Temporal Trends of Flame Retardants in Lake Ontario lake trout (1979-2004)

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Introduction

Lake trout (*Salvelinus namaycush*) has been used as a sentinel indicator species for studies on temporal trends of halogenated organic pollutants in Canadian and US monitoring programs. Changes in the inputs of chemicals into the environment are reflected in changes in concentrations of chemical contaminants in wildlife over time. For new and emerging chemicals, there is a general paucity of information regarding emissions and as such, constructing historical concentration profiles is the only means of assessing the chronology of contamination.

Flame retardants have come under fire from regulators because of their potential toxicity and ubiquity in the environment. The ones based on bromine have been the focus of considerable scientific research. Some formulations have recently, albeit reluctantly, been phased out by the industry. It is not unreasonable to anticipate that those flame retardants removed from commerce will likely be replaced with unregulated ones, *i.e*., those that have not gone under the rigors of independent scientific testing. For example, the penta-brominated diphenyl mixture, which the industry ceased production of in 2004, has been replaced by bis(tribromophenoxy)ethane (BTBPE)[1]. Little is currently known about the potential toxicity of this compound yet it has already been detected in air samples from the United States and also in biota from a freshwater lake in Canada[2,3].

Our knowledge of the 75 bromine based flame retardants in commerce is limited. Much work has been done on the brominated diphenyl ethers and on tetrabromobisphenol-A while the remaining others have received little to no attention. Our objective in this study was to gain an understanding of the temporal trends of 'newer' bromine and chlorine based flame retardants in fish. In addition to BTBPE, the other bromine-based flame retardants that we focused on were: hexabromocyclododecane (HBCD), decabromodiphenylethane (DBDPE) and tetrabromobisphenol A bis(allyl ether) (TBBPA-AE). Dechlorane Plus (DP), a chlorinated flame retardant recently identified in air and sediments from the United States was also included in our study[2].

Materials and Methods

Lake trout (4 year olds from 1979, 1983, 1988, 1993, 1998, 2004, *n=5* for each year) were collected from Lake Ontario as part of the Department of Fisheries and Oceans long term monitoring program in the Great Lakes. Fish were homogenized whole then stored frozen in glass jars at -80°C until analysis in the archive maintained by the Great Lakes Laboratory for Fisheries and Aquatic Sciences. Samples were thawed and approximately 10 g of material (wet weight) were placed in a stainless steel accelerated solvent extraction vessel (300 mL). The top of the vessel was spiked with a suite of recovery internal standards including BDE 71, 126, 197, 207 and, ^{13}C-labelled α, β, γ-HBCD isomers. Extracts were reduced in volume (10 mL) and a portion of the extract (1 mL) was used for lipid determination. Lipids from the remaining extract were removed using an automated gel permeation chromatography and the extracts were fractionated on a column of Florisil. The elution sequence off the Florisil can be found elsewhere[3]. Samples were spiked with a known amount of an instrument performance internal standard prior to LC or GC-injection. BTBPE, DBDPE and the *syn*- and *anti*- isomers of DP were analyzed using an Agilent 5973 GC-MSD fitted with a 10 m × 0.25 mm id DB-5 capillary column (0.25 μm film thickness, J&W Scientific, CA). Splitless injections of 2 μL were made by a 7683 Agilent autosampler with the injector set isothermally at 280°C.

The initial oven temperature was set at 90 ºC with no hold time, ramped at 20 ºC/min to 310 ºC and held for 5 minutes. MS analysis was performed in the electron capture negative ionization mode using methane as the buffer gas. Source and quad temperatures were both set to 150 ºC. Detection of BTBPE, PBEB and DBDPE was done under selected ion monitoring conditions (SIM) using the $[Br]^-$ ions (*m/z* 79, 81) while the *m/z* 651.8 and 653.8 ions were used for the DP isomers[2]. HBCD was quantified as described previously[4,5]. TBBPA-AE was also analyzed by LC/MS/MS using the parent to daughter ion transition of *m/z* 582.7 to *m/z* 526.4. In all cases, quantification was achieved using an external standard solution.

Results and Discussion

Plots of the chemical concentrations (ng/g, wet weight) versus sampling year are shown in Figure 1(a-c). Because portions of whole homogenized fish material were analyzed we felt it more meaningful to report concentrations on a wet weight basis. Of the BFRs analyzed, only the DBDPE was consistently below detectable levels in all our samples. Total HBCD concentrations were consistently greater than all the other BFRs analyzed in this study and ranged from 1.2 to 5.1 ng/g (wet weight), with a temporal trend that varied little or perhaps even declined in recent years. This was surprising given that regulatory actions against PBDEs were expected to result in increased use of HBCD. Concentrations in this study are similar to the mean of 1.8 ng/g reported for Lake Ontario lake trout collected in 2002[6].

There was a statistically significant positive linear relationship ($p<0.04$) between BTBPE concentrations and time. BTBPE concentrations in lake trout range from below detectable levels to 0.5 ng/g wet weight; on a lipid weight basis BTBPE concentrations in lake trout from Lake Ontario were amount 10 times greater than the range reported for biota from lake Winnipeg[3]. An increase in BTBPE concentrations can be expected to continue as this compound has already begun to replace the penta-BDE mixture in commercial applications.

