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Spatial and Temporal Trends of Mercury Concentrations in Young-of-the-Year Spottail Shiners (*Notropis hudsonius*) in the St. Lawrence River at Cornwall, ON

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Abstract The St. Lawrence River at Cornwall, Ontario is an "Area of Concern" because of mercury (Hg) biomagnification from bottom sediments. To assess the spatial and temporal distribution of Hg in the food web, young-of-the-year (YOY) spottail shiners (*Notropis hudsonius*) were collected in August 2005 from five sites along the Cornwall waterfront within a Hg-contaminated zone and two reference zones. The results were compared to analyses made between 1979 and 2000 by the Ontario Ministry of the Environment. Total Hg concentrations in spottail shiners from the contaminated zone were significantly higher than in reference zones, confirming previous observations. Within the contaminated zone, there were significant differences in Hg concentrations among three sites spaced about 500 m apart, consistent with a high degree of site fidelity of YOY fish and suggesting a possible internal source of Hg. Hg concentrations in spottail shiners are decreasing regionally, although year-to-year variability was high, particularly in the contaminated zone. Stable isotope analyses of spottail shiners did not reveal any differences in nitrogen isotope composition among zones that would indicate differences in food-web structure and Hg biomagnification. However, carbon sources at an upstream reference zone were not the same as within the Area of Concern. Differences in carbon isotope composition at two sites within the contaminated zone corresponded to differences in Hg concentrations, consistent with a unique internal source of Hg. The variation in Hg contamination of YOY spottail shiners over fine spatial and temporal scales provide important insights about the potential release of Hg from contaminated sediments and the role of climate in regional trends. Sessile YOY fish provide a precise indicator for demonstrating these differences and for assessing their cause.

Keywords Mercury · Young-of-the-year fish · Stable isotopes · Aquatic food web · Monitoring

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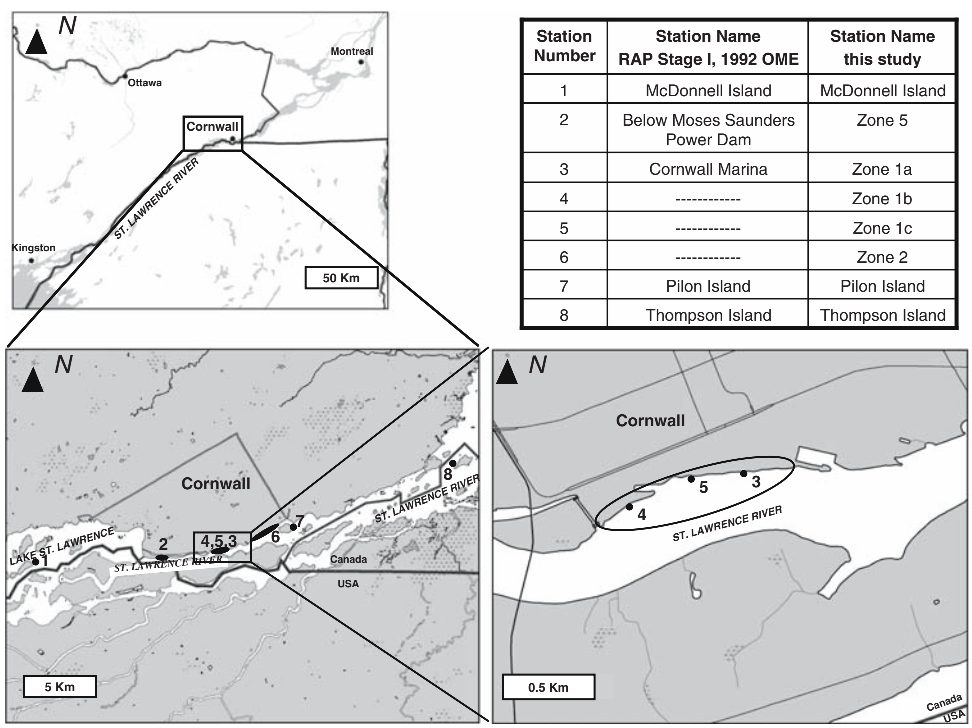
In 1985, the International Joint Commission identified the Cornwall–Massena section of the St. Lawrence River as 1 of 43 Areas of Concern (AOCs) within the Great Lakes and the St. Lawrence River basin (Environment Canada 1992). This AOC stretches 80 km, from the Moses Saunders Power Dam to the eastern end of Lake St. Francis, and includes waters shared by Canada, the United States, and the Mohawks of Akwesasne. As a result, the St. Lawrence River Remedial Action Plan (RAP) was implemented to assess the major environmental impairments. Mercury (Hg) contamination was identified as a primary concern due to elevated concentrations in sediments of the North Channel at Cornwall (Richman and Dreier 2001). Along the north shore, there are three depositional zones where sediment Hg concentrations exceeded background concentrations and the Ontario Ministry of the Environment (OME) sediment quality guidelines (Environment Canada 1992).

