

BROMINATED AND CHLORINATED FLAME RETARDANTS IN LAKE ONTARIO, CANADA, LAKE TROUT (*SALVELINUS NAMAYCUSH*) BETWEEN 1979 AND 2004 AND POSSIBLE INFLUENCES OF FOOD-WEB CHANGESNARGIS ISMAIL,<sup>†</sup> SARAH B. GEWURTZ,<sup>‡</sup>§ KERRI PLESKACH,<sup>†</sup> D. MICHAEL WHITTLE,<sup>||</sup> PAUL A. HELM,<sup>§</sup> CHRIS H. MARVIN,<sup>#</sup> and GREGG T. TOMY<sup>\*†††</sup><sup>†</sup>Great Lakes Institute for Environmental Research, University of Windsor, 401 Sunset Avenue, Windsor, Ontario N9B 3P4, Canada<sup>‡</sup>Department of Chemistry, Brock University, 500 Glenridge Avenue, St. Catharines, Ontario M9P 3V6, Canada<sup>§</sup>Ontario Ministry of the Environment, Environmental Monitoring and Reporting Branch, 125 Resources Road, Toronto, Ontario M9P 3V6, Canada<sup>||</sup>Department of Fisheries and Oceans, Great Lakes Laboratory for Fisheries Aquatic and Sciences,<sup>#</sup>Environment Canada, National Water Research Institute, 867 Lakeshore Road, Burlington, Ontario L7R 4A6<sup>†††</sup>Departments of Chemistry and Environment and Geography, University of Manitoba, Winnipeg, Manitoba R3T 2N6, Canada

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**Abstract**—Concentrations of non-polybrominated diphenyl ether (PBDE) brominated (hexabromocyclododecane [HBCD], 1,2-bis[2,4,6-tribromophenoxy]ethane [BTBPE], and pentabromoethylbenzene [PEB]) and chlorinated (Dechlorane Plus [DP] as well as short- and medium-chain chlorinated paraffins [SCCP and MCCP, respectively]) flame retardants were evaluated in archived Lake Ontario, Canada, lake trout (*Salvelinus namaycush*) samples collected between 1979 and 2004. Polybrominated diphenyl ethers also were analyzed to provide a point of reference for comparison to previous studies. Concentrations of the dominant PBDE congeners (BDEs 28, 47, 99, 100, 153, and 154) increased significantly from 1979 until the mid-1990s, then either leveled off or decreased significantly between 1998 and 2004, a result that corresponds to those of previous studies. In contrast, BDE 209 increased approximately fourfold between 1998 and 2004. The temporal trends of the non-PBDE flame retardants varied, with sum ( $\Sigma$ ) HBCD and DP showing significant overall decreases; BTBPE,  $\Sigma$ SCCP, and  $\Sigma$ MCCP showing parabolic trends; and PEB showing no overall change during the study period. Because many of the non-PBDE chemicals may be used as replacements for penta- and octa-BDE mixtures, these results will provide a baseline to evaluate future usage patterns. Possible changes in food-web structure, evaluated through stable nitrogen isotopes ( $\delta^{15}\text{N}$ ), may be influencing our interpretations of contaminant trends in lake trout and are hypothesized to be partially responsible for the observed decrease in concentrations of BDEs 28, 47, 99, 100, 153, and 154 between 1998 and 2004. Retrospective analyses evaluating temporal trends in stable isotope values at the base of the food web, however, are recommended to test this hypothesis further.

## INTRODUCTION

The global market demand for flame retardant chemicals has been growing rapidly because of increasing use of polymers in a wide variety of materials [1]. Of the flame retardants, the polybrominated diphenyl ethers (PBDEs) have received the most research attention, culminating in the recent banning of the penta- and octa-BDE mixtures by the European Union and several states in the United States as well as in the voluntary phase-out of these mixtures in the United States and Canada in 2006 (<http://www.bsef.com>). The deca-BDE mixture, which consists of greater than 97% of decabromodiphenyl ether, is not currently banned [2].

Perhaps not unexpectedly, the penta- and octa-BDE mixtures are now being replaced with brominated compounds that have not been subjected to rigorous, independent environmental testing. Hexabromocyclododecane (HBCD) is a bioaccumulative and persistent, high-production-volume chemical [3,4] used mainly in polystyrene foam in building construction [1], and it may be used as an alternative to PBDEs in some applications [5]. In addition, 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), a replacement chemical for the octa-BDE mixture [6], has been detected in biota [6–8], and concentra-

tions were highest in the surficial layer of a Lake Ontario, USA, sediment core [9]. Another brominated flame retardant, 2,3,4,5,6-pentabromoethylbenzene (PEB), has been detected in North American air [10] and herring gull eggs [6] as well as in glaucous gulls from the Norwegian Arctic [8], although this chemical may only be produced at low volumes [10].

Chlorinated compounds continue to be used as flame retardants, but to a lesser extent than brominated compounds [1]. Dechlorane Plus (DP), a high-production-volume chemical, was recently detected in air, sediment, and biota from the Great Lakes [6,11,12]. In addition, short-chain chlorinated paraffins (SCCPs) and medium-chain chlorinated paraffins (MCCPs) are used as flame retardants and plasticizers in vinyl plastics, rubber, paints, adhesives, and sealants [13,14]. The SCCPs have been termed persistent toxic substances by the United Nations Environment Program [15] (<http://www.chem.unep.ch/Pts/regreports/Europe%20full%20report.pdf>) as well as Category 3 carcinogens and Dangerous for the Environment by the European Union [14]. Furthermore, Environment Canada recently concluded that both SCCPs and MCCPs are toxic to the environment and human health as defined under the Canadian Environmental Protection Act [16] ([http://www.ec.gc.ca/CEPARRegistry/documents/subs.list/ChlorinatedParaffins/CPs\\_followup.pdf](http://www.ec.gc.ca/CEPARRegistry/documents/subs.list/ChlorinatedParaffins/CPs_followup.pdf)).

Lake trout (*Salvelinus namaycush*) is a top predator in the Great Lakes and a useful indicator species, because it accu-

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mulates contaminants to detectable concentrations and integrates exposure through its food web [17,18]. Eggs from the herring gull (*Larus argentatus*), another top predator, also have been used for this purpose [6,19]. Programs monitoring a variety of species are important in examining temporal trends, because species like lake trout and herring gulls have different diets and bioenergetics and respond to changing ecosystem dynamics in different ways [20,21].

In the present study, we investigated the temporal trends of brominated (HBCD, BTBPE, and PEB) and chlorinated (DP, SCCP, and MCCP) flame retardants in Lake Ontario, Canada, lake trout from 1979 to 2004. These temporal trend data are important for prioritizing current-use chemicals for management actions. Results from the present study also provide a baseline from which to assess the environmental occurrence of alternative flame retardants as usage patterns change following the withdrawal of the penta- and octa-BDEs from the marketplace. To our knowledge, the present study represents one of the first time trends of non-PBDE flame retardants in Great Lakes lake trout and of BTBPE and PEB in biota worldwide. Although PBDEs in Lake Ontario lake trout samples have been evaluated previously [18,22], we included the temporal trends of eight PBDE congeners (including BDE 209) to provide a point of reference in comparing trends of the other flame retardant chemicals in the trout. Furthermore, because changing food-web structure also may influence temporal trends [19], we assessed this possibility by considering the stable isotopes of nitrogen ( $\delta^{15}\text{N}$ ) and carbon ( $\delta^{13}\text{C}$ ) as well as the relative differences in fish growth to determine if trend interpretations in this data set would be impacted.

