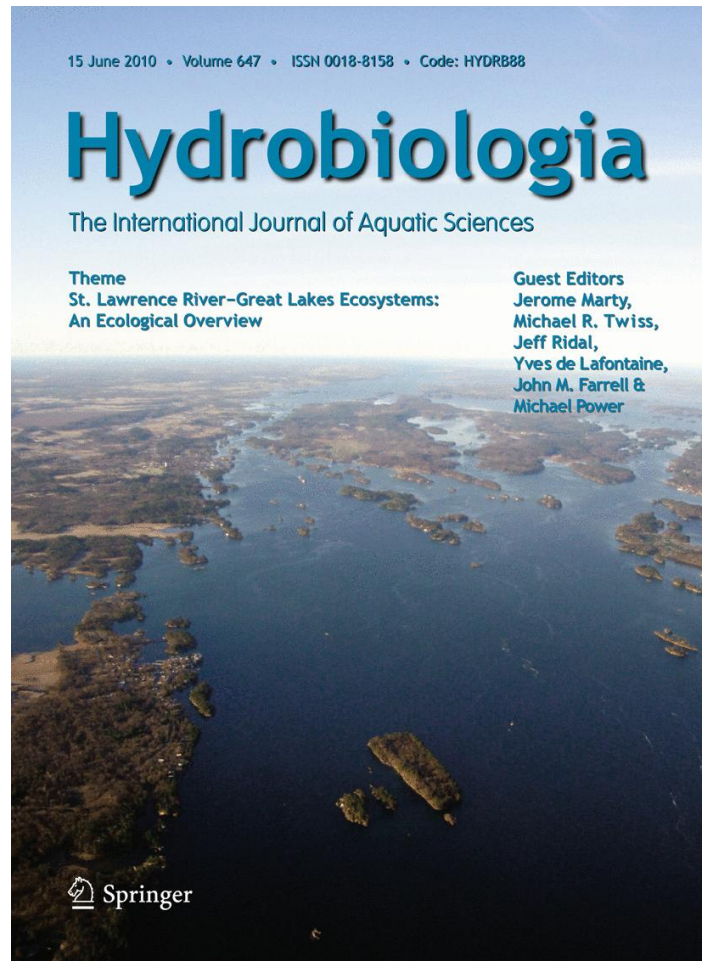


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Potential causes of enhanced transfer of mercury to St. Lawrence River Biota: implications for sediment management strategies at Cornwall, Ontario, Canada

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Abstract We examined factors and pathways involved in the transfer of mercury (Hg) to the food web in St. Lawrence River embayments near Cornwall, Ontario, where natural remediation of contaminated sediments (eventual burial by settling of cleaner sediments) has been adopted as a management strategy. Yellow perch (*Perca flavescens*) from one of the study zones (Zone 1) along the river by Cornwall contained significantly higher total mercury (THg) concentrations than perch from other equally contaminated zones. While THg concentrations in benthic invertebrates did not vary among contaminated zones, THg concentrations in yellow perch and invertebrate prey recovered from the perch stomachs

were 1.5–2.5 times higher in Zone 1 than those from other zones, suggesting that prey selection affects THg accumulation more than habitat location. No significant differences were found in THg concentrations among different prey species within Zone 1, although there were significant differences in THg concentrations in the same prey species within Zone 1. In contrast, THg concentrations among different prey species increased significantly with trophic level in other contaminated and reference zones. The lack of correspondence between trophic position and THg accumulation in Zone 1 suggests two possibilities: (1) yellow perch in Zone 1 are highly mobile and are assimilating THg from a wide range of prey across Zone 1 with variable THg concentrations and (2) there may be an important non-dietary source of THg to the Zone 1 food web. Potential waterborne Hg sources to Zone 1 were investigated. Whereas THg and MeHg values in discharges from a disused canal were similar to Zone 1 surface water values (0.97 and 0.04 ng l⁻¹, respectively), concentrations in storm sewer and combined sewer overflows discharging in the vicinity of Zone 1 were 19–45-fold (THg) and 2–4-fold (MeHg) higher than upstream river water. Contributions of Hg to the water column from sediment–water diffusion, estimated using a simple, well-mixed reactor model, ranged 0.05–0.1% of the surface water THg concentration and 1–2% of the MeHg concentration measured in summer months in Zone 1. Although not investigated in the other zones, a strong correlation ($r^2 = 0.82$) was found between

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MeHg in porewater and amphipod concentrations in Zone 1, indicating that the sediment porewater is bioavailable and likely an important pathway for transfer of sediment Hg to the foodweb. Large areas of Zone 1 contain bark deposits and produce high rates of gas ebullition, and may not provide favourable conditions for progressive burial with clean sediments and attenuation of Hg transfer to biota through natural remediation. Careful monitoring of surface sediment concentrations and biota is required in these areas. Failure to reduce concentrations of Hg in these media would indicate alternative or additional management measures are required.

Keywords Mercury · Sediment · Biota · Fish · Bioaccumulation · St. Lawrence River

Introduction

Mercury (Hg) contamination of aquatic environments is ubiquitous, particularly in areas with a history of industrial activity such as in the lower Great Lakes of North America. Continuous transformations among the different chemical and physical forms of Hg in the atmosphere, water, sediments and soils constitute the global cycle of Hg in the environment. Elemental Hg is efficiently transported throughout the globe, and even the remote Canadian North shows signs of Hg pollution (Morel et al., 1998).

Hg in water is usually determined as total (THg) or as methylmercury (MeHg), the form which is most efficiently bioaccumulated because of its propensity to bind to sulphur amino acids and proteins via its affinity for sulphur groups. Typically, over 90% of the Hg in fish is MeHg accumulated primarily through diet (Hall et al., 1997; Trudel et al., 2000; Trudel & Rasmussen, 2006). MeHg can cross the blood/brain barrier when associated with cysteine and is a potent neurotoxin (Harada, 1995). Consumption advisories have been developed for most inland waters in North America that limit the amount of fish a person should consume. Currently in Ontario, Canada, Hg contamination is responsible for 85% of consumption restrictions for sport-fish from over 1,500 lakes and rivers (Ontario Ministry of the Environment (OME) 2007).

Once Hg has entered an aquatic system, it can bind with organic and inorganic ligands which limit its mobility within the sediment. MeHg concentrations in

the aquatic environment are controlled by the relative efficiency of microbial methylation and demethylation (Ullrich et al., 2001). At the sediment–water interface, Hg can be methylated by sulphate-reducing bacteria to MeHg (Kamman et al., 2005). The factors controlling the concentrations of MeHg in aquatic systems are complex and the relationships among Hg input, sediment chemistry and overlying water conditions are important in its production and distribution (Bloom et al., 1999; Kamman et al., 2005).

Despite recent progress, there are few solid and consistent data describing the rates of formation, degradation and uptake of MeHg in lakes and rivers, which is a major limitation to informed management of contaminated sediments. Mixing and transport in river systems add to the complexity of managing Hg contamination and can make source identification challenging (Waldron et al., 2000).

The International section of the St. Lawrence River from the mouth of Lake Ontario to where the river enters fully into Canada at the intersection of the Ontario, New York and Quebec borders is a critical freshwater resource for shipping, power generation, tourism, and sport and commercial fishing. This section has a long industrial history including chemical, pulp and paper, and aluminium production. It also became a major international shipping route following the construction of the St. Lawrence Seaway (est. 1959) and the Moses–Saunders Dam (est. 1958) at Cornwall–Massena (Richman & Dreier, 2001). As a consequence, the river's ecosystem has been affected by chemical pollution, habitat degradation and a variety of other impacts. Hg contamination of fish has been a prominent public health issue for decades.

Based on the extensive degradation of the aquatic environment, the river near Cornwall, Ontario, from the Moses–Saunders dam downstream to the Beauharnois Dam in Quebec has been designated a Great Lakes “Area of Concern (AOC).” In response, a Remedial Action Plan (RAP) was developed to remediate and manage each of the stressors within the AOC and to assess progress through programs of research and monitoring (St. Lawrence River RAP Team, 1997; Richman & Dreier, 2001).

The sources of Hg to the AOC include historical point sources at Cornwall, tributaries discharging agricultural and wetland runoff, diffuse sources from Lake Ontario and from long-range atmospheric transport and deposition. The location and characteristics of

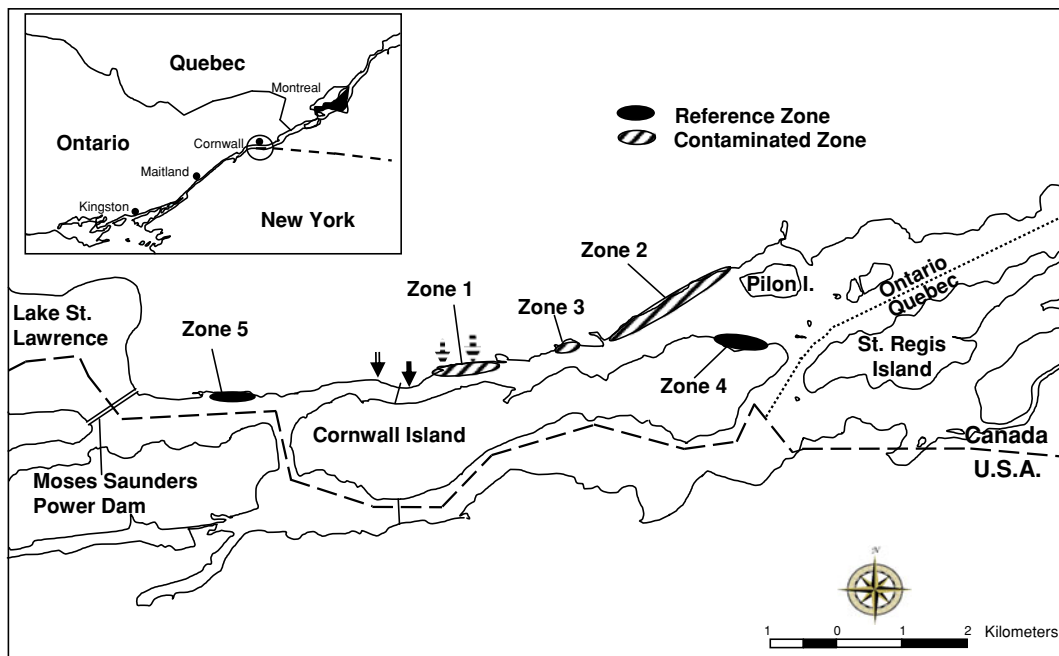


Fig. 1 Map of study zones (adapted from Fowlie et al., 2008). Zones 1, 2 and 3 contain contaminated sediment, and Zones 4 and 5 serve as reference zones. Also shown are the locations of the sewer outfalls in the vicinity of Zone 1. These outfalls include the storm sewer outfall for the former Domtar/ICI