These zones include the following: Zone 1 at Lamoureux Park, the westernmost zone downstream of a pulp and paper mill and a chlor-alkali plant; Zone 2, the largest and most eastern location downstream of a rayon manufacturer; and Zone 3, the smallest zone in between Zones 1 and 2 (Fig. 1). Despite the discontinued use of mercurial slimicides by the pulp mill in 1970 and the ultimate closure of all industries (the rayon mill in 1992, the chlor-alkali mill in 1995, and the pulp mill in 2006), sediment Hg concentrations along the Cornwall waterfront remain above the severe-effect level (Delongchamp 2006; Environment Canada 1997).

Within Zone 1, the total Hg (THg) concentrations in yellow perch (*Perca flavescans*) 12 cm or larger exceed guidelines for human consumption (0.26 ppm; OME 2006; Fowlie 2006). This is in contrast to Zone 2, where concentrations of total Hg in sediments are somewhat higher than in Zone 1, but concentrations in the same size perch are lower and within the guidelines for human consumption. This difference could not be attributed to differences in the average size, growth rate, or condition factor of yellow perch (Environment Canada 1997; Fowlie 2006).

This paradox might be explained by unique ecological characteristics of Zone 1, such as a greater abundance of highly contaminated prey, a more complex food-web structure leading to greater biomagnification, or a localized internal source of Hg, such as an unexpected effluent discharge or a greater release of Hg from contaminated sediments. A recent survey indicated no unusual Hg concentrations in groundwater or storm sewers (Project Trackdown, C. deBarros, OME, Kingston ON, personal communication), but there is an abundance of subsurface deposits of wood fibers in the sediments of Zone 1 (Biberhofer and Rukavina 2002). Rates of methane evasion that were 5-fold to 20-fold greater than those of CO_2 suggest an increased rate of methane production from these deposits (Poissant et al. 2007; H_2S not measured). In addition to resuspending Hg-contaminated sediments and porewater, methane bubbling might also be associated with increased rates of Hg methylation. Compared to Zone 2, sediments of Zone 1 have high concentrations of solid-phase MeHg and high MeHg-to-THg ratios in surface sediments and porewaters (Delongchamp 2006).

One approach for locating potential internal sources of Hg to Zone 1 is to monitor species that are more sessile than perch and that represent a specific habitat. Young-of-the-year (YOY) forage fish, such as the spottail shiner (*Notropis hudsonius)*, are intra-annual indicators of local contamination by persistent chemicals. Because their home range is limited by their size (<1 km; OME 2005a), YOY spottail shiners have the potential to reflect local conditions and to provide fine-scale and precise geographic and temporal information about contaminant distributions (Suns and Rees 1978). Since 1975, temporal and spatial trends of contaminants in spottail shiners have been monitored throughout the Great Lakes and the St. Lawrence River basin as part of the OME Nearshore Juvenile Fish Contaminants Surveillance Program and the Great Lakes International Surveillance plan (Environment Canada 1997). In this study, YOY spottail shiners sampled along the shore of the



Station Number	Station Name RAP Stage I, 1992 OME	Station Name this study
1	McDonnell Island	McDonnell Island
2	Below Moses Saunders Power Dam	Zone 5
3	Cornwall Marina	Zone 1a
4	------------	Zone 1b
5	------------	Zone 1c
6	------------	Zone 2
7	Pilon Island	Pilon Island
8	Thompson Island	Thompson Island

Fig. 1 Spottail shiner collection sites, Hg-contaminated zones [Z1 (Sites a, b, c), Z2, Z3], and industrial sources of Hg within the St. Lawrence River, Cornwall, ON. The inset table indicates the correspondence between names for sampling sites used by OME (2005b) and names for the same sampling sites used in this study

Cornwall AOC were analyzed to reflect the distribution of bioavailable Hg among contaminated and reference zones and to determine the temporal trends in Hg contamination by comparison with data collected previously by the OME.

