Journal of Great Lakes Research 37 (2011) 148–159

Contents lists available at ScienceDirect

Journal of Great Lakes Research

journal homepage: www.elsevier.com/locate/jglr

Trends of legacy and emerging-issue contaminants in Lake Simcoe fishes

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ARTICLE INFO

Article history:
Received 5 August 2009
Accepted 23 March 2010
Available online 12 August 2010

Communicated by Stephanie Guildford

Index words:
Lake Simcoe
Sport fish
Mercury
Polychlorinated biphenyl PCB
Polybrominated diphenyl ether PBDE
Temporal trend

ABSTRACT

The temporal trends of legacy contaminants (i.e., mercury, PCBs, and DDT) and the current status of both legacy and emerging-issue (polybrominated diphenyl ethers (PBDEs) and polychlorinated naphthalenes (PCNs)) chemicals were examined in sport fishes from Lake Simcoe. Mercury concentrations decreased statistically significantly with time in lake trout, cisco, smallmouth bass, and yellow perch, consistent with assumed loading patterns. In contrast, mercury in largemouth bass, northern pike, and walleye showed a random relationship with time and increased statistically significantly with time in whitefish. Such differences among species suggest the influence of food-web processes (e.g., nutrient inputs and invasive species) in controlling temporal patterns of mercury in Lake Simcoe fishes. Concentrations of total-PCB and total-DDT in lake trout and whitefish generally followed an exponential decay pattern, with concentrations stabilizing during the 1990s. Current concentrations of legacy contaminants were, for the most part, below fish consumption guidelines for the general population. The risk associated with fish consumption to the sensitive population of women of child bearing age and children under 15 was of more concern for the larger, predatory fishes due to elevated mercury and PCBs. Recent measurements of PCNs and PBDEs were not of concern to Lake Simcoe sport fish consumers, although continued monitoring of fish contaminant levels is recommended in light of possible further loadings to this system. Contaminant related issues in Lake Simcoe sport fishes were of less or similar concern compared with the North American Great Lakes.

Introduction

Lake Simcoe, the largest inland lake in southern Ontario outside the Great Lakes, is a valuable natural, social, and economic resource. The Lake Simcoe recreational fishery is worth more than $100 million dollars per year and accounts for 15% of all angling efforts in Ontario (Eimers et al., 2005; LSEMS, 2008). Fish species most often targeted are lake trout (*Salvelinus namaycush*), lake whitefish (*Coregonus clupeaformis*), and yellow perch (*Perca flavescens*), although cisco (*Coregonus artedi*), northern pike (*Esox lucius*), and smallmouth bass (*Micropterus dolomieu*) are also important (Evans et al., 1996; LSEMS, 2008). Given the importance of the Lake Simcoe fishery, it is important to evaluate the risk of stressors, such as contaminants, to sport fish consumers.

The presence of contaminants has been identified as a potential threat to the ecological health of Lake Simcoe (LSSAC, 2008). In the Simcoe watershed, dichlorodiphenyltrichloroethane (DDT) was used intensively as a pesticide in agriculture and in mosquito control programs until restrictions were introduced in 1970, and methyl mercury was used for seed treatment until it was phased out between 1970 and 1972 (Frank et al., 1978). Sources of these and other contaminants could also include runoff from sanitary landfill sites and sewage-sludge disposal areas, urban stormwater runoff, and atmospheric deposition (OMOE, 1978). Increasing urban land use, which presently represents 6% of the watershed (LSRCA and OMOE, 2009), may also be contributing to contaminant loadings to the lake (LSEMS, 2008). Indeed, recent sediment data suggest that Barrie, Ontario (population of 128,000) was a source of previously regulated organic contaminants such as polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) (Helm et al., 2010-this issue). However, atmospheric deposition associated with the large urban and industrial areas to the southwest of Lake Simcoe was also likely important (Helm et al., 2010-this issue). Sediment concentrations of polybrominated diphenyl ether (PBDE) flame retardants were also associated with Barrie, but to a lesser extent than the historical contaminants, and atmospheric deposition from sources originating from areas of higher population density appeared to have a dominant

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0380-1330/$ – see front matter
doi:10.1016/j.jglr.2010.07.001

contribution (Helm et al., 2010-this issue). Presently, sport fish consumption restrictions have been advised for the larger sized individuals of lake trout, walleye (*Sander vitreus*), smallmouth bass, largemouth bass (*Micropterus salmoides*), lake whitefish, burbot (*Lota lota*), common carp (*Cyprinus carpio*), and bowfin (*Amia calva*) (OMOE, 2009).

The Lake Simcoe Science Advisory Committee (LSSAC) has put forward an objective to achieve contaminant levels in fishes that do not cause consumption restrictions and to ensure that long-term trends in contaminant levels are declining (LSSAC, 2008). However, the last study which documented contaminant trends in Lake Simcoe fishes presented data only up until 1976 (Frank et al., 1978). Frank et al. (1978) found that concentrations of DDT and polychlorinated biphenyls (PCBs) generally declined between 1970 and 1975–1976. In contrast, for the most part, mercury did not change during this same time period (Frank et al., 1978). Since the 1970s, the population in the Lake Simcoe watershed (currently ~400,000) has more than doubled (Eimers et al., 2005) and is expected to increase (LSSAC, 2008). In addition, the Lake Simcoe food web has changed dramatically due to processes such as nutrient inputs and exotic species invasions (LSSAC, 2008). There is thus a need to include more recent data in temporal trend analyses and to assess the risk of contaminant exposure to sport fish consumers.

The first objective of this study was to perform a comprehensive data analysis of temporal trends of legacy contaminants (DDT, mercury, and PCB) in Lake Simcoe fishes. The second objective was to assess the current status of both legacy and emerging-issue (PBDEs and PCNs) chemicals by comparing recent measurements to fish consumption guidelines as well as to data for Great Lakes sport fishes.

Methods

The Sport Fish Contaminant Monitoring Program (SFCMP) of the Ontario Ministry of the Environment (OMOE, Canada), in partnership with the Ontario Ministry of Natural Resources (OMNR) and other agencies/institutes, has been monitoring sport fishes from Lake Simcoe for a suite of toxic chemicals since the 1970s. Fishes were collected in the late summer or early fall by gill netting and trawling primarily at Georgina Island (44.396°, −79.299°) and Strawberry Island (44.554°, −79.336°) although collection site was not recorded consistently for every species and year. Upon collection, total length, weight, and gender of each fish were recorded, and a skinless, boneless fillet of the dorsal muscle was removed and stored frozen at −20 °C until analysis.

Chemical analyses

All chemical analyses were performed at the OMOE, which is accredited by the Canadian Association for Laboratory Accreditation. These methods have been previously published (Kolic et al., 2009; OMOE, 2006, 2007a,b,c), and are described briefly in Appendix A. All fish samples collected were analyzed for mercury and 65% and 53% of lake trout and whitefish, respectively, were analyzed for both total-PCB and total-DDT (Table A1). Some lake trout ($n=16$ and 11) and whitefish ($n=10$ and 5) were also analyzed for dioxins, furans and dioxin-like PCBs, and PCNs and PBDEs, respectively.

Data analysis

Data from the different collection sites were pooled in order to be consistent with data treatment in the *Guide to Eating Ontario Sport Fish* (OMOE, 2009) and because site information was not available for every year. The results of this study should thus be considered representative of Lake Simcoe on a system-wide basis. There were no significant differences (ANCOVA, $p<0.01$) in length-adjusted concentrations among locations (for the years that this information was available) except for mercury in walleye collected in 1999. This is not surprising considering that surficial sediment concentrations of organochlorines (Helm et al., 2010-this issue) and mercury (Landre et al., 2010-this issue) were also relatively uniform across the lake, with the exception of Kempenfelt Bay (where no fishes were collected). Further, the larger fishes (i.e., lake trout, whitefish, and walleye) have relatively large home ranges and likely integrate their exposure over the collection sites (Scott and Crossman, 1998).