## MATERIALS AND METHODS

### Materials

Individual native PBDE congeners 71, 126, 156, 197, and 207 (purity, >99%); labeled ( $^{13}\text{C}$  and  $\text{d}_{18}$ ) diastereoisomers of HBCD ( $\alpha$ ,  $\beta$ , and  $\gamma$ ; purity, 99.8%); BTBPE; PEB; mixture of BDE congeners, syn and anti-DP; and the fish tissue standard reference material (WMF-01) were obtained from Wellington Laboratories. The SCCPs and MCCPs were from Dover Chemicals. Acetone, hexane, and dichloromethane (DCM) distilled in glass-grade solvents were obtained from Caledon Labs. Optima-grade methanol, water, Florisil (60–100 mesh), and Ottawa sand were obtained from Fisher Scientific.

### Sample collection, extraction, and cleanup

Lake trout (age, four to five years) were collected from Lake Ontario north of Main Duck Island, a location assumed to be representative of the eastern basin of the lake, as part of long-term monitoring by the Great Lakes Laboratory for Fisheries and Aquatic Sciences (GLLFAS). Fish were collected every four to six years (1979, 1983, 1988, 1993, 1998, and 2004), with five individuals (four in 1979) per time point. These samples were selected for inclusion in the present study to balance the need to evaluate accumulation of in-use chemicals and statistical considerations while maintaining the integrity of the GLLFAS archive. As such, we consider the reported concentration trends as being indicative of long-term trends in the lake trout.

Individual whole fish were homogenized then stored frozen in glass jars at  $-80^\circ\text{C}$  in the Great Lakes Specimen Bank maintained by the GLLFAS until analysis. Extraction and cleanup were performed at the Freshwater Institute and have

been described previously [7,23–26]. Briefly, tissues were thawed, weighed, and mixed with Hydromatrix® (cleaned at  $600^\circ\text{C}$  for 6 h; Varian), then loaded into a 100-ml extraction cell, spiked with the recovery internal standard solution (containing BDEs 71, 126, 197, and 207 [10  $\mu\text{l}$  of a 0.45 ng/ $\mu\text{l}$  solution] as well as [ $^{13}\text{C}$ ] $\alpha$ -, [ $^{13}\text{C}$ ] $\beta$ -, and [ $^{13}\text{C}$ ] $\gamma$ -HBCD [10  $\mu\text{l}$  of a 1 ng/ $\mu\text{l}$  solution]), and topped with Ottawa sand (an inert material used to fill any void volume in the cell). The samples were extracted in 1:1 DCM:hexane by accelerated solvent extraction (ASE 300; Dionex Canada). Extracts were dried over anhydrous sodium sulfate, reduced in volume, and filtered through a 1- $\mu\text{m}$  polytetrafluoroethylene syringe filter. Lipid content was determined gravimetrically in an aliquot of each extract, with the remains cleaned of lipids using gel-permeation chromatography eluting with 1:1 DCM:hexane. The extracts were then reduced to 1 ml in hexane and fractionated through a Florisil chromatography column. The PBDEs and DP were collected in fraction 1 (F1; 40 ml of hexane, then 20 ml of 85:15 hexane:DCM), whereas HBCD isomers and BTBPE were in fraction 2 (F2; 7 ml of 85:15 hexane:DCM, then 50 ml of 50:50 hexane:DCM). The SCCPs, MCCPs and PEB eluted into both fractions.

### Instrumental analysis

Before analysis, final extracts were spiked with instrument-performance internal standard solutions; BDE 156 in both F1 and F2; and  $\text{d}_{18}$ - $\alpha$ -,  $\beta$ -, and  $\gamma$ -HBCD isomers in F2. The PBDEs and DP (F1), BTBPE (F2), and PEB were analyzed by gas chromatography (GC)–low-resolution electron-capture negative-ion mass spectrometry on an Agilent 6890 GC coupled to an Agilent 5973 mass-selective detector. Quantitation was based on external standard solutions, monitoring  $m/z$  79/81 for the PBDEs, BTBPE, and PEB and  $m/z$  651/653 for the DP isomers. More detailed instrument conditions have been published previously [7,24]. The HBCD isomers were analyzed in F2 by liquid chromatography–tandem mass spectrometry as described elsewhere [23]. Pentabromoethylbenzene, SCCPs, and MCCPs were analyzed after the above analyses by combining the F1 and F2 fractions. The SCCPs and MCCPs were analyzed by GC–high-resolution capture negative-ion mass spectrometry using a Kratos instrument according to previously reported conditions [25,26].

### Quality control

Chromatographic peaks were identified based on retention times and on agreement of target/qualifier ion and transition ratios with standard values. Procedural blanks consisting of clean Hydromatrix® and Ottawa sand were extracted and analyzed with each sample set, and high-performance liquid chromatography and GC instrument solvent blanks were included to monitor for possible carryover. Method detection limits were calculated from procedural blanks as the mean plus three standard deviations of blank value, or based on a signal to noise ratio of five for compounds that were not detected in the blanks. The PBDEs were detected in procedural blanks, with congener method detection limits ranging from 0.05 to 1.03 ng/g wet weight, as were BDE 209, PEB, and DP, with method detection limits of 0.23, 0.21, and 0.01 ng/g wet wt, respectively. Small amounts of SCCPs and MCCPs were present in the procedural blanks and usually were less than 10% of that present in samples. The HBCD isomers ( $\alpha$ ,  $\beta$ , and  $\gamma$ ) and BTBPE were not detected in blanks; method detection limits from fortified blanks ranged between 0.001 and 0.01

ng/g wet weight for the HBCD isomers and was 0.005 ng/g wet weight for BTBPE.

Average recoveries of the PBDE recovery internal standards (BDEs 71, 126, 197, and 207) in all samples were  $85\% \pm 3\%$  (mean  $\pm$  standard error,  $n = 42$ ), which were used for compounds determined by GC. An initial prescreening of a fish from each sampling year revealed that these congeners were present at undetectable levels. Recoveries of the [ $^{13}\text{C}$ ] $\alpha$ -HBCD, [ $^{13}\text{C}$ ] $\beta$ -HBCD, and [ $^{13}\text{C}$ ] $\gamma$ -HBCD isomers in samples were  $67\% \pm 4\%$ ,  $61\% \pm 2\%$ , and  $75\% \pm 2\%$ , respectively. Additionally, the fish tissue standard reference material was processed in triplicate with samples, with mean concentrations deviating from reported values by 5, 16, 11, 8, 12, and 2% for BDEs 28, 47, 100, 99, 154, and 153, respectively (*Supporting Information*, Fig. S1 [<http://dx.doi.org/10.1897/08-162.S1>]). Reported concentrations were recovery-corrected with the PBDE or HBCD recovery values. The PBDE, PEB, SCCPs, MCCPs, and DP values were blank corrected.

