Historic brownfields and industrial activity in Kingston, Ontario: Assessing potential contributions to mercury contamination in sediment of the Cataraqui River

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ABSTRACT

The waterfront of historic Kingston, Ontario (pop: 113,000) has been used for industrial activities for over a century. More than 40 industries have existed within the inner harbour, and while many of these industries are no longer present, the properties that they operated on remain as potential sources of persistent contamination to the present day, including mercury. To assess the extent and distribution of total mercury (THg) contamination, 21 sediment cores as well as pore water samples were collected within the inner harbour of Kingston. The spatial distribution of THg in the surface sediment is not homogenous; with concentrations in the surface sediment along the southwestern shoreline, adjacent to the former industrial properties, are significantly greater ($p < 0.01$) than the rest of the inner harbour, and were above the Federal severe effect limit (>2000 ug/kg;) guideline for sediment. MeHg was detected in some sediment cores, and was found to have a significant, positive correlation with [THg] in the surface sediment (0–5 cm). THg was not found in storm sewer discharges, but was detected in terrestrial soil near the Kingston Rowing Club at a concentration of more than 4000 ug/kg. Significant [THg] was detected in runoff draining from contaminated shoreline soils, indicating that erosion from terrestrial sources may be an ongoing source of Hg to the sediment. It can be concluded that there is an increased risk over time to surrounding ecosystems where properties with historical contamination are not remediated until they are developed.

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1. Introduction

Concerns about the potential impact that contamination originating from abandoned industrial sites (brownfields) has been raised; particularly as it is estimated that there are between 400,000 and 500,000 brownfields in the US (Litt and Burke, 2002), 300,000 to 1.5 million sites in Europe (van Calster, 2004) and over 30,000 in Canada (National Round Table on the Environment and the Economy, NRTEE, 2003). The City of Kingston (Ontario, Canada) has several key historical brownfields along its waterfront, which are sources of long-standing controversy, and have provided a challenge for remediation approaches. In particular, the Kingston Inner Harbour on the Cataraqui River (Fig. 1), whose gradually sloping western shoreline has been utilized by industries for more than a century, has experienced repeated contamination events. Former industries include a coal gasification plant, a former tannery and lead smelter, manufacturing and fabrication companies, a municipal dump, a woollen (textile) mill, a gristmill, shipyards, a fuel depot, and a railway corridor (Malroz Engineering Inc., 2003).

While many of the industries along Kingston's southwestern shoreline are no longer present, the properties that they operated on remain as potential contamination sources to the Cataraqui River and Lake Ontario. Previous analysis of sediment quality in the inner harbour has found elevated levels of several contaminants including PCBs, PAHs and metals such as chromium, copper and lead, in the sediment spatially closer to the former industries along the southwestern shoreline (Bennett, 2003; Stokes, 1977). While no studies have examined the distribution of mercury (Hg) in the sediment of the inner harbour in detail, THg concentrations (THg) were measured in the surface sediment taken by the Ministry of the Environment in 2002 during Project Trackdown, following the removal of PCB-contaminated surface sediment. THg concentrations were found to be more than twice the severe effect limit (SEL), which defines sediment greater than 2000 ug/kg as being heavily polluted and potentially toxic to biota (International Joint Commission, 2006).

The contamination issues associated with mercury have many implications for the socioeconomic and ecosystem health of the region. Presently, the shorelines of the inner harbour are used for