For temporal trend analysis, the focus was on mercury, total-PCB and total-DDT (sum of *p,p′*-DDT, *o,p′*-DDT, *p,p′*-DDD, and *p,p′*-DDE). Other chemicals were either mostly below detection limits (OCS, HCB, mirex, photomirex, toxaphene, and chlordane) or were only measured in more recent time periods (PCDD/Fs, DL-PCBs, PCNs, and PBDEs). Due to data availability, lake trout and whitefish were focused on as these species were collected and analyzed at multiple time points. However, mercury concentrations were also available for cisco, largemouth bass, northern pike, smallmouth bass, walleye, whitefish, and yellow perch. For all contaminants, non-detect values were substituted with one half of the detection limit, allowing consistency with previously published temporal trend studies (Bhavsar et al., 2007; DeVault et al., 1996; Huestis et al., 1996; Suns et al., 1993) and the *Guide to Eating Ontario Sport Fish* (OMOE, 2009). The frequency of detection for each chemical/species combination was, on average, 99%, and in all cases was greater than 75% (Table A1).

Although hydrophobic organic chemicals such as PCBs and DDT partition preferentially into the lipid portion of organisms (Gobas and Morrison, 2000), concentrations were not lipid normalized because guideline levels are expressed on a wet-weight basis and this better reflects levels to which humans are exposed. Further, several recent temporal and spatial trend studies of organic contaminants in biota have also expressed data on a wet-weight basis (Bhavsar et al., 2007; French et al., 2006; Hickey et al., 2006), which allows consistency with our results. However, the temporal trends of total-PCB and total-DDT were also evaluated on a lipid-weight basis in order to assess the influence of lipid on contaminant trends.

Contaminant concentrations often increase with fish length (Miller, 1994; Somers and Jackson, 1993). In order to account for the influence of length, fish within a limited size range were included into the analysis similar to other contaminant trend studies (Bhavsar et al., 2007; French et al., 2006; Gewurtz et al., 2010). For lake trout and walleye, size ranges of 55–65 and 45–55 cm were used, respectively, to be consistent with those employed by Bhavsar et al. (2007) in their evaluation of PCBs in the Great Lakes. For the other species, a consistent approach for choosing the size range was followed: first, the grand mean length across years for each chemical/species combination was calculated, and second, a size range of 11 cm centered at the mean was selected, to be consistent with the size range chosen by Bhavsar et al. (2007). Significant differences (ANOVA, $p<0.05$) in mean length among years were then determined for the selected fish. If there were significant differences, unplanned multiple comparisons were performed with the Tukey test to identify years showing significant differences. If most pair-wise comparisons showed no significant differences in length, a size range of 11 cm was kept. Otherwise the size range was narrowed and significant differences in length were tested for the narrowed size range. The length range selected for each fish species and chemical are shown in Table A2 and Fig. A1. Table A2 also shows the results of the ANOVA and Tukey test used to test for significant differences in length among years.

Temporal trends of individuals within the limited size range were evaluated using the common first-order exponential decay model:

$$C_t = C_0 e^{k_2 t} \quad (1)$$

where C_0 and C_t are concentrations initially and at time t (years elapsed from the start of the available record), respectively, and k_2 is the apparent first-order rate constant. Use of the decay model allows direct comparison of our results with those who have used a similar model in temporal trend studies in the Great Lakes (DeVault et al., 1996; French et al., 2006; Huestis et al., 1996; Paterson et al., 2005). This model is intrinsically linear when log-transformed and was estimated by ordinary least-squares linear regression ($\ln C_t = \ln C_0 + k_2 t$). Individual concentration data for each time point were included to incorporate the variability of each year in our regression analysis, as recommended by Zar (1984), consistent with several previous studies (Hickey et al., 2006; Huestis et al., 1996; Paterson et al., 2005). However, temporal trend analysis using arithmetic means was also performed (DeVault et al., 1996; French et al., 2006), which led to similar results except that both r^2 and p-values were generally greater because the use of mean values does not incorporate variability within years and lowers the power associated with the tests.

The temporal trends were also evaluated by three additional statistical approaches in order to determine if the assessment of trends was robust. First, a coarse-grained time analysis was performed by comparing concentrations at two representative time periods: 1970–1979 and 1999–2007 for mercury, and 1977–1983 and 2005–2006 for total–PCB and total-DDT. These time periods were selected to maximize data availability for a comparison of past to recent contaminant concentrations. The non-parametric Kruskal–Wallis test was used to test for significant differences among time periods due to non-normal distributions (Shapiro–Wilk, $p<0.05$) for some chemicals/species. The second and third approaches evaluated how the use of fish within a limited size range influenced the analysis. The regression based ANCOVA approach described by Hebert and Keenleyside (1995) was applied to mercury in cisco, largemouth bass, northern pike, walleye, and yellow perch. These data, unlike other chemicals/species, were consistently related to length, and the slopes of the relationship between the logarithm of concentration and length were parallel among years (ANCOVA, $p>0.05$). Both concentration and length were log-transformed prior to the analysis since their relationship is typically assumed to follow a power function (Bhavsar et al., 2008a; Scheider et al., 1998). Finally, a power function for length was added into the exponential decay model as follows:

$$C_{t,L} = C_0 e^{k_2 t} + aL^b \tag{2}$$

where $C_{t,L}$ is the concentration at time t (years elapsed from the start of the available record) and length L (cm), a is a constant and b is the power of the relationship between concentration and length. Values of b greater than zero indicate a positive relationship between concentration and length and b values not significantly different from zero suggest independence between concentration and length. The model was estimated using a least-squares loss function and fitted with the Levenberg–Marquardt Algorithm. Length and time were not correlated for mercury in lake trout, cisco, largemouth bass, and walleye, and for total-PCB in lake trout and whitefish. For the other chemical and species combinations, r^2 was less than 0.10 indicating that the extent of multicollinearity was slight. In order to assess if consideration of fish length in Eq. (2) was necessary, Akaike's Information Criterion (AIC) was used to determine the level of support associated with the addition of the power function for length compared with the original exponential decay model (Eq. (1) using all data) (Burnham and Anderson, 2002). AIC_c (AIC corrected for small sample size) was calculated for both equations according to Burnham and Anderson (2002), with the better-fitting model having the lower AIC_c. ΔAIC_c (ΔAIC_c = larger AIC_c − smaller AIC_c) was then determined for the weaker equation, where $\Delta AIC_c<2$ suggests substantial evidence for the applicability of the weaker model to the data in relation to the stronger model and $\Delta AIC_c>10$ indicates that the weaker model is very unlikely (Burnham and Anderson, 2002).

The current state of contamination was assessed with respect to risk to sport fish-eating humans using the consumption guidelines employed by the OMOE (OMOE, 2009). These consumption guidelines are derived from tolerable daily intakes from the Food Directorate of Health Canada. The focus of this analysis was on lake trout, whitefish, and yellow perch as these are the most commonly consumed species in Lake Simcoe (Evans et al., 1996; LSEMS, 2008), although all species for which data were available were reported. All major chemicals for which data were available and guideline values exist were considered, i.e., mercury, total-PCB, OCS, HCB, total-DDT, mirex, photomirex, toxaphene, chlordane, PCDD/Fs, and DL-PCBs. PCNs and BDE-47, -99, -153, and -209 were also evaluated using the interim OMOE fish consumption guidelines for these chemicals. The consumption risk for PCNs was assessed along with PCDD/Fs and DL-PCBs using 2,3,7,8-tetrachlorodibenzo-*p*-dioxin toxic equivalent (TEQ) concentrations based on OMOE guidelines. TEQs were calculated by summing the multiplication of congener specific concentrations with their respective toxic equivalency factors (TEFs). The 2005 mammalian World Health Organization (WHO) TEF values were used for PCDD/Fs and DL-PCBs (Van den Berg et al., 2006). The WHO has not assigned TEFs to PCNs, although they were recognized as chemicals that should be included in the TEF scheme (Van den Berg et al., 2006). Thus PCN TEQs were calculated using proposed TEFs from Puzyn et al. (2007). For PBDEs, the first level of interim OMOE consumption guidelines based on the draft tolerable daily intakes from the United States Environmental Protection Agency (Donohue and Galal-Gorcheve, 2007) are: BDE-47—120 ng/g, BDE-99—120 ng/g, BDE-153—240 ng/g, and BDE-209—8200 ng/g. There were no significant ($p>0.05$) increasing or decreasing trends from 2000 onwards for any chemical/species combination except for mercury in lake trout and thus this period was assumed to represent current conditions in terms of contaminants. The only exceptions were for PCDD/Fs, DL-PCBs, PCNs, and PBDEs, which were only analyzed in lake trout and whitefish collected in 2006 and 2005, respectively. Fish of all sizes were used in the comparison to consumption guidelines.