#### Stable isotope $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ analysis

Carbon and nitrogen isotope analyses were accomplished by continuous-flow ion ratio mass spectrometry using a GV-Instruments<sup>®</sup> IsoPrime attached to a peripheral temperature-controlled EuroVector<sup>®</sup> elemental analyzer (University of Winnipeg Isotope Laboratory) using previously described methods [7]. Briefly, freeze-dried fish tissues were ground, loaded into tin capsules, and analyzed along with internally calibrated carbon and nitrogen standards (Pharma and Casein proteins:  $\delta^{13}\text{C} = -22.95$  and  $-26.98\%$  Vienna PeeDee Belemite, respectively;  $\delta^{15}\text{N} = 5.00$  and  $5.94\%$  IAEA-N-1, respectively). The delta values of carbon ( $\delta^{13}\text{C}_{\text{cell}}$ ) and nitrogen ( $\delta^{15}\text{N}_{\text{cell}}$ ) represent deviations from the standards, such that

$$\delta_{\text{sample}} = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \cdot 10^3$$

where  $R$  is the  $^{13}\text{C}$  to  $^{12}\text{C}$  or  $^{15}\text{N}$  to  $^{14}\text{N}$  ratio in the sample and the standard. Analytical precision, as determined from the analysis of duplicate samples, was  $\pm 0.16\%$  for  $\delta^{13}\text{C}$  and  $\pm 0.18\%$  for  $\delta^{15}\text{N}$ .

#### Data analyses

Data are presented on a lipid-normalized basis because of the assumption that chemicals are predominantly associated with the lipid portion of the fish, as has been the practice in previous contaminant trend studies [18]. We repeated the analysis on a wet-weight basis, however, to compare our results with those of studies that reported temporal concentration trends in this manner (*Supporting Information*, Figs. S2 and S3) [17]. Data are presented as the mean  $\pm$  standard error of the mean unless noted otherwise in the text.

Common first-order exponential growth ( $\ln C_t = \ln C_0 + k_1 t$ ) and decay ( $\ln C_t = \ln C_0 - k_2 t$ ) models were used to describe contaminant trends, where  $C_0$  and  $C_t$  are the initial concentration and concentration at time  $t$ , respectively, and  $k_1$  and  $k_2$  are rate constants, ensuring that our results are directly comparable to those of other studies using similar models [18,22,27]. Doubling-times and half-lives were calculated as  $\ln(2)/k_1$  and  $-\ln(2)/k_2$ , respectively. Individual concentration data for each time point were included to incorporate the variability for each year in our regression analysis, as recommended by Zar [28], consistent with several previous studies [17,20,29]. We repeated the regression analyses using the median concentration value at each year to facilitate comparisons with others who have used this approach [30], but this analysis

did not change any of the discussions or conclusions of the present study.

Analysis of variance was used for tests of significant differences among years, followed by the Tukey honestly significant-difference test for post hoc comparisons. The data were log-transformed before these analyses to meet the assumptions of normality and homogeneity of variances. Analysis of covariance was used for tests of significant differences in slopes of regression lines.

## RESULTS AND DISCUSSION

### PBDEs

We first present the temporal trends of PBDEs to assess how they compare to previous measurements of PBDEs in Lake Ontario lake trout [18,22,31]. The concentration trends (lipid wt) of the eight PBDEs (BDEs 28, 47, 85, 99, 100, 153, 154, and 209) that we analyzed in trout collected between 1979 and 2004 are shown in Figure 1 and in the *Supporting Information* (Table S1 and, on a wet-wt basis, Fig. S2 [<http://dx.doi.org/10.1897/08-162.S1>]). The concentration trends of most PBDEs evaluated (BDEs 28, 47, 99, 100, 153, and 154) showed a generally increasing trend between 1979 and either 1993 or 1998 (Fig. 1), with doubling-times ranging from 3.5 to 8.1 years during this time period (Table 1). Between 1998 and 2004, however, the PBDE concentrations either leveled off (BDE 154) or decreased significantly (analysis of variance,  $p < 0.05$ ; BDEs 28, 47, 99, 100, and 153). Our observations are consistent with the trend patterns previously observed in both Lake Ontario lake trout and herring gull eggs [18,22,27], and these findings have been attributed to the phasing out of the penta- and octa-BDE mixtures [22,27].

To compare with other results in Great Lakes fish, the concentrations of the sum of BDEs 47, 99, 100, and 153 in trout collected during 1998 and 2004 in our study ( $281 \pm 11$  and  $220 \pm 11$  ng/g wet wt, respectively) are consistent with those reported by Carlson and Swackhamer [31] in 2000 for lake trout from Lake Ontario ( $212 \pm 18$  ng/g wet wt). In other reports, however, PBDE concentrations in Lake Ontario lake trout represented by the sum of BDEs 47, 99, 100, and 153 ranged from 1.3 ng/g wet weight in 1980 to 97 ng/g wet weight in 2000 [18] and from 1.4 ng/g wet weight in 1980 to 71 ng/g wet weight in 1997 [22]. These levels are lower than our mean concentrations, which ranged from  $20 \pm 3$  ng/g wet weight in 1979 to  $281 \pm 11$  ng/g wet weight in 1998. The reason for this discrepancy is unknown, because the fish analyzed in each of the studies were of similar size and age. We also found good agreement between our results and reference material values (*Supporting Information*, Fig. S1). With the exception of Carlson and Swackhamer [31], however, there has been low replication in these studies, with  $n = 1$  composites having 4 to 10 fish in each sample [22],  $n \leq 3$  composites having five fish in each composite [18], and  $n = 4$  or 5 individuals (the present study), and perhaps these differences are indicative of the natural variability of PBDEs in the trout. Differences also could relate to the use of individual compared with composite samples.

Concentrations of BDE 209 were consistently detected in samples throughout the study period and ranged from  $2.3 \pm 0.5$  to  $12 \pm 5.3$  ng/g lipid ( $0.27 \pm 0.03$  to  $1.3 \pm 0.8$  ng/g wet wt). To our knowledge, BDE 209 has not been reported previously in Great Lakes fish, with the exception of trace amounts of BDE 209 being detected in a Lake Superior smelt sample [32]. In contrast to the other PBDE congeners, a large

