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Thirty-Year Time Series of PCB Concentrations in a Small Invertivorous Fish (*Notropis Hudsonius*): An Examination of Post-1990 Trajectory Shifts in the Lower Great Lakes

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Abstract

The production and use of polychlorinated biphenyls (PCBs) have been restricted in North America since the 1970s; yet, PCBs are still detected in all components of the Great Lakes ecosystems. Our objective was to determine how total PCB (PCB_T) concentrations in spottail shiner (*Notropis hudsonius*) changed over the period 1975–2007 in the lower Great Lakes. Trends were best described by three basic models: (1) piecewise models where concentrations followed a decreasing trend before the break point (T) and an increasing trend post-T (Lake St. Clair, eastern Lake Erie, and upper Niagara River); (2) piecewise models where concentrations decreased both pre- and post-T but where the rate of decline post-T was less than that pre-T (western Lake Erie and Niagara River's Tonawanda Channel); and (3) linear models where concentrations declined at a constant rate across the entire temporal range (lower Niagara River and western Lake Ontario). Piecewise models best described the trends in shallow areas that are susceptible to full water-column mixing whereas constant-slope models best described trends in deeper areas. For piecewise models, T typically occurred during the years 1988–1992. Two events coincided with this timing: (1) a sustained shift towards warming summer temperatures and (2) the proliferation of dreissenid mussels (*Dreissena* spp.). The weight-of-evidence suggests that the dreissenid invasions were a more likely driving factor behind the observed trends.

Key words: Great Lakes; Lake St. Clair; Niagara River; Lake Ontario; Lake Erie; polychlorinated biphenyls; environmental change; climate change; invasive species; dreissenids; *Dreissena*; *Notropis hudsonius*.

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Introduction

Polychlorinated biphenyls (PCBs) were widely used as insulators in electronic devices and in the formulation of some pigments and waxes, elastomers, plastics, sealants, cutting oils, pesticides, lacquers and varnishes, and flame retardants (Verschueren 1996). There is a 50-year history of PCB use in North America: the compounds were first manufactured in the 1920s, peak usage occurred in the mid-1960s, and they were effectively banned in Canada and the United States by 1977 (Wong and others 1995). PCBs are structurally stable in the environment and many congeners can readily volatilize at ambient summer temperatures; thus, despite being banned for more than three decades, they continue to enter surface waters, including the Laurentian Great Lakes, from contaminated sites and infrastructures (Samara and others 2006; Diamond and others 2010) and via atmospheric deposition (Venier and Hites 2010).

PCBs are still detected in virtually all components of Great Lakes ecosystems including water and suspended particulates (Robinson and others 2008; Miller and Hornbuckle 2010), bottom sediments (Li and others 2009), phytoplankton (Trowbridge and Swackhamer 2002), invertebrates (Jude and others 2010), fishes (Bhavsar and others 2007), amphibians and reptiles (Bishop and Gendron 1998; Ashpole and others 2004), birds (Venier and others 2010), and mammals including people (Basu and Head 2010). PCBs are strongly non-polar (log K_{ow} = 3.9–7.8); therefore, when PCBs are present in aquatic systems, concentrations are lowest in water (Meng and others 2008), moderate in organic-rich sediments (Marvin and others 2004), and highest in lipid-rich biota (Carlson and others 2010). PCB biomagnification in a typical Great Lakes food chain occurs such that if concentrations are in the order of 0.001 ng g^{-1} (1 ng L^{-1}) in water, they would be in the orders of about 1 ng g^{-1} (wet weight) in algae, 10 ng g^{-1} in zooplankton, 100 ng g^{-1} in invertivorous fish, and 1,000 ng g^{-1} in piscivorous fish (compare Trowbridge and Swackhamer 2002; Stapleton and Baker 2003; Meng and others 2008). PCBs enter the food chain at the algal level primarily through bioconcentration, but higher trophic levels accumulate PCBs mostly from their food (Skoglund and others 1996). The biological and ecological risks presented by PCBs in the Great Lakes region are considerable and have been comprehensively reviewed by Hornbuckle and others (2006).

The first records of PCB concentrations in Great Lakes fishes date back to the 1960s, with the first temporal trends being published in the mid-1980s (De Vault and others 1986) and the early 1990s (Schmitt et al. 1990; Suns and others 1991; Borgmann and Whittle 1991). More-recent temporal studies have revealed that PCB concentrations in Great Lakes fishes declined exponentially from the mid-1970s (when PCBs were banned) through the mid-1980s but that the rate of decline has been very slow, if not negligible, since the late 1980s/early 1990s (Stow and others 1995; Gewurtz and others 2010; Carlson and others 2010). Periodic oscillations in PCB concentration, within the overall downward trajectory, have been attributed to variations in food-web related and climatic variables (French and others 2006). It is concerning that the decline of PCB concentrations in Great Lakes fishes has been stalling over the past 20 years. Even more concerning, recent analyses indicate that PCB concentrations in adult walleye (*Sander vitreus*) and lake trout (*Salvelinus namaycush*) have been increasing, albeit slowly, in Lake Erie since the late 1980s/early 1990s (Bhavsar and others 2007); these apparent trend reversals are counterintuitive because PCBs have not been manufactured in North America for many years.

Temporal PCB trends in Great Lakes fishes have mostly been derived from concentrations in large-bodied species such as coho salmon (*Oncorhynchus kisutch*), chinook salmon (*O. tshawytscha*), lake trout, and walleye because these species are often targeted by anglers and because PCB concentrations are highest in these high-trophic-level piscivores. These species can move considerable distances throughout the Great Lakes over their lifespan; therefore, PCB concentrations in adults reflect an integration of several years of accumulation/losses and exposure rates that vary across the basin. Precise interpretations of temporal PCB trends based on concentrations in adult piscivores are further complicated because the trophic position of such species changes with age and size and because the transference of PCBs to these species is dependent on the structure, and number, of lower trophic levels which can vary temporally and spatially in the Great Lakes (Kwon and others 2006). Thus, the inter-annual variability of PCB concentrations in adult piscivores would not be expected to correlate tightly with concurrent variations in PCB loading and bioavailability, shifts in food-web structure or other dynamic habitat features including climatic factors.