complex (▼) upstream of Zone 1, the Brookdale Avenue CSO (▼), and the Pitt St. and Amelia St. storm sewers (⊞). Details on the locations and geophysical characteristics of the sediments are provided in Rukavina (2000) and Biberhofer & Rukavina (2002)

the sediments most heavily contaminated by deposits of heavy metals and organic contaminants have been described previously (Richman & Dreier, 2001). In fast-moving rivers, sediment deposition and accumulation occurs only in regions where flow is restricted. There are three main contaminated depositional zones along the Cornwall waterfront: Zones 1, 2 and 3 (Fig. 1). Each zone is characterized by a high degree of spatial heterogeneity in sediment type and composition (Rukavina, 2000; Biberhofer & Rukavina, 2002). Two nearby reference sites, located opposite to the river channel from the Cornwall waterfront and upstream of Cornwall, are relatively uncontaminated and have been designated as Zones 4 and 5, respectively. Despite the closure of the main industrial sources of Hg to the river, concentrations in the zones with historically contaminated sediments remain high. Hg concentrations in most samples exceed Ontario's Lowest Effects Level Sediment Quality Guideline of 200 ng g^{-1} for total Hg (THg) on a dry weight basis and many exceed the Severe Effects Level of 2000 ng g^{-1} THg (dw).

After a review of data from an array of studies on Hg concentrations in sediment, sediment toxicity and

sediment stability, and of the potential for Hg transfer from sediment to biota (Grapentine et al., 2003), a management strategy has been adopted to leave the sediments in place and to allow natural remediation to occur through eventual burial by sedimentation of low Hg content. The management strategy is based on evidence that although these sediments were highly contaminated, they exhibited low toxicity, supported healthy benthic communities, were resistant to resuspension and erosion, and showed a low potential for Hg transfer to benthos (Golder Associates Ltd, 2004). The strategy recognized the need for continued research and more complete environmental data to further characterize factors affecting MeHg production, sediment–water interactions and concentrations of MeHg in biota, especially fish. Additional research was required because elevated Hg concentrations in yellow perch (*Perca flavescens*) and other sentinel fish species have been found in Zone 1, the upstream contaminated site (Fowlie et al., 2008). In addition, Hg concentrations in adult walleye (*Sander vitreus*) from Lake St. Francis, the portion of the river downstream of the Moses–Saunders dam and the historical industrial

sources at Cornwall, are about two times higher than in upstream populations and exceed the fish consumption advisory limit for Ontario.

This report summarizes research to examine pathways for mercury transfer from sediments via the food chain to fish and to determine if there is significant Hg transfer from these contaminated sediments. THg and MeHg concentrations were measured in surface water and suspended solids, stormwater, zooplankton, amphipods, fish prey (stomach contents) and fish (yellow perch) and have been compared with published data on sediments (DeLongchamp et al., 2009a, b) and detailed studies on spatial and temporal patterns of Hg accumulation in fish (Choy et al., 2008; Fowlie et al., 2008). While our work focused on the St. Lawrence River, these investigations outline approaches to investigate Hg fate and transport in aquatic food webs that are relevant to other aquatic ecosystems, particularly major rivers where high flow rates physically structure ecosystems by controlling sedimentation and contaminant distribution.

Materials and methods

Surface water samples were collected in pre-cleaned 50-ml polypropylene centrifuge tubes for THg (Fisherbrand, ThermoFisher Scientific, Waltham, MA) and 1 l HDPE bottles for MeHg (Nalgene, ThermoFisher Scientific, Waltham, MA) using a gloved hand. Samples from mid-depth (3–5 m below the surface) were obtained using a pre-cleaned GO-Flo[®] sampler. Each sampling event consisted of five samples taken along a straight line transect at equal intervals across each zone. Due to the longer length of Zone 2, five samples were taken in both the west (2W) and east (2E) half of the zone. Zone 2W contains the highest concentrations of sediment Hg of all Zones (Richman & Dreier, 2001). Surface and mid-depth water samples were taken in August 2004 at surface and at mid-depth. In 2005, surface water samples were taken in late May, late July and late September to examine seasonal differences. Stormwater and canal water samples were taken by grab sample or by pole sampler from the effluent stream at its point of entry to the river. Filled sample tubes were double-bagged immediately and stored on ice during transport to the laboratory. THg samples were preserved with BrCl and MeHg samples with HCl in a clean room facility within hours of sampling.

Suspended solids were collected from surface water samples onto pre-cleaned and pre-weighed glass fibre-filters with nominal 1.2 µm pore-size (GF/C, Whatman, Maidstone, England) and dried to constant weight. Temperature, dissolved oxygen and specific conductivity measurements were made in the field using calibrated handheld meters (YSI, Yellow Springs, OH).

Zooplankton samples were collected at three sites within each zone with a 150-µm mesh net using multiple vertical hauls sufficient to sample ~2500 l of water. Care was taken during sampling not to disturb bottom sediments. Samples were processed as described by Ridal et al. 2006. Our sampling gear did not have an appropriate mesh size to collect small rotifers, which can dominate zooplankton biomass in the St. Lawrence River (Basu et al., 2000), but our focus was on the larger zooplankton consumed by fish. Fish were collected using a range of capture techniques including gill nets (two 15 m panels of 25, 33 and 64 mm stretched mesh, set 1–2 h), trap nets (set 18–24 h), seine nets (10 m, 3 or 4 pulls) and angling with baited lines. Fish were killed and frozen immediately for storage. Stomach contents of yellow perch were processed as described in detail by Yanch (2007). The proportion of stomach mass for each prey type was expressed as a percentage of the proportion of its mass divided by the total stomach content mass. Prey occurrence was expressed as the number of times a given prey item was identified in yellow perch stomachs (the percentage of the number of stomachs in each category). Skinless dorsal white muscle tissue from above the lateral line was used for THg analysis.

MeHg concentrations were determined in river and stormwater samples by capillary gas chromatography coupled with atomic fluorescence spectrometry (GC-AFS) as described by Cai et al. (1996). The method detection limit (MDL) is estimated as 0.02 ng l⁻¹. Water samples were analysed for THg using pre-oxidation by BrCl and SnCl₂ reduction with pre-concentration by two-stage gold amalgamation, followed with detection using cold vapour atomic fluorescence spectroscopy (CV-AFS). The analysis was conducted using a Tekran 2600 system following the modified US EPA Method 1631 Revision E for Hg analysis (US EPA, 2002). The MDL was estimated as 0.2 ng l⁻¹. Analysis of trip and procedural blanks consisting of de-ionized water revealed no Hg contamination during THg analysis or during MeHg

extraction and analysis. Recoveries of spiked samples were between 90 and 115% for THg and 95–105% for MeHg. Coefficients of variations for analyses of field replicates ($n = 11$) were 19% for THg and 26% for MeHg for these low level samples. Canal water samples were analysed by Flett Analytical, Winnipeg, Manitoba, using similar methods for THg and by distillation, ethylation, purge and trap and CV-AFS for MeHg. Analysis of trip and procedural blanks consisting of de-ionized water revealed no Hg contamination during THg analysis or during MeHg extraction and analysis. Analysis of replicate samples between the two laboratories showed no significant differences for THg ($P = 0.32$, $n = 8$) and MeHg ($P = 0.20$, $n = 6$).

Biota samples were freeze dried and homogenized prior to analysis at the University of Ottawa using a high-temperature combustion Nippon Automated Hg Analyser SP-3D (Nippon Instruments Corporation, Osaka, Japan) with a detection limit of 0.001 ng g^{-1} . This technique is a three-step method which includes thermal decomposition, dual-step concentration by gold amalgamation and detection by cold-vapour atomic absorption spectroscopy. Suspended solids were measured directly on filters with blank correction for the filter material. The standard quality assurance/quality control program included analysis of blanks, standards and standard reference materials (DORM2). QA/QC samples comprised 5% of the samples analysed. The University of Ottawa laboratory routinely participates in inter-laboratory quality assurance programs run by the Canadian Food Inspection Agency. Typical coefficient of variation (CV) or precision values for sediments and biota were $\sim 5\%$ and recovery values for standard reference material ranged from 93 to 105%. Wet weight THg concentrations in yellow perch dorsal muscle were converted to dry weight using an 80% moisture content factor from data on Great Lakes yellow perch (González et al., 2006).

Carbon and N stable isotope analyses were performed at the Queen's Facility for Isotope Research (Geological Sciences and Geological Engineering, Queen's University, Kingston, Canada). Samples of yellow perch ($n = 40$) and prey items ($n = 160$) were analysed for stable isotopes of N and C. Approximately 0.4–0.5 mg of sample was weighed into tin capsules, combusted in the presence of oxygen and converted to a gas (N_2 or CO_2) in a Costech Elemental Analyzer (Costech Instruments, Milan, Italy) and passed to a stable isotope mass spectrometer (Finnigan Delta

PLUS Isotope Ratio Mass Spectrometer, Bremen, Germany) that uses Continuous Flow Technology (ThermoFinnigan, Bremen, Germany).