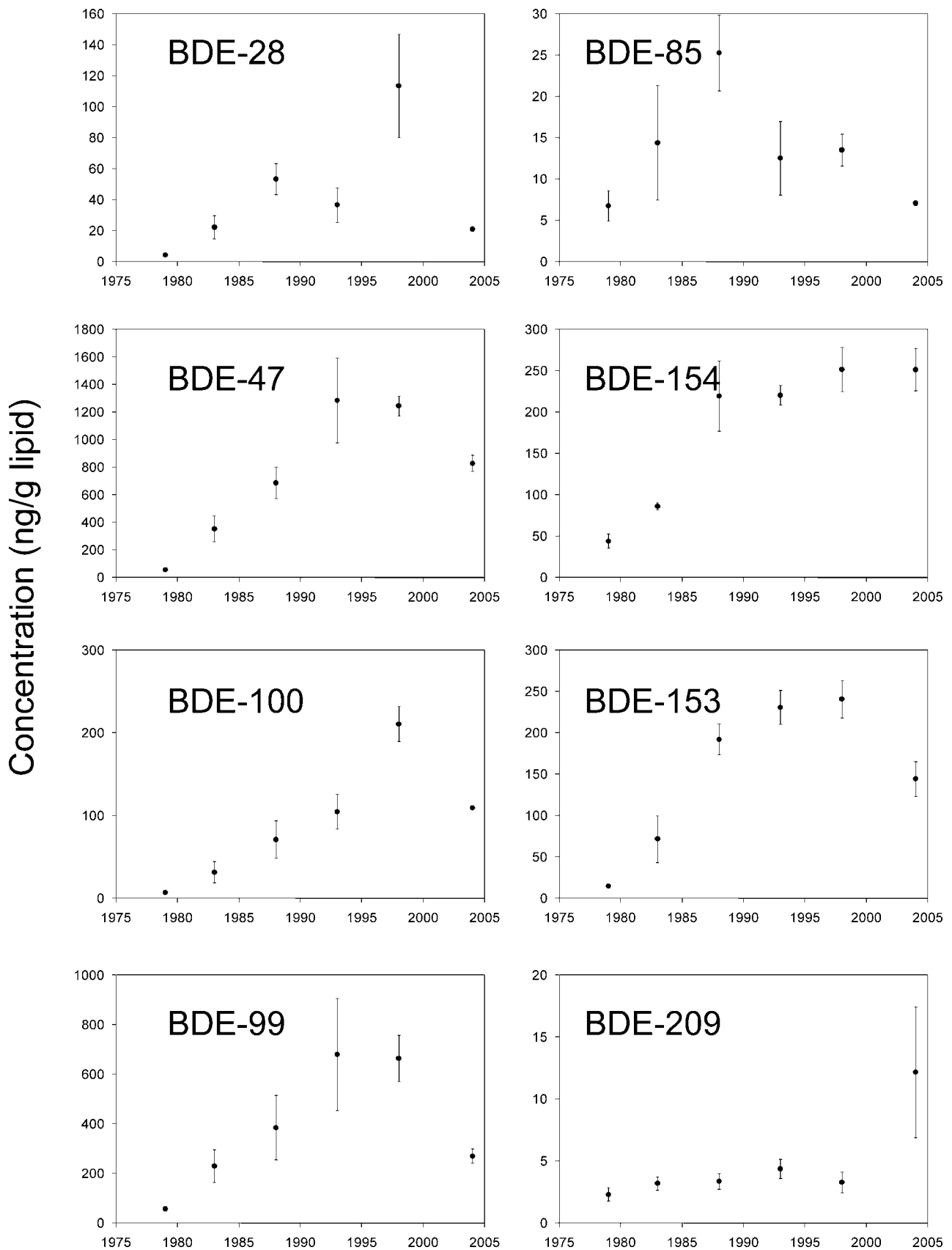


Fig. 1. Temporal trends of eight polybrominated diphenyl ether (PBDE) congeners (ng/g lipid) in Lake Ontario, Canada, lake trout (*Salvelinus namaycush*). Values are presented as the mean  $\pm$  standard error of the mean.

Table 1. Doubling-times ( $t_2$ ) or half-lives ( $t_{1/2}$ ) of various brominated and chlorinated flame retardants during the time period indicated<sup>a</sup>

	Year range	Doubling-time/ half-life (year)	95% Confidence interval <sup>b</sup>	<i>p</i>	<i>r</i> <sup>2</sup>
ΣPBDE	1979–1993	$t_2 = 4.2$	3.2–6.0	<0.001	0.74
BDE 28	1979–1998	$t_2 = 5.4$	3.7–10.1	<0.001	0.47
BDE 47	1979–1993	$t_2 = 3.5$	2.6–5.2	<0.001	0.70
BDE 100	1979–1998	$t_2 = 4.1$	3.3–5.3	<0.001	0.79
BDE 99	1979–1993	$t_2 = 4.4$	3.0–8.2	<0.001	0.57
BDE 154	1979–1998	$t_2 = 8.1$	6.1–12.0	<0.001	0.69
BDE 153	1979–1998	$t_2 = 5.2$	3.9–7.7	<0.001	0.66
BDE 209	1979–2004	$t_2 = 19.3$	10.1–217	<0.05	0.18
ΣHBCD	1979–2004	$t_{1/2} = 33$	18.0–176	<0.05	0.19
α-HBCD	1979–2004	$t_{1/2} = 40$	19.7–1019	0.06	0.13
β-HBCD	1979–2004	$t_{1/2} = 14$	9.6–24.4	<0.001	0.46
γ-HBCD	1979–2004	$t_{1/2} = 16$	9.5–48.7	<0.01	0.26
BTBPE	1979–1993	$t_2 = 5.9$	3.9–13.0	<0.01	0.47
DP	1979–2004	$t_{1/2} = 14$	9.9–24.0	<0.001	0.47
ΣSCCP	1988–2004	$t_{1/2} = 6.1$	4.3–10.9	<0.001	0.59
ΣMCCP	1979–1998	$t_2 = 15$	7.4–1049	0.05	0.19

<sup>a</sup> Data are presented only regarding those compounds for which the corresponding exponential relationship was either significant ( $p < 0.05$ ) or marginally significant ( $p < 0.10$ ). BTBPE = 1,2-bis(2,4,6-tribromophenoxy)ethane; DP = Dechlorane Plus; HBCD = hexabromocyclododecane; ΣMCCP = sum of medium-chain chlorinated paraffins; PBDE = polybrominated diphenyl ether; ΣSCCP = sum of short-chain chlorinated paraffins.

<sup>b</sup> Calculated according to Zar [28].

(approximately fourfold) increase in BDE 209 occurred between 1998 and 2004. A similar increasing trend for BDE 209 after the year 2000 was found in Great Lakes herring gull eggs [27]. The continued increase of BDE 209 through 2004 is not surprising, because the deca-BDE mixture remains in the marketplace [27] (<http://www.bsef.com>). There also was a significant increase in concentrations between 1979 and 2004, with a doubling-time of 19 years ( $p < 0.05$ ) (Table 1 and Fig. 1). Considerable variation was found in BDE 209 concentrations, however, especially in 2004, and the  $r^2$  value for the first-order exponential growth model was only 0.18. It is important to note that BDE 209 is debrominated into lower-brominated congeners by fish [33,34], and the observed trout body burden of BDE 209 likely underestimates the true uptake of this congener.