The objective of this study was to use total PCB (PCB_T) concentrations in spottail shiner (*Notropis hudsonius*, Cyprinidae) to assess long-term PCB trends (1975–2007) at sites located along the Canadian side of the lower Great Lakes and to explore the factors associated with temporal variations. Spottail shiner are a small-bodied fish (64–76 mm TL, total length) that spawns in the spring or early summer (Scott and Crossman 1998). The species is well suited for site-specific bioindicator programs because they have a small home range (<1 km distance), and because they have a narrowly defined trophic position such that they feed exclusively on benthic invertebrates and zooplankton (Scott and Crossman 1998; Marcogliese and others 2006). Given their low trophic position and small home range, PCB concentrations in spottail shiner might be expected to change relatively quickly in response to changes in PCB exposure and bioavailability. On this basis, it was predicted that the spottail shiner bioindicators used in this study would provide improved resolution to the PCB trend reversals observed in Lake Erie (*above*) with this, in turn, offering an opportunity to explore linkages between temporal variations in PCB concentration and environmental factors.

METHODS

Study Area

The Laurentian Great Lakes contain approximately 20% (23,000 km^3) of the world's fresh surface water. The highly industrialized watershed (521,830 km^2) has a population of more than 33 million people. This study was undertaken in the lower Great Lakes (Erie and Ontario), Lake St. Clair, and Niagara River for which data on PCB_T concentrations in spottail shiner were monitored from 1975 to 2007 at 19 sites (Figure 1).

Lake St. Clair is relatively small having a surface area (A_o) and volume (V) of 1,115 km^2 and 3.4 km^3, respectively. For its A_o, Lake St. Clair is very shallow having mean ($\overline{Z}$) and maximum (Z_m) depths of 3.0 and 6.4 m. Lake Erie has the largest A_o (25,700 km^2), but it is smaller than Lake Ontario with respect to V (484 km^3) due to its shallow $\overline{Z}$ (19 m) and Z_m (64 m). Lake Ontario's A_o, V, $\overline{Z}$, and Z_m are 18,960 km^2, 1,640 km^3, 86 m, and 244 m, respectively.

Niagara River drops 99 m over its 56-km length; mean monthly discharges are 4,800–7,300 $m^3\ s^{-1}$ and thalweg velocities are about 0.6–3.0 $m\ s^{-1}$ (Masse and Murthy 1990; Crissman and others 1993). The $\overline{Z}$ upstream of Niagara Falls is 4.5 m; the river is deeper downstream of the falls where pool depths can be 30–65 m. Water transparency in the river is high because the channel is eroded to bedrock and Lake Erie traps particulates.

Currently, PCBs enter the Great Lakes mostly via atmospheric deposition (Venier and Hites 2010) and from contaminated dumps and urban landscapes (Samara and others 2006; Diamond and others 2010). Direct sources to Lake St. Clair include Clinton River (Leach 1991) and industrial sites near Sarnia (Oliver and Bourbonniere 1985). Detroit River accounts for 90% of the tributary inflow to Lake Erie and it is the lake's main PCB contributor (Drouillard and others 2006; Heidtke and others 2006). PCBs enter Detroit River via streams that run through metro Detroit (Kauss and Hamdy 1985; Kannan and others 2001) and with leachates from sites near Grosse Island (Heidtke and others 2003). PCBs enter western Lake Erie in pulses when water velocities in Detroit River increase as a result of a wind-induced west to east seiche in the lake (Drouillard and others 2006). PCB sources to eastern Lake Erie include Big Creek and Grand River (Murdoch 1980; Frank and others 1991). Lake Ontario's primary PCB source is Niagara River which accounts for more than 80 and 50% of the lake's tributary inflow and sediment load, respectively (Kemp and Harper 1976; Carter and Hites 1992). PCB loads to Niagara River originate from sites that drain into the Tonawanda Channel; these include Love Canal and the 102nd Street and Hyde Park dumps (Howdeshell and Hites 1996; Marvin and others 2007).

Sample Collection/Processing

Nineteen near-shore sites (1–2 m depth) were seined for spottail shiner over the period 1975–2007 through Ontario Ministry of Environment's (OMOE) *Sportfish Contaminant Monitoring Program* (SFCMP): Lake St. Clair (sites 1–3), western (sites 4 and 5) and eastern (sites 6 and 7) Lake Erie, Niagara River (sites 8–14), and western Lake Ontario (sites 15–19) (Figure 1). Sampling was undertaken once annually during the autumn (September or October). It was not feasible to sample every site during each of the 33 sampling years. Sites 2–4, 7–12, 16, 18, and 19 were sampled 14–16 times. Sites 5 and 13–15 were sampled more frequently (18–23 times) and sites 1, 6, and 17 were sampled less frequently (7–12 times). Forty-five percent of the samples were collected during or before 1989 with the rest being collected during or after 1990.

The TL (nearest mm) of each spottail shiner was measured then individuals were allocated randomly into groups of 10 fish (a composite).