Quality control and quality assurance included duplicate assays for 15% of the samples ($\delta^{15}\text{N}$: $\text{CV} = 1.5 \pm 0.1$; $\delta^{13}\text{C}$: $\text{CV} = 0.9 \pm 0.2$) and replicate assays for 10% of the samples ($\delta^{15}\text{N}$: $\text{CV} = 2.4 \pm 0.2$; $\delta^{13}\text{C}$: $\text{CV} = 1.6 \pm 0.3$). Experimental precision based on the standard deviation of replicated reference standards was 0.4‰ for the international N standard, ammonium sulphate [Certified Reference Material (CRM) 8548, International Atomic Energy Agency, Vienna, Austria] and 0.1‰ for the C standard, graphite (nbs21). The recovery of standard materials for $\delta^{15}\text{N}$ was 101%, and 99% recovery was obtained for $\delta^{13}\text{C}$. In order to calibrate the system, two internal reference materials were analysed every five samples. CVs were 23% for $\delta^{15}\text{N}$ and 5% for $\delta^{13}\text{C}$ for lipid normalized Atlantic salmon ($n = 17$) and 8% for $\delta^{15}\text{N}$ and 2% for $\delta^{13}\text{C}$ ($n = 18$) for red tilapia. Because of the deleterious effects of the lipid removal on $\delta^{15}\text{N}$ analysis (Sotiropoulos et al., 2004), stable isotope results were not lipid normalized.

Data were analysed with SigmaStat 3.0 (Systat Software, Point Richmond, CA, USA), JMP 6.0 (SAS Institute, Cary, NC, USA) or Minitab 14 (Minitab, State College, PA, USA). Log transformations of concentrations were used when they improved normality or reduced heteroscedasticity. Null hypotheses were rejected at $P < 0.05$. Statistical approaches involved parametric analyses as t tests and one- and two-way analyses of variance (ANOVA), as well as their non-parametric equivalents, Wilcoxon and Kruskal–Wallis analyses on ranks. For analysis of stomach content data, post hoc tests such as the Holm–Sidak test assessed differences in Hg concentrations among sites, prey items and the effect of year and zone. Holm–Sidak tests were used for both pair-wise comparisons and comparisons versus a control group to remove the bias inherent in multiple comparisons.

Results

Surface water and suspended solids

THg concentrations in surface whole water samples ranged from 0.20 to 3.07 ng l^{-1} (Table 1). No significant differences were found between surface and

Table 1 Summary of the total and methyl mercury concentrations in different media from the St. Lawrence River near Cornwall, ON, Canada

Matrix	Total Hg (Average, <i>N</i> , Min-Max)					Methyl Hg (Average, <i>N</i> , Min-Max)				
	1	2	3	4	5	1	2	3	4	5
Surface water (ng l ⁻¹)	0.97 (25) 0.55–3.07	0.85 (50) 0.16–2.69	0.51 (10) 0.36–1.12	0.48 (20) 0.20–0.85	0.47 (20) 0.20–0.49	0.04 (25) <0.20–0.17	0.03 (50) <0.02–0.06	0.02 (10) <0.02–0.03	0.03 (20) <0.20–0.09	0.03 (20) <0.02–0.05
Suspended sediments (ng g ⁻¹ dw)	343 (2) 324–364	486 (2) 236–1001	n.a.	n.a.	149 (2) 141–158	n.a.	n.a.	n.a.	n.a.	n.a.
Zooplankton (ng g ⁻¹ dw)	502 (2) 410–594	608 (4) 384–1130	245 (2) 169–321	111 (2) 98–15	102 (2) 81–124	10.6 (2) 10.4–10.8	12.0 (4) 7.5–16.0	9.2 (2) 8.3–10.0	n.a.	8.5 (2) 7.4–9.6
Sediment (ng g ⁻¹) Top 1 cm (1)	625 (3) 557–727	566 (4) 442–780	811 (2) 405–1217	n.a.	16 (1)	39.8 (3) 34.5–45.5	13.9 (4) 9.4–18.6	12.3 (2) 9.6–15.1	n.a.	0.24 (1)
Sediment (ng g ⁻¹) Top 10 cm (2)	774 (4) 378–1646	2238 (10) 379–5568	1744 (2) 610–2879	104 (6) 53–159	n.a.	2.4 (4) 1.4–5.4	2.6 (10) 0.7–4.8	n.a.	0.8 (6) 0.4–1.6	n.a.
Benthos (ng g ⁻¹ dw) (2)	338 (8) 114–502	300 (25) 31–1642	666 (5) 244–1623	118 (11) 51–374	93 (2) 92–94	23.3 (8) 4.5–26.2	22.9 (25)	68.3 (5) 25.9–108	20.8 (11) 8.1–67.2	18.0 9.3–26.8

Shown are the average values (number of samples) and minimum and maximum values. Suspended sediment data were not sampled in Zone 4, and insufficient suspended sediments were collected to determine MeHg concentrations. Insufficient zooplankton samples were available in Zone 4 for MeHg analysis

(1)—Delongchamp et al. (2009a, b); (2)—Grapentine et al. (2003)

Benthic invertebrate values are the average for snails, chironomids and amphipods

n.a. Not available

mid-depth samples ($P > 0.05$, $n = 46$). THg concentrations did vary seasonally between zones and within some zones (Fig. 2). THg concentrations in Zones 1 and 2W were greater than Zone 2E and reference Zones 4 and 5 in May 2005 ($F = 11.7$, $P < 0.001$, $df = 4$, 24), and, in July 2005, greater than Zone 2E and Zone 5 ($F = 8.5$, $P < 0.001$, $df = 3$, 19). However, no differences were observed in THg concentrations between zones in late September samples ($F = 2.5$, $P = 0.058$, $df = 5$, 29). THg concentrations in May were lower than July and September samples in Zones 1, 2E, 2W and 5 ($P < 0.001$). No May data are available for Zones 3 and 4.

In contrast, there were no significant differences in MeHg concentrations in water samples between zones, but there were some seasonal differences within the zones ($P < 0.001$). MeHg concentrations in Zones 2E and 5 followed the pattern September > July > May, while concentration patterns were July ~ September > May for Zone 2W. There were no seasonal differences found for MeHg concentrations in Zone 1 ($F = 1.31$, $P = 0.310$, $df = 2$, 13).

Overall, temperature and specific conductivity data for all water samples were very uniform between zones for each sampling event, although Zone 1 temperatures (24.0 ± 0.2 SE) were greater than other zones (23.6 ± 0.03 SE) in July ($H = 13.3$, $P = 0.010$, $df = 4$, 25). Average water temperatures ($^{\circ}\text{C}$) were 10.6 ± 0.02 SE, 23.7 ± 0.06 SE, 19.8 ± 0.01 SE in May, July and September, 2005 sampling events, respectively. Average specific conductivity values ($\mu\text{S cm}^{-1}$) were 299 ± 1 SE, 295 ± 1 SE, 294 ± 1 SE in May, July and September, respectively.

The concentrations of total suspended solids were low, with very similar values in the contaminated zones (0.49 – 0.64 mg l⁻¹), with values of 0.29 and 1.2 mg l⁻¹ in reference Zones 4 and 5, respectively. The concentration in Zone 5 was significantly greater than suspended solid values from the other zones ($F = 4.33$, $P = 0.018$, $df = 4$, 22). The majority of the suspended material was inorganic, with the organic fraction estimated from loss on ignition ranging from below detection to 25%. THg concentrations in suspended solids ranged from 236 to

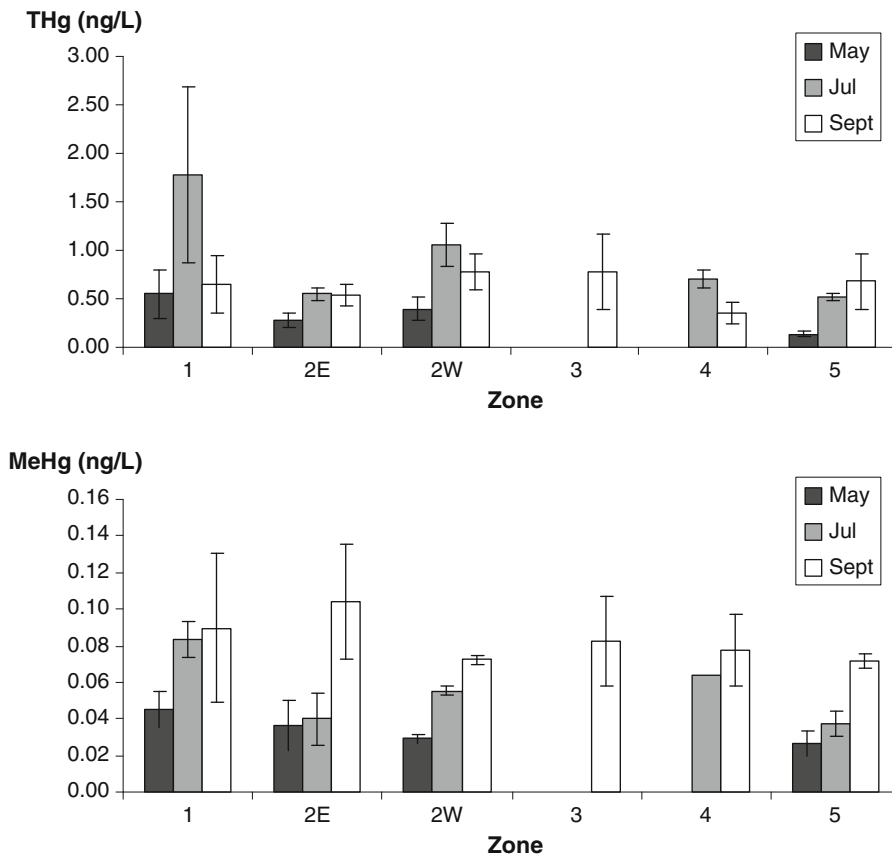


Fig. 2 Surface water concentrations of THg (ng l^{-1}) and MeHg (ng l^{-1}) for zones sampled in May, July and September in 2005. Shown are mean values with 95% confidence intervals

1010 ng g^{-1} in contaminated Zones 1 and 2, from 152 to 464 ng g^{-1} in Zone 4 and from 141 to 158 ng g^{-1} dw in Zone 5. No differences between reference and contaminated zone values were found on pooled samples ($F = 2.30$, $P = 1.73$, $df = 1, 8$), but the low number of analyses provided little statistical power. Based on the measured values for suspended solids, it is estimated that suspended particulates made up to 20% of the THg in the whole water samples.

