Monitoring of Fish in Zone 1 and at Reference Sites to Determine Trends in Bioavailability of Mercury

Final Report Provided to Ontario Ministry of the Environment
in support of the St. Lawrence River (Cornwall)
Remedial Action Plan

ST. LAWRENCE RIVER
RESTORATION COUNCIL

Prepared by the

St. Lawrence River Institute of Environmental Sciences

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Report prepared for the Ontario Ministry of the Environment, Eastern Region, Kingston, ON, in support of the St. Lawrence River (Cornwall) Remedial Action Plan and the Canada-Ontario Agreement.

St. Lawrence River Institute of Environmental Sciences
2 St. Lawrence Drive
Cornwall, ON

Corresponding author:
jridal@riverinstitute.ca

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Executive Summary

Spottails and small Yellow Perch collected in 2011 along the Cornwall waterfront and at reference sites were analysed to establish spatial and temporal trends in fish mercury concentrations. The analysis indicates that concentrations along the Cornwall waterfront have decreased by 1.6 to 2.5-fold over the past decade. The largest decrease in concentrations occurred in the embayment near Lamoureaux Park (Zone 1), a popular angling site where fish exceeding the fish consumption limit for the sensitive population have been previously found. Mercury concentrations in 2011 for Yellow Perch (72 ng/g ww for 125 mm fish) in Zone 1 are well below the fish consumption guideline of 260 ng/g ww, although larger fish more typically kept by anglers for consumption would have higher concentrations.

Variations of Yellow Perch concentrations between recent years for similarly-sized fish in Zone 1 (118 ng/g ww in 2010) suggests that interannual variations may be significant, possibly relating to climactic conditions including stormwater inputs to the zone. The closure of Domtar Fine papers and cessation of discharges from the combined industrial sewer upstream of Zone 1 may be a factor contributing to the decline in fish mercury concentrations by decreasing mercury and/or nutrient inputs to the river, and therefore the delivery of bioavailable mercury to downstream zones.

Despite temporal declines, statistically significant spatial differences were found for fish mercury concentrations at different sites within Zone 1, and as well between Zone 1 and an upstream reference site for both Yellow Perch and Spottails. These data indicate that delivery of bioavailable mercury to Zone 1 remains enhanced compared to reference zones. Further investigation of stormwater inputs to the Cornwall waterfront to identify ongoing fugitive sources, as well as continued water quality and fish monitoring within Zone 1 is recommended.

Introduction

The Ministry of Natural Resources (MNR) undertakes fish monitoring in Lake St. Francis every second year and provides samples to the Ministry of the Environment (MOE) for contaminant analysis. The MOE uses this data to publish the *Guide to Eating Ontario Sports Fish*. However, the MNR fish sampling does not include sites in Zone 1 along the Cornwall waterfront where elevated mercury concentrations in localized fish (e.g. Spottail Shiners, small Yellow Perch) have been previously documented (Choy et al., 2008, Fowlie et al., 2008). Zone 1 is a publicly accessible site by land (via Lamoureaux Park) and attracts recreational anglers throughout the year. Therefore, this project is a contribution to the monitoring of fish concentrations in and near this zone.

In addition, the MOE has maintained a long-term monitoring program for Spottail Shiners as part of the Nearshore Juvenile Fish Contaminants Surveillance Program. Young of the Year (YOY) Spottails have been sampled in the Cornwall AOC to reflect the distribution of bioavailable Hg among contaminated and reference zones and to determine the temporal trends in Hg contamination. The last YOY sampling was conducted in 2005 (Choy et al., 2008).

Purpose of this Project

Fish collections of small perch and spottail shiners are to be undertaken in 2011 and analysed for their mercury contents. The results will be compared with past data to ascertain whether mercury concentrations in these fish are stable or declining.