Our first objective was to determine if Hg concentrations in YOY spottail shiners reflected the broad differences among zones observed for species such as yellow perch (Fowlie 2006). The specific null hypothesis was H_{o1}: there is no difference in Hg concentrations of spottail shiners between contaminated Zone 1 and two reference zones (MacDonnell Island and Zone 5, upstream; Fig. 1). Our second objective was to determine, in conjunction with OME's Project Trackdown, whether there was a unique contaminant source in Zone 1. Recognizing the limited home range of spottail shiners, our null hypothesis was H_{o2}: Hg concentrations in YOY fish sampled at three sites at 500-m intervals along the shoreline of Zone 1 would show no differences in Hg concentrations. The third objective was to identify temporal trends of Hg within the AOC using current and previously collected data by OME's Nearshore Juvenile Fish Contaminants Surveillance Program. Our assumption was that Hg concentrations should decrease following the trends evident throughout the Great Lakes basin, except at zones where there is an ongoing Hg input. The null hypothesis was H_{o3}: there are no trends of decreasing Hg concentrations in spottail shiners sampled from any zone. The analysis of OME data also enabled a second test of H_{o1}. Our last objective was to determine if differences in fish Hg concentrations among zones could be explained by differences in the aquatic food web, as indicated by stable isotope ratios. Changes in the number of trophic levels will change the extent of biomagnification, and spottail shiner diets are known to vary among locations. For example, within Lake Erie, small cladocerans and copepods composed the majority of the diet of YOY spottail shiners, but they might also feed on chironomids, algae, and detritus (Hartman et al. 1992). Stable nitrogen isotope ($\delta^{15}N$) values increase 3–4‰ with every trophic transfer, so that differences in isotope ratios among locations might reflect trophic position and baseline nitrogen input. Stable carbon isotope ($\delta^{13}C$) values show an increase of about 0–1‰ but might vary according to the primary producers at the base of the food web (Peterson and Fry 1987). Hence, our last hypothesis was H_{o4}: there are no differences among zones in ratios of stable isotopes of nitrogen and carbon in spottail shiners.

Materials and Methods

Fish Capture

Young-of-the-year spottail shiners were collected with a 0.6-cm mesh seine net (1.9 m × 18.5 m) from July to late August 2005 within the Cornwall AOC. There was one shoreline sampling site within each of two reference zones (McDonnell Island and Zone 5) and three sampling sites within one downstream contaminated zone (Zone 1; i.e., Sites a, b, and c, each 500 m apart; Fig. 1). MacDonnell Island and Site a of Zone 1 were used by OME as part of their YOY surveys (Environment Canada 1997) and provided a basis for comparison of new to existing data. Following the OME protocol, spottail shiners were identified by a large black spot at the base of their caudal fin, and fish shorter than 60 mm were assumed to be YOY (OME 2005a). The mass and length of each fish captured were recorded, as well as the time, date, and global positioning system (GPS) coordinates for each seine haul. Fish were wrapped individually in aluminum foil, given an identification number, and frozen in polyethylene bags at -20°C. Species identification was corroborated by Brendan Jacobs of the Raisin River Conservation Authority, Cornwall, ON, who verified the correct identification of three preserved specimens from Site a.

Hg Analysis

Whole YOY spottail shiners were homogenized for Hg analysis following the OME Forage Fish Monitoring Program standard protocols (OME 2005a). Forty-two spottail shiners from MacDonnell Island, Zone 5, and Zone 1 (Sites a, b, and c) were frozen in liquid nitrogen and crushed into a powder using a mortar and pestle. Homogenates were reweighed, with 0.05 g of wet tissue measured for Hg content. Samples were analyzed individually for THg at the University of Ottawa using a Nippon Hg Analyser SP-3D (Nippon Instruments Corporation, Osaka, Japan) with a detection limit of 0.001 ng/g (Fowlie 2006). Each sample was analyzed with 0.1 M NaOH buffer, calcium hydroxide [$Ca(OH)_2$], activated alumina (Al_2O_3), and 1:1 sodium carbonate (Na_2CO_3) as additive agents. Two replicates of the certified reference material, DORM-2, (4.64 ± 0.26 mg/kg; National Research Council of Canada, Ottawa, ON) were run for quality control (our results: 4.47± 0.326 mg/kg). Each sample was run in duplicate and had a coefficient of variation (CV) of less than 2%. The THg concentrations of 5% HNO_3, aluminum foil rinsed in 5% HNO_3, the rinsate, and unrinsed aluminum foil were also tested to verify that samples were not contaminated in storage. The concentration of Hg extracted with 5% HNO_3 from the aluminum foil was 0.37 ng/g with a CV of 8.8% (n = 2), which represents <1% of the sample values. Concentrations of Hg extracted from the unrinsed foil (3.0 ng/g), foil rinsed in 5% HNO_3 (8.12 ng/g), and 5% HNO_3 (0.36 ng/g) were also low.