Stormwater and other inflows

Zone 1 receives discharges from the Pitt St. and Amelia St. stormwater outfalls, the Brookdale Ave. combined sewer overflow (CSO) and the outflow of the former Cornwall Canal (Fig. 1). Although low, median values of THg (ng l^{-1}) in canal (0.69, $n = 6$) and stream (0.61, $n = 7$) outflows were higher than

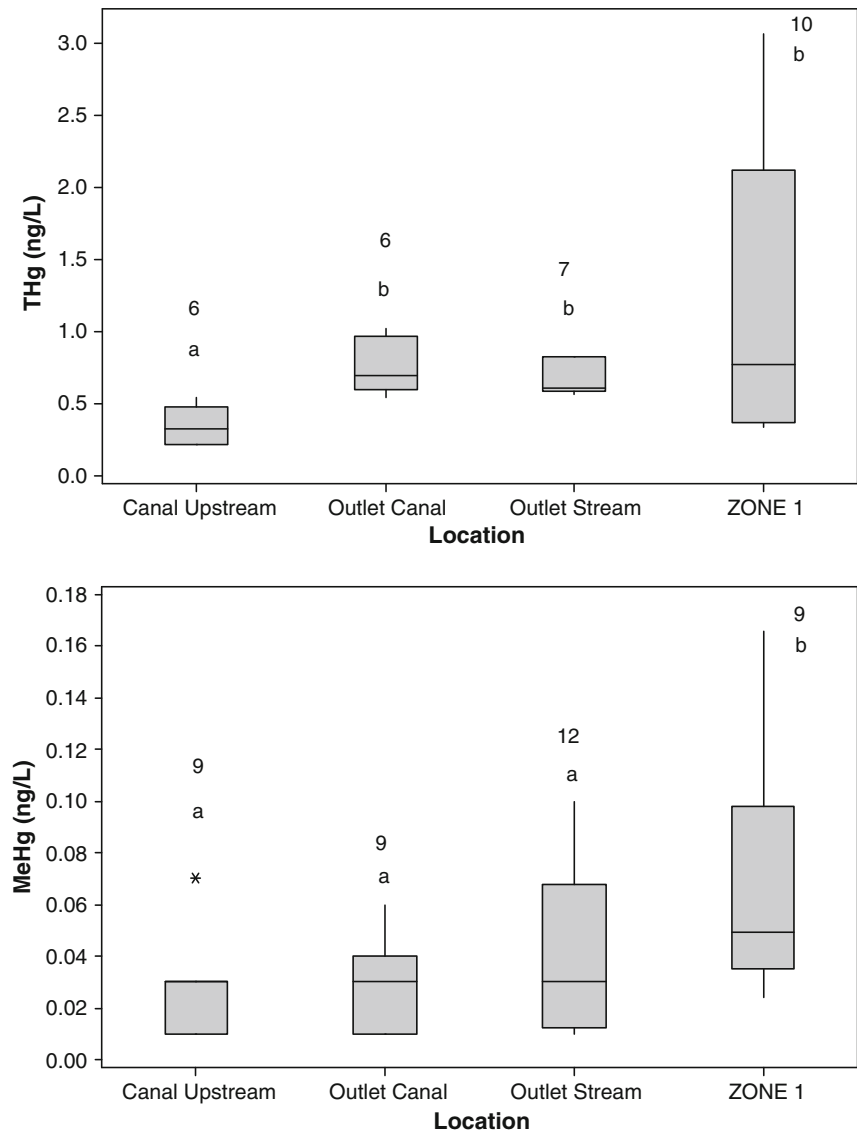
(bars). Zones 2E and 2W correspond to the east half and west half of Zone 2, respectively. Samples were not taken in Zone 3 for May and July and in Zone 4 in May

canal inflow values (0.32, $n = 6$) based on a Kruskal–Wallace test ($P = 0.003$, $H = 11.67$, $df = 2$, Fig. 3). MeHg values were low with the same median (0.03 ng l^{-1}) for all samples (Fig. 3). Canal outflow THg and MeHg values were similar to Zone 1 surface water values (Table 1). In contrast, the median THg and MeHg concentrations for upstream river water, sampled at the same time, were 19–45-fold (THg) and 2–4-fold (MeHg) lower than storm sewer and CSO values, respectively.

Zooplankton

In terms of zooplankton diversity, cladocerans and copepods were collected most frequently, with copepods making up 79–95% of all zooplankton collected. Of the copepods, *Cyclopidae* (70–90%) and *Diaptomidae* (10–30%) were the most abundant. The cladoceran population was also composed of *Daphnidia*

Fig. 3 Boxplots comparing median and interquartile ranges of THg (ng l^{-1}) and MeHg (ng l^{-1}) data for surface water samples collected in 2005 from the upstream portion of the Cornwall canal near its outflow from the Moses–Saunders dam, from downstream outlet sites into Zone 1 at the canal outlet, from a constructed stream that is sourced from the canal and in Zone 1. Due to the MeHg data distribution for the Canal Upstream samples, the median and third quartiles have the same value and occur as a single line. Sample numbers are shown above each box. Sample boxes sharing the same letters are not statistically different ($P > 0.05$)



(40–90%) and *Bosminidae* (10–60%). In addition, other invertebrate organisms such as ostracods, chironomids, amphipods, hydrachnids and trichopterans were collected in low numbers. The non-indigenous *Bythotrephes longimanus* was also found in zooplankton hauls. Total zooplankton densities were very low during the sampling events at all sites. Total sample masses from the vertical hauls (a mixture of zooplankton and seston) ranged from 11 to 63 $\mu\text{g l}^{-1}$ in July (mostly seston) and 13–71 $\mu\text{g l}^{-1}$ in August of which ~30–50% was zooplankton (Ridal et al., 2006). Therefore, zooplankton dry mass was negligible in July and is estimated to range from 4 to 36 (mean 18) $\mu\text{g l}^{-1}$ at the sample sites in August.

The results of the total Hg analysis for July and August pooled zooplankton samples within each zone are summarized in Table 1. THg values ranged from 124 to 594 ng g^{-1} dw in July and from 81 to 1131 ng g^{-1} dw in August. There were insufficient data for statistical analysis, but a similar pattern for relative THg concentrations for each zone was evident for both sampling dates. THg values were 2.4–6-fold higher in the zones that contained the most contaminated sediment (1 and 2) compared to the reference site (Zone 5). Zone 3, the smallest contaminated zone had intermediate values. MeHg concentrations ranged from 7.5 to 14.5 ng g^{-1} dw in July and from 7.4 to 16.0 ng g^{-1} dw in August (Table 1).

Prey items

Stomach contents of perch collected from Zones 1, 2, and 4 in 2005 and 2006 were analysed to more accurately track Hg transfer in the food web, reduce the effort and complexity of invertebrate sampling, provide a direct measure of the dietary exposure of fish and avoid sample contamination by sediments. Amphipods were the most frequent prey type detected and made up $47 \pm 34\%$ of the diet mass of the yellow perch. Other common prey items were isopods, chironomids, trichoptera and small fish (Fig. 4), the percent occurrence of the prey varied annually, seasonally and among zones (Yanch, 2007).

Both yellow perch and their amphipod prey items from Zone 1 had the highest THg concentrations (Fig. 5), yellow perch were 1.5 times higher than those from Zone 2 and 2.5 times higher than those from Zone 4. Results of a one-way ANOVA indicated that there was a significant difference in THg concentrations of amphipods among zones ($F = 87.9$, $P < 0.001$, $df = 2$, 68). Holm-Sidak post hoc tests revealed that THg concentrations of amphipods from Zone 1 were significantly higher, 3.5-fold, than those of Zones 2 and 4 (Fig. 5).

Mean THg concentrations of all common prey types from each zone are compared in Fig. 6. One-way ANOVAs were conducted to determine if there were significant differences among THg concentrations of all prey items within each zone (for those prey items where $n > 5$ in each zone). In Zone 1, there was no significant difference in THg

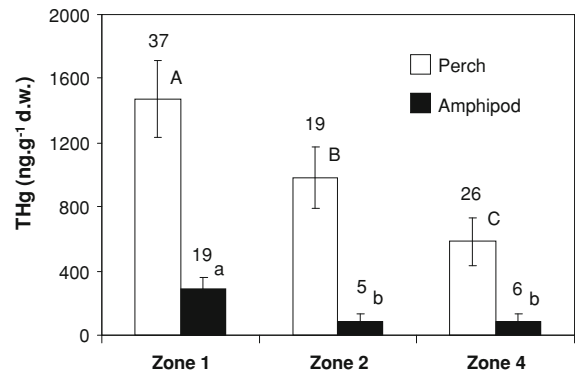


Fig. 5 A comparison among zones of THg concentrations ($\text{ng g}^{-1} \text{d.w.}$) in yellow perch and in amphipods collected from their stomachs. The error bars represent the 95% confidence limits and the numbers refer to sample sizes. Mean (\pm SE) length was 140 ± 2 cm. Samples within a species that are significantly different have different letters (ANOVA, $P < 0.05$)

concentrations of prey items ($F = 1.057$, $P = 0.396$, $df = 6$, 51). In contrast, there were significant differences in THg concentrations among prey items from Zones 2 and 4. In particular, Holm-Sidak post hoc tests reveal that in Zone 2, fish and *Bythotrephes* contained significantly more THg (2.5 times) than amphipods ($F = 3.3$, $P = 0.029$, $df = 4$, 22), and in Zone 4 fish contained significantly more THg than all other prey items ($F = 5.8$, $P = 0.002$, $df = 4$, 26). THg concentrations of fish from Zone 4 were 4.8 times higher than chironomids.