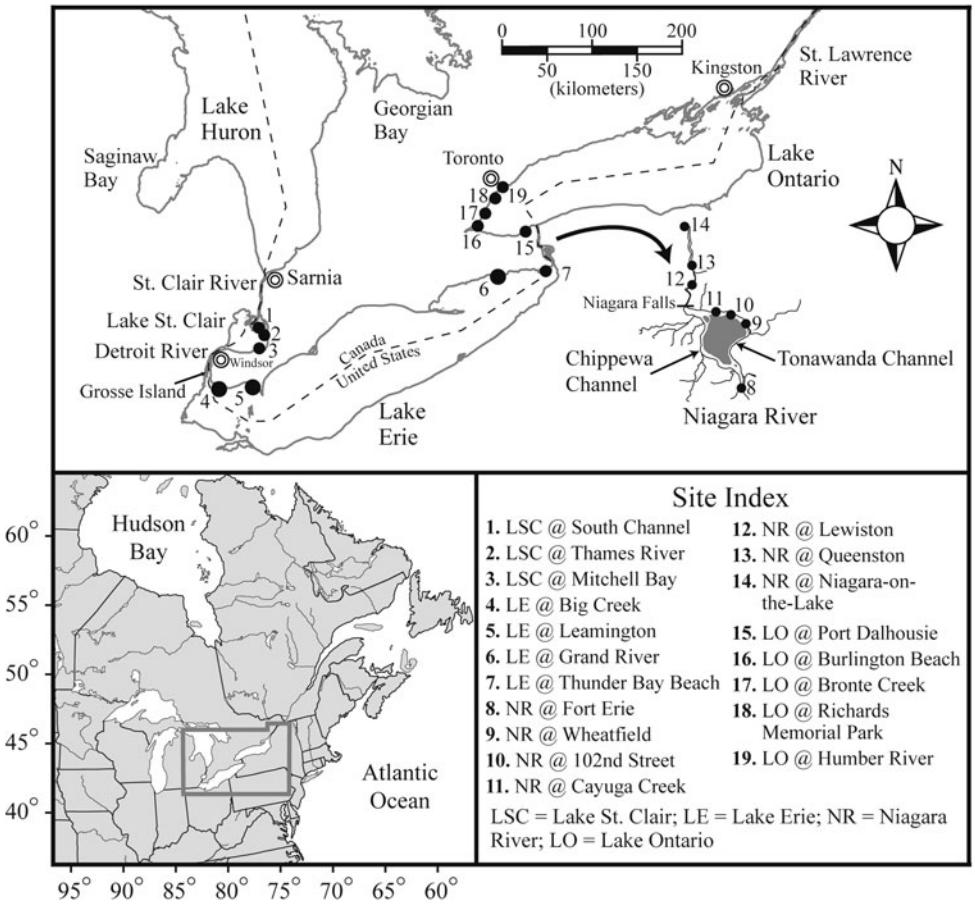

Figure 1. Spottail shiner sampling sites in the lower Laurentian Great Lakes, Lake St. Clair, and Niagara River (1975–2007).

Composites were wrapped in aluminum foil, put into a sealed plastic bag, and then frozen. On average, six 10-fish composites were produced at each sampling site per year. Upon return to the laboratory, the composites were thawed, then homogenized. Homogenates were transferred to 20 ml scintillation vials and stored in the dark at −20°C until analyzed for %lipid and PCB_T concentration.

Analytical Techniques

The whole-body spottail shiner composites were analyzed for PCB_T concentration and %lipid at OMOE laboratories (Toronto, ON). PCB_T concentrations were determined by OMOE Method E3136 (Bhavsar and others 2007). Lipid determinations were performed as per French and others (2006).

Chromatography techniques used in the 1970s separated PCB congeners into 23 peaks at most but the capillary columns used in recent times separate almost all congeners. To standardize long-term PCB_T data, the resolution of recent techniques was detuned to that of the 1970s with PCB_T concentrations over the study period being calculated by summing the concentration equivalents of the 23 peaks. PCB_T concentrations were quantified against commercial Aroclor standards (4:1 Aroclor 1254: 1260).

To ensure data quality and comparability, the OMOE organics laboratory routinely analyzes certified-clean matrix blanks (contamination test), certified calibration solutions (accuracy test), matrix and surrogate spikes (analyte recovery test), and sample and calibration solution duplicates (within- and between-run precision tests) with each sample batch. The laboratory is also routinely audited by Canadian Association for Laboratory Accreditation Inc. (Ottawa, ON). Method performance is also tested through inter-laboratory calibration studies (for example, Northern Contaminants Program and Quality Assurance of Information for Marine Environmental Monitoring in Europe).

Temporal Trends (1975–2007)

PCB_T concentrations were log transformed and temporal trends at each site were based on the average (of transformed values) concentration for each sampling year. Three models were used to describe temporal trends: (1) linear least-squares regression of PCB_T concentration versus time across the entire temporal range; (2) two-segment piecewise regression (that is, broken-stick regression) to determine if and when slope characteristics changed (for example, Pekarik and Weseloh 1998); and (3) zero-slope regression across the entire temporal range. Statistical analyses were performed with STATISTICA™ 7.0 (StatSoft, Inc. 2004). The piecewise model was:

$$f = \begin{cases} \frac{y_1(T-t)+y_2(t-t_1)}{T-t_1}, \text{ for } t_1 \leq t \leq T \\ \frac{y_2(t_2-t)+y_2(t-T)}{t_2-T}, \text{ for } T \leq t \leq t_2 \end{cases} \quad (1)$$

where t is the sampling year, t_1 is the earliest year in time series (start point), t_2 is the latest year in time series (end point), T is the break point year, y_1 is the slope prior to T, and y_2 is the slope after T. T was determined with the quasi-Newton method which uses an iterative convergence procedure to minimize model loss functions. For the zero-slope model, the slope was constrained to zero and the Y-intercept estimated; this model was run to test a scenario wherein PCB_T concentrations in spottail shiner did not change over time and where concentrations varied among sites as represented by differences in regression intercepts. The Akaike Information Criterion (AIC) was computed as a measure of the relative strength of each model. Model selection was based on ΔAIC (=model AIC − lowest AIC) following Burnham and Anderson's (2002) guidelines: (1) the models being compared are very similar in terms of how well they fit the data if ΔAIC is less than 2; (2) there is considerable evidence that the models being compared are different in terms of how well they fit the data if ΔAIC is between 3 and 7; and (3) the models being compared are very different in terms of how well they fit the data if ΔAIC is greater than10.

Several sites were located in close proximity to one another; for example, sites 1–3 in Lake St. Clair, 4 and 5 in western Lake Erie, and 6 and 7 in eastern Lake Erie (Figure 1). Regression analyses were performed on each site independently and on pooled data from geographically close sites. If the relative strength of regression models was improved when data were combined, the pooled data were used to describe temporal trends.

Results

Data Standardization

PCBs were detected in 86% (N = 1,744) of the spottail shiner composites at concentrations up to 3,640 ng g^{-1}; the overall average/median concentration was 215/132 ng g^{-1} (Table 1). The lipid content of the composites was 0.1–10.8% (25th–75th percentiles = 1.6–3.1%) with the mean/median being 2.6/2.2%. Pearson correlations of PCB_T concentration versus %lipid were computed for each set of samples; they were not significant in 94% of the 292 cases. For the significant cases, the relationship between PCB_T concentration and %lipid was always linear across the range of fish length but Y-intercepts and slopes were not consistent among sites or sampling years and the trend lines did not pass through the origin (Figure A1). Thus, there was not a consistent method by which PCB_T concentrations could be standardized to remove the effects of variations in %lipid without the risk of introducing bias to the trend analysis (compare Hebert and Keenleyside 1995). Temporal PCB_T trends were, therefore, based on wet-weight (ww) concentrations. Temporal trends based on %lipid-standardized PCB_T concentrations (PCB_T/[%lipid/100], a common standardization method) are presented in Supplemental Materials Appendix for comparison (Figure A2).

Temporal Trends (1975–2007)

The AIC was lowest for the piecewise model (Eq. 1) relative to the constant-slope and zero-slope models for all 19 sites; therefore, all ΔAICs were computed relative to the piecewise model (Table 2). Three temporal patterns were identified: PATTERN 1 piecewise regression model—characterized by $y_1 < 0$ and $y_2 > 0$ (PCB_T concentrations followed a decreasing trend before T and an increasing trend after T); PATTERN 2 piecewise regression model—characterized by $y_1 < 0$ and $y_2 < 0$ where $y_1 > y_2$ (the rate at which PCB_T concentrations declined slowed after T); and PATTERN 3 linear regression model—characterized by a constant negative slope across the temporal range such that the ΔAIC of the piecewise model relative to the linear model was less than 2 (Table 2). The common characteristic of the three temporal patterns was the declining PCB_T concentration (y_1 = −0.126 to −0.036) from t_1 to T (Table 2).