Historical data (OME 2005b) from spottail shiners of the same age and length were used to determine temporal patterns of total Hg concentrations in YOY spottail shiners at Site a in Zone 1, MacDonnell Island, Pilon Island, and Thompson Island (Fig. 1). The OME analyses indicated a mean of 4.13 mg/kg (n = 20) for the DORM-2 certified reference material and a CV of 8.9% (n = 117) (Russell and Prashad 2005).

Stable Isotope Analysis

Stable isotope concentrations were measured in the Queen's Facility for Isotope Research (Geological Sciences and Geological Engineering, Queen's University). Twenty-eight spottail shiners from MacDonnell Island, Zone 5, and Sites a, b, and c in Zone 1 were analyzed for stable isotopes of nitrogen and carbon (about five per site). Subsamples of whole-fish homogenates were freeze-dried to a constant weight (30 h) and ground with a mortar and pestle. An aliquot of 4–5 mg dry weight was weighed into tin capsules and combusted in a Costech Elemental Analyzer (Costech Instruments, Milan, Italy) coupled to a Finnigan Mat Delta Plus XP stable isotope mass spectrometer using Continuous Flow Technology (ThermoFinnigan, Bremen, Germany). Stable isotope values were determined from mass and isotope balance calculations:

$$\delta^{15}N \text{ or } \delta^{13}C = [(R_{sample}/R_{standard}) - 1] \times 1000$$

The $R_{standard}$ for $\delta^{15}N$ was the international standard atmospheric nitrogen and the $R_{standard}$ for $\delta^{13}C$ was the international standard Pee Dee Belemnite (PDB). Quality control and quality assurance included duplicate assays of every sixth sample (CV < 1.5%) and multiple measurements of blanks (empty tin capsules). Sulfanomide (0.3–0.4 mg), international nitrogen standard ammonium sulfate (Certified Reference Material 8548; 0.3 mg), and an in-house carbon standard uc-1 (University Carbon-1) (0.3 mg) were run every 10–12 samples. Based on the standards, the precision for both $\delta^{13}C$ and δ^{15} N values was ±0.3‰. To establish a comparative basis for isotope ratios, data for spottail shiners were plotted against the results of stable isotope ratios for zebra mussels (baseline), oligochaetes, yellow perch, and walleye (*Sander vitreus*) (data from Fowlie 2006).

Data Analysis

All data were analyzed using SigmaStat 3.0 and SigmaPlot 9.0 (Systat Software, Point Richmond, CA, USA). One- and two-way analyses of variance (ANOVAs) and all pairwise multiple comparison tests (Holm-Sidak test) were used to assess the differences in Hg concentrations and isotope values.

Results

Hg Concentrations: Spatial Trends

In 2005, the mean (± SE) total Hg concentrations on a wet-weight basis in YOY spottail shiners over all sites from Zone 1 (69 ± 6.5 ng/g) were significantly higher than in Zone 5 (50 ± 9.7 ng/g) and MacDonnell Island (34.2 ± 9.7 ng/g) (ANOVA, F = 16.4, $p < 0.001$, df = 2; Fig. 2A).

The differences among zones observed in 2005 were consistent with those of previous OME surveys (Fig. 2B; OME 2005b). In the OME survey, concentrations at Site a of Zone 1 were significantly higher than at MacDonnell Island, Thompson Island, and Pilon Island (ANOVA, F = 32, $p < 0.001$, df = 3). At Site a of Zone 1, there was a 1.9-fold increase in mean Hg concentrations of spottail shiners relative to MacDonnell Island in 2005 and a 1.7-fold increase from 1979 to 2005.

Within Zone 1, the mean concentrations of THg ranged from 60 to 80 ng/g, and concentrations from Site c of Zone 1 were significantly higher than those from Site b (Holm–Sidak test: t = 2.51, p = 0.017). There were no relationships