Mean THg concentrations of amphipods in Zone 1 changed from month-to-month indicating seasonal

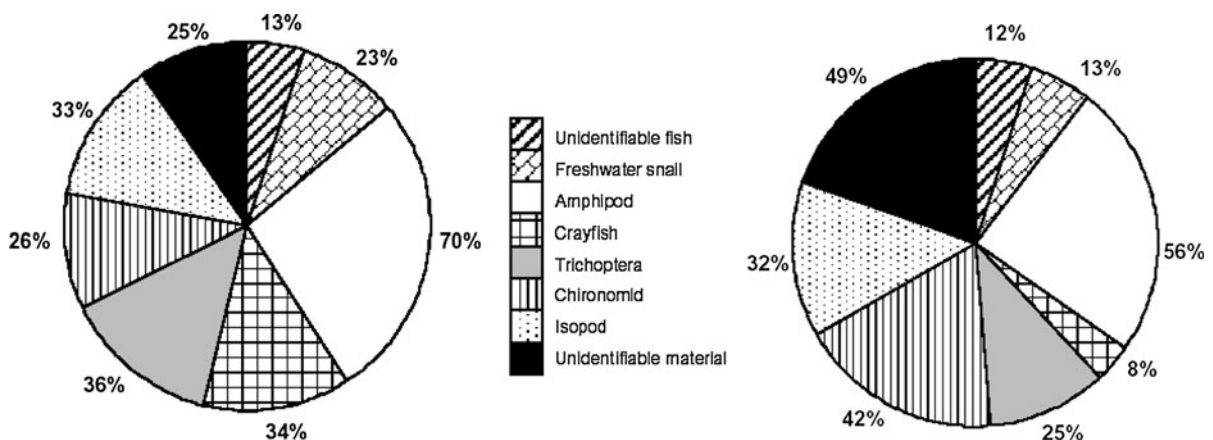
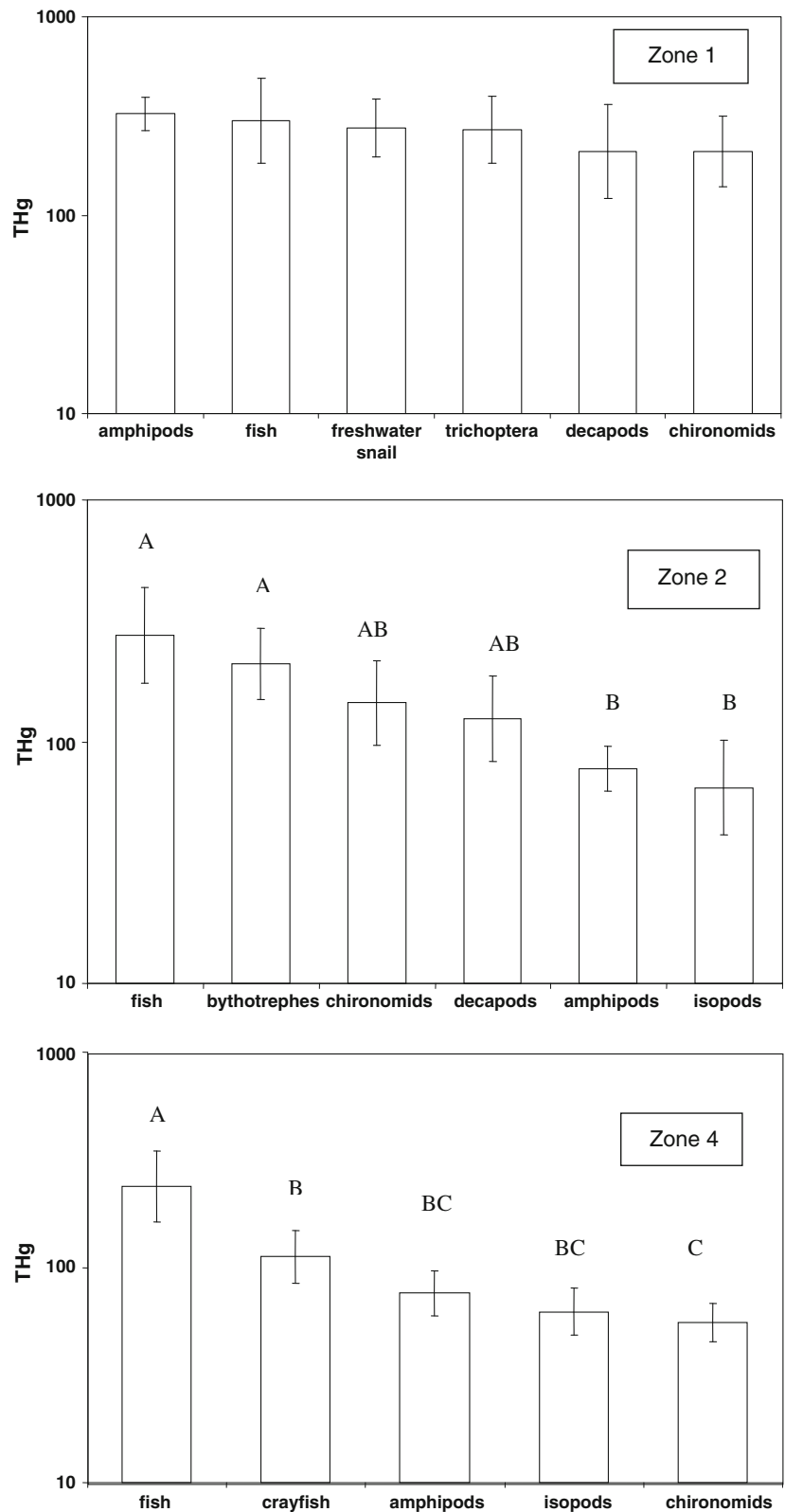


Fig. 4 Percent occurrence of the eight most common prey types consumed by yellow perch in 2005 (left, $n = 201$ fish stomachs) and 2006 (right, $n = 106$ fish stomachs). 2005 stomach content data from Fowlie et al. (2008)

Fig. 6 A comparison of THg ($\text{ng g}^{-1} \text{dw}$) in the most abundant perch prey from the different study zones. Shown are geometric mean values and 95% confidence intervals of THg in each prey type. Bars sharing the same letters are not significantly different ($P > 0.05$). There were no differences in the THg concentrations between perch prey from Zone 1



differences in THg concentration. In fact, results of Holm-Sidak post hoc tests reveal that THg concentrations of amphipods in June are significantly higher than THg concentrations in July and August (one-way ANOVA: $F = 9.3$, $P = 0.001$, $df = 3, 67$). The nitrogen stable isotope ratios, $\delta^{15}\text{N}$, for the amphipod prey, an indicator of relative trophic position, were similar (Kruskal–Wallis; $H = 3.0$, $P = 0.22$, $df = 2$): 9.1 ± 0.6 in Zone 1, to 9.6 ± 0.5 in Zone 2 and 9.5 ± 0.7 in Zone 4.

Discussion

Recent data illustrate relatively consistent and widespread contamination by Hg in the sediment of the St. Lawrence River along the Cornwall waterfront compared with reference zones. THg concentrations in surface sediments range $378\text{--}5568 \text{ ng g}^{-1} \text{ dw}$ in contaminated zones compared with values ranging from 16 to $159 \text{ ng g}^{-1} \text{ dw}$ in reference zones (Table 1). These patterns reflect the historical Hg inputs to the river and the present hydrological regimes in the vicinities of the discharges (Richman & Dreier, 2001). Strong currents limit mixing across the river, and shoreline inputs to the river remain localized in areas of low flow or are carried downstream along the shore (Carignan et al., 1994).

A comparison of the sediment data suggests that while recently deposited surficial sediments are less contaminated in total Hg than deeper, older sediments in zones 1, 2 and 3, they are more contaminated in MeHg. THg concentrations in the top 1 cm of sediment cores are 1.2–4.0 times lower than the Hg values for the top 10 cm measured by Grapentine et al. (2003); while MeHg concentrations in the top 10 cm of sediments from the three contaminated zones are 5–16-fold lower than in the top 1 cm of sediment. Since only one analysis is available for Zone 5, the variability in the sediment concentrations from this zone is not known. The proportion of MeHg in the top 1 cm of sediment is $\sim 6\%$ in Zone 1 compared to 2.5% in Zone 2 suggesting conditions favour greater methylation of Hg in Zone 1 than in Zone 2 (DeLongchamp et al., 2009a).

THg concentrations in benthos (snails, chironomids and amphipods) reported by Grapentine et al. (2003) range from 3.2 to 7.2-fold higher in Zones 1–3 than in Zone 5 (Table 1). MeHg concentrations in

benthic invertebrates are similar among zones with the exception of Zone 3, where average concentrations are about threefold higher than in all other zones.

Fowlie et al. (2008) found THg concentrations in yellow perch and other sentinel fish are higher in Zone 1 than other zones. The Hg content of yellow perch is linearly related to fish length and is consistently and significantly more contaminated at Zone 1, with concentrations about 2.3–3.6 times higher than at other contaminated and reference zones for a standard length (Fig. 7). Similar differences among sites are found for pumpkinseed (*Lepomis gibbosus*) and rock bass (*Ambloplites rupestris*), while the relationship for brown bullheads (*Ameiurus nebulosus*) is less clear due to small sample size (Fowlie et al., 2008). Their study also revealed that in May, the Hg-length relationship is highly variable ($r^2 = 0.12$), with no statistical differences among zones. The linearity of the relationship improves month-by-month, and by August, the relationship in Zone 1 is statistically distinct from those of all other zones ($r^2 = 0.78$), but is more variable again in September. Coincidentally, there are shifts in population demographics. Perch collected in summer months are exclusively juvenile (<15 cm long; <age 3+), sexually immature and actively feeding. In contrast, the collection in May provides larger (15–30 cm), older (age 3 to 7+), non-feeding and sexually mature perch, apparently moving in to spawn in the slow moving and vegetated waters of Zone 1. These fish have low Hg concentrations, equivalent to fish from reference zones. Therefore, the seasonal signal of Hg in yellow perch is consistent with the fish population dynamics in zone 1. A decreased variability between log Hg-length relationships in yellow perch sampled during summer months reflects fish residency and contaminant accumulation within the zone (Fowlie et al., 2008).