Trends at sites 1–3 (Lake St. Clair; Figure 2A), 6 and 7 (eastern Lake Erie; Figure 2C), and 8 (upper Niagara River; Figure 2D) followed PATTERN 1 such that PCB_T concentrations in spottail shiner declined from the mid-1970s to T (years 1989–1991) followed by an increasing trend to 2007 (Table 2). At site 8, the moderately high ΔAIC of the linear model (ΔAIC = 9.2) relative to the piecewise model was due to the low PCB_T concentrations in 1989 when concentrations in all

Table 1. Summary Statistics for PCB_T Concentrations in Spottail Shiner Composites from Sites in the Lower Great Lakes Region (1975–2007)

Site	n	>DL (% n)	PCB_T Range (ng g^{-1} ww)	PCB_T IQR[a] (ng g^{-1} ww)	PCB_T Median (ng g^{-1} ww)	PCB_T Average (ng g^{-1} ww)
(a) Lake St. Clair						
1	52	63	<DL–150	<DL–60	32	40
2	68	54	<DL–100	<DL–38	20	26
3	99	42	<DL–170	<DL–32	<DL	31
(b) Lake Erie						
4	90	100	40–774	91–396	152	239
5	139	97	<DL–2,370	134–358	211	291
6	70	71	<DL–155	<DL–55	39	50
7	106	48	<DL–200	<DL–42	<DL	36
(c) Niagara River						
8	90	76	<DL–277	20–77	40	55
9	80	100	58–788	128–316	210	244
10	77	100	84–746	160–330	220	252
11	67	100	95–1,078	150–508	230	353
12	79	87	<DL–820	60–219	80	152
13	104	92	<DL–561	41–147	85	111
14	144	100	14–1,000	100–250	150	212
(d) Lake Ontario						
15	131	95	<DL–1,200	110–273	207	222
16	91	100	35–950	140–312	184	270
17	54	100	60–420	110–200	160	168
18	99	95	<DL–2,500	121–301	211	314
19	104	100	60–3,640	178–967	407	797

n is the number of composites analyzed and DL is the analytical detection limit.
[1]Interquartile range (25th–75th percentiles).

seven composites were below the detection limit, DL (Figure 2D; Table 2). The raw data indicated that no PCB_T concentrations at site 8 were less than DL from 1982 to 1985 (site was not sampled in 1986). In 1987, 3 of 7 spottail shiner composites had PCB_T concentrations less than DL with 3 of 5 and 2 of 6 composites having PCB_T concentrations below DL in 1993 and 1994, respectively; the frequency of non-detects decreased each year thereafter to the end of the record. Thus, the preponderance of non-detects observed in 1989 at site 8 was consistent with the pre-T downward concentration trend and the upward post-T trend. The concentration minimum at site 8 in 1989 also coincided with concentration minima observed at nearby sites 6 and 7 (eastern Lake Erie; Figure 2C, D). Therefore, it was concluded that the PCB_T concentration minimum at site 8 in 1989 was ''real'' as opposed to being an artifact.

Temporal trends at sites 4 and 5 (western Lake Erie) and 9–11 (Niagara River's Tonawanda Channel) followed PATTERN 2 such that PCB_T concentrations in spottail shiner declined from mid-1970s to T (1988 for sites 4 and 5, and 1994 for sites 9–11) with the rate of concentration decline slowing after T (Figure 2B, E; Table 2). Trends at sites 12–14 (lower Niagara River; Figure 2F), 15–17, and 18 and 19 (western Lake Ontario; Figure 2G, H) followed PATTERN 3 such that there was no advantage to using a piecewise model over a log-linear model to describe the trends ($\Delta AIC = 0.6$–1.9; Table 2). However, graphical analysis combined with the comparatively low AICs for piecewise models for these sites suggest that the rate of PCB_T concentration decline slowed slightly starting at the years 1987–1992 (Figure 2F–H; Table 2).

Temporal trends and break points based on lipid-standardized PCB_T concentrations were nearly identical to those based on wet-weight concentrations for all locations except sites 8, 9–11, and 18 and 19 (Figures 2D, E, H and A2d, e, h; Tables 2 and A1). At sites 9–11, trends based on wet-weight concentrations followed PATTERN 2 (Table 2) whereas trends based on lipid-standardized concentrations were described about equally as well by PATTERN 2 and PATTERN 3 (Table 1A). Conversely, trends at sites 18 and 19 followed

Table 2. Break Point, T (Year when PCB_T Trend Trajectory Changed), and Slope of Pre-T (y_1) and Post-T (y_2) Regression Segments for Average PCB_T Concentrations in Spottail Shiner Composites versus Sampling Year (1975–2007)

Site grouping	Piecewise regression			ΔAIC			Temporal pattern (*see* text)
	T (year)	y_1 (Pre-T)	y_2 (Post-T)	Piecewise regression	Linear regression	Zero-slope linear regression (model Y-intercept)	
(a) Lake St. Clair							
(i) Sites 1–3 combined	1991	−0.052	+0.032	0.0	13.5	15.3 (1.3)	PATTERN 1
(b) Lake Erie							
(i) Western region (sites 4 and 5 combined)	1988	−0.059	−0.012	0.0	3.8	29.4 (2.3)	PATTERN 2
(ii) Eastern region (sites 6 and 7 combined)	1990	−0.089	+0.040	0.0	36.6	43.1 (1.4)	PATTERN 1
(c) Niagara River							
(i) Upper reach (site 8)	1989	−0.126	+0.021	0.0	9.2	10.5 (1.6)	PATTERN 1
(ii) Tonawanda Channel (sites 9–11 combined)	1994	−0.036	−0.002	0.0	3.6	27.9 (2.4)	PATTERN 2
(iii) Lower reach (sites 12–14 combined)	1992	−0.042	−0.013	0.0	1.9	34.5 (2.0)	PATTERN 3
(d) Lake Ontario							
(i) Sites 15–17 combined	1989	−0.039	−0.016	0.0	0.7	22.5 (2.2)	PATTERN 3
(ii) Sites 18 and 19 combined	1987	−0.072	−0.036	0.0	0.6	27.9 (2.4)	PATTERN 3

ΔAIC (Akaike Information Criterion) estimates are shown for temporal trends based on two-segment piecewise regression (Eq. 1), linear regression across the entire temporal range, and fixed-slope linear regression (that is, slope fixed to zero under the presumption that average PCB_T concentrations remained constant over the study period). Statistics shown were calculated from trends shown on Figure 2 (based on wet-weight concentrations).