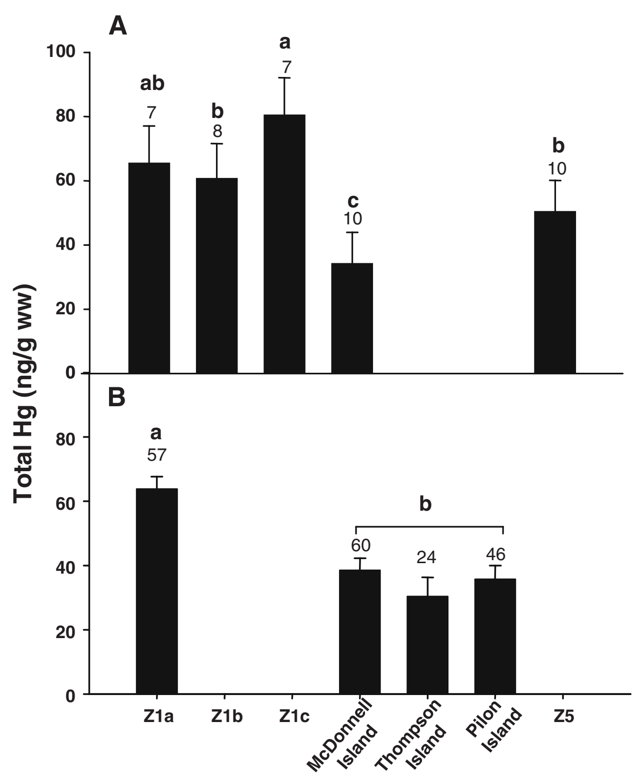


Fig. 2 Mercury concentrations of YOY spottail shiners sampled from the St. Lawrence River at Cornwall in 2005 (panel A, this study) and between 1979 and 2000 (panel B; OME 2005b). Treatments sharing the same letter are not significantly different from each other. Error bars represent 95% confidence limits; samples sizes are shown for each mean

between Hg concentrations and length or mass of spottail shiners ($p > 0.05$).

Hg Concentrations: Temporal Trends

A two-way ANOVA indicated that total Hg concentrations in YOY spottail shiners varied significantly with year of capture ($F = 10.7$, $p < 0.001$, df = 10) and zone ($F = 44.3$, $p < 0.001$, df = 3). Between 1979 and 2005, there was a weak negative correlation between Hg concentrations and time over all four zones ($r = -0.24$, $p < 0.001$). Despite the high variability among years, concentrations were highest at Zone 1, except in 1987, when concentrations were equal at the three zones sampled.

Between 1979 and 2000, the negative linear relationship between Hg concentration and time was strongest for fish from Thompson Island ($r = -0.92$, $p < 0.001$, $n = 7$), weaker for MacDonnell Island ($r = -0.39$, $p = 0.006$, $n = 10$), and insignificant for Site a of Zone 1 and Pilon Island ($n = 10$ and 7, respectively).

Stable Isotope Analysis

The δ^{15}N values of YOY spottail shiners showed little variability, with means ranging from 11.7‰ to 12.3‰ (Fig. 3), and no significant differences among zones (ANOVA: $F = 1.49$, $p = 0.24$, $df = 4$). There was a greater variation in δ^{13}C values, which ranged from –12‰ to –22.0‰ (Fig. 4), and significant differences among zones (ANOVA: $F = 14.5$, $p < 0.001$, df = 4). Values for δ^{13}C in fish from MacDonnell Island (mean of –20.0 ± 1.52‰) were significantly lower than for fish from Zones 1 and 5,

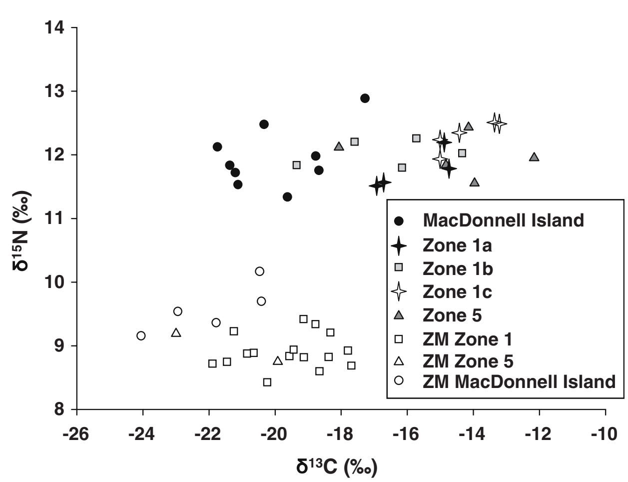


Fig. 3 The δ^{15}N and δ^{13}C values of YOY spottail shiners ($n = 28$) and zebra mussels (ZM; $n = 23$; Fowlie 2006) from five locations in Lake St. Lawrence (LSL) and at Cornwall