Methods

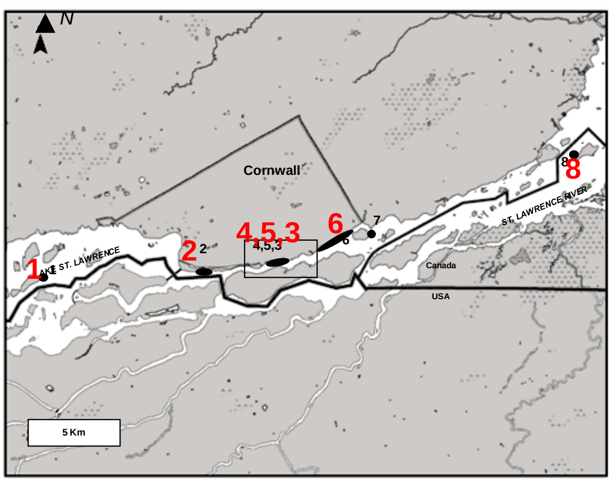
Sampling by seine net was conducted in July, August and Sept 2011 for small perch and YOY fish at Cornwall waterfront sites and at reference sites (Figure 1). Target species were Spottails Shiners and small Yellow Perch at all sites. Additional samples of Pumpkinseed and Round Gobies were also collected but not analysed.

Sampling position and fish morphological data were collected in the field. Perch samples were returned to the lab and fish dorsal muscle was collected, weighed and frozen in plastic cryovials. Spottails were stored whole at 20^{o}C prior to analysis. Small amounts of sample were also taken for stable isotope analysis.

Samples were transferred on ice to the University of Ottawa where analyses were conducted at the University of Ottawa mercury laboratory under the supervision of Dr. Alex Poulain. Spottails (whole fish) and yellow perch dorsal muscle were freeze-dried and then ground to a powder using mortar and pestle. All samples were analysed for THg using established methods (Ridal et al., 2009). To check a subset of spottail shiners were analyses for MeHg using capillary gas chromatography coupled with atomic fluorescence spectrometry (GC-AFS) as described by Cai et al. (1996).

THg values in units of dry weights were converted to wet weight values using a previously determined factor of 80% moisture for yellow perch fish tissue (Evano 2011). To determine the factor for whole spottail shiners, 10 whole fish were dried at 105^{o}C to a constant weight resulting in a mean value of 77% moisture content. The difference in percent moisture reflects the skeletal contributions of the minnow to the mass. All mercury concentrations are reported as wet weight values. Analysis of a subset of the samples using methyl mercury (MeHg) methods indicated that 99% (±1% SE, n=10) of the mercury in the Spottails from the sampling sites was in the methylated form.

Differences in Spottail Shiner concentrations between sites were assessed using one-way and two-way analysis of variance (ANOVA) and Dunnett's method was applied to test for differences between sites with the upstream control site, Zone 5. Yellow perch data were analysed using a one-way ANOVA for THg data that did not vary with fish length and analysis of covariance (ANCOVA) with total fish length as the covariate. In the ANCOVA approach, the data were fitted to a general model for all data to test for differences in slopes between the individual data sets. If slopes were equivalent, the interaction term was removed and the data sets compared based on values of the intercepts for the relationship between log THg and length with site and date using a Tukey`s post hoc test. Statistical analysis was conducted using JMP v.8 software.



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	PilonIsland	PilonIsland
8	Thompson Island	Thompson Island

Figure 1. Sample sites for this project (from Choy et al., 2008)

Results

Spottails ranged 42-75 mm in total length with an overall mean of 55 mm. Spottails are generally considered YOY up to 60 mm in length (MOE 2005). 5 of 8 MacDonnell Island Spottails exceeded this length and the mean value was statistically greater than the other sites (ANOVA, $F = 4.7$, $p < 0.001$, df=7). As a result, the MacDonnel Island fish were excluded from the statistical comparison, and the Zone 5 fish were used as the upstream reference site for comparison of THg concentrations in Spottails between sites. Site Z1a was also excluded from the statistical analysis due to low sample numbers (n=2).