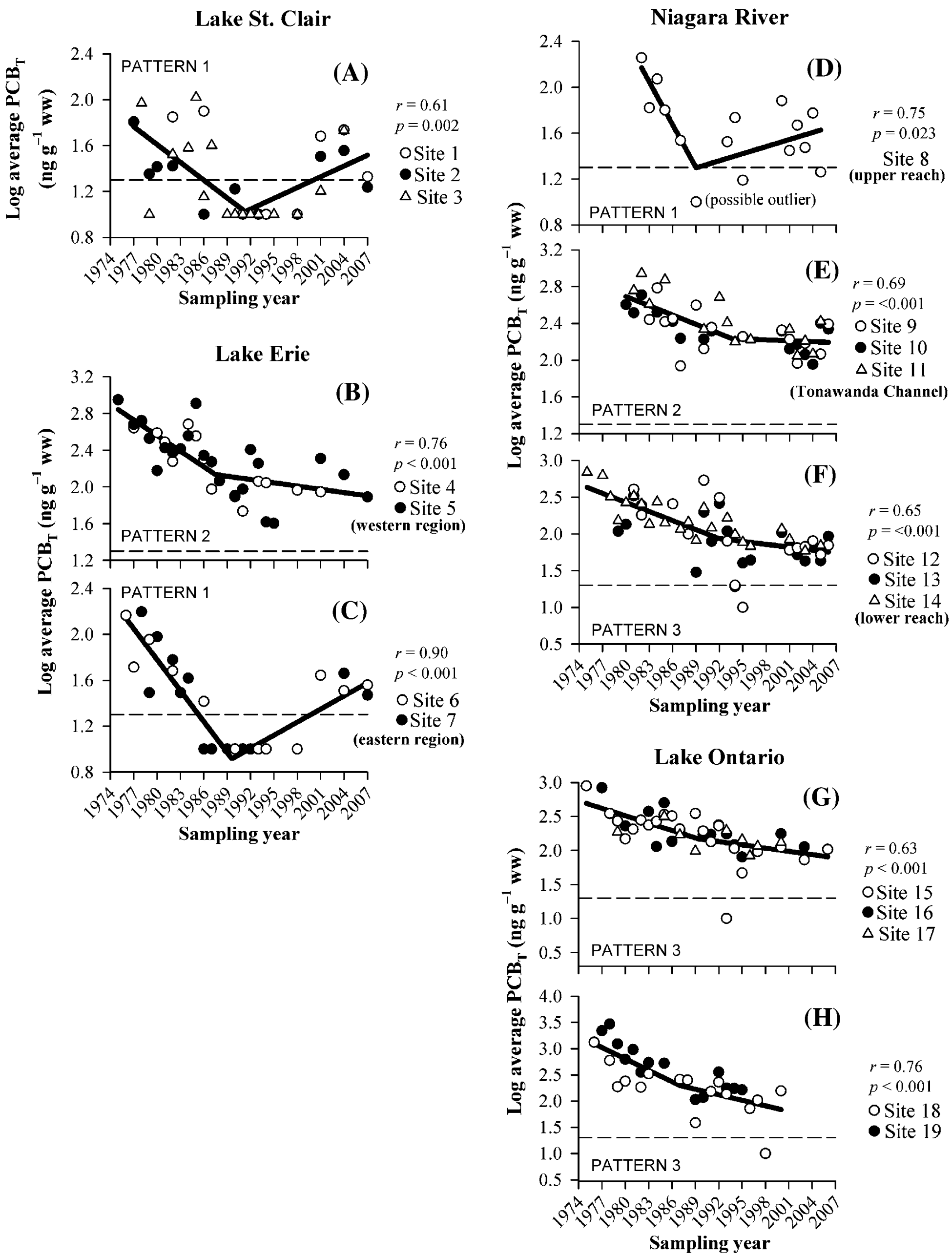

Figure 2. Piecewise regression analysis of average PCB_T concentration in whole-fish spottail shiner composites versus sampling year for sites **A** 1–3 in Lake St. Clair, **B** 4 and 5 in western Lake Erie, **C** 6 and 7 in eastern Lake Erie, **D** 8 in upper Niagara River, **E** 9–11 in Niagara River's Tonawanda Channel, **F** 12–14 in lower Niagara River, **G** 15–17 in western Lake Ontario, and **H** 18 and 19 in western Lake Ontario. *The dashed line* is the analytical detection limit (20 ng g^{-1}). Summary statistics for regressions are provided in Table 2.

PATTERN 2 when PCB_T concentrations were lipid standardized but the linear model (PATTERN 3) described the trend at these sites about as well as the piecewise model when wet-weight concentrations were used (Tables 2 and A1). The largest discrepancy between trends based on wet-weight versus lipid-standardized PCB_T concentrations was for site 8 (upper Niagara River) with *T* being 1989 versus 1994, respectively. The trend at site 8 was best described by PATTERN 1 when wet-weight concentrations were used whereas PATTERN 3 described the temporal trend about as well as PATTERN 1 when lipid-standardized concentrations were used (Tables 2 and A1). The very low PCB_T concentrations observed at site 8 in 1989 (*above*) did not affect the trend as much when concentrations were lipid standardized; however, PCB_T concentrations did appear to increase subtly after *T* even when concentrations were lipid standardized (Figures 2D and A2d).

Linkage to Climate Change and Species Invasions

PCB_T break points most often occurred between the years 1988–1992 (Table 2). This timing coincided with two events: (1) a sustained shift towards warming summer temperatures (Figure 3) and (2) the proliferation of dreissenid mussels (Figure 4). Piecewise analysis of the standardized residuals of daily average summer (June through August) air temperatures at Kingston, Toronto, and Windsor versus year (1975–2007) identified an abrupt, and sustained, temperature shift starting in 1991 (Figure 3). At Kingston, 10 of 15 summers prior to 1991 were cooler than average; pre-1991 temperatures at Toronto and Windsor were similarly cool (Figure 3). There was a warming trend from 1992 to 2007 such that the warmest seven summers occurred after 1992 with summer 2005 being the warmest (Figure 3). The timing of this climatic shift coincided well with the temporal PCB_T break points (Tables 2 and A1). However, PCB_T concentrations were actually negatively correlated ($r = -0.44$, $P = 0.014$) with average daily summer air temperature at sites 12–14 for the post-*T* period. Although not statistically significant, the correlations of PCB_T concentration versus post-*T* average summer temperature were also consistently negative for sites 4 and 5, 8, and 15–17 ($r = -0.38$ to -0.32, $P = 0.120$–0.288).