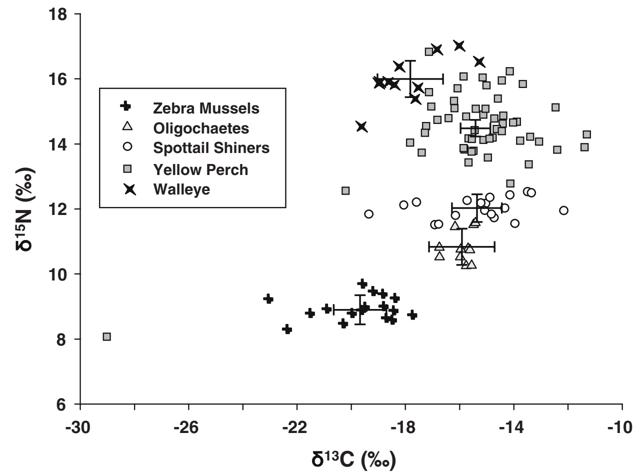


Fig. 4 Carbon and nitrogen isotope values of YOY spottail shiners (this study) and other species (Fowlie 2006) from the St. Lawrence River at Cornwall in 2005. Error bars represent 95% confidence limits ($n = 110$)

and there was a significant difference between δ^{13}C values of Sites b and c of Zone 1 (Holm–Sidak test: $t = 2.19$, $p = 0.04$). The stable isotope ratios suggest that spottail shiners occupied an intermediate position in the aquatic food web (Fig. 4).

Discussion

Spatial Trends in Total Hg

The THg concentrations in YOY spottail shiners from Zone 1 were significantly higher than in fish from Zone 5 and MacDonnell Island, which corresponds to observations for yellow perch (Fowlie 2006; Golder Associates 2004), and proximity to major sources of Hg (Environment Canada 1997). This spatial distribution was similar to that of previous data collected by OME (Fig. 2). Hence, we have rejected the first null hypothesis and conclude that distributions of Hg concentrations in spottail shiners reflect the patterns demonstrated by other fish species and that the food web at Zone 1 is indeed more contaminated than in other zones.

Within Zone 1, the Hg concentrations of YOY spottail shiners from Site c were significantly higher (33%) than concentrations from Site b; concentrations at Site a were intermediate and not significantly different from the other two sites. The data suggest considerable heterogeneity in the sources and distribution of Hg in Zone 1. However, they do not correspond to observations by OME's 2006 survey (Project Trackdown) that there were no unusual concentrations of Hg in groundwater and storm sewers in areas of the city of Cornwall adjacent to Zone 1 (C.

Debarros, OME, personal communication). Hence, the higher inputs of Hg to the Zone 1 food web might originate with existing Hg stored in the sediments, perhaps due to increased rates of methylation, increased bioturbation of sediments by fish or invertebrates, or increased disturbance of Hg-contaminated sediments by bubbles of methane released from subsurface beds of wood fiber. All Hg concentrations in spottail shiners were well below the Great Lakes Water Quality Agreement objective for the protection of aquatic life of 500 ng/g (Environment Canada 1992).

Temporal Trends of Hg in Spottail Shiners and Other Regions of the Great Lakes

In general, Hg concentrations in YOY spottail shiners have declined significantly over time at the four zones for which there were previous sampling data. Although we can reject the null hypothesis of no decrease in Hg with time, the trends were highly variable, with concentrations highest in 1988 and 1991. Further, the temporal trends varied among zones. The strongest or most consistent declines in Hg concentrations were observed at the upstream zone (MacDonnell Island) and the downstream zone furthest from Cornwall (Thompson I). In contrast, the temporal trend was much weaker for contaminated Site a of Zone 1 and not significant for Pilon Island, the downstream reference zone closest to Zone 1. Across other areas of the Great Lakes, Hg concentrations in YOY spottail shiners declined significantly and appeared to stabilize at many sites from 1976 to 1982, including five sites at Lake Erie, Lake Ontario, Leamington, and Niagara-on-the-Lake (Suns et al. 1985). Therefore, it appears that a Great Lakes regional trend toward decreasing contaminant concentrations in aquatic biota (Huestis et al. 1996; Koster et al. 1996) is reflected in the Hg concentrations of spottail shiners at the reference sites, but that the trend is less pronounced at Cornwall, perhaps due to ongoing inputs of Hg to Zone 1.

Similar results have been observed for other fish species in the St. Lawrence River AOC near Cornwall. In 1989, Hg concentrations peaked in yellow perch and northern pike in Lake St. Francis, with no sampling in 1988 (Environment Canada 1997). For yellow perch, walleye, and northern pike, Hg concentrations decreased from the 1970s until the early 1990s, when concentrations stabilized. Significant declines in Hg concentrations have also been demonstrated in many organisms within the Great Lakes, such as walleye and herring gulls (*Larus argentatus;* Koster et al. 1996; Scheider et al. 1998; Weis 2004), likely due to improved industrial practices and specific control programs (*e.g.*, Lake St. Clair, Scheider et al. 1998). Similar improvements have been made at Cornwall, and the current management strategy relies on the natural accumulation of clean sediments to decrease Hg contamination of surface sediments (Golder Associates 2004).