The level of concern to Lake Simcoe sport fish consumers in relation to the Great Lakes was next evaluated by comparing the concentrations of contaminants that were consistently detected (i.e., mercury, total-PCB, total-DDT, PCDD/Fs, DL-PCBs, PCNs, and PBDEs). For mercury, total-PCB, and total-DDT the fish size ranges reported in Table A2 were used in this analysis. Lengths of 59–69 cm were used for PCDD/Fs and DL-PCB and all sizes for PCNs and PBDEs were included (47–76 and 52–64 cm for lake trout and whitefish, respectively). Data from 2000 onwards were assumed to represent current conditions in order to be consistent with the analysis above. There were no significant increasing or decreasing trends ($p>0.05$) in this time period for 75% of the chemical/species/lake combinations. The assumptions of ANOVA were not met (e.g., the variances were significantly heterogeneous—Bartlett's test for homogeneity of variances $p<0.05$, and the data did not fit normal distributions—Shapiro–Wilk, $p<0.05$). Therefore, the Kruskal–Wallis test was used to test for significant differences among sites, with unplanned multiple comparisons performed on mean ranks of all pairs of groups (Siegel and Castellan, 1988). For PCNs and PBDEs, fillet measurements were not available for the Great Lakes. Thus these measurements were compared to PBDE and PCN concentrations in whole lake trout (60–70 cm) collected from Lake Ontario in 2004 (Gewurtz et al., 2009; Ismail et al., 2009). Since Ismail et al. (2009) only measured BDE-28, -47, -85, -99, -100, -153, -154, and -209, these congeners were used to represent $\sum$PBDE in this analysis. The comparison for PCNs and PBDEs should be treated with caution because contaminant concentrations of hydrophobic contaminants in whole fish samples generally exceed those in fillet because of fatty internal organs (Amrhein et al., 1999).

All statistical analyses were performed using STATISTICA 7.0 (StatSoft Inc., Tulsa, OK, USA).

Results and discussion

Temporal trends

For mercury, the exponential decay model fit to year-specific data for fish within the limited size range suggested differential trends for various species (Fig. 1, Table A3). Concentrations in lake trout, cisco, smallmouth bass, and yellow perch decreased significantly ($p<0.001$), concentrations in largemouth bass, northern pike and walleye did not change significantly ($p>0.05$), and concentrations in whitefish increased significantly ($p<0.001$) with time.

The results of the three additional statistical approaches applied to the mercury data support these findings, which show that they are robust. With regards to the comparison between 1970s/early 1980s data to more recent measurements (i.e., the coarse-grained time analysis), the results were the same as the exponential model (Fig. A2). When the ANCOVA approach was applied to fish of all sizes, the overall trends did not change in largemouth bass, northern pike, and yellow perch (Table A3 and Fig. A3) and there were no significant differences between the two curves (ANCOVA, $p>0.05$). In contrast, for walleye, mercury decreased significantly ($p<0.05$) when the ANCOVA approach was used to account for length. However, the r^2 value was only 0.03 (Table A3), suggesting that time only explained a small proportion of the variability in concentration. The addition of the power function for length to the exponential decay model (Eq. (2)) resulted in a considerably better model fit compared with Eq. (1) when applied to fish of all lengths: Eq. (1) had ΔAIC_c values greater than 75, suggesting that Eq. (2) was a significant improvement compared with Eq. (1) (Table A4). For the most part, model applications to fish within limited size ranges were consistent with the results of Eq. (2) (Tables A3 and A4). The exceptions were that the significant decrease in mercury observed over time for cisco was no longer present and there was a significant increase for northern pike that was not found in the other analyses (Table A4).

Historical mercury data for whitefish, cisco, and yellow perch caught during the 1920s, 1950s, and 1960s were reported by OMOE (1978) and are shown in Fig. A4. These fishes, which were obtained from the Royal Ontario Museum and analyzed in the 1970s, were

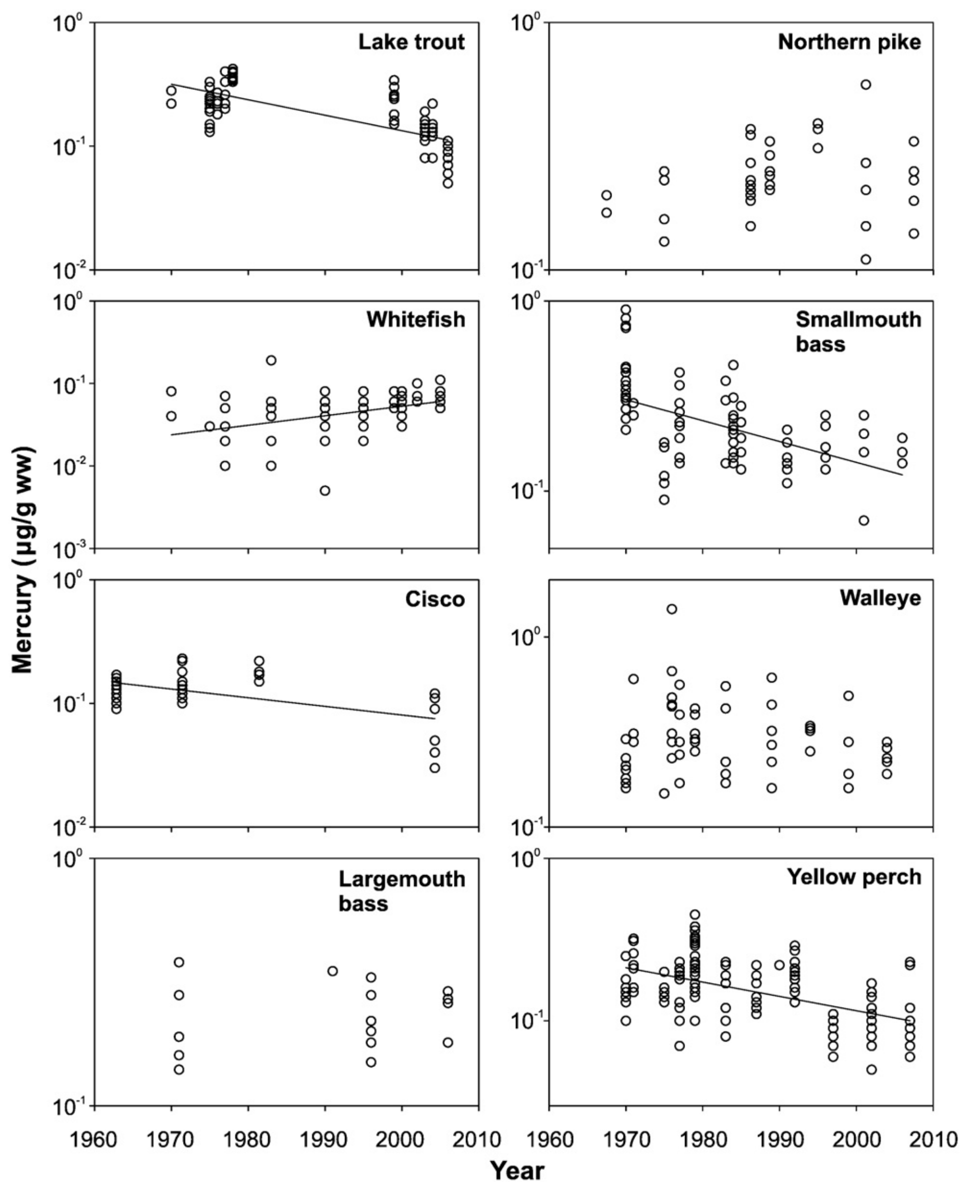

Fig. 1. Temporal trends of mercury (µg/g ww) in fishes from Lake Simcoe. The solid line represents the trend from the first-order exponential decay model ($C_t = C_0 e^{k_2 t}$) and is displayed when $p<0.05$. Only fish within a specific size range were included in this analysis.

generally smaller than the size range of fishes included in the temporal trend analysis (Fig. A4). Further, their mercury levels may have been influenced by the preservation process (Gibbs et al., 1974). Nonetheless, these results suggest that for whitefish and cisco, mercury levels in the 1920s–1960s were generally similar to those in the 1970s. For yellow perch, 1952 mercury concentrations were comparable to 1980s levels but below peak concentrations observed between the 1960s and 1970s.