### HBCD

Total concentrations (Σ) of all HBCD isomers (α, β, and γ) ranged from  $16 \pm 3.5$  to  $33 \pm 3.0$  ng/g lipid ( $2 \pm 0.2$  to  $4 \pm 0.6$  ng/g wet wt). Tomy et al. [4] previously reported a ΣHBCD concentration of  $1.7 \pm 0.73$  ng/g wet weight in 2002 Lake Ontario lake trout, which is comparable to our average 1998 and 2004 concentration of  $2.8 \pm 0.27$  ng/g wet weight. The ΣHBCD showed a significant, exponential, declining trend during the sampling years, with a half-life of 33 years ( $p < 0.05$ ) (Table 1 and Fig. 2), although the  $r^2$  value for this regression was only 0.19. Similar to what was observed by Tomy et al., α-HBCD was the dominant isomer, with concentrations ranging from  $15.1 \pm 1.4$  to  $27.4 \pm 8.7$  ng/g lipid ( $1.7 \pm 0.20$  to  $3.4 \pm 0.43$  ng/g wet wt). Although an overall decrease of α-HBCD occurred over time (Fig. 2), the relationship was not significant ( $p = 0.06$ ). The β- and γ-HBCD concentrations ranged from  $0.16 \pm 0.03$  to  $0.94 \pm 0.27$  and  $1.4 \pm 0.3$  to  $6.5 \pm 1.9$  ng/g lipid, respectively ( $0.03 \pm 0.003$  to  $0.11 \pm 0.03$  and  $0.23 \pm 0.04$  to  $0.77 \pm 0.22$  ng/g wet wt, respectively). Both β- and γ-HBCD decreased exponentially ( $p < 0.001$ ), with half-lives of 14 and 16 years, respectively. Processes that are influencing the slower decline of α-HBCD compared with β- and γ-HBCD may include changes to the source of loadings

over time and/or bioisomerization of β- and γ-HBCD to α-HBCD [35], and this merits further study.

The temporal trends of HBCD reported in the literature are highly conflicting. Sellstrom et al. [30] found a doubling of ΣHBCD in guillemot eggs from the Baltic Sea over their study period (1969–2001), although concentrations have appeared to level off since the mid-1990s. Concentrations have increased exponentially, however, in Californian sea lions (*Zalophus californianus*) stranded between 1993 and 2003 [36]. More consistent with the present study, Vorkamp et al. [37] reported a nonstatistically significant decrease of ΣHBCD in peregrine falcon (*Falco peregrinus*) eggs from southern Greenland between 1986 and 2003 ( $p = 0.22$ ). Likewise, in the Canadian Arctic, ΣHBCD decreased from 1976 to 1987, and then again in 2004, in Ivory Gull eggs [38]. The reason for the differences observed among these studies is not clear. Although it is difficult to interpret differences in trends because of limited information regarding industrial production and usage, the global market demand for HBCD increased from 15,900 metric tons in 1999 to 16,700 metric tons in 2001 [36]. Industry, however, is undertaking voluntary measures to limit emissions at production and handling sites [5]. Perhaps the application and effectiveness of such measures are location specific.

### BTBPE

Concentrations of BTBPE in the lake trout increased exponentially ( $p < 0.01$ ) between 1979 ( $0.6 \pm 0.3$  ng/g lipid or  $0.07 \pm 0.03$  ng/g wet wt) and 1993 ( $2.6 \pm 0.6$  ng/g lipid or  $0.24 \pm 0.03$  ng/g wet wt), with a doubling-time of six years (Table 1 and Fig. 2). Concentrations peaked in 1993, however, and then decreased by 40% between 1993 and 2004, although the trend was not significant ( $p > 0.05$ ). Our average 1998 and 2004 concentration of  $1.9 \pm 0.3$  ng/g lipid was greater than those of emerald shiner ( $0.95$  ng/g lipid), goldeye ( $0.33$  ng/g lipid), white sucker ( $0.13$  ng/g lipid), and burbot ( $0.79$  ng/g lipid) collected from Lake Winnipeg, Canada, in 2002 [7].

To our knowledge, the present study is one of the first reports of BTBPE time trends in biota. In a Lake Ontario

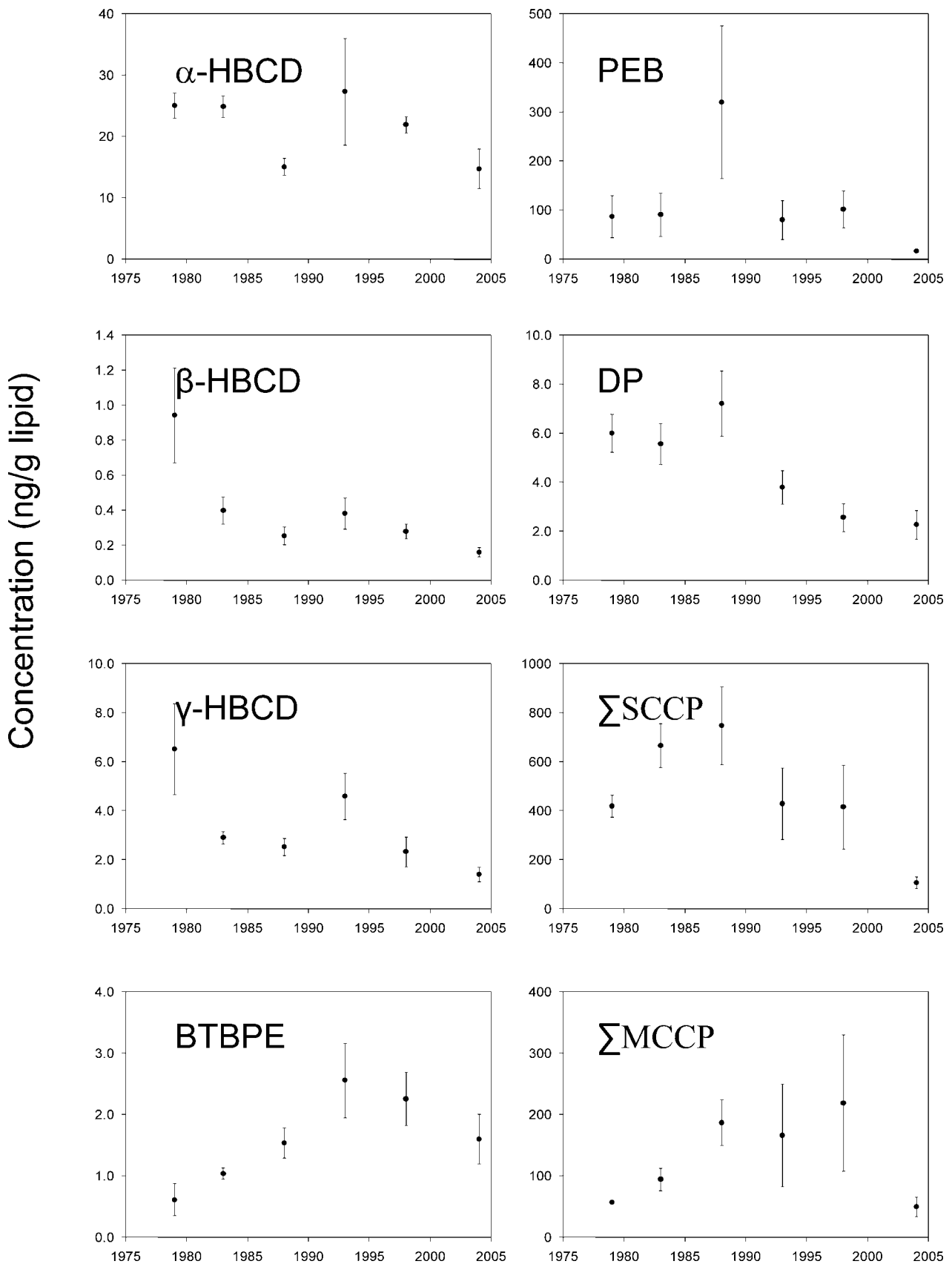


Fig. 2. Temporal trends of brominated ( $\alpha$ -hexabromocyclododecane [HBCD],  $\beta$ -HBCD,  $\gamma$ -HBCD, 1,2-bis[2,4,6-tribromophenoxy]ethane [BTBPE], and pentabromoethylbenzene [PEB]) and chlorinated (Dechlorane Plus [DP], short-chain chlorinated paraffins [ $\Sigma$ SCCP], and medium-chain chlorinated paraffins [ $\Sigma$ MCCP]) flame retardants (ng/g lipid) in Lake Ontario, Canada, lake trout (*Salvelinus namaycush*). Values are presented as the mean  $\pm$  standard error of the mean.

sediment core, however, BTBPE increased consistently, starting in the early 1980s, and the highest concentrations (a sixfold increase) were observed in surficial sediment, which corresponded to the year 2000 [9]. Because BTBPE is now being used as a replacement chemical for the octa-BDE mixture [6], our results will provide a baseline to evaluate future usage patterns.