Choy et al. (2008) measured Hg in young-of-the-year spottail shiners (*Notropis hudsonius*) collected along the shore, assuming that site fidelity would provide a detailed picture of spatial differences in Hg sources. Spottail THg concentrations are higher in Zone 1 than in other zones, confirming a similar pattern from earlier studies by the Ontario Ministry of the Environment (Choy et al., 2008). Significant differences are detected in THg concentrations among three sampling sites within Zone 1 spaced

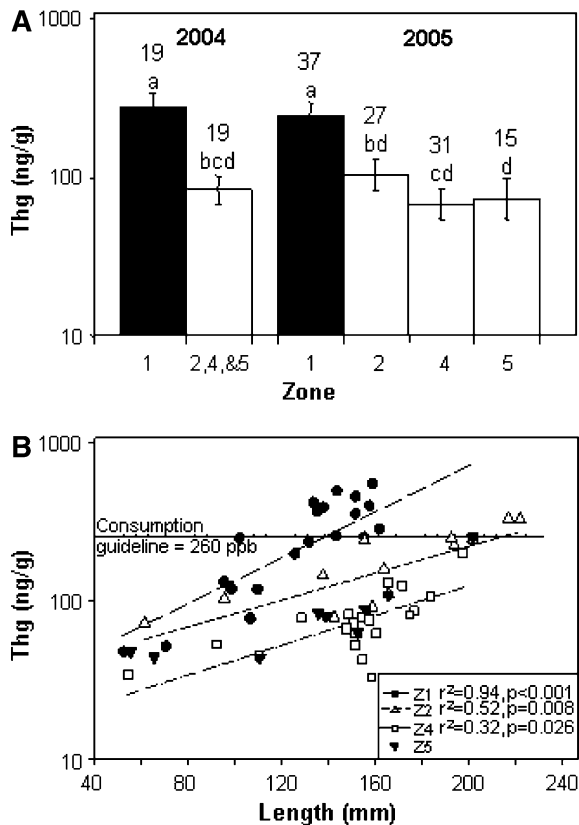


Fig. 7 Total mercury concentrations (THg ng g^{-1} w.w.) (and 95% confidence limits) in yellow perch collected from Hg-contaminated (1 and 2) and reference zones (4 and 5) of the St. Lawrence River at Cornwall (ON) from June to August in 2004 and 2005. Panel A shows data standardized mathematically to the average length of capture, 147 mm total length. Sample sizes are indicated above each bar, and bars sharing the same letters are not statistically different ($P > 0.05$). Panel B shows fish length-Hg relationships for yellow perch captured in August of 2004 and 2005. Only significant regressions are shown. The horizontal line is the Ontario fish consumption advisory of 260 ng g^{-1} for sensitive human populations such as children, pregnant women and frequent consumers of fish (Ontario Ministry of the Environment, 2007). Figure from Fowlie et al. (2008) (used with permission from the Journal of Great Lakes Research)

about 500 m apart. In particular, mid-zone THg concentrations measured in young-of-the-year spottail shiners are higher than those in areas on either side, suggesting high site fidelity of the young-of-the-year fish and a possible internal source of Hg in Zone 1.

The importance of these fish data is the discovery of significant differences in the extent of food-web contamination by Hg in the same species over

relatively short (<2 km) distances between zones, and seasonal variations in contamination that in some months obscure the geographic pattern. Hence, routine annual monitoring of Hg in fish to protect human consumers may not accurately estimate the risk if the temporal and spatial scales of sampling do not reflect the temporal and spatial variations in Hg concentration.

What sources, therefore, could account for the differences in fish concentrations among sites? Through examination of stable isotope, fish age and biomass data Fowlie et al. (2008) determined that the pattern of contamination of fish from the different zones cannot be explained by differences in growth rate, condition factor, diet composition or trophic position. By a process of elimination of the main factors that typically determine Hg concentrations in biota, the cause of Hg contamination is likely a unique source of Hg to biota in Zone 1. However, the possibility that Hg accumulation is controlled by a factor that has not been considered or by interactions among factors which on their own are not significant cannot be discounted.

The data for Hg concentrations in fish and their prey obtained from stomach content analysis provide unique insights into the transfer of Hg to the food web in Zone 1 compared to other zones. Amphipods from stomachs of yellow perch show the same zone-to-zone differences in Hg concentrations as the fish they were sampled from, with high values of Hg in prey from Zone 1 (Fig. 5, 6). Because perch and amphipod $\delta^{15}\text{N}$ do not vary among the zones (Yanch, 2007; Fowlie et al., 2008), there are no significant differences in food chain length that might explain differences in Hg concentration.

The stomach content analysis indicates that benthos formed the majority of the diet in the fish sampled, underscoring the importance of sediment Hg to contamination of fish at these sites. While smaller zooplankton are not commonly detected in the stomach content analysis, the invasive *Bythotrephes longimanus* (the spiny water flea) was found in 11% of the perch stomachs examined (Yanch, 2007), although it is a minor component of zooplankton net hauls. These data also illustrate that an assessment of the relative abundance of prey in the environment does not accurately portray the diet composition of perch. This finding is important, because prey selection could increase or decrease THg concentrations

in perch relative to concentrations predicted from the relative abundance of prey items in the environment. Zooplankton THg values (81–1131 ng g⁻¹ dw) are highest in the zones that contain the most contaminated sediment and are lowest at the reference site. MeHg concentrations in zooplankton samples range from 7.4 to 16.0 ng g⁻¹ dw, but unlike THg do not show strong site to site differences.

In contaminated Zone 2 and reference Zone 4, there are significant differences in THg concentrations among different prey species, with less THg accumulating in lower trophic level prey, such as isopods, than in prey at a higher trophic level, such as fish (Fig. 6). In contrast, no significant differences are found in THg concentrations among prey in Zone 1. The lack of correspondence between trophic position and Hg accumulation in Zone 1 suggests two alternate hypotheses for the ambiguous biomagnification trends. First, if excess Hg is accumulated via the gills, all species will accumulate Hg to a similar extent because they all encounter similar water–tissue concentration gradients in a well-mixed environment. However, given the significant variation in THg concentrations in spottail shiners (Choy et al., 2008) and amphipods (Razavi, 2008) from different sites across Zone 1, the second explanation could be that the high mobility of yellow perch in Zone 1 allows the fish to assimilate a wide range of THg concentrations from variably contaminated prey items across Zone 1. This process would lead to confounding biomagnification trends in the food web of Zone 1 (Yanch, 2007).

The biological data demonstrate the differences in Hg delivery to the food web among the zones and indicate the possibility of unique source(s), either external (e.g. runoff, storm sewer) or internal to the site (e.g. enhanced release from sediments via sediment resuspension and/or porewater). While delivery of Hg to aquatic systems from atmospheric deposition is well known, it is not likely a source of such fine scale differences in Hg concentrations. Therefore, the three most plausible mechanisms for enhanced delivery of Hg to biota in Zone 1 are diffusion and advection of sediment porewater, sewer inputs and resuspension of sediments.

Sediment–water diffusion fluxes based on the concentration gradient between the Hg concentration in the top 1 cm of interstitial fluid and the overlying water column Hg concentration have been estimated

(Delongchamp, 2006, 2009b). The calculated diffusive flux of THg from porewater to the overlying water of Zone 1 ranges from 1.2 to 6.8 ng cm⁻² year⁻¹ ($n = 2$), while MeHg flux had a smaller range from 1.2 to 4.0 ng cm⁻² year⁻¹ ($n = 3$). Values found for the two other contaminated zones were 9.1–48.2 ng cm⁻² year⁻¹ for THg and 1.5–14.6 ng cm⁻² year⁻¹ for MeHg. Assuming these data are representative of the diffusive fluxes from the sediments during the summer months, the contribution of Hg from sediments to the water column and its influence on observed water concentrations in Zone 1 can be estimated using a very simple model. Here, we assume complete mixing (field measurements of temperature and conductivity showed no depth stratification), a mean depth of 7 m, a sediment area of 25,000 m² (Biberhofer & Rukavina, 2002), a water renewal time of 0.1 day based on depth-averaged current speeds estimated as 0.05 m s⁻¹ (Nettleton, 2004) for a water mass travelling the 500 m along the flow axis of the zone, and no other losses (the most conservative scenario). The model suggests that diffusion of Hg from sediments contributes 0.05–0.1% of the THg concentration (mean value of 1.07 ng l⁻¹) and 1–2% of the MeHg concentration (mean value of 0.04 ng l⁻¹) measured in summer months in Zone 1. Comparatively, values for zones 2 and 3 are estimated as 1–3 and 0.3%, respectively, for THg, and 3–28 and 9% in the same zones, respectively, for MeHg, using sediment areas of 360,000 m² (Rukavina, 2000) and 13,000 m² (Biberhofer & Rukavina, 2002) and water renewal times of 0.25 day and 0.06 day for Zones 2 and 3, respectively. Therefore, the contributions from sediment–water diffusion to the THg concentrations measured in the bulk surface waters at these sites would be negligible. MeHg contributions are more important, given the very low levels of MeHg in the water column; however, these increases would be difficult to detect given our typical CV ($\pm 26\%$) for duplicate MeHg measurements. The sediment–water diffusion values do not take into account Hg contributions from bioturbation, bioirrigation, ebullition and resuspension of sediments which affect the extent of exchange across the sediment–water interface (Aller & Aller, 1998).