Sediment core data, as well as comparisons between 1970s and 1997–2000 sediment data suggest that, in general, loadings of mercury to the Great Lakes peaked during the 1920s–1970s, but then generally decreased (Marvin et al., 2004; Pirrone et al., 1998). This pattern occurred at locations influenced primarily by atmospheric deposition as well as those impacted by local point sources. In Lake Simcoe, mercury has not been analyzed in sediment cores, which prevents a detailed loadings assessment. However, surficial sediment mercury concentrations were lower in 2008 compared to 1977 (Landre et al., 2010-this issue; OMOE, 1978), which fits the loading pattern observed in the Great Lakes. The significant decrease from the 1970s onwards observed in lake trout, smallmouth bass, and yellow perch were consistent with assumed loadings. Although mercury concentrations in cisco declined significantly ($p<0.0.001$) between 1977 and 2006 (Figs. 1 and A3), the trend followed a parabolic curve, with increasing concentrations between 1977 and 1990 ($p<0.01$), and a significant decrease in 2006 ($p<0.01$). However, this trend was likely influenced by the fact that there was no sampling between 1990 and 2006. The temporal trends of mercury in largemouth bass, northern pike, walleye, and whitefish did not decrease significantly from the 1970s onwards, which suggests the influence of changing food web processes for these species, due to factors such as nutrient inputs and invasive species, as discussed below.

Several previous studies of fishes either in or nearby the Great Lakes have found that mercury has stabilized or in some cases increased since the 1980s–1990s, following consistent decreases in the 1970s–1980s (Bhavsar et al., 2010; French et al., 2006; Gewurtz et al., 2010; Monson, 2009; Scheider et al., 1998). In Lake Simcoe, the trends since the 1980s–1990s depended on the species (Fig. 1). For example, mercury concentrations in yellow perch and smallmouth

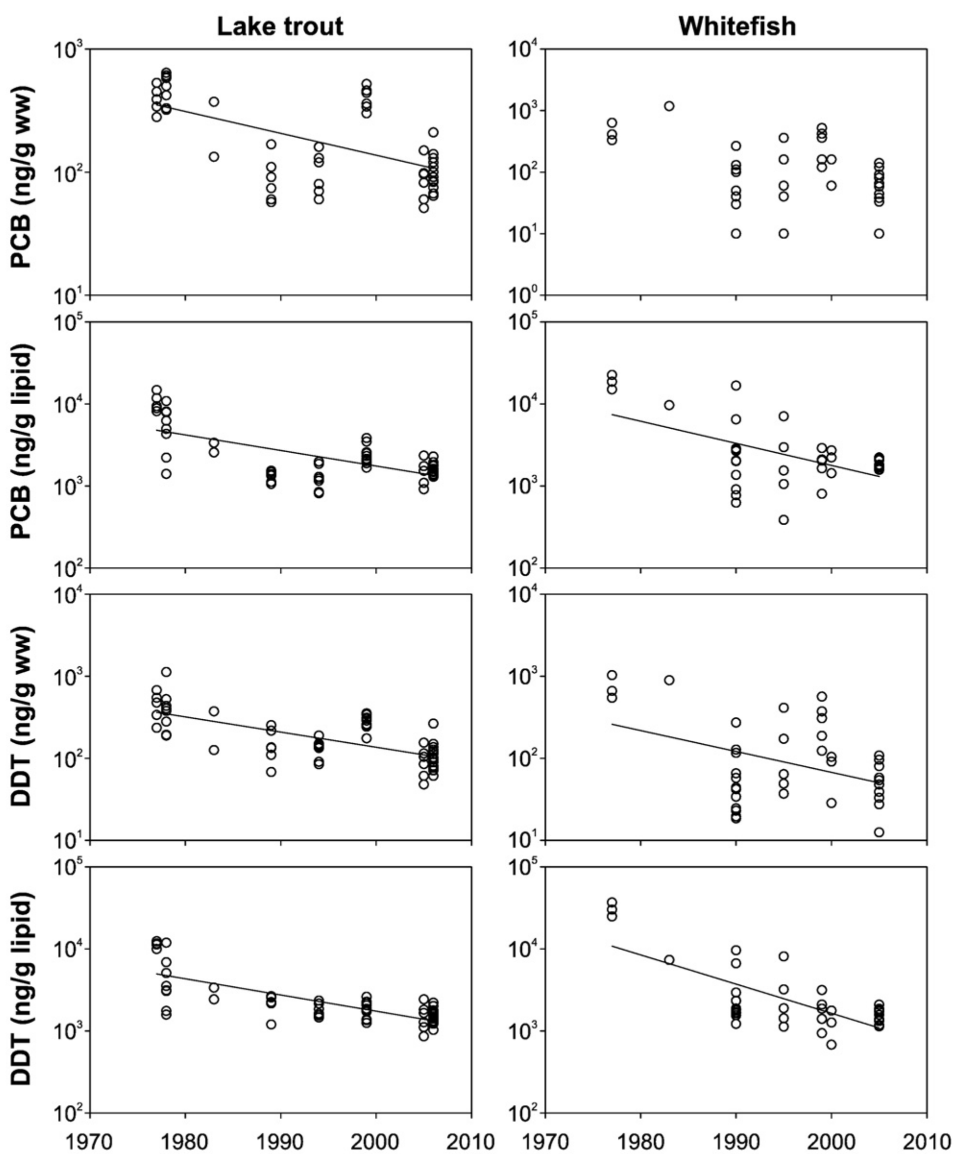

Fig. 2. Temporal trends of total-PCB and total-DDT (ng/g) on both a wet and lipid weight basis in lake trout and whitefish from Lake Simcoe. The solid line represents the trend from the first-order exponential decay model ($C_t = C_0 e^{k_2 t}$) and is displayed when $p<0.05$. Only fish within a specific size range were included in this analysis.

bass were stable during this time period, similar to general patterns observed in fishes in or nearby the Great Lakes. However, mercury concentrations in 2006 lake trout decreased to levels that were significantly lower ($p<0.01$) than any other year, and in whitefish concentrations increased significantly between 1990 and 2005 ($p<0.001$).

With regards to total-PCB and total-DDT, when the exponential decay model was applied to individuals within a limited size range, total-PCB in lake trout and total-DDT in lake trout and whitefish decreased significantly ($p<0.01$) over time (Fig. 2 and Table A3). In whitefish, although concentrations of total-PCB between 1990 and 2005 were generally lower than the late 1970s to early 1980s, the trend did not follow an exponential decay pattern ($p>0.05$). However, these trends were likely influenced by the limited number of data points in 1977 and 1983, and a peak in lipid content in 1983 (Fig. 2). The r^2 values for the fit of the exponential decay model increased in all cases when the organochlorine data were expressed on a lipid, rather than a wet-weight basis.