Mean THg concentrations on a wet weight basis in YOY Spottails Shiners ranged from 15 ng/g in Zone 1a to 36 ng/g in Zone 1c (Table 1). Mean THg concentrations were significantly higher at Zone 1b, Zone 1c, and Thompson Island than Pilon Island and the reference site, Zone 5 (ANOVA, $F=5.6$, $p<0.001$, df=5). The results for Zone 1a and MacDonnell Island were not included in the comparison between sites.

Table 1. Summary of sites, numbers of fish analysed, mean total length, and size range. NA indicates no analysis was undertaken of fish collected at the site.

Site	Spottails			Yellow Perch		
	N	Average size, mm (range)	Average THg ng/g ww (±SE)	N	Average size, mm (range)	Average THg ng/g ww (±SE)
MacDonnell Island	8	62 (53-75)	30±6	NA	NA	NA
Zone 5	8	55 (46-63)	24±3	8	107 (104-110)	41±5
Zone 1a	2	50 (49-50)	15±1	8	128 (94-165)	55±7
Zone 1b	8	51 (42-59)	34±2	6	130 (94-165)	110±20
Zone 1c	8	56 (54-61)	36±2	12	106 (81-150)	61±8
Zone 2	8	58 (50-62)	27±1	8	165 (145-190)	96±4
Pilon Island	8	55 (50-59)	23±2	NA	NA	NA
Thompson Island	8	54 (50-57)	32±2	NA	NA	NA

Yellow Perch samples ranged 81-190 mm in total length. Samples from Zone 2 and Zone 5 were collected within narrow size ranges. The Zone 2 fish are significantly longer than the Zone 5 fish (ANOVA, $p<0.001$). Mean THg concentrations (±SE) in these two zones were 41(±5) and 96 (±4) but direct comparison of the THg concentrations from these two sites is not be appropriate because of the differences in fish sizes.

THg concentrations in dorsal muscle of Yellow Perch from Zones 1a, 1b and 1c ranged 18-185 ng/g and were correlated with total length (Figure 2). The general model is significant (r^2= 0.68, p < 0.0001, n=26) with Zones 1a and 1B significantly different than the general model but not Zone 1c. The test for collarity of slopes was accepted, and the post hoc test for different intercepts indicated that fish from Z1B and Z1C were similar but statistically different than fish from Z1a (p<0.05).