Zebra mussels *(Dreissena polymorpha*) were inadvertently introduced to the Great Lakes in the mid-1980s; quagga mussels (*D. bugensis*) were first seen in the lakes in 1989 (Figure 4). Dreissenids were well established across the Great Lakes basin by 1990, at which time densities in Lake St. Clair and western Lake Erie exceeded 10^3 m^{-2} and 10^5 m^{-2}, respectively, at some locations (MacIsaac and others 1992; Figure 4). Dreissenid densities in Lake Erie have declined somewhat since the initial invasions, such that in 2002 lake-wide mean densities were about 2,000 m^{-2} (strongly dominated by quagga mussels) with maximum densities being in the order of 20,000 m^{-2} (Patterson and others 2005). Densities in Lake St. Clair have remained relatively stable such that lake-wide average and maximum densities were about 1,800 m^{-2} and 8,000 m^{-2} (strongly dominated by zebra mussels), respectively, in 2001 (Hunter and Simons 2004). Based on surveys undertaken in 2001 and 2003 it was estimated that dreissenids occupied 50–80% of Lake Erie's bottom area (including profundal zones) and that populations extended from near-shore through central regions of Lake St. Clair (Hunter and Simons 2004; Patterson and others 2005). In 2003, zebra mussel densities up to 1,000 m^{-2} were observed at a few near-shore sites in Lake Ontario, however, the species had become quite rare in Lake Ontario on a whole-lake basis (Watkins and others 2007). In comparison, quagga mussels were present along the entire shoreline of Lake Ontario in 2003, colonizing to depths greater than 90 m and attaining densities up to 50,000 m^{-2} (Watkins and others 2007). Dreissenids have colonized nearly the entire length of Niagara River to depths of at least 10 m (Richman and Somers 2010).

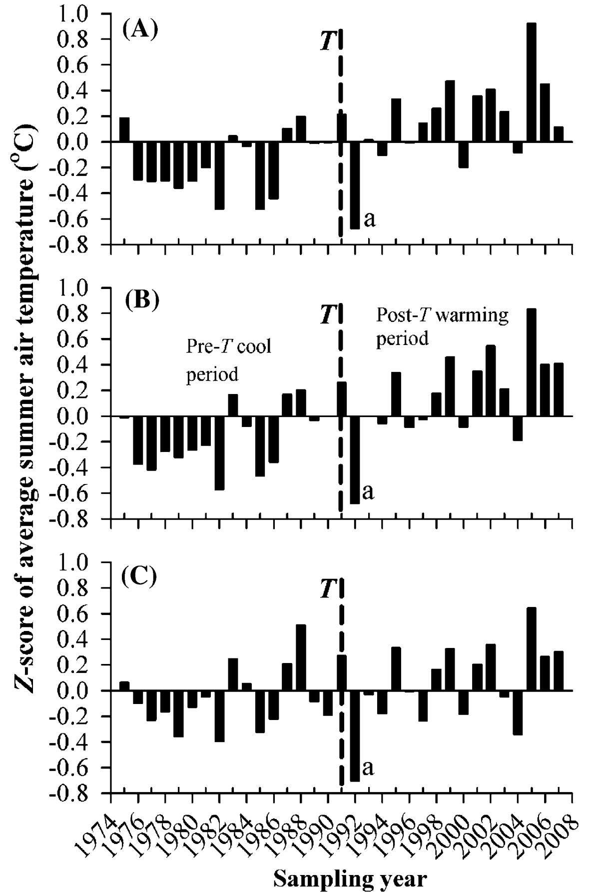

Figure 3. Standardized residuals (*Z*-score) of average daily summer (June 1 to August 31) air temperatures at **A** Norman Rogers Airport (Kingston, eastern Lake Ontario region), **B** Lester B. Pearson Airport (Toronto, western Lake Ontario region), and (**C**) Windsor International Airport (Windsor, western Lake Erie/Lake St. Clair region). Pre-*T* is the time period before break point year (1991 in all cases) and Post-*T* is the time period after break point year (piecewise regression of *Z*-score of average summer air temperature versus year). Daily average temperatures were obtained from Environment Canada's National Climate Data and Information Archive (http://climate.weatheroffice.gc.ca/climateData/canada_e.html).

Discussion

PCB_T concentrations in spottail shiner declined at all lower Great Lakes sites from the mid-1970s to

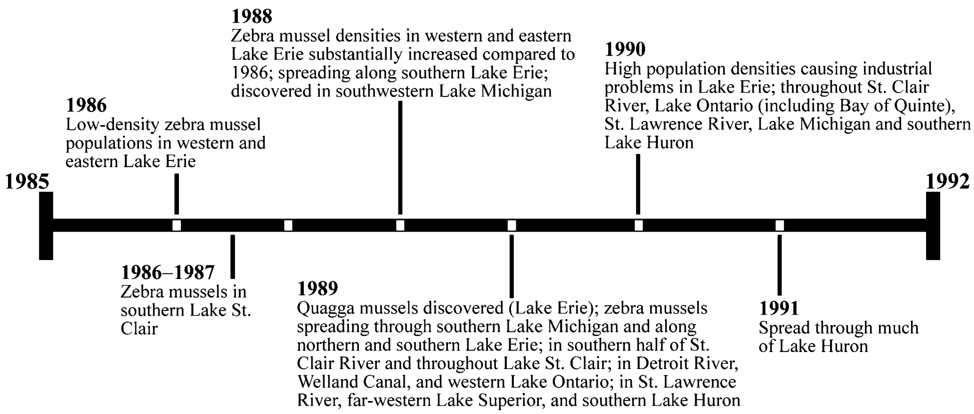

Figure 4. Early invasion history of zebra mussels and quagga mussels in the Laurentian Great Lakes (1985–1992). Timeline based on the results of an extensive review of the literature.

around 1990 (Figure 2). Complete trend reversals occurred in Lake St. Clair, eastern Lake Erie, and upper Niagara River such that PCB_T concentrations in spottail shiner have been increasing at these locales since about 1990 (Figure 2A, C, D). The trend reversals observed at these Great Lakes locales are consistent with Bhavsar and others' (2007) conclusion that PCB_T concentrations in Lake Erie's walleye and lake trout populations have been increasing for the past 20 years. As predicted, the trajectory shifts observed in spottail shiner (an invertivore) were considerably more pronounced than the shifts observed in walleye and lake trout which are high-trophic-level piscivores. A subsequent study by Sadraddini and others (in revision) similarly shows that PCB_T trends in freshwater drum (*Aplodinotus grunniens*), which feed primarily on benthic macroinvertebrates (including dreissenids), have switched to weakly increasing trajectories in Lake Erie.