Enhanced resuspension in Zone 1, as compared to other zones, may remobilize sediment bound Hg providing a source of Hg to biota (Montgomery et al., 2000; Ullrich et al., 2001). Our analysis of bulk

suspended particulate concentrations show consistently low concentrations at all sites (below ~ 1.5 mg l⁻¹). THg concentrations in suspended particulates range from 149 ng g⁻¹ dw in the reference zone to a high of 619 ng g⁻¹ in Zone 2. Our results for suspended particulate concentrations are similar to those reported by Lepage et al. (2000) for samples collected with cylindrical sediment traps located at various sites in the Cornwall AOC and at reference site above the Moses–Saunders dam. In that study, dry weight concentrations of THg in settling sediment average 1150 ± 380 ng g⁻¹ in Zone 2 compared with an average concentration of 170 ± 50 ng g⁻¹ at the upstream reference station. The collections using sediment traps suspended near the river bottom (i.e. Lepage et al., 2000) are more likely to contain resuspended bottom sediments than the surface water sampling used in the current study. The large variations of THg concentrations in suspended particulates among zones suggest a dynamic exchange between the background suspended particulates drifting into each zone (i.e. by advection) and the thin transient layer (the hydrosol) in contact with the bulk sediments of the zone. The exchange between bulk sediments and the top layer is consistent with fast mixing rates in surface sediments implied by the radiometric data collected from sediment cores (Delongchamp, 2006). MeHg concentrations in top sediments do not vary as broadly from zone to zone as THg concentrations, and our techniques are not sufficiently sensitive to permit analysis of MeHg in the suspended particulates.

There have been investigations conducted in Zone 1 to delineate the influence of woody debris and high rates of methane gas production in Zone 1 on Hg transfer to the water column and biota (Poissant et al., 2007; Razavi, 2008; Fathi, 2009). These studies confirm the complexity of this zone, with large deposits of decaying bark and wood chips overlain by fine-grained sediments with high concentrations of Hg. It is estimated that 72% of the muddy deposit in this zone contains high gas content (Biberhofer & Rukavina, 2002). Low wood fibre sites yield well-preserved sediment cores where Hg levels clearly represent historical deposition patterns. However, deposition patterns in cores from high wood fibre sites are mixed and not amenable to ²¹⁰Pb dating, suggesting sediment mixing or episodic deposition events (Fathi, 2009). Gas ebullition from decaying

wood chips would be one possible cause of mixing and resuspension of contaminated sediment.

Razavi (2008) investigated the relationships among amphipod abundance, amphipod Hg concentrations, gas ebullition rate, and surface sediment (top 5 cm) and porewater Hg concentrations. While no relationship is found between the rate of gas ebullition and MeHg concentration in amphipods, a significant relationship between porewater and amphipod methyl Hg concentrations is obtained, albeit for a relatively small number of data points ($r = 0.82$, $n = 8$, Fig. 8). This study represents one of the first investigations linking MeHg concentrations in sediment porewater and benthos and requires further confirmation.

Other potential waterborne sources of Hg to Zone 1 include the outflow of water from the former Cornwall canal system and intermittent inputs of Hg from combined sewer overflows and storm sewers. Levels of THg in canal and stream outflow samples are twofold higher than upstream canal samples indicating inputs of Hg along the canal, but there are no discernable differences for MeHg values. At times of peak flows (typically spring and fall), combined sewer and storm sewer discharges may represent sources of episodic inputs of Hg into the zone (Table 2). Concentrations of THg in the effluents were below the Ontario Provincial Water Quality Objective of 200 ng l⁻¹ except for one instance where the Brookdale CSO samples averaged 267 ng l⁻¹ based on duplicate sample values of 42 and 493 ng l⁻¹. Such a large variation in duplicate

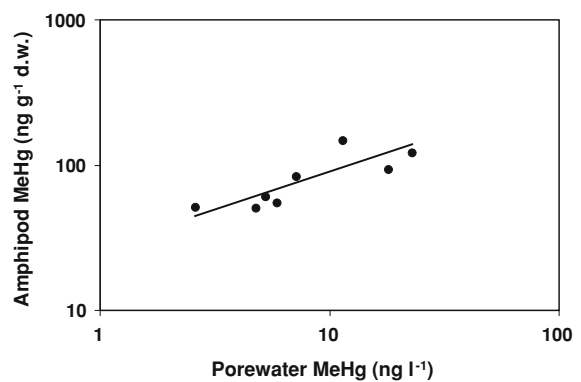


Fig. 8 Log scale relationship between amphipod methylmercury (MeHg) and porewater MeHg concentrations ($r = 0.82$, $P = 0.011$, $n = 8$). From Razavi (2008)

Table 2 Concentrations of total and methyl mercury (mean of duplicate samples) in sewer discharges potentially influencing Zone 1 during Brookdale CSO overflow events

Date	Precip (mm)	Brookdale CSO		Pitt St. CSO		Amelia Storm		River	
		Total Hg (ng l ⁻¹)	Methyl Hg	Total Hg (ng l ⁻¹)	Methyl Hg	Total Hg (ng l ⁻¹)	Methyl Hg	Total Hg (ng l ⁻¹)	Methyl Hg
08-07-07	21.2	103	0.52	5.63	0.16	14.6	0.24	0.27	0.04
27-11-07	13	0.73	0.02	4.50	0.02	1.08	0.03	0.16	0.04
08-01-08	5	267	0.21	6.97	0.07	2.72	0.06	0.59	0.06
04-04-08	5.5	12.1	0.18	5.10	0.13	0.34	0.16	0.15	0.15
09-07-08	32	3.39	0.05	4.62	0.08	2.04	0.05	0.40	0.03
Geometric Mean		15.2	0.11	5.29	0.07	1.97	0.08	0.27	0.05
Proportion relative to river		56	2	19	1	7	2	1	1

Values shown are for the Brookdale Avenue and Pitt St. combined sewer outfalls (CSO), and Amelia St. stormwater outfall. Also shown are surface water samples taken upstream of the sewer inputs and the proportion of mean outfall concentrations to the river mean value. Precipitation values are recorded for the prior 24 h to sampling at a recording station within 1 km of the sampling sites

samples likely reflects variations in the particulate load for Brookdale CSO events. For instance, the ranges in CSO effluent concentrations were comparable to municipal raw sewage values ranging from 2 to 150 ng l⁻¹ for THg and 0.5–4 ng l⁻¹ for MeHg from Winnipeg, MB, Canada (Bodaly et al., 1998). The overall high variability in results may represent the influence of a number of factors, including the timing of the sampling relative to the duration of the storm event (Lee et al., 2002), and the sampling method used. The runoff from the Pitt St. storm sewer, which has an outfall that is above the river water level, was sampled directly into a sampling container. The Pitt Street CSO system rarely overflows and therefore samples likely consist of ground water and other incursions to the system. In contrast, the Brookdale CSO and Amelia St. storm sewer outfalls are submerged in the river, and samples of the discharge plume were collected with a container on a pole. These samples are affected by varying amounts of mixing with river water at the two sites. No alternative access points are readily available in the terminal parts of these two sewer systems without requiring confined space entry protocols, which would have greatly encumbered the sampling.

CSO and stormwater runoff events, therefore, represent a unique source of THg and associated organic matter to Zone 1. Although concentrations of total Hg and MeHg from the CSO are much higher than those in the stormwater discharges, CSO events occur only during significant storms (5–10 times per year), while stormwater discharges occur during most

rainfall events. These shoreline discharges may create areas of influence that provide temporarily elevated Hg concentrations in nearshore areas near sewer outfalls and contribute to spatial differences in spottail shiner Hg concentrations detected by Choy et al. (2008). As small fish are components of the diet of summer perch (Fig. 4), consumption of shiners could contribute to elevated Hg concentrations in perch from Zone 1.

Another external source of Hg is the discharge from a remnant industrial storm sewer associated with the industrial complex ~750 m upstream of Zone 1. It includes stormwater inputs from a former pulp and paper mill and a chlor-alkali plant (Fig. 1). In 2008, Hg was detected in a stormwater grit chamber that received run-off from the two industrial properties and this run-off is directed to the river via a diffuser situated in the main channel (C. deBarros, Ontario Ministry of the Environment, pers. commun., 2009). However, details on the extent of this source are not presently available and further investigation is required.

Conclusions

Investigations into the transfer of Hg to the foodweb in a historically contaminated section of the St. Lawrence River provide several new insights into transport and pathways of this contaminant that may account for greater Hg contamination of yellow perch and other fish species in Zone 1 compared with fish

from nearby zones with similar levels of sediment contamination. While Hg contamination in invertebrates collected directly from sediments do vary among contaminated zones, prey recovered from perch stomachs are significantly more contaminated in Zone 1 than other study zones. Hence, prey selection may be an important factor contributing to site-specific Hg accumulation.

Yellow perch and amphipods from each zone have similar $\delta^{15}\text{N}$ values indicating that trophic structures do not vary among zones and are not a determinant of differences in Hg contamination in yellow perch. However, unlike other study zones, all prey species from Zone 1 are variably contaminated, with significant difference in same species from different regions within Zone 1 (Choy et al., 2008; Razavi, 2008). These observations suggest two alternate hypotheses, including the enhanced delivery of Hg to biota to this zone, possibly via direct uptake from water, and highly mobile yellow perch consuming prey from across Zone 1 with a wide range of THg concentrations.

Three possible sources of Hg delivery to Zone 1 have been identified and include: diffusion of Hg from porewater; gas ebullition contributing to advection of Hg from porewater and resuspension of sediments; and inputs of methyl and total Hg from canal discharges, CSOs and storm sewers. There is a strong correlation between MeHg in porewater and amphipod concentrations in Zone 1, indicating that the sediment porewater is bioavailable and an important pathway for transfer of sediment Hg to the foodweb. The possibility that bioavailable MeHg is released from sediment porewater by diffusion and by disturbance is relevant to the existing sediment remediation strategy of natural remediation in Zone 1. Specifically, areas where sediments overlie bark deposits and produce high rates of gas ebullition may not provide favourable conditions for progressive burial with clean sediments and attenuation of Hg transfer to biota through natural remediation. Continued monitoring of surface sediment concentrations and biota is required in these areas. Failure to reduce concentrations of Hg in these media would indicate that active sediment management options may be necessary. On-going efforts are also needed to better understand the significance of Hg discharges from old industrial zones and CSOs on Hg levels in biota from Zone 1. If these are the sources of excess Hg in Zone 1, the natural attenuation strategy will not

reduce Hg concentrations in biota of Zone 1; a strategy of storm sewer management would be more appropriate.