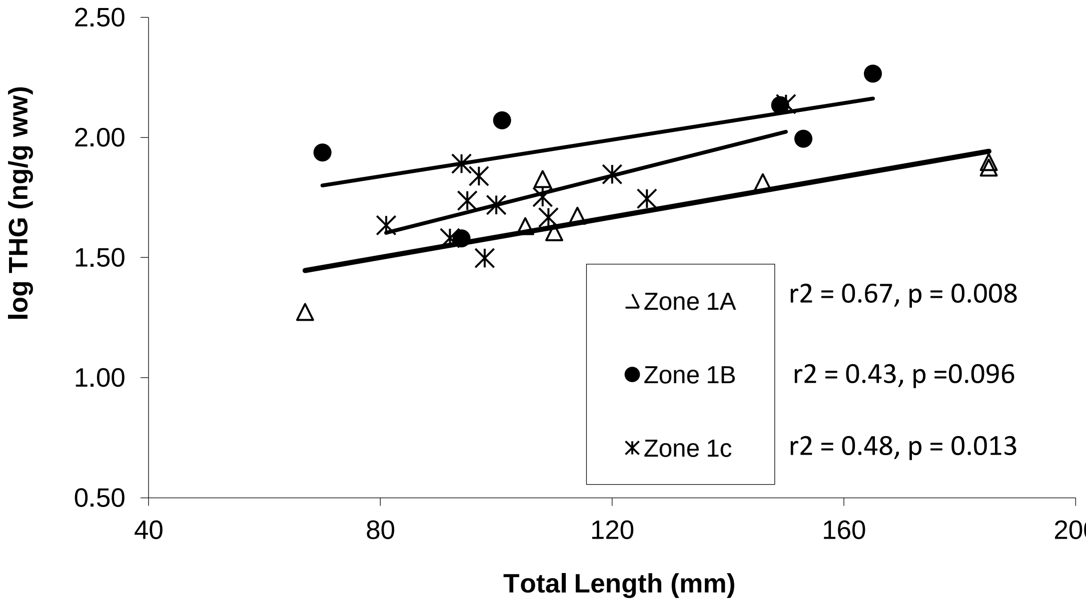


Figure 2. Concentration (log THg) – length (mm) relationships for Yellow Perch from sites in Zone 1. Significant differences were found between the relationship between Zones 1A and 1C.

Discussion

Spatial Trends

The 2011 Spottail data follow similar spatial patterns as previously reported by Choy et al., 2008. In 2011, THg concentrations in Spottails from Zone 1b and 1c were approximately 1.4-fold higher than Zone 5 and Pilon Island (Figure 3). In 2005, THg concentrations in Spottails were approximately 1.4-fold greater in Zone 1 than Zone 5. Spottails collected between 1979 and 2000 from site Zone 1a had approximately 1.8-fold greater THg concentrations than fish collected near MacDonnell, Thompson and Pilon Islands.

In 2011, Spottail THg concentrations from Zone 2 and MacDonnell Island had intermediate concentrations although MacDonnell Island fish were significantly larger than those from other sites. Spottails collected at Thompson Island had similar concentrations as at Zone 1b and Zone 1c sites. The relative high THg concentrations in Spottails at Thompson Island are consistent with a recent survey of small yellow perch concentrations in Lake St. Francis (Ridal et al., 2011). In that work, greatest THg concentrations were found in areas several km downstream of Cornwall particularly those influenced by tributary inputs.

We observed similar spatial patterns for Yellow Perch as Spottails. THg concentrations in the Yellow Perch were significantly greater from Zone 1b and Zone 1c sites than from the downstream Zone 1a site (closer to the Cornwall Marina). Zones 1b and 1c sites contain more extensive shallow littoral areas and comprise a greater proportion of the contaminated sediment deposit (Ridal et al, 2009, Eveno 2011). Current speeds in Zone 1 are low and the nearshore circulation pattern is such that the discharge from a stormwater pipe is carried into Zone 1b. These distinct features may account for the differences observed between fish even within a very small geographic area.

Temporal Trends

Overall the 2011 Spottails from Zone 1 averaged 33±3 SE ng/g compared with 69±7 ng/g in 2005 (Choy et al., 2008, Figure 3). Similarly, Spottails from Zone 5 in 2011 were approximately 50% lower than the average value in 2005 of 50±10 SE ng/g. A two-way ANOVA shows a significant difference between sites between years (2005 vs 2011 data) with the strongest effect being years (F ratio=95.2, $p=<0.001$ for years versus F ratio=11.1 for sites, $p<0.001$). A t-test conducted on Least Square Mean differences (year effect) yielded significant differences ($p<0.05$) between years for sites tested (i.e. Zones 1a, 1b, and 5).

To examine for temporal trends in Yellow Perch, we compared the 2011 data from Zone 1 (all data combined) against data collected in 2002 (Ridal, unpublished data), and 2004 and 2005 (Fowlie et al., 2008). We limited our comparisons to fish collected in July and August to match the time period of the sampling in 2011. The ANCOVA indicates that the general model for logTHg versus fish length is highly significant ($r^2=0.78$, n=71, $p<0.0001$) and the slopes for different years are collinear ($p=0.782$). Removing the interaction term from the analysis, and comparing years by a Tukey HSD indicates that 2011 data were significantly different ($p<0.001$) than the 2002, 2004 and 2005 data which were all similar and not significantly different from each other (Figure 4).