Similar to mercury, the results of the three additional statistical approaches applied to total-PCB and total-DDT corresponded well to these findings. With respect to the coarse-grained time analysis, both total-PCB and total-DDT concentrations declined significantly ($p<0.001$) between the late 1970s/early 1980s and the mid-2000s in lake trout and whitefish (Fig. A2). The assumptions of the ANCOVA approach were not met for either PCB or DDT data. However, the comparison of Eq. (1) with Eq. (2) showed that consideration of length was not important when the models were applied to total-PCB and total-DDT in fish of all sizes: Eq. (2) had ΔAIC_c values greater than 500, suggesting that this model was very unlikely compared with Eq. (1) (Table A4). This provides evidence that length did not influence the temporal trends of these chemicals, even when all fish lengths were included in the analysis. As such, the exponential decay

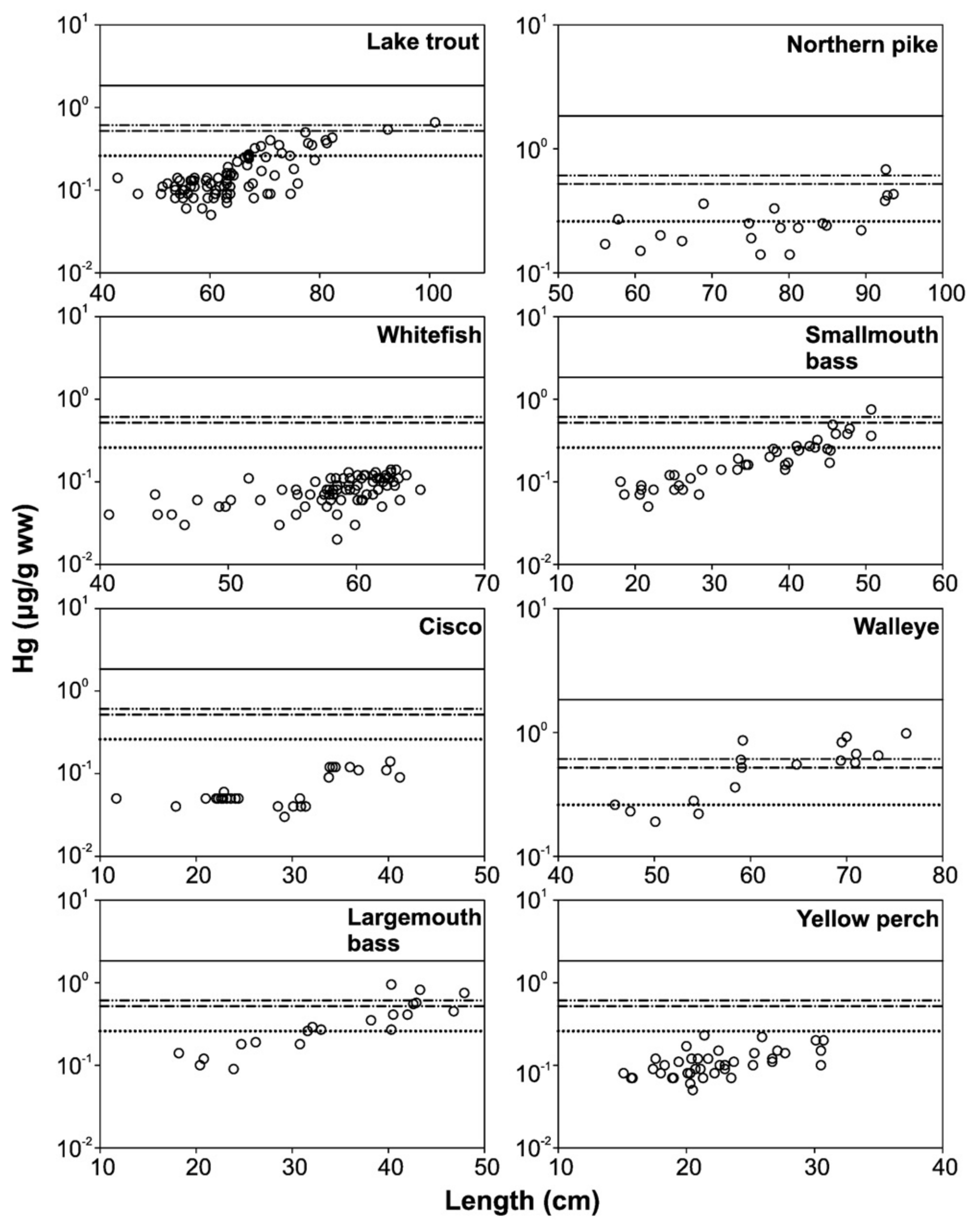

Fig. 3. Mercury (µg/g ww) versus length in fishes collected in 2000–2007 from Lake Simcoe in relation to the OMOE sport fish consumption guidelines. Fish of all sizes were included in this figure. The dotted, dash-dotted-dash, dash-dotted-dotted-dash, and solid lines represent the first level consumption restriction guideline for the sensitive population (0.26 µg/g ww), the complete restriction guideline for the sensitive population (0.52 µg/g ww), the first level consumption restriction guideline for the general population (0.61 µg/g ww), and the complete restriction guideline for the general population (1.84 µg/g ww), respectively.

model was also applied to fish of all sizes, where the overall results generally remained the same (Fig. A5 and Tables A3 and A4).

The concentrations of total-PCB and total-DDT have leveled off since the 1990s on both a wet and lipid weight basis (Fig. 2). Similar patterns were previously observed for these chemicals in the Great Lakes (Bhavsar et al., 2007; Hickey et al., 2006) and have been attributed to changes in food web structure and sources (e.g., increasing relative importance of atmosphere and historically contaminated sediment compared to fresh sources) (Gobas et al., 1995; Stow et al., 1995).

Temporal trends of individual DDT isomers can provide information on the relative importance of different sources because commercial formulations of DDT consisted of primarily *p,p′*-DDT (75%) and *o,p′*-DDT (20%) (Hesselberg et al., 1990; Murty, 1986) but these parent compounds are biotransformed to metabolites such as *p,p′*-DDE and *p,p′*-DDD in fish (Kwong et al., 2008). According to the exponential decay model, all DDT isomers, similar to total-DDT, decreased significantly ($p<0.05$) over time in lake trout and whitefish on both a wet and lipid weight basis (except for *p,p′*-DDD in whitefish on a wet weight basis) (results not shown). However, *p,p′*-DDE decreased at a significantly slower rate (ANCOVA, $p<0.05$) than the other isomers causing its relative importance to increase over time in both lake trout and whitefish (Fig. A6). Further, this metabolite dominated the isomer distribution (contribution to total-DDT = 50–74%). This provides evidence of a switch from fresh sources of technical DDT (e.g., from agriculture and mosquito control programs) to more weathered sources (e.g., atmosphere and recycling from sediment) following restrictions in 1970. The fact that of the two DDT metabolites examined, *p,p′*-DDE was consistently greater than *p,p*-DDD is not surprising since *p,p′*-DDE is more bioaccumulative and more slowly eliminated from fish compared with *p,p′*-DDD (Kwong et al., 2008).

Changing food-web processes in Lake Simcoe are likely influencing these temporal trends because its food web has changed dramatically since the late 1960s as a result of factors such as eutrophication, invasive species, and fish-stocking practices. Changing diet and bioenergetics have been relatively well studied in Lake Simcoe whitefish and lake trout compared to other fishes. For whitefish, food web processes may be especially important because mercury increased significantly between the 1970s and 2000s ($p<0.001$), which is opposite to assumed loadings patterns (see discussion above). However, upon closer examination of mercury trends in whitefish (Fig. 1), it is evident that concentrations only began increasing from the 1990s onwards. Several changes occurred in the Lake Simcoe whitefish population in the late 1980s–early 1990s. For example, before the 1990s, the whitefish catch was predominantly wild fish, whereas after the 1990s, the population was made up mostly of hatchery-reared fish (Amtstaetter, 2002). Although the wild whitefish are generally larger and older than stocked fish, their growth rates and size at age are similar (Amtstaetter, 2002). However, the growth rates of both stocked and wild fish increased dramatically following 1992 (Amtstaetter, 2002), which corresponds approximately to the zebra mussel (*Dreissena polymorpha*) invasion (veligers were detected in 1992 and they became widespread in 1994–1995). Zebra mussels, as well as the spiny waterflea (*Bythotrephes* sp., invaded in 1993), are now the first and fourth most