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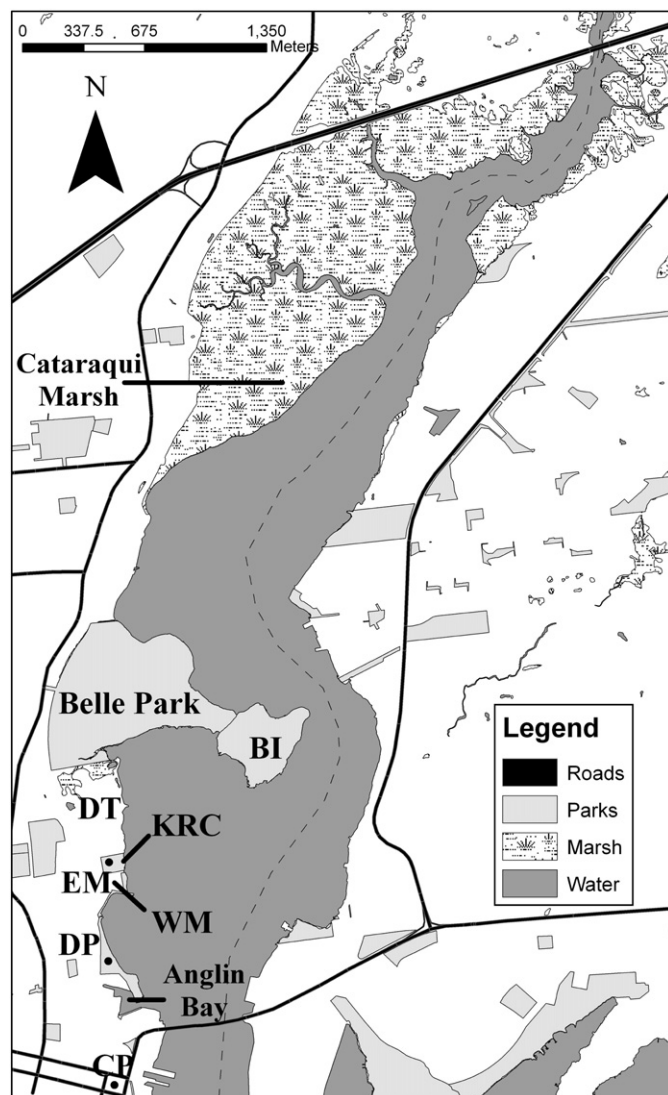
Fig. 1. Map of the Cataraqui River before it drains into Lake Ontario, bound by the LaSalle Causeway to the south and highway #401 to the north, with the approximate location of the navigation channel shown (dashed line). Former and current anthropogenic land use properties of interest are identified: Davis Tannery & Lead Smelter (DT), Kingston Rowing Club (KRC), former Kingston Woolen Mill (WM), former Kingston Coal Gasification Plant (CP) and two parks, Emma Martin Park (EM) and Douglas Park (DP).

commercial, residential and park lands in addition to current and former industrial properties (Fig. 1). Aquatic recreational activities, including rowing, sailing, fishing and boating are important to city residents and visitors. In addition, there is at least one known commercial fishery and two bait fisheries. The northern stretch of the inner harbour is dominated by the provincially significant Cataraqui Marsh (Fig. 1), which occupies approximately 3.5 km of the shoreline, and is an important spawning site for many key fish species and migratory stopping (Malroz Engineering Inc., 2003). As a result, it is urgent to quantify the extent and potential sources of THg contamination in the inner harbour and assess the mobility of THg in the system. This study will examine the distribution of THg in the sediment, the water column, pore water, and soil samples along the lower Cataraqui River at Kingston. Our goal is to assess whether Hg loading to the inner harbour sediments is an ongoing process, and what role former and current use of industrial properties play in its spatial distribution of Hg within the sediment.

2. Material and methods

2.1. Site description

The Cataraqui River, one of two distinct river systems that comprise the World Heritage Site Rideau Canal connecting Ottawa to Kingston, drains 930 km^2 of primarily rural, Canadian Shield bedrock before it empties into Lake Ontario through Kingston's inner harbour. The mouth of the river, which defines the inner harbour of Kingston and our study area (Fig. 1), is considered an embayment of Lake Ontario (Crysler and Latham Ltd., 1977) and extends approximately 5 km north until it meets provincial highway #401. While the Inner Harbour is not a 'true' estuary by definition of salinity mixing, its hydrological patterns indicate a mixing region typical of estuaries, where sediment from upstream tributaries mix with sediments from the inlet to Lake Ontario (Crysler and Latham Ltd., 1977).

The Cataraqui Wetlands Conservation Area, just south of the Highway 401 causeway, is home to 206 different bird species, 51 different plant species, and 36 reported fish species (Blancher, 1984). The shorelines of the inner harbour are important spawning areas for local fish species such as bass, perch and pike, as well as for migrating carp (Ecologistics Limited, and Water and Earth Science Associates Ltd., 1984; Blancher, 1984; Malroz Engineering Inc., 1999). At the south, where the inner harbour exits into Lake Ontario, the boundary is typically delimited by the LaSalle Causeway, a lift-bridge allowing boating traffic to enter the inner harbour (Fig. 1). Navigation channels leading from Lake Ontario through the Rideau Waterway have been maintained by occasional dredging by Transport Canada, going past the inner harbour (Fig. 1).