To illustrate the changes in Yellow Perch concentrations over time, the size-length relationships for 2005 were used to predicted values for same length fish as collected at sites in 2011 (Table 2). THg concentrations for 125 mm fish from sites in Zone 1 in 2011 is 114 ng/g (62%) lower than 2005 predicted values. For Zone 2, the mean THg value is 74 ng/g (44%) lower than the predicted value from 2005 for 165 mm Yellow Perch (mean length of 2011 fish from that zone). On the other hand, the mean THg value in fish from the Zone 5 from 2011 is only 30 ng/g (30%) lower than the value predicted for 107 mm Yellow Perch in 2005.

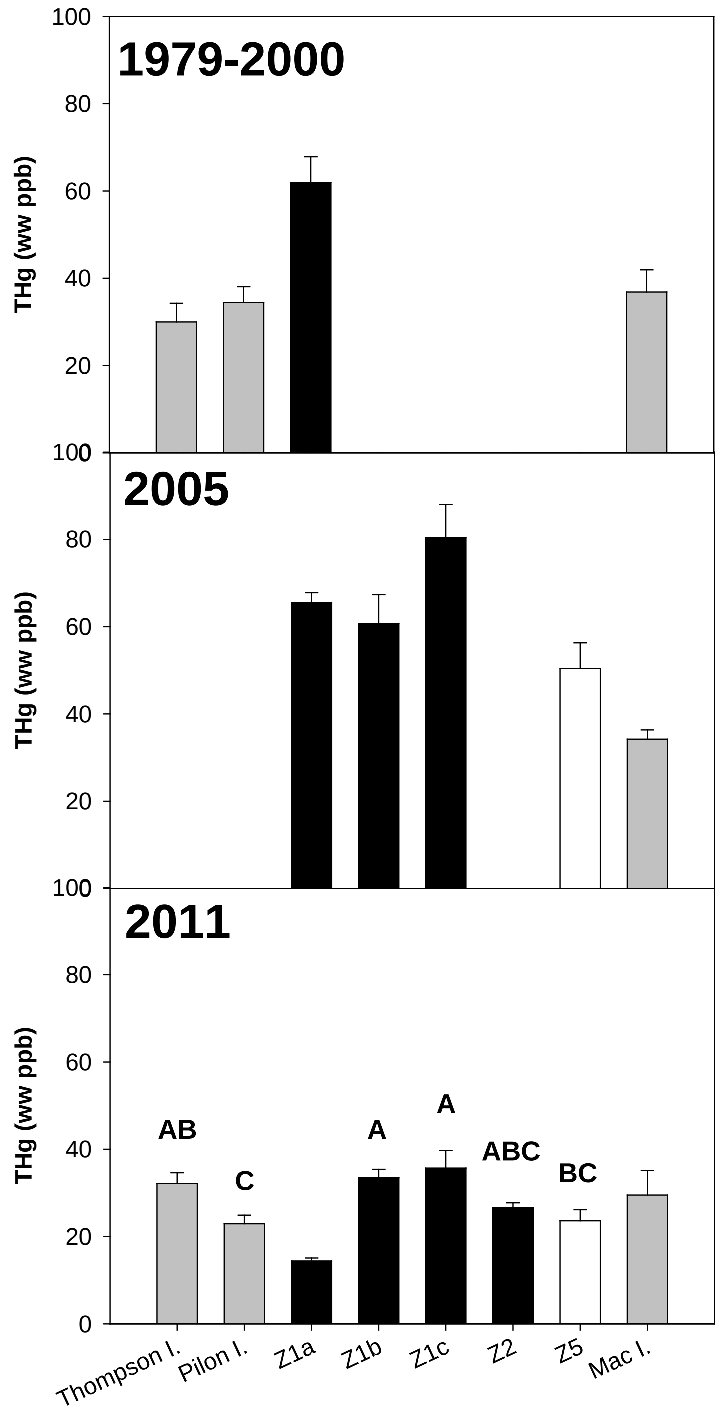


Figure 3. Concentrations of total mercury (THg) in spottail shiners on a wet weight basis from different sites in the St. Lawrence River in 2011 and comparison with historical data as reported in Choy et al., 2008. For the 2011 data, bars with different letters are statistically different. The