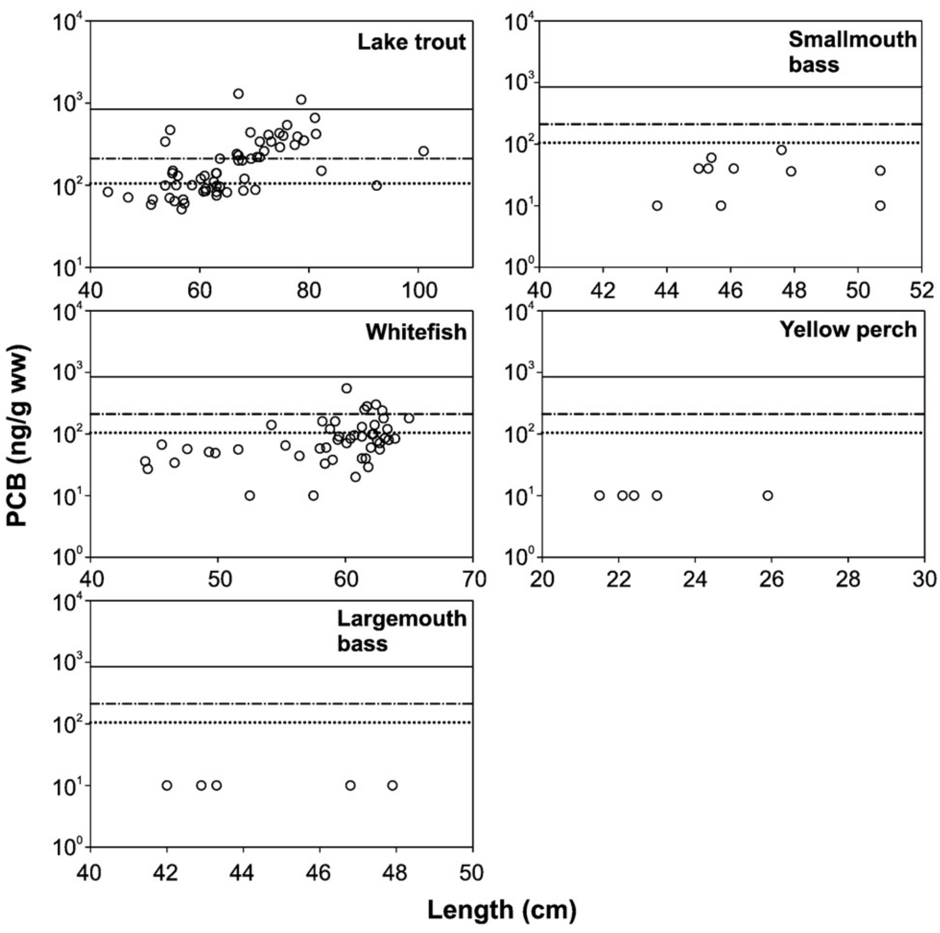

Fig. 4. Total-PCB (ng/g ww) versus length in fishes collected in 2000–2007 from Lake Simcoe in relation to the OMOE sport fish consumption guidelines. Fish of all sizes were included in this figure. The dotted, dash-dotted-dash, and solid lines represent the first level consumption restriction guideline for the sensitive and general populations (105 ng/g ww), the complete restriction guideline for the sensitive population (211 ng/g ww), and the complete restriction guideline for the general population (844 ng/g ww), respectively.

common whitefish prey items by weight and may have played a role in increasing whitefish growth rates (Amtstaetter, 2002). Increased growth is generally associated with lower contaminant concentrations (Gobas and Morrison, 2000). However, a switch in diet and/or the transfer of energy from pelagic to benthic habitats caused by the zebra mussels (Morrison et al., 1998) or increased food consumption related to the growth, are possible processes that could be contributing to increasing whitefish concentrations from 1990 onwards.

The diet of lake trout (whose population consists primarily of stocked fish) has also undergone large changes since the beginning of data collection in the 1970s (MacRae, 2001). During the late 1970s to early 1980s, the diet of lake trout consisted primarily of cisco, rainbow smelt (*Osmerus mordax*), and emerald shiner (*Notropis atherinoides*). However, following the collapse of the cisco population in the early 1980s, rainbow smelt became the primary diet item. During the early 2000s, lake trout began consuming more spoonhead sculpin (*Cottus ricei*), possibly in response to declining rainbow smelt populations. Although the condition of lake trout did not change in response to these diet changes (MacRae, 2001), smelt have higher contaminant concentrations compared to other forage fishes (Mathers and Johansen, 1985). The high abundance of smelt in the lake trout diet may have prevented further decreases in mercury between 1983 and 1999 and the incorporation of more sculpin may have been responsible for the sudden drop in levels between 2003 and 2006 (Fig. 1). It is evident that additional evaluation of the effect of food-web processes on temporal trends in whitefish and lake trout is needed, especially considering that in contrast to mercury, PCB and DDT concentrations did not seem to reflect these diet changes.

Comparison to consumption guidelines

Mercury was generally not of concern in the most commonly eaten Lake Simcoe fish species (Fig. 3). Concentrations in whitefish (<65 cm) and yellow perch (<35 cm) were sufficiently low to not result in any fish restriction in both the sensitive (children under 15 and women of child-bearing age) and general populations. For lake trout, concentrations in all but the largest sized individual (101 cm) were below the first consumption limit guideline of 0.61 μg/g ww for the general population. However, 42% of the larger sized lake trout (>65 cm) exceeded the first consumption limit of 0.26 μg/g ww for the sensitive population.

Mercury was also not of concern in cisco of all size ranges sampled (<40 cm) (Fig. 3). Most mercury measurements for <90 cm northern pike, <45 cm smallmouth bass, and <55 cm walleye were also in the range (<0.26 μg/g) that would be deemed safe for consumption by both populations without any restriction. However, mercury in all 40–50 cm largemouth bass exceeded the guideline for the first level restriction for the sensitive population (0.26 μg/g), and some exceeded both the complete and first level restriction guidelines for the sensitive and general populations, respectively. The guideline exceedances for large-sized largemouth bass (>40 cm), northern pike (>90 cm), and walleye (>55 cm) are especially of interest given that mercury in these species are not decreasing statistically significantly over time.

Total-PCB concentrations in all 21–26 cm yellow perch, 42–48 cm largemouth bass, and 43–51 cm smallmouth bass were either close to the detection limit or below all consumption guidelines for both the sensitive and general populations (Fig. 4). However, PCB levels in the large size of more commonly consumed lake trout (>50 cm) and whitefish (>55 cm) were of more concern with frequent exceedances of the complete (211 ng/g) and first level restriction guidelines (105 ng/g) for the sensitive and general populations, respectively (Fig. 4). Given that PCB levels have stabilized in lake trout and whitefish, further decreases below the consumption guidelines will likely be slow.

The total-TEQ concentrations of the dioxin-like compounds (PCDD/Fs, DL-PCBs, and PCNs) were below the complete restrictive guideline for the general population (21.6 pg/g ww TEQ) in all lake trout and whitefish collected (Fig. 5). However, the two largest (>70 cm) lake trout had concentrations well above the complete restrictive guideline for the sensitive population (5.4 pg/g ww). With respect to total-TEQ, DL-PCBs, PCDD/Fs, and PCNs contributed 72 ± 1.3, 23 ± 1.5, and 4.4 ± 0.3%, respectively, in lake trout and 62 ± 3.3, 31 ± 1.7, and 7.1 ± 1.8%, respectively, in whitefish (mean ± standard error of the mean), indicating that these exceedances were primarily related to PCBs.

