders-of-magnitude higher in concentration than the replacement BFRs. The detection of DBDPE, a replacement of Deca-BDE that has been detected mainly in sediment, sludge and dust, was surprising given its high log K_{ow} (13.6) and low predicted bioavailability⁹. Its detection in eels may be related to their benthic characteristic and direct contact with sediment. Some non-BDE flame retardants have been measured in Lake Ontario biota. Concentrations of BTBPE and PBEB in lake trout (1979-2004) had a peak of 2.6 ng/g lw and 320 ng/g lw¹⁰, respectively. The trends in halogenated flame retardants reported here add to the existing information for the Lake Ontario food web, and indicate flame retardants that may warrant further study.

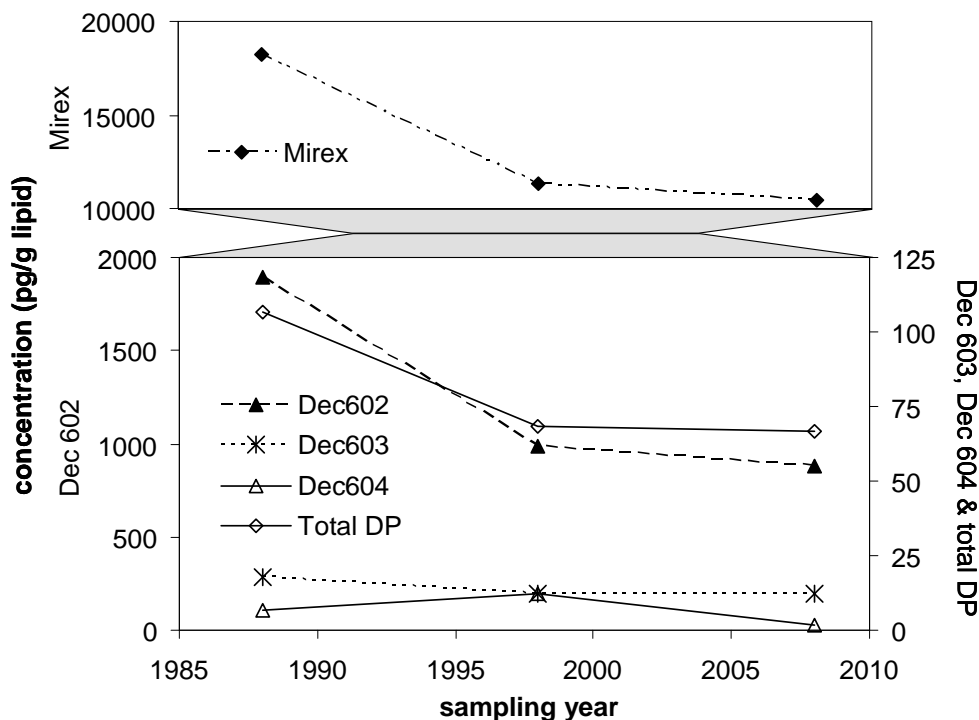


Figure 2: Temporal trend in mirex, Dec 602, 603, and 604, and total DP in American eel collected in Lake Ontario. Dec 602 was the only compound to show a statistically significant change in concentration over time (between 1988 and 1998).

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