#### PEB

The concentrations of PEB ranged from  $17 \pm 3$  to  $320 \pm 156$  ng/g lipid ( $5 \pm 2$  to  $17 \pm 6$  ng/g wet wt) and showed no relationship with time ( $p > 0.05$ ) (Fig. 2). To our knowledge, the present study represents one of the first reported time trends of PEB in the environment, and PEB was only recently detected in air and biota [6,8,11]. Pentabromoethylbenzene was used as an additive flame retardant in the 1970s and 1980s, with a production of 45 to 450 tons per year in 1977. By 1986, however, its production decreased to between 5 and 225 tons per year [10]. In the United States, current production, if any, is confidential [10]. Hoh et al. [10] hypothesized that there could be fresh emissions of PEB in Chicago, because they observed relatively high concentrations in the Chicago atmosphere in July 2003. Our results support the hypothesis of recent emissions to the environment, because no consistent decrease was found in concentration with time. Although the lowest PEB concentrations were observed in 2004, no significant differences were found in concentrations among years ( $p > 0.05$ ).

#### DP

Concentrations of DP ranged from  $2.3 \pm 0.6$  to  $7.2 \pm 1.3$  ng/g lipid ( $0.31 \pm 0.07$  to  $0.85 \pm 0.20$  ng/g wet wt) (Fig. 2). The DP concentrations decreased significantly ( $p < 0.001$ ) during the sampling period, with a half-life of 14 years (Table 1), which was not significantly different ( $p > 0.05$ ) from the 17-year half-life of DP observed in Niagara River suspended sediment collected between 1980 and 2002 [12]. A similar trend also was observed in a Lake Ontario, USA, sediment core, with a large increase beginning in the 1970s, although concentrations peaked later in 1994 [9]. Sverko et al. [12] hypothesized that usage/production of DP may be decreasing or that modern manufacturing processes currently release less free DP into the environment. In contrast to the present study, however, DP concentrations in Lake Erie, USA, walleye did not show a significant relationship with time [11]. Whether DP finds use as a replacement to PBDEs in some applications remains to be determined.

#### SCCPs and MCCPs

For  $\Sigma$ SCCP and  $\Sigma$ MCCP, Lake Ontario lake trout concentrations ranged from  $107 \pm 23$  to  $748 \pm 158$  ng/g lipid ( $17 \pm 3$  to  $91 \pm 18$  ng/g wet wt) and from  $50 \pm 16$  to  $187 \pm 37$  ng/g lipid ( $7.9 \pm 2$  to  $34 \pm 15$  ng/g wet wt), respectively. In comparison, Houde et al. [39] found  $\Sigma$ SCCP and  $\Sigma$ MCCP concentrations of  $34 \pm 14$  and  $24 \pm 9.8$  ng/g wet weight, respectively, in Lake Ontario lake trout collected in 2001. These data are comparable to our  $\Sigma$ SCCP concentrations ( $47 \pm 30$  and  $17 \pm 3$  ng/g wet wt in 1998 and 2004, respectively) as well as our  $\Sigma$ MCCP concentrations ( $25 \pm 13$  and  $8 \pm 2$  ng/g wet wt in 1998 and 2004, respectively), collected during a similar time period.

The  $\Sigma$ SCCP showed an increasing (but nonsignificant) trend in the trout from 1979 until 1988 and then decreased signif-

icantly until 2004, with a half-life of six years ( $p < 0.001$ ) (Table 1 and Fig. 2). In comparison,  $\Sigma$ SCCP concentrations in a sediment core from the Niagara basin of Lake Ontario peaked in the 1970s and have decreased since that time [40]. Tomy et al. [41] also recently reported consistent decreases in beluga whale blubber from Hendrickson Island and Pangnirtung in the Canadian Arctic. The  $\Sigma$ MCCP concentrations increased significantly from 1979 until 1998 ( $p = 0.05$ ), then decreased in 2004 to less than the 1979 levels (Table 1 and Fig. 2). In a sediment core from Switzerland,  $\Sigma$ MCCP increased since 1965, reaching a maximum in the surface sediment [42].

#### Potential influence of food-web processes

Variations in food-web processes may be influencing our interpretation of temporal trends, because the Lake Ontario food web has changed since the 1970s [43]. Values of  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  commonly are used in studies to evaluate food-web processes [44]. The  $\delta^{15}\text{N}$  values provide information about the trophic levels at which organisms feed, with increases of approximately 2 to 4‰ for each trophic level, whereas  $\delta^{13}\text{C}$  is useful for evaluating the origin of carbon used by an organism [44].

In the present study,  $\delta^{15}\text{N}$  increased significantly ( $p < 0.01$ ) from 1979 ( $15.6\text{‰} \pm 0.29\text{‰}$ ) to 1988 ( $16.8\text{‰} \pm 0.19\text{‰}$ ), then remained stable to 1998 ( $16.7\text{‰} \pm 0.10\text{‰}$ ), and decreased significantly ( $p < 0.001$ ) from 1998 to 2004 ( $14.9\text{‰} \pm 0.26\text{‰}$ ) (Fig. 3). The decrease between 1998 and 2004 of approximately 2‰ may represent a full trophic level, because a large variability in trophic fractionation is found among species [44]. The  $\delta^{13}\text{C}$  values decreased linearly ( $p < 0.001$ ,  $r^2 = 0.37$ ) from 1979 ( $-27.7\text{‰} \pm 0.24\text{‰}$ ) to 2004 ( $-30.0\text{‰} \pm 0.32\text{‰}$ ) at a rate of 0.07‰ per year.

These changes in stable isotopes do not necessarily imply changes to the lake trout diet, because they also could be reflective of temporal variations in loadings or changes at the base of the food web [44]. Unfortunately, to our knowledge, no previous studies have evaluated changes to stable isotopes at the base of the Lake Ontario food web between 1979 and 2004. Stable isotope trends were reported, however, in two Lake Ontario sediment cores collected in 1993 and 1994 [45], overlaying our 1979 to 1993 data points. The  $\delta^{13}\text{C}$  values in these cores decreased from the 1970s or 1980s to the top of the cores, which corresponds to the trend in fish, which was attributed to decreased productivity in Lake Ontario, because  $^{12}\text{C}$  is preferentially taken up during photosynthesis [45]. This suggests that at least during the period between 1979 and 1993, the decrease in  $\delta^{13}\text{C}$  in Lake Ontario lake trout was caused by changes at the base of the food web as a result of declining primary productivity. In contrast to  $\delta^{13}\text{C}$ , the  $\delta^{15}\text{N}$  values in the sediment cores were relatively constant between 1979 and 1993 [45]. Therefore, this provides some circumstantial evidence suggesting that the  $\delta^{15}\text{N}$  trends observed in the trout could represent changes to fish trophic position.