Concentrations of the four PBDE congeners were below fish consumption guidelines in all 46–77 cm lake trout and 52–64 cm whitefish (Fig. 6). Concentrations of BDE-153 and -209 in both lake trout and whitefish were at least 2- and 3-orders of magnitude below the first restriction levels of 240 and 8200 ng/g ww, respectively. However, the BDE-47 concentrations of 34 and 56 ng/g ww in the two largest lake trout (>70 cm) were closer to the first advisory level of 120 ng/g ww. BDE-47 and -99 were major constituents of the Penta-BDE technical mixture (La Guardia et al., 2006) although their commercial use has decreased as a result of bans or voluntary phase-outs (http://www.bsef.com). Not surprisingly, their concentrations no longer appear to be increasing exponentially in southern Ontario biota (Batterman et al., 2007; Gauthier et al., 2008; Ismail et al., 2009), although there are likely still loadings into these systems (Samara et al., 2006). However, BDE-209, which is not currently banned, appears to be increasing in nearby Great Lakes biota (Gauthier et al., 2007; Ismail et al., 2009) and has peaked in the upper layers of a Lake Simcoe sediment core (Helm et al., 2010-this issue). BDE-209 metabolically and photolytically debrominates to lower brominated congeners (Christiansson et al.,

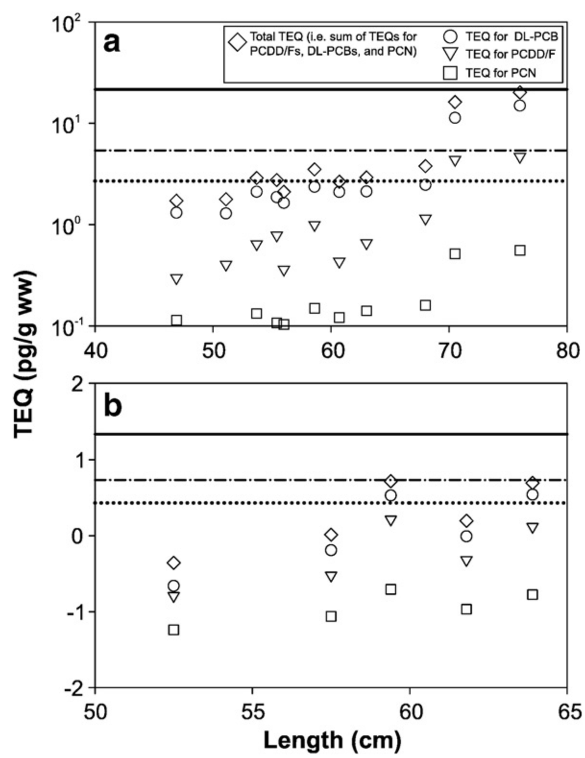

Fig. 5. DL-PCB, PCDD/F, and PCN TEQ concentrations (pg/g ww) versus length in (a) lake trout and (b) whitefish collected in 2006 and 2005, respectively, from Lake Simcoe in relation to the OMOE sport fish consumption guidelines. The dotted, dash-dotted-dash, and solid lines represent the first level consumption restriction guideline for the sensitive and general populations (2.7 pg/g ww), the complete restriction guideline for the sensitive population (5.4 pg/g ww), and the complete restriction guideline for the general population (21.6 pg/g ww), respectively. Fish of all sizes were included in this figure.

2009; Stapleton et al., 2006). Although its debromination down to tetra- and penta-BDEs (including BDE-47 and -99) has not been observed in up to a 5-month period in fish (Stapleton et al., 2006), modeling work suggests that it may be possible for lower brominated congeners to be formed over the long-term (Bhavsar et al., 2008b). As such, it could be speculated that the debromination of BDE-209 is potentially a source of lower brominated congeners in Lake Simcoe fishes.

No other chemical evaluated (OCS, HCB, total-DDT, mirex, photomirex, toxaphene, and chlordane) exceeded consumption guidelines in the fishes evaluated (results not shown), suggesting that they are not presently of concern to the humans consuming Lake Simcoe sport fishes.

Comparison to Great Lakes sport fishes

Concentrations of legacy contaminants (mercury, total-PCB, total-DDT, PCDD/F) in Lake Simcoe lake trout and whitefish within a limited size range were either significantly less ($p<0.05$) or similar ($p>0.05$) compared to Great Lakes fishes (Fig. 7). For example, total-PCB and mercury in Lake Simcoe lake trout were significantly less ($p<0.05$) than in all the other Great Lakes and in Lakes Ontario, Huron, and Superior, respectively. Mercury in lake trout from Lakes Erie and Georgian Bay were similarly low compared to Lake Simcoe. On average, PCDD/F and DL-PCB TEQ in both Lake Simcoe lake trout and whitefish were less than in the other Great Lakes but only significantly so ($p<0.05$) in Lakes Ontario, Huron (lake trout), and Erie (whitefish). For the most part, mercury and total-PCB in whitefish as well as DDT in both lake trout and whitefish were not significantly different ($p<0.05$) compared to the Great Lakes. However, DDT is sufficiently low in all Ontario Lakes to not be a consumption-limiting contaminant (OMOE, 2009). On average, concentrations of PBDEs and PCNs in lake trout were approximately an order of magnitude lower in Lake Simcoe compared with Lake Ontario (Table 1). These results correspond to those in sediment (Helm et al., 2010-this issue) and suggest that for

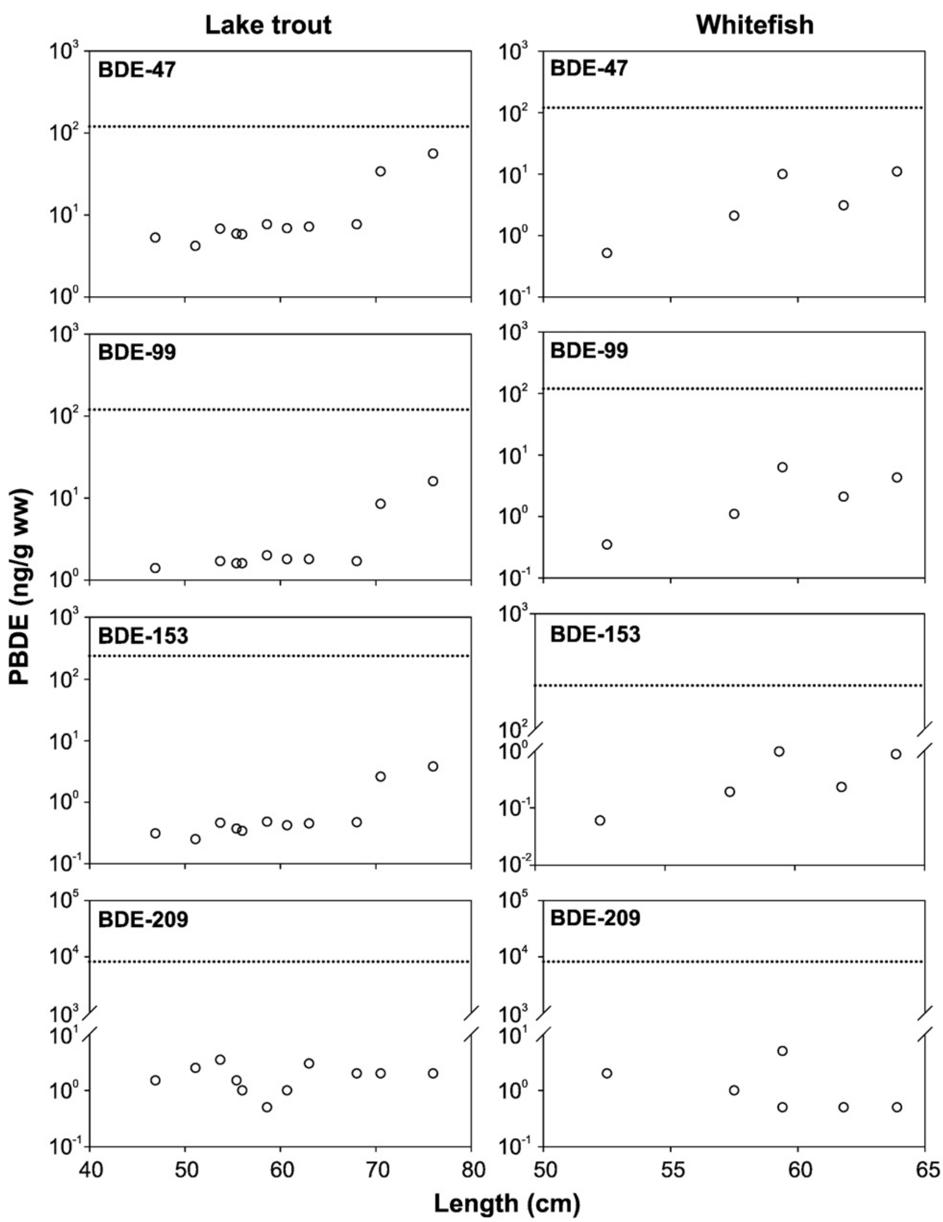

Fig. 6. Concentrations of BDE-47, -99, -153, and -209 (ng/g ww) versus length in lake trout and whitefish collected in 2006 and 2005, respectively, from Lake Simcoe in relation to the OMOE sport fish consumption guidelines. The dotted lines represent the first level interim OMOE consumption guidelines (120, 120, 240, and 8200 ng/g for BDE-47, -99, -153, and -209, respectively). Fish of all sizes were included in this analysis.