Despite an overall decrease in Hg concentrations of spottail shiners over time, there was a sharp reversal of the trend at MacDonnell Island and Site a of Zone 1 from 1997 to 2005, typical of the high year-to-year variability that obscures the temporal trends. Time series analyses of Lake Ontario chinook salmon support similar trends, with increasing Hg concentrations from 1999 to 2003 (French et al. 2006). The high concentrations of Hg during the late 1980s and early 1990s might be linked to warmer temperatures and drier weather. Warmer epilimnetic temperatures have been correlated to increased Hg concentrations in yellow perch, walleye, and other fish species (Bodaly et al. 1993). Elevated temperatures can increase Hg concentrations in fish by increasing mercury methylation rates in sediments, shortening the ice-cover period, and releasing Hg from watersheds (Evans et al. 2005). Both 1988 and 1991 were strong La Niña and El Niño years (Smith and Sardeshmukh 2000). Of the years sampled for Hg, 1991 had the highest annual temperature (8.4°C), whereas 1989 (6.6°C), 1993 (6.6°C), and 1997 (6.9°C) had the lowest temperatures (Environment Canada 2006) and the lowest Hg concentrations in spottails (Fig. 5). Interactions among climate, temperature, and Hg concentrations in fish have been reported recently for coho and chinook salmon feeding on alewifes in Lake Ontario (French et al. 2006). Warmer summer temperatures correspond with strong El Niño years and a decline in salmonine Hg concentrations. Because salmon preferentially feed on large alewifes, warmer temperatures would increase survival among YOY alewifes and, therefore, increase competition

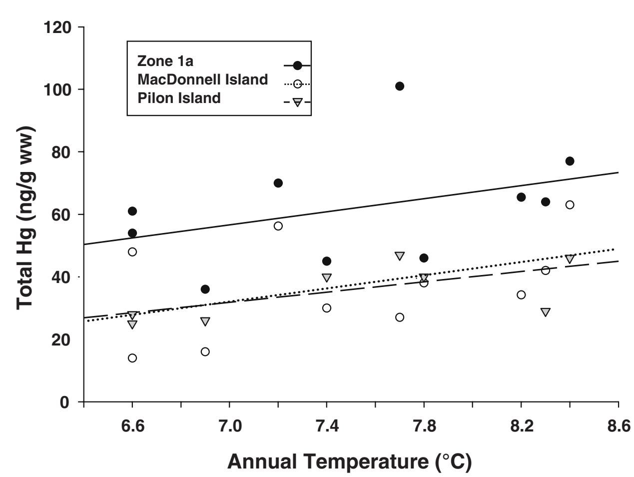


Fig. 5 Mean Hg concentrations of YOY spottail shiners from three zones of the St. Lawrence River at Cornwall compared to annual air temperatures between 1979 and 2005. The correlation coefficients (r) for the three zones were 0.38 for Zone 1a, 0.43 for MacDonnell Island, and 0.64 for Pilon Island (n = 28)

for resources. Increased competition for food might cause a decline in fish size among alewifes and, therefore, a decline in Hg transfer to salmon.

Mercury concentrations in walleye of Lake St. Clair and eastern Lake Ontario have also increased from 1990 to 1994 (Scheider et al. 1998), similar to the increase observed for spottail shiners in 1991. In a comparison of trends in Hg among sportfish from Lake St. Clair from 1971 to 1997, Weis (2004) found an increase in Hg concentrations in walleye and small mouth bass during the 1990s, with concentrations stabilizing in yellow perch and carp. It appears that despite restrictions placed on Hg output and predicted declines across the Great Lakes, environmental factors such as temperature might play a major role in the uptake of Hg to aquatic systems. It would be useful to make a detailed analysis of the interactions among temperature, water flow, and Hg concentrations in fish to determine if a multifactorial model could define clearer temporal trends and to determine if long-term climate change has an influence on contaminant dynamics in a major river system.