The largest change to both  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  in lake trout occurred between the 1998 and 2004 sampling time points, and no sediment core data are available to indicate whether this resulted from changes occurring at the base of the food web. Nonetheless, in 1998, the round goby (*Neogobius melanostomus*) was first observed in Lake Ontario and now represents the second most abundant diet item (36% of overall diet mass) of lake trout after alewife (*Alosa pseudoharengus*) [43]. Round gobies primarily consume dreissenids and mysids

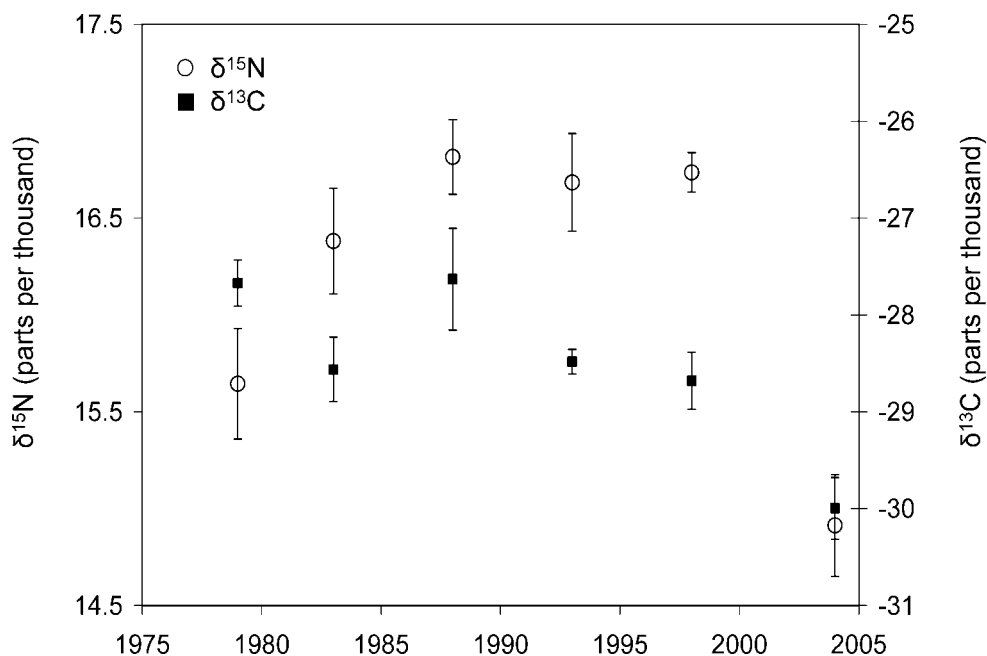


Fig. 3. Temporal trends of  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  in Lake Ontario, Canada, lake trout (*Salvelinus namaycush*) collected between 1979 and 2004. Values are presented as the mean  $\pm$  standard error of the mean.

(*Mysis relicta*) [46]. This switch in the lake trout food web since 1998 may be a factor in the significant change in  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  observed at this time.

It is important to note that the exact mechanism for the change in  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  between 1998 and 2004 cannot be evaluated with our data. Furthermore, the bioenergetics of lake trout also likely have changed as a result of dietary shifts, and  $\delta^{15}\text{N}$  does not track bioenergetics in the same manner as contaminants do [47]. Therefore, the incorporation of stable isotope values into our analyses should be treated as a hypothesis. Further evaluations of temporal changes in food-web tracers in Lake Ontario as well as a retrospective analysis of temporal changes in stable isotopes at the base of the food web are recommended.

Adjusting temporal concentration trends for changes in  $\delta^{15}\text{N}$  (trophic position) has the potential to influence the interpretation of contaminant trends [19]. We used a first-order, linear-regression approach, which is described in detail by Hebert and Weseloh [19] and by Hebert and Keenleyside [48], to account for possible changes in fish trophic position. For this approach, the natural logarithm of contaminant concentration is regressed with  $\delta^{15}\text{N}$  values, and the residuals, rescaled by adding the grand mean contaminant concentration, represent concentrations adjusted for  $\delta^{15}\text{N}$  values [19,48]. The analysis-of-covariance interaction term between year and  $\delta^{15}\text{N}$  was not significant ( $p > 0.05$ ), indicating no significant difference between the slopes of the regression lines among years for all contaminants.

Figure 4 shows a comparison of temporal trends of BDEs 47, 99, 153, and 209 adjusted and unadjusted for  $\delta^{15}\text{N}$ , and each of the  $\delta^{15}\text{N}$ -adjusted PBDE congener trends are shown in the Supporting Information (Fig. S4 [http://dx.doi.org/10.1897/08-162.S1]). Following adjustment, the BDE congener doubling-times between 1979 and either 1993 or 1998 were not significantly different from the unadjusted data ( $p > 0.05$ ) (Supporting Information, Table S2 [http://dx.doi.org/10.1897/08-162.S1]), suggesting that food-web changes did not

influence temporal trends of these PBDEs up until 1993 or 1998. After adjustment, however, a significant concentration decrease no longer existed between 1998 and 2004 for BDEs 28, 47, 99, and 100 ( $p > 0.05$ ), and concentrations of BDEs 153 and 154 increased significantly between these two time periods ( $p < 0.05$ ). This indicates that food-web changes may be at least partially responsible for the observed decrease in PBDE concentrations between 1998 and 2004. This result may have important implications. Even though the exact mechanism for the change in  $\delta^{15}\text{N}$  values between 1998 and 2004 cannot be determined in the present study and  $\delta^{15}\text{N}$  may not be tracking all the food-web processes influencing contaminant accumulation [47], our data suggests that a better knowledge of recent alterations in the Lake Ontario food web is needed to more accurately interpret changes in lake trout body burdens in terms of PBDE loadings.

Adjustment for  $\delta^{15}\text{N}$  did not change the temporal trend pattern for BDE 209 (Fig. 4) and for HBCD, PEB, and DP (Supporting Information, Fig. S5 and Table S2 [http://dx.doi.org/10.1897/08-162.S1]). For BTBPE, adjustment for  $\delta^{15}\text{N}$  did not result in a significant change to the exponential increase in BTBPE between 1979 and 1993 ( $p > 0.05$ ) (Supporting Information, Table S2), but this adjustment did cause a leveling off of concentrations between 1993 and 2004 (Supporting Information, Fig. S5). For  $\Sigma\text{SCCP}$ , adjustment for  $\delta^{15}\text{N}$  changed its pattern such that concentrations peaked in 1983 and then declined significantly ( $p < 0.01$ ), with a half-life of 12 years, and for  $\Sigma\text{MCCP}$ , the increase between 1979 and 1998 was no longer significant following adjustment (Supporting Information, Table S2 and Fig. S5).