Trend reversals did not occur at sites in western Lake Erie, Niagara River's Tonawanda Channel, the lower Niagara River, or in western Lake Ontario. At these sites, however, the rate at which PCB_T concentrations declined in spottail shiner after T was slower than the rate of decline in years preceding T (Figure 2B, E–H). The slowing rates of PCB_T decline in spottail shiner from these Great Lakes locales, as opposed to a switch to increasing concentration trajectories, is the trend most often reported for piscivorous fishes in the Great Lakes (Stow and others 1995; French and others 2006; Carlson and others 2010).

It seems clear that the pre-1990 period of rapid PCB_T decline was in direct response to regulatory actions by North American governments. However, the factors responsible for the PCB_T trend reversals, and the slowing rates of PCB_T decline, in Great Lakes fishes are poorly understood. An obvious explanation for the PCB_T trend reversals in Lake St. Clair, eastern Lake Erie and upper Niagara River would be that PCB loads to these locales have been increasing post-T (that is, since about 1990). If recent increases in PCB_T concentrations in spottail shiner were in fact due to increased loadings, concurrent increases in bottom sediment PCB concentrations would be expected, as has been the case for paralleling polybrominated diphenyl ether concentrations in Great Lakes sediment and fish (Qui and others 2007; Ismail and others 2009). PCB concentrations in Great Lakes bottom sediments have, however, decreased exponentially since the mid-1970s and trend reversals are not evident in sediment profiles (Marvin and others 2004; Li and others 2009). Moreover, PCB concentrations in the Great Lakes water column have decreased steadily over time and trend reversals in the water column have not been observed (Jeremiason and others 1994; Marvin and others 2007). Given that PCB_T concentrations in Great Lakes fishes have increased, or slowed in their rate of decline, in response to concurrent decreases in PCB loading, it can be reasonably inferred that the recent trends in fish are the results of within-lake/river processes that are increasing the bioavailability of the PCB pool.

Temporal break points for PCB_T concentrations in spottail shiner occurred between 1987 and 1994 with T most often occurring between 1988 and 1992 (Figure 2; Table 2). This timing coincided with two events: (1) a sustained shift towards warming summer temperatures (Figure 3) and (2) the proliferation of dreissenid mussels (Figure 4), both of which could have affected the cycling and bioavailability of PCBs in the lower Great Lakes region. Near-shore water temperatures in the lower Great Lakes would have increased during the post-1991 period of warming summer air temperatures because water temperature in the region is positively correlated with air temperature during open-water seasons (French and others 2006; Sharma and others 2008). Austin and Colman (2007) estimated that water temperatures in Lake Superior increased by more than 1°C/decade since the mid-1980s, with this rate of warming actually exceeding the rate at which air temperatures in the region warmed. The fact that PCB_T concentrations in spottail shiner increased at some Great lakes locales during the post-1991 warming period (Figures 2, 3) might suggest that warming temperatures somehow increased the bioavailability of the within-lake PCB pool. However, PCB_T concentrations in spottail shiner were negatively correlated with summer temperature during the post-1991 warming period. This trend is consistent with French and others (2006) who showed that PCB_T concentrations in adult Lake Ontario salmon decreased when summer temperatures increased. Similarly, comparisons of PCB_T concentrations and bioaccumulation factors in fish across latitudinal and elevational gradients typically show that concentrations are highest in colder environments (for example, Jarque and others 2010; Sobek and others 2010). This is because PCB elimination and fish growth rates generally increase with increasing ambient temperature (Nfon and Cousins 2007; Paterson and others 2007). Moreover, warming summer air temperatures would be expected to decrease the exposure of Great Lakes biota to PCBs because the rate at which PCBs volatilize from water and terrestrial surfaces increases with increasing temperature (Buehler and other 2004; Choi and others 2010; Venier and Hites 2010). Studies by Meng and others (2008) support the idea that warming temperatures are reducing PCB concentrations in the Great Lakes water column such that they demonstrated that PCB losses from Lake Superior are primarily from volatilization to the atmosphere and that the Great Lakes, as a whole, are net contributors of PCBs to the atmosphere. Due to the processes described above, it seems reasonable to rule out the possibility that the PCB_T trend reversals, and slowing rates of PCB_T decline, observed in Great Lakes fishes are attributable to warming trends in the region; in fact, the available evidence would suggest that warming temperatures should actually *decrease* PCB_T concentrations in fish.

As indicated, the PCB_T break points also coincided well with the proliferation of dreissenid mussels (Figures 2, 4; Table 2). Previous studies have shown that, through their immense water-filtering and nutrient-assimilation capacities, dreissenids have affected the fundamental limnology of the lower Great Lakes and Lake Huron. For example, dreissenids have accelerated the re-mineralization of limiting nutrients (for example, N, P, Si) by excreting them in dissolved form and by eliminating them in their feces and pseudofeces wherefrom they enter the microbial and detrital systems (Johengen and others 1995; Makarewicz and others 2000). Small dreissenids excrete N and P at a molar ratio of about 5:1 and this has been linked to the shift in planktonic dominance towards N_2-fixing cyanobacteria in western Lake Erie and Lake Huron (Arnott and Vanni 1996; Fishman and others 2010). Filtering by dreissenids removes large amounts of particulates from the water column such that they removed 6.4×10^6 tonnes of phytoplankton (26% total primary production) from the water column of western Lake Erie in 1990 (Madenjian 1995). Particulate removal by dreissenids has doubled the thickness of the euphotic zone in many regions of the Great Lakes (DePinto and Narayanan 1997; Vanderploeg and others 2002). In turn, increases in transparency have shifted the foci of productivity and nutrient cycling from the water column to littoral benthic areas where dense *Cladophora* and macrophyte beds have grown despite the efforts of nutrient abatement programs (Skubinna and others 1995; Hecky and others 2004). Given that dreissenids affect water-column properties in the Great Lakes to the extent of altering the productivity and structure of benthic and planktonic communities, it seems highly plausible that they have altered PCB cycling in the lakes. Indeed, conceptual and food-web based bioaccumulation models have demonstrated that dreissenid populations have the potential to affect PCB dynamics on basin-wide scales in the Great Lakes (DePinto and Narayanan 1997; Morrison and others 1998).