Our research highlights a unique feature of large river ecosystems that must be recognized to understand the distribution of Hg; i.e. the effect of the linear physical structure of strong, unidirectional current flows. The physical structuring of the river at Cornwall has created significant heterogeneity of aquatic habitat, food webs and fish population dynamics that interact to enhance heterogeneity of Hg sinks, transfer routes and biomagnification.

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References

- Aller, R. C. & J. Y. Aller, 1998. The effect of biogenic irrigation intensity and solute exchange on diagenetic reaction rates in marine sediments. *Journal of Marine Research* 56: 905–936.
- Basu, B. K., J. Kalff & B. Pinel-Alloul, 2000. Midsummer plankton development along a large temperate river: the St. Lawrence River. *Canadian Journal of Fisheries and Aquatic Sciences* 57(Suppl. 1): 7–15.
- Biberhofer, J. & N. A. Rukavina, 2002. Data on the distribution and stability of St. Lawrence River sediments at Cornwall, ON. National Water Research Institute, Environment Canada. Contribution Number 02-195.
- Bloom, N. S., G. A. Gill, S. Cappellino, C. Dobbs, L. Mcshea, C. Driscoll, R. Mason & J. Rudd, 1999. Speciation and cycling of mercury in Lavaca Bay, Texas, sediments. *Environmental Science and Technology* 33: 7–13.
- Bodaly, R. A., J. W. M. Rudd & R. J. Flett, 1998. Effect of urban sewage treatment on total and methyl mercury concentrations in effluents. *Biogeochemistry* 40: 279–291.
- Cai, Y., R. Jaffé, A. Alli & R. D. Jones, 1996. Determination of organomercury compounds in aqueous samples by capillary gas chromatography-atomic fluorescence spectrometry following solid-phase extraction. *Analytica Chimica Acta* 334: 251–259.
- Carignan, R., S. Lorrain & K. Lum, 1994. A 50-yr record of pollution by nutrients, trace metals, and organic chemicals

- in the St. Lawrence River. Canadian Journal of Fisheries and Aquatic Sciences 51: 1088–1100.
- Choy, E. S., P. V. Hodson, L. M. Campbell, A. R. Fowlie & J. J. Ridal, 2008. Spatial and Temporal Trends of Mercury Concentrations in Young-of-the-Year Spottail Shiners (*Notropis hudsonius*) in the St. Lawrence River at Cornwall, ON. Archives of Environmental Contamination & Toxicology 54: 473–481.
- Delongchamp, T. M., 2006. Mercury dynamics in sediments of the St. Lawrence River near Cornwall, Ontario. M.Sc. Thesis, University of Ottawa, Ottawa, ON, Canada.
- Delongchamp, T. M., D. R. S. Lean, J. J. Ridal & J. M. Blais, 2009a. Sediment mercury dynamics and historical trends of mercury deposition in the St. Lawrence River area of concern near Cornwall, Ontario, Canada. Science of the Total Environment 407: 4095–4104.
- Delongchamp, T. M., J. J. Ridal, D. R. S. Lean, L. Poissant & J. M. Blais, 2009b. Mercury transport between sediments and the overlying water of the St. Lawrence River Area of Concern near Cornwall, Ontario, Canada. Environmental Pollution (accepted).
- Fathi, M., 2009. Benthic flux of total mercury (THg) and methyl mercury (MeHg) between contaminated sediments and the overlying water column in the St. Lawrence River. M.Sc. Thesis, University of Ottawa, Ottawa, ON, Canada.
- Fowlie, A. R., P. V. Hodson & M. B. C. Hickey, 2008. Spatial and seasonal patterns of mercury concentrations in fish from the St. Lawrence River at Cornwall, Ontario: implications for monitoring. Journal of Great Lakes Research 34: 72–85.
- Golder Associates Ltd., 2004. Evaluation of Sediment Management Options for the St. Lawrence River (Cornwall) Area of Concern. Report submitted to: Ontario Ministry of the Environment, Kingston, ON, Canada: 107 pp, ISBN 04-1112-017.
- González, S., G. F. Flick, S. F. O'Keefe, S. E. Duncan, E. Mclean & S. R. Craig, 2006. Composition of farmed and wild yellow perch (*Perca flavescens*). Journal of Food Composition and Analysis 19: 720–726.
- Grapentine, L., D. Milani & S. Mackay, 2003. Assessment of the potential for mercury biomagnification from sediment in the St. Lawrence River (Cornwall) Area of Concern. Environment Canada Publication, National Water Research Institute, Burlington, ON, Canada.
- Hall, B. D., R. A. Bodaly & R. J. P. Fudge, 1997. Food as the dominant pathway of methylmercury uptake by fish. Water, Air and Soil Pollution 100: 13–24.
- Harada, M., 1995. Minamata disease: methylmercury poisoning in Japan caused by environmental pollution. Critical Reviews in Toxicology 25: 1–24.
- Kamman, N. C., A. Chalmers, T. A. Clair, A. Major, R. B. Moore, S. A. Norton & J. B. Shanley, 2005. Factors influencing mercury in freshwater surface sediments of northeastern North America. Ecotoxicology 14:101–111.
- Lee, J. H., K. W. Bang, L. H. Ketchum, J. S. Choe & M. J. Yu, 2002. First flush analysis of urban storm runoff. The Science of the Total Environment 293: 163–175.
- Lepage, S. J., H. Biberhofer & S. Lorrain, 2000. Sediment dynamics and the transport of suspended matter in the upstream areas of Lake St. Francis. Canadian Journal of Fisheries and Aquatic Sciences 57(Suppl 1): 52–62.
- Montgomery, S., M. Lucotte & L. Cournoyer, 2000. The use of stable carbon isotopes to evaluate the importance of fine suspended particulate matter in the transfer of methylmercury to biota in boreal flooded environments. Science of the Total Environment 261: 33–41.
- Morel, F. M., A. M. L. Kraepiel & M. Amyot, 1998. The chemical cycle and bioaccumulation of mercury. Annual Review of Ecology and Systematics 29: 543–566.
- Nettleton, P., 2004. Hydrodynamic Modelling of the St. Lawrence River at Cornwall in Support of Sediment Remediation Development by the MOE Eastern Region. Ontario Ministry of the Environment, Environmental Monitoring & Reporting Branch, Modelling Section, Toronto, ON: 30 pp.
- Ontario Ministry of the Environment, 2007. Guide to eating Ontario sport fish 2007–2008, 24th ed., revised. Queen's Printer for Ontario, Canada.
- Poissant, L., P. Constant, M. Pilote, J. Canário, N. O'Driscoll, J. Ridal & D. Lean, 2007. The ebullition of hydrogen, carbon monoxide, methane, carbon dioxide and total gaseous mercury from the Cornwall Area of Concern. Science of the Total Environment 381: 256–262.
- Razavi, N. R., 2008. Role of bubbling from aquatic sediments in mercury transfer to a benthic invertebrate in the St. Lawrence River, Cornwall, Ontario. Master's Thesis, Queen's University, Kingston, ON, Canada.
- Richman, L. A. & S. I. Dreier, 2001. Sediment contamination in the St. Lawrence River along the Cornwall, Ontario waterfront. Journal of Great Lakes Research 27: 60–83.
- Ridal, J., B. Doran, O. Nwobu, & D. R. S. Lean, 2006. Assessment of Mercury Concentrations in Zooplankton Populations in the Zones of Contaminated Sediments and Comparison to Reference Sites in the St. Lawrence River (Cornwall) Area of Concern. Report to the Ontario Ministry of the Environment, Kingston, Ontario, Canada: 28 pp.
- Rukavina, N. A., 2000. Sedimentology of contaminated St. Lawrence River sediments at Cornwall, Ontario. NWRI Contribution No. 00-052, National Water Research Institute, Burlington, Ontario, Canada: 130 pp.
- Sotiropoulos, M. A., W. M. Tonn & L. I. Wassenaar, 2004. Effects of lipid extraction on stable carbon and nitrogen isotope analyses of fish tissues: potential consequences for food web studies. Ecology of Freshwater Fish 13: 155–160.
- St. Lawrence River RAP Team, 1997. St. Lawrence River RAP Team. Remedial Action Plan for the St. Lawrence River (Cornwall) Area of Concern. Stage 2 Report: The Recommended Plan. Environment Canada, Environment Ontario, ISBN 0-7778-6881-4.
- Trudel, M. & J. B. Rasmussen, 2006. Bioenergetics and mercury dynamics in fish: a modelling perspective. Canadian Journal of Fisheries and Aquatic Sciences 63: 1890–1902.
- Trudel, M., A. Tremblay, R. Schetagne & J. B. Rasmussen, 2000. Estimating food consumption rates of fish using a mercury mass balance model. Canadian Journal of Fisheries and Aquatic Sciences 57: 414–428.
- Ullrich, S. M., T. W. Tanton & S. A. Abdrashitova, 2001. Mercury in the aquatic environment: a review of factors affecting methylation. Critical Reviews in Environmental Science and Technology 31(3): 241–293.

- United States Environmental Protection Agency, 2002. Method 1631, revision E. USEPA, Office of Water, Office of Science and Technology, Engineering and Analysis Division (4303), 1200 Pennsylvania Avenue NW, Washington, DC, 20460.
- Waldron, M. C., J. A. Colman & R. F. Breault, 2000. Distribution, hydrologic transport, and cycling of total and methyl mercury in a contaminated river-reservoir-wetland system (Sudbury River, eastern Massachusetts). *Canadian Journal of Fisheries and Aquatic Sciences* 58: 1080–1091.
- Yanch, L. E., 2007. Assessing the spatial and temporal patterns of total mercury, $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ in yellow perch and their prey items from a contaminated site, St. Lawrence River, Cornwall, ON. Master's Thesis, Queen's University, Kingston, ON, Canada.