Growth also can influence contaminant trends in fish through the process of growth dilution, whereby increases in body weight reduce or dilute the internal concentration in the fish [49]. The relative changes in growth rates among years for the fish of the present study can be evaluated by assessing differences in weight and length, because all fish were of a similar age (five years for fish collected in 1988, 1993, 1998,

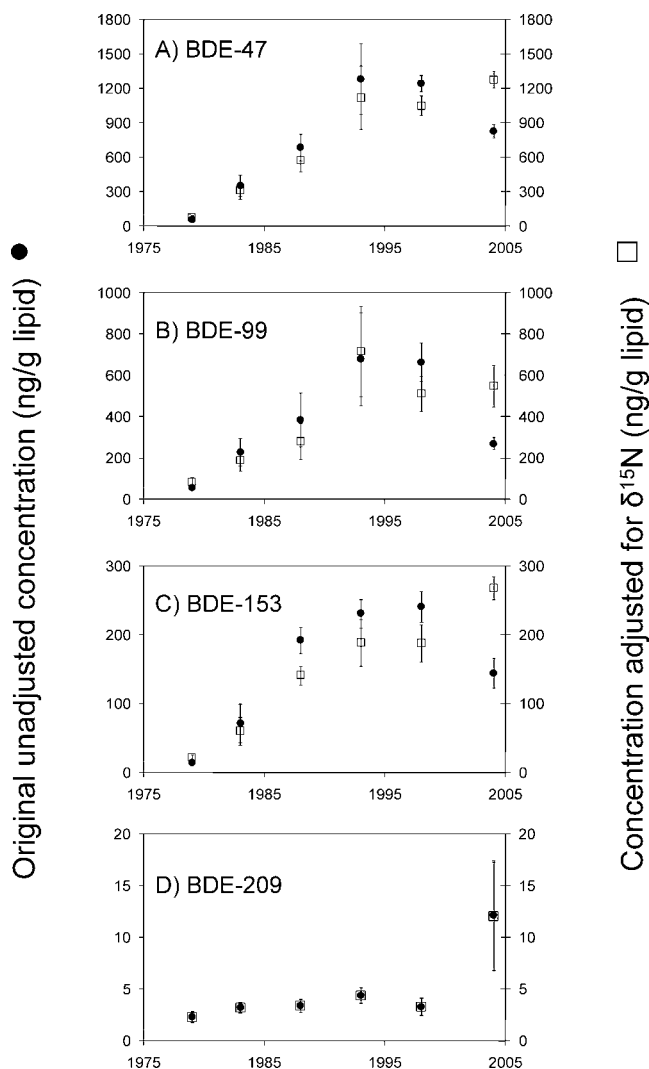


Fig. 4. Temporal trends of (A) brominated diphenyl ether (BDE) 47, (B) BDE 99, (C) BDE 153, and (D) BDE 209 (ng/g lipid) in Lake Ontario, Canada, lake trout (*Salvelinus namaycush*), using original, unadjusted concentrations and concentrations that have been adjusted for  $\delta^{15}\text{N}$ . Values are presented as the mean  $\pm$  standard error of the mean.

and 2004 and four and five years for fish collected in 1979 and 1983). Lake trout collected in 2004 had a significantly higher weight ( $p < 0.05$ ) compared with fish from any other year. These 2004 fish also were longer than those in any other year (although only significantly so compared to 1988,  $p < 0.05$ ) (*Supporting Information*, Table S3 [<http://dx.doi.org/10.1897/08-162.S1>]). This provides evidence that the fish collected in 2004 may have been growing faster than in any other year. We hypothesize that if fish from 2004 were, indeed, growing at a faster rate compared with the other time points, then this also could be a factor influencing the observed leveling off or decrease of BDEs 28, 47, 99, 100, 153, and 154 at this time point.

Finally, metabolic biotransformation of the contaminants by the lake trout has the potential to influence contaminant concentrations, because some of the compounds included in the present study (PBDE congeners and HBCD isomers) can be biotransformed in fish [34,35]. Bhavsar et al. [50] suggested that the impact of biotransformation on observed concentrations may be minimal for PBDE congeners susceptible to both

biodegradation and bioformation (BDEs 28, 47, 85, 99, 100, 153, and 154). Nonetheless, further modeling work is recommended to quantify the influence of biotransformation on our results.

#### SUPPORTING INFORMATION

**Table S1.** Concentrations (ng/g lipid) of brominated and chlorinated flame retardants in Lake Ontario, Canada, lake trout (*Salvelinus namaycush*). Values are presented as the mean  $\pm$  standard error of the mean.

**Table S2.** Doubling-times ( $t_2$ ) or half-lives ( $t_{1/2}$ ) of various brominated and chlorinated flame retardants adjusted for  $\delta^{15}\text{N}$  during the time period indicated.

**Table S3.** Lake Ontario, Canada, lake trout (*Salvelinus namaycush*) sample information.

**Fig. S1.** Comparison of concentrations between certified brominated diphenyl ether (BDE) values in Wellington fish standard reference material (SRM) and measurements made by Department of Fisheries and Oceans (DFO) laboratory. Each bar represents the mean  $\pm$  standard error of the mean in the measurement ( $n = 3$ ).

**Fig. S2.** Temporal trends of eight polybrominated diphenyl ether congeners (ng/g wet wt) in Lake Ontario, Canada, lake trout (*Salvelinus namaycush*). Values are presented as the mean  $\pm$  standard error of the mean.

**Fig. S3.** Temporal trends of brominated [ $\alpha$ -hexabromocyclododecane (HBCD),  $\beta$ -HBCD,  $\gamma$ -HBCD, 1,2-*bis*(2,4,6-tri-bromophenoxy)ethane (BTBPE), and pentabromoethylbenzene (PEB)] and chlorinated [Dechlorane Plus (DP), short-chain chlorinated paraffins ( $\Sigma\text{SCCP}$ ), and medium-chain chlorinated paraffins ( $\Sigma\text{MCCP}$ )] flame retardants (ng/g wet wt) in Lake Ontario, Canada, lake trout (*Salvelinus namaycush*). Values are presented as the mean  $\pm$  standard error of the mean.

**Fig. S4.** Temporal trends of eight polybrominated diphenyl ether (PBDE) congeners (ng/g lipid) in Lake Ontario, Canada, lake trout (*Salvelinus namaycush*), where concentrations have been adjusted for  $\delta^{15}\text{N}$ . Values are presented as the mean  $\pm$  standard error of the mean.

**Fig. S5.** Temporal trends of brominated [ $\alpha$ -hexabromocyclododecane (HBCD),  $\beta$ -HBCD,  $\gamma$ -HBCD, 1,2-*bis*(2,4,6-tri-bromophenoxy)ethane (BTBPE), and pentabromoethylbenzene (PEB)] and chlorinated [Dechlorane Plus (DP), short-chain chlorinated paraffins ( $\Sigma\text{SCCP}$ ), and medium-chain chlorinated paraffins ( $\Sigma\text{MCCP}$ )] flame retardants (ng/g lipid) in Lake Ontario, Canada, lake trout (*Salvelinus namaycush*), where concentrations have been adjusted for  $\delta^{15}\text{N}$ . Values are presented as the mean  $\pm$  standard error of the mean.

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