Previous studies have found that the distribution of other metals such as Cr, Cu and Pb tends to be concentrated in plumes and highly variable along the shoreline adjacent to former industrial sites (Bennett, 2003). The Davis Tannery Site (Fig. 1), a highly contaminated brownfield, showed a wide range of THg concentrations measured in soils (100–7710 ug/kg), and sediment (370–870 ug/kg) by Stokes (1977). Soil concentrations measured 17 years later by Decommissioning Services Ltd (1994) showed a similar range of THg in soils (50–15,000 ug/kg). Extensive remediation efforts are yet to be applied to the property, and has remained vacant since the Tannery's closure. It is important to note, that while Belle Park Landfill (1952–1974) has been the subject of long-standing controversy for the release of hazardous materials since its closure, Hg has not been detected (<0.0001 mg/L) during any of the well monitoring programs since 1999 (Malroz Engineering Inc., 2003). As a result, the majority of the sampling effort focused along the southwestern shoreline of the inner harbour.

2.2. Water sampling

Physiochemical parameters of river column water within the Inner Harbour were measured at four core sampling locations (C3, R3, C12, and C14) in June of 2007, with a Hydrolab DS5X water quality sonde. Parameters included spectrometric chlorophyll-a analyses and luminescent dissolved oxygen (LDO) (Table 1). Storm sewer water was

Table 1
Water physiochemical parameters measured at four core sampling locations in June 2007.

Location (depth)	Chlorophyll-a (g/L)	pH	Temperature (°C)	LDO (mg/L)
C3 (1.3 m)	4.0	9.55	24.8	104
C3 (2 m)	5.5	8.90	24.04	53.1
R3 (1.3 m)	1.3	9.27	25.68	118.8
R3 (2.3 m)	2.3	8.63	24.73	63.9
C12 (1 m)	2.1	9.52	24.96	167.5
C12 (1.5 m)	2.3	9.50	24.87	151.2
C14 (1.3 m)	3.1	9.43	25.6	107
C14 (2.1 m)	2.4	8.54	24.46	47.2

collected from 3 storm sewers during rain events at three of the four monitoring points (MP 2, MP 3, and MP 4) on the Cataraqui River (Fig. 3) and from overland flow from two locations (MP 1 and MP 2) thrice over the course of a year. The storm sewers at Douglas Park N. and Douglas Park S. were at river water levels, so sampling of those outflows most likely contained some quantity of diluted river water in addition to sewer water. The storm sewer south of the former Woollen Mill was above the water level and could be collected directly from that sampling location. Overland flow samples were collected where rills had formed and also contained visibly eroding soil from the shoreline. To get an estimate of the importance of particulates in THg loading, the last MP 1 runoff sample from the Rowing Club was split into two and one subsample filtered (0.45 um). During one of the sampling periods, snow was on the ground so snow pack samples were collected in addition to overland flow from MP 1 and both storm sewers in Douglas Park. Snow samples were placed in a Whirlpak and then thawed in a cool water (4 °C) bath prior to preservation and storage. All water and snowmelt samples were immediately acidified with 5% nitric acid and 5% potassium dichromate solution by volume and refrigerated until analysis.

2.3. Soil sampling

Soils were sampled along the western shoreline adjacent to the southwestern shoreline, on and near former industrial properties. Forty soil samples (S1–S40) were taken at a 0–10 cm profile using plastic sterile scoops, with each location sampled as a composite; three random scoops within a 1.5 m radius were placed into a Whirlpak, homogenized by hand within the bag, and immediately frozen until the time of analysis.

2.4. Sediment coring

Sediment cores were collected using a Glew gravity corer (Glew, 1989) from six locations in October of 2005 (C1–C6), two in October of 2006 (C13, C14), and the remaining six in November of 2006 (C7–C12) (Fig. 2). The 7.5-cm diameter (inside dimensions) coring tubes were cleaned with 10% nitric acid prior to coring, and sediment cores were extruded and sectioned the day of sampling at 1-cm intervals on land. Extruded sections were scraped into sterile Whirlpaks, using 10% nitric acid to clean the extruder and knife between samples, and immediately frozen. Additional samples were obtained from seven deep cores collected using a percussion corer (7.5 cm diameter) in September 2006 by the Royal Military College (RMC) Kingston, which ranged in depth from 30 to 110 cm, sectioned by 5 cm intervals.