Both isomers of DP were consistently detected in all our samples analyzed to date (animals from 2004 and some from 1979 are yet to be analyzed). There was also a small but statistically significant decrease ($p<0.01$) in total DP concentrations between 1979 and 1998 which is somewhat consistent with the profile of DP in a sediment core from Lake Erie[2]. Hoh *et al*. (2006) did not find any correlation between DP concentrations and the year of fish sampling. On a lipid weight (lw) basis, the range in ΣDP concentrations for late trout in our study (0.17 – 0.81 ng/g, lw) are similar to the range reported for walleye from Lake Erie (0.14 – 0.91 ng/g, lw). Work is ongoing to characterize the relative amounts of both DP isomers in our fish samples.

The TBBPA-AE compound is a derivative of TBBPA used commercially as a reactive BFR. Being a reactive-type BFR and the fact that our detection limits on the LC/MS/MS are high (~ 50 pg on-column, ESI negative ion mode) it is not surprising that it was detected in only a small number of samples. An elution profile of the *m/z* 582.7 to *m/z* 526.4 ion transition of TBBPA-AE is shown in Figure 2. TBBPA-AE concentrations, which was only detected in samples from 1997 (*n=1*), 1998 (*n=3*) and 2004 (*n=1*), were 1.2, 1.7 and 0.2 ng/g wet weight, respectively.

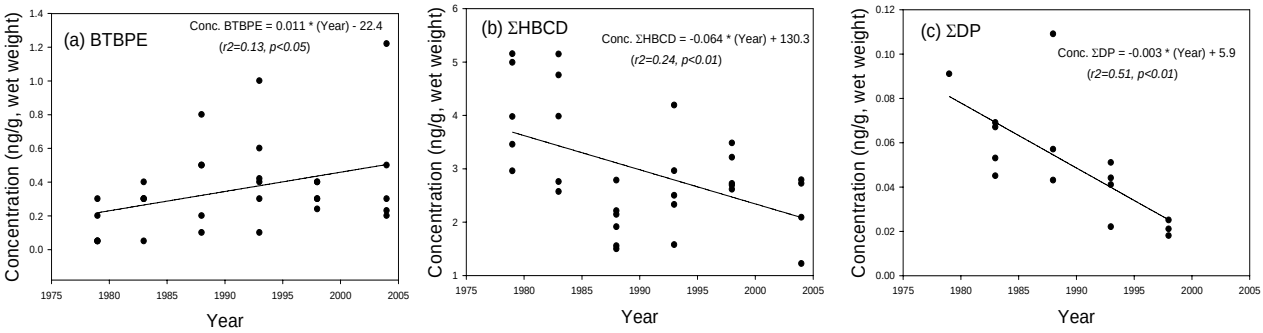

Figure 1. Change in concentrations of (a) BTBPE, (b) ΣHBCD and (c) ΣDP in Lake Ontario lake trout over time. Results of the linear regression are given in each plot. Some animals remain to be analyzed.

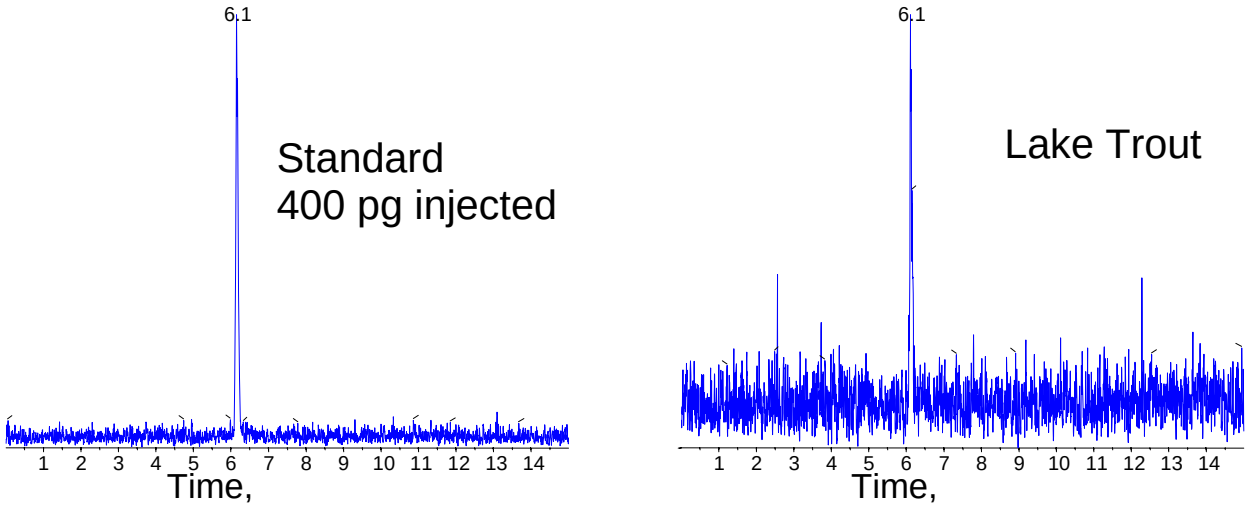

Figure 2. MRM (*m/z* 582.7 to *m/z* 526.4) elution profile of TBBPA-AE in an external standard solution (left panel) and an extract of a Lake Ontario lake trout (right panel).

While temporal trends of chemicals in food webs have become a necessary aspect of contaminant fate and assessment studies, this study indicates care must be taken in interpreting the observed trends. Food web disruptions in Lake Ontario continue, and the impact of this on bioaccumulation and biomagnification of POPs remain unknown. Additional analyses for other legacy and current-use POPs in the samples included in this study may clarify the preliminary observations for the compounds examined. As well, the monitoring of multiple indicators of contaminant temporal trends and chemical fate, including multimedia (other species & sediment cores for example) and multiple chemical comparisons (legacy & current-use) are recommended to compensate for system specific (in this case Lake Ontario) dynamics that may otherwise confound our understanding.

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