data from Z1a and MacDonnell Island were excluded from the analysis. Z1a had low sample

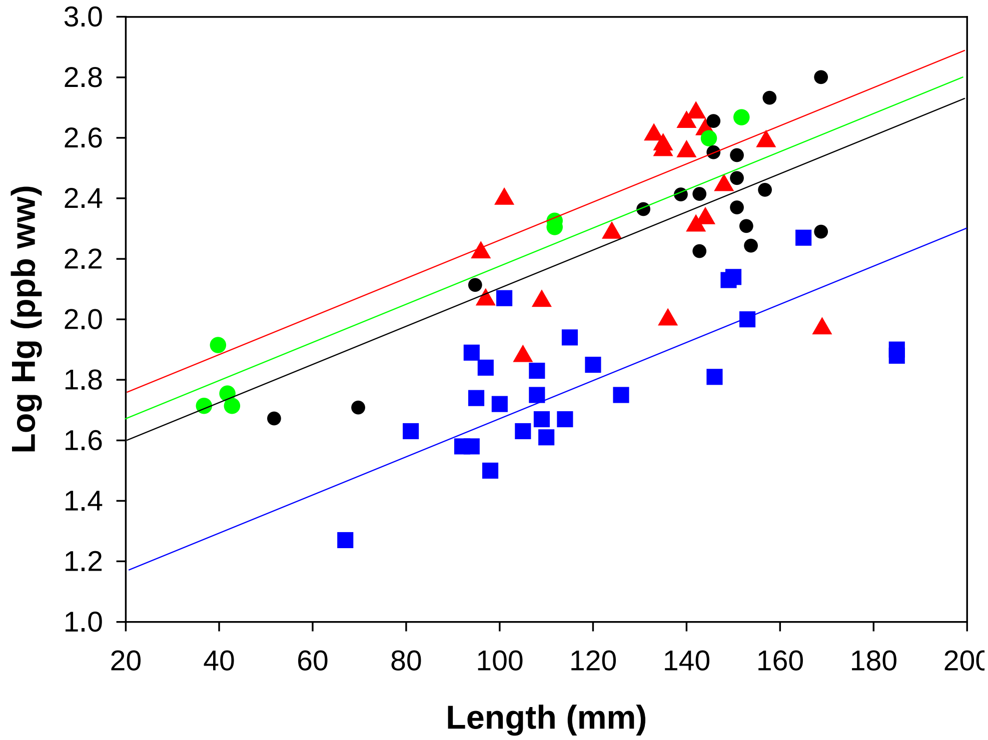


Figure 4. Comparison of log transformed mercury concentrations in Yellow Perch from Zone 1 as a function of fish length between 2002 (green circles), 2004 (triangles), 2005 (black triangles) and 2011 data (blue squares). The 2011 data are significantly different than those from earlier years ($p<0.001$).

numbers for (n=2), MacDonnell Island fish were significant longer than those from other sites.

Table 2. THg concentrations in Yellow Perch from 2011 compared against concentrations predicted from size-concentration relationships for same length fish from 2005 (Fowlie et al 2008). Also provided for comparison are fish collected in Zone 1 in 2010 (Evano 2011, n=45). NA indicates that concentration-fish length relationship was not significant; * shown are the geometric mean THg data for zones 2 and 5 for 2011. The Smearing Estimator is used to account for retransformation bias and is the mean of the antilog of the residual errors of the regression fit.