Although water-column PCB concentrations have been declining in the Great Lakes (*above*), modeling studies have shown that dissolved-phase PCB concentrations have increased in Lake Erie due to the removal of particulates by dreissenids (DePinto and Narayanan 1997; Morrison and others 1998). An analogous process occurs in Lake Superior which has been affected minimally by the dreissenids. Suspended particle concentrations are naturally low in Lake Superior and, therefore, about 80% of water-column PCBs are in dissolved forms (Eisenreich 1987; Jeremiason and others 1994). Dreissenids also excrete unassimilated PCBs in dissolved phases which are more bioavailable than particulate-phase PCBs (DePinto and Narayanan 1997; Morrison and others 1998). Thus, the PCB trend reversals and slowing rates of PCB decline observed at the survey sites might be due, at least in part, to concurrent increases in PCB bioavailability resulting from dreissenid-mediated reductions in water column particulate concentrations.

The effects that dreissenids have on water-column properties are most pronounced in shallow lake regions where there is full water-column mixing (Vanderploeg and others 2002; Noonburg and others 2003). From a whole-lake perspective, dreissenid populations filter the entire volumes of Lake St. Clair, Lake Erie, and Lake Ontario about once every 3, 5, and 333 days, respectively (Vanderploeg and others 2002). Proportional filtering rates are highest in Lake St. Clair and Lake Erie because they are comparatively shallow, thus permitting dreissenids to occupy much of the bottom areas, and because these lakes have smaller volumes. The high A_o:V of Lake St. Clair and Lake Erie make them susceptible to complete water-column mixing (Schertzer and others 1987; Leach 1991) and this mixing also enhances filtering rates by exposing dreissenid beds to high proportions of the water volume. The high relative intensities of dreissenid filtering in Lake St. Clair and Lake Erie might explain why complete trend reversals occurred in these lakes (Figure 2A, C). Interestingly, complete trend reversals in Lake Erie occurred in the eastern basin but not in the western basin where rates of PCB_T decline have just dramatically slowed (Figure 2B, C). The degree of change in the PCB_T concentration trajectory in Lake Erie appears to be directly related to dreissenid abundance such that the most-recent benthic survey indicates that dreissenids (mostly quagga mussels) are considerably more abundant in the eastern basin than in the western basin (Patterson and others 2005). PCB_T concentrations in Lake Ontario spottail shiner would, from this view point, be less influenced by dreissenids because filtering intensity is lower in this lake; thus, complete trend reversals did not occur in Lake Ontario (Figure 2G, H).

Flushing rates are high in Niagara River and, because the river's channel is eroded to bedrock and Lake Erie is an upstream sediment trap, transparency in the river was high even prior to the dreissenid invasions. These factors might explain why complete PCB_T trend reversals did not occur in the Tonawanda Channel or in the lower reaches of the river (Figure 2E, F). The trend reversal observed at site 8 (upper Niagara River) was likely the result of influences emanating from eastern Lake Erie where complete PCB_T trend reversals occurred (Figure 2C, D).

There are other mechanisms through which dreissenids can facilitate PCB transfers in the food web. Great Lakes dreissenid populations produce millions of tonnes of nutrient-rich feces and pseudofeces annually, and these wastes are often concentrated with organochlorines including PCBs (Madenjian 1995; DePinto and Narayanan 1997). Bruner and others (1994a) demonstrated that PCBs enter Great Lakes food chains when contaminated feces/pseudofeces are consumed by benthic detritivores. Spottail shiner is heavily reliant on benthic invertebrates for food; thus, their food-related exposure to PCBs has likely increased since the dreissenid invasions. PCBs in dreissenids can also by-pass spottail shiner and be transferred directly to higher trophic levels. For example, a portion of the PCB_T in dreissenids is transferred to waterfowl including lesser scaup (*Aythya affinis*), greater scaup (*A. marila*), and bufflehead (*Bucephala albeola*), and to fish such as the invasive round goby (*Neogobius melanostomus*) which are major predators of dreissenids (Bruner and others 1994b; Mazak and others 1997; Ray and Corkum 1997). Holeck and others (2004) described a similar interaction between zebra mussels and round goby that has killed thousands of Great Lakes waterfowl. Zebra mussels accumulate the toxin botulinum which is produced by *Clostridium botulinum*. Botulinum is then transferred to round goby when they eat zebra mussels; it is then transferred to waterfowl when they eat round goby—waterfowl can be overcome by type-E botulism.

Dreissenids can also affect PCB dynamics in the Great Lakes through physical processes. The surface roughness of dreissenid colonies causes localized deposition of fine-textured particles and these particles are sinks for hydrophobic pollutants including PCBs when they are enriched with organics (Howell and others 1996; Marvin and others 2002). This localized sediment contamination might further promote PCB transfers to benthic detritivores, thereby promoting the transfer of PCBs to higher trophic levels.

Three species, in addition to zebra and quagga mussels, invaded the Great Lakes at times corresponding to the temporal break points: (1) common rudd (*Scardinius erythrophthalmus*) in 1989, (2) round goby in 1990, and (3) tubenose goby (*Proterorhinus marmoratus*) in 1990 (Mills and others 1993). The trophic position of spottail shiner is below that of these species; thus, the influence that these species have on PCB transfers to spottail shiner is likely minimal compared to the influence of dreissenids. However, there is evidence that a synergism between dreissenids and round goby has caused Hg concentrations in smallmouth bass (higher trophic position than spottail shiner) to increase in western Lake Erie (Hogan and others 2007). This synergism involves the following trophic transfer of Hg: sediment sources $\rightarrow$ dreissenids $\rightarrow$ round goby $\rightarrow$ smallmouth bass which feed extensively on round goby (Hogan and others 2007).

In conclusion, long-term data show that PCB_T concentrations in spottail shiner have either been increasing, or slowing in decline, over the past 20 years. Changes in trend trajectories were not related to concurrent increases in PCB loading to the lower Great Lakes but rather to within-lake processes affecting PCB bioavailability. Trajectory changes coincided with both a sustained shift towards warming summer temperatures and the dreissenid mussel invasions; however, the weight-of-evidence suggests that the dreissenid invasions were a more likely driving factor behind the observed trends. PCBs continue to enter the Great Lakes from contaminated sites and urban infrastructures and, at least seasonally, via atmospheric deposition; thus, PCBs will continue to be detected in Great Lakes fishes into the foreseeable future.

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