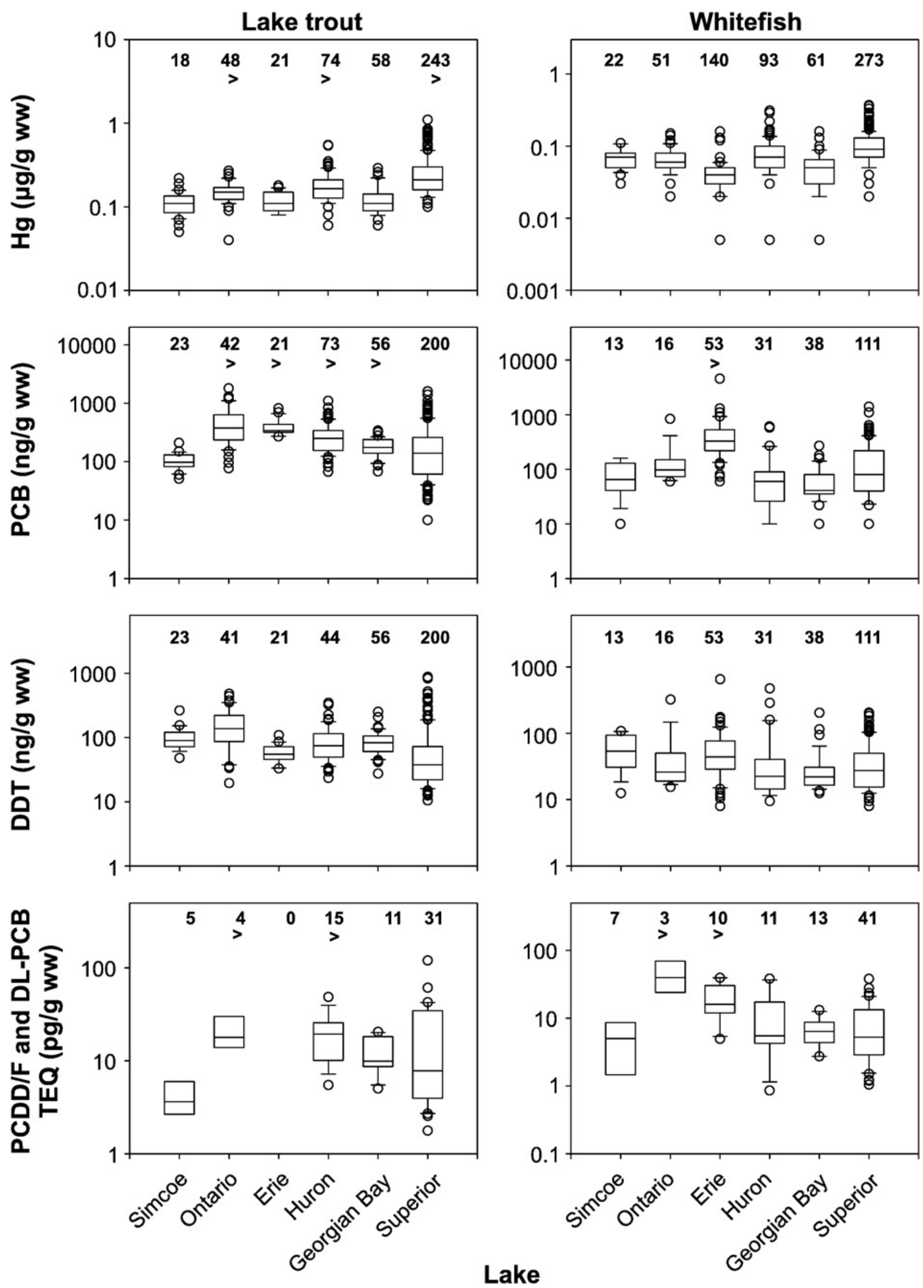

Fig. 7. Concentrations of mercury, total-PCB, total-DDT, and total-TEQ of PCDD/F and DL-PCB in Lake Simcoe lake trout and whitefish in comparison to the Great Lakes. The fishes were collected from 2000 onwards. The ">" symbol denotes lakes where the fish concentrations were significantly ($p<0.05$) greater than in Lake Simcoe and the numbers represent sample size. Only fish within a limited size range were included in this analysis.

the chemicals evaluated in this study, contaminant-related concerns for Lake Simcoe sport fish consumers are generally less or similar compared to the Great Lakes.

Table 1
Concentrations of ∑PBDE (ng/g ww) and ∑PCN TEQ (ng/g ww) in Lake Simcoe lake trout and whitefish collected in 2006 and 2005, respectively, in comparison to lake trout collected from Lake Ontario in 2004 (Gewurtz et al., 2009; Ismail et al., 2009).

Lake	Species	Chemical	n	Mean	SE[a]	Min	Max
Lake Simcoe	Lake trout	∑PBDE	11	24	8.2	9.0	94
		∑PCN	11	0.20	0.05	0.09	0.56
	Whitefish	∑PBDE	5	12	4.0	3.2	22
		∑PCN	5	0.12	0.03	0.06	0.20
Lake Ontario	Lake trout	∑PBDE	5	273	19	217	334
		∑PCN	5	3.7	1.6	1.6	10

[a] SE = standard error of the mean.

Conclusions

In conclusion, concentrations of total-PCB and total-DDT have generally declined in Lake Simcoe sport fishes (lake trout and whitefish) between the 1970s and 2007. However, the rate of concentration decrease has slowed since the 1980s–1990s, which is similar to the trends reported in Great Lakes fishes. In contrast, for mercury, the temporal trend varied among species. Mercury in lake trout, cisco, smallmouth bass, and yellow perch decreased statistically significantly with time, similar to the organochlorines and assumed loading patterns. However, concentrations in largemouth bass, northern pike, and walleye showed a random relationship with time, and mercury in whitefish increased statistically significantly with time. These trends were demonstrated using four different statistical approaches, which provide confidence in the findings. The results of this study, along with the observations from fishery studies, suggest that changes in food web, bioenergetics, and life history due to factors including eutrophication and invasive species, may be influencing mercury trends in Lake Simcoe fishes. If more than two species had been available for total-PCBs and total-DDT such differences in trends might also have been observed. This suggests that use of one fish species to evaluate temporal trends may provide misleading information.

Contaminant concentrations were, for the most part, below the "complete restriction" consumption guidelines for the general population. The only exception was for the largest (>60 cm) lake trout, where concentrations of PCBs either approached or exceeded this most restrictive guideline. The risk to the sensitive population was of more concern for the larger, predatory fishes (lake trout, largemouth bass, northern pike, smallmouth bass, and walleye for mercury, and whitefish for PCBs). PCNs and PBDEs were below the consumption guidelines for the measured species. Overall, contaminant related issues appear to be of less or similar concern than in the Great Lakes.

Acknowledgments

We thank Andre Vaillancourt (OMOE), Steve Petro (OMOE), and the staff at the OMNR for coordinating field work, and the staff at the Laboratory Services Branch of the OMOE for chemical analysis. This project was partially supported by funding from the OMOE Best in Science Research Program-Grant Funding Agreement 89023.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.jglr.2010.07.001.

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