Year	Zone	Slope	Intercept	Smearing Estimator	Fish Length (mm)	Predicted THg (ww)
2005	1	0.00823	1.22	1.05	125	186
	2	0.00404	1.55	1.03	165	170
	5	0.00359	1.41	1.07	107	67
2010	1	NA	NA	NA	116	118
2011	1	0.00479	1.23	1.07	125	72
	2	NA	NA	NA	165	96*
	5	NA	NA	NA	107	42*

Our analysis indicates that there have been significant declines in THg concentrations of fish along the Cornwall waterfront. Spottail THg concentrations have declined approximately 2-fold since 2005 at both Zones 1 and 5. Yellow Perch concentrations have declined by approximately by a factor of 2.5 in Zone 1 and a factor of 1.8 in Zone 2. The 2010 data from Zone 1 are a factor of 1.6 lower than 2005 data suggesting some interannual variability in perch concentrations in this zone. A 30% decline in Yellow Perch concentrations at Zone 5 since 2005 is similar to the decline in Spottails over the same time period at that site.

It would be expected that declines in concentrations would be proportionately greater for larger Yellow Perch feeding at a higher trophic level due to the biomagnification effect which typically represents a 3-5 times increase in concentrations between trophic levels. For instance, a 3-fold difference exists between the mean value (265 ng/g ww) for 144 mm Yellow Perch in Zone 1 reported by Fowlie et al., (2008) and the value for similar sized fish (89 ng/g ww) predicted using the concentration-size relationship regression for 2011 Zone 1 fish.

Overall, the results suggest that sources of mercury and/or mercury methylation rates in these Zones have been curtailed over the past decade. A number of actions may be responsible for decreasing inputs of Hg to downstream Zones since 2005. The most potentially significant factor has been the cessation of the operations of the Domtar Fine Papers mill which closed in 2006. Decommissioning included several activities that may have decreased sources of mercury from the industrial complex, including possible fugitive discharges from stormwater drains. A grit chamber leading to the Domtar diffuser and reported containing high concentrations of mercury has been pumped clean (Madeleine Rose, Paris Holdings, personal communication). Stormwater from the site is now primarily directed to the Cornwall water treatment plant.

The closing of Domtar Fine Papers also represented a reduction in nutrient discharge to the river which would likely have decreased biofilm production along the downstream zones. Biofilms are important sites for mercury methylation and production of bioavailable mercury (Planas et al, 2006; Eveno 2011, Hamelin et al, 2011).

In addition to clean up activities, administrative controls have been implemented along the Cornwall waterfront as part of the Cornwall Sediment Strategy which has reduced activities which may disturb sediments.

Conclusions and Recommendations

Analysis of sentinel fish (Spottails and small Yellow Perch) indicates that fish mercury concentrations in Zones along the Cornwall waterfront have decreased by 1.6 to 2.5-fold over the past decade with the largest decrease in concentrations occurring in the embayment near Lamoureaux Park (Zone 1), a popular angling site where fish exceeding the fish consumption limit for the sensitive population have been previously found. Mean THg concentrations in 2011 for yellow perch (72 ng/g ww for 125 mm fish) are well below the fish consumption guideline of 260 ng/g ww, although larger fish more typically kept by anglers for consumption would have higher concentrations. Variations of Yellow Perch concentrations between recent years for similarly sized fish (2010 vs 2011) suggests that interannual variations may be significant, possibly relating to climactic conditions including stormwater inputs to the zone.

Despite temporal declines, statistically significant spatial differences were found for fish Hg concentrations at different site within Zone 1 and between Zone 1 and an upstream reference site for both Yellow Perch and Spottails. These data indicate that delivery of bioavailable mercury to Zone 1 remains enhanced compared to reference zones. Further investigation of stormwater inputs to identify sources, as well as continued water quality and monitoring of fish within Zone 1 is recommended.

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