Stable Isotope Composition

Because there were no statistical differences among zones in δ^{15}N values of YOY spottail shiners, we accepted the null hypothesis and concluded that YOY spottail shiners occupied the same trophic position in all zones. In other words, the higher concentrations of Hg in spottail shiners at Site c of Zone 1 cannot be explained on the basis of more trophic levels and a more complex food web relative to other zones. Spottail shiners occupy a trophic position well above baseline organisms such as mussels and mid-way between benthic oligochaetes and yellow perch and walleye. Within many of the Great Lakes, yearling spottail shiners were the dominant prey of 1–3-year-old and yearling walleye (Hartman and Margraf 1992; Parsons 1971). Hence, spottail shiners are potential conduits of Hg to yellow perch and walleye, although total concentrations are relatively low. In Zone 1, benthic invertebrates such as amphipods sampled from the stomachs of yellow perch contained much higher concentrations of Hg (100–800 ng/g; Yanch 2007) than did spottail shiners (30–80 ng/g) and might be a more important source of Hg to other fish species. The dominant transfer route of Hg to spottail shiners might be seston (*i.e.*, zooplankton plus associated suspended nonliving materials), which contains MeHg concentrations estimated at 10 ng/g in Zone 1 and 7 ng/g in Zone 5 in August 2005 (Ridal et al. 2006).

We rejected the hypothesis that there were no variations among zones in δ^{13}C values because of observed significant differences between Sites b and c within Zone 1 and between MacDonnell Island and all other zones. The difference in δ^{13}C values of spottail shiners within Zone 1 corresponds to a significant difference between Sites b and c in Hg concentrations, suggesting a possible common source of carbon and Hg. One explanation could be the accelerated release of Hg from sediments caused by methane bubbling from wood fiber.

The unique δ^{13}C values of spottail shiners at MacDonnell Island might indicate that they consumed different dietary items than in other zones or that there were regional influences on baseline δ^{13}C values (*i.e.*, a different source of carbon from primary production). Our seining site at MacDonnell Island was influenced by a strong Main Channel current, estimated at 0.4–0.6 m/s (Ridal et al. 2005). Our other seining sites in the AOC had much slower water currents, estimated at less than 0.1 m/s (Ridal et al. 2005). The higher water velocity at MacDonnell Island might have decreased the boundary-layer thickness for primary producers, leading to more negative δ^{13}C values than at Zones 1 and 5. Thicker boundary layers trap greater concentrations of dissolved inorganic carbon, leading to less discrimination between the heavier and lighter isotopes and a more positive δ^{13}C value (France 1995; Hecky and Hesslein 1995). Higher water velocity might also favor phytoplankton over benthic algae at MacDonnell Island; benthic algae are enriched in δ^{13}C by more than 7‰ compared to phytoplankton (France 1995; Hecky and Hesslein 1995; Trudeau and Rasmussen 2003).

A stronger current might also deplete proportions of particulate organic carbon in the water from the Main Channel compared with slack water areas, lowering the ^{13}C content (Barth and Veizer 1999; Barth et al. 1998). As a limiting nutrient for plant and algal growth, nitrogen might not have been affected by the "dilution effect" at MacDonnell Island. Because the Main Channel of Lake St. Lawrence drains directly from Lake Ontario, some of the particulate organic matter (POM) in Main Channel water originates from Lake Ontario (Barth and Veizer 1999; Barth et al. 1998). Lake Ontario is supersaturated with CO_2, and benthic invertebrates such as oligochaetes contain much lower δ^{13}C values than those in the Cornwall AOC (Fowlie 2006; Leggett et al. 1999). Hence, the δ^{13}C values of spottail shiners from MacDonnell Island might reflect an external source of carbon (*i.e.*, Lake Ontario), whereas the carbon in fish from the other zones might represent primary production typical of local littoral habitats (*i.e.*, by macrophytes or periphyton).

Conclusions

The concentration of THg in YOY spottail shiners from Zone 1 was elevated relative to other zones along the Cornwall waterfront, suggesting a continuing input of Hg to aquatic food webs, but there was no clear indication of a specific shoreline point source. The data confirmed observations of elevated Hg concentrations in other fish species and demonstrated important fine-scale differences in Hg contamination not observed in regional-scale monitoring. Although temporal trends indicate that Hg concentrations in spottail shiners have decreased overall from 1979 to 2005, these trends might be influenced locally by Hg inputs to Zone 1, and high variability might reflect the influence of year-to-year differences in temperature and water flow. Differences in Hg concentrations among zones were not related to differences in the structure of aquatic food webs and were likely due to geographic variations in the source of Hg.

These results demonstrate the importance of scale in understanding the distribution of Hg in aquatic food webs. They also confirm the value of YOY sessile fish as a precise tool for discriminating differences in Hg contamination over small intervals of space and time.

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