2.5. Pore water sampling

Small-volume pore water samples were obtained from three cores with a Millipore Hazardous Waste Filtration Unit, using a 142-mm Advantec Glass Fiber Filter with a pore size of 0.45 um and vacuum extracted using nitrogen gas up to 50 psi and stored in amber glass vials with Teflon lids. Only a limited number of samples could be analyzed, so cores C3 and C14 were chosen due to high concentrations of THg in the sediment, their proximity to biologically productive areas, and because bubbling from disturbed sediments was observed in these two areas, which has been shown to be correlated with increased transport and bioaccumulation of Hg in some studies (Pak and Bartha, 1998). Core C12 was chosen as a reference site as it contained the lowest concentrations of THg, and was upstream from the industrial sites in a highly productive area near the Cataraqui Marsh. In order to achieve a lower detection limit for THg in pore water, four large-volume pore water samples (1000 mL) were collected in acid-cleaned Teflon bottles using drive-point 12-inch PVC piezometers with a 0.2 μm filter from the sampling point PW at the Kingston Rowing Club docks (Fig. 3) attached to a peristaltic pump
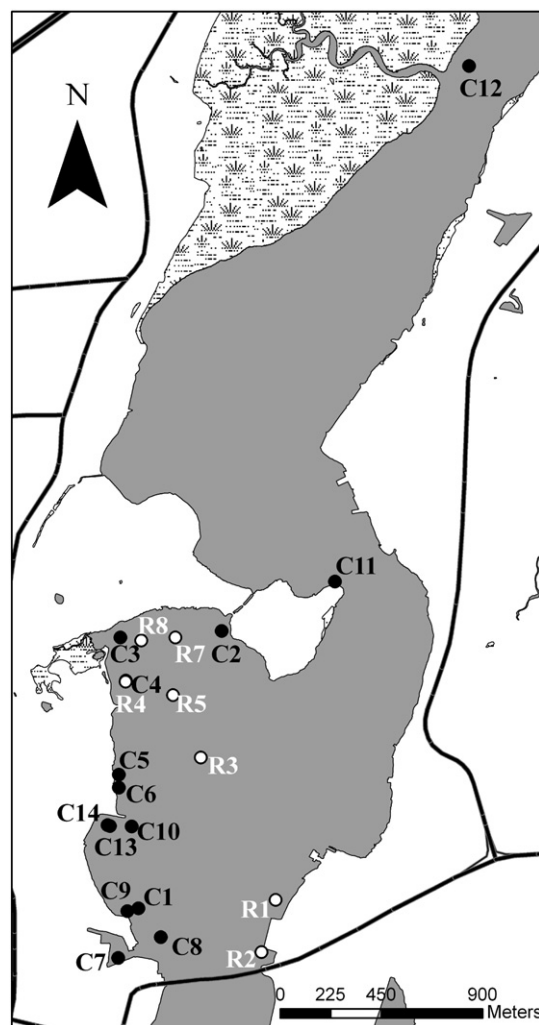

Fig. 2. Map of core sampling locations. Note that C13 and C14 appear as one point, as they are only a few meters apart.

with acid-cleaned silicone tubing. All pore water samples were immediately acidified with 5% nitric acid and 5% potassium dichromate solution by volume and refrigerated until analysis.

2.6. Core dating

Sediment core dating of four selected intervals (0–1, 12–13, 20–21 and 34–35) from core C3 was done on freeze–dried sediment in epoxy-sealed plastic test tubes using an Ortec 92X gamma ray spectrometer for 80,000 s. Gamma counts for the radioisotopes ^{137}Cs, ^{214}Bi and ^{210}Pb (dpm/g), corrected for density, date sampled, and efficiency were recorded at the Paleoecological Environmental Assessment and Research Laboratory at Queen's University. C3 was chosen as it was collected in a relatively undisturbed deep core furthest from the navigation channel near Belle Island. There was no exponential decrease in ^{210}Pb and no distinguishable peaks in the ^{137}Cs or ^{214}Bi signals were observed. Since the ^{210}Pb signal decreased from 11.35 to 3.54 dpm/g from the top of the core to the bottom over a depth of 30 cm in a linear fashion (Fig. 4), and with a natural half-life of 22.3 years, this likely indicates a period of sedimentation of only around 35–40 years for the 21 cm-long core. This time frame is well after the former industrial properties around Belle Island were closed, and the lack of ^{137}Cs signal suggests that sediment was high in organic content and/or may be subjected to high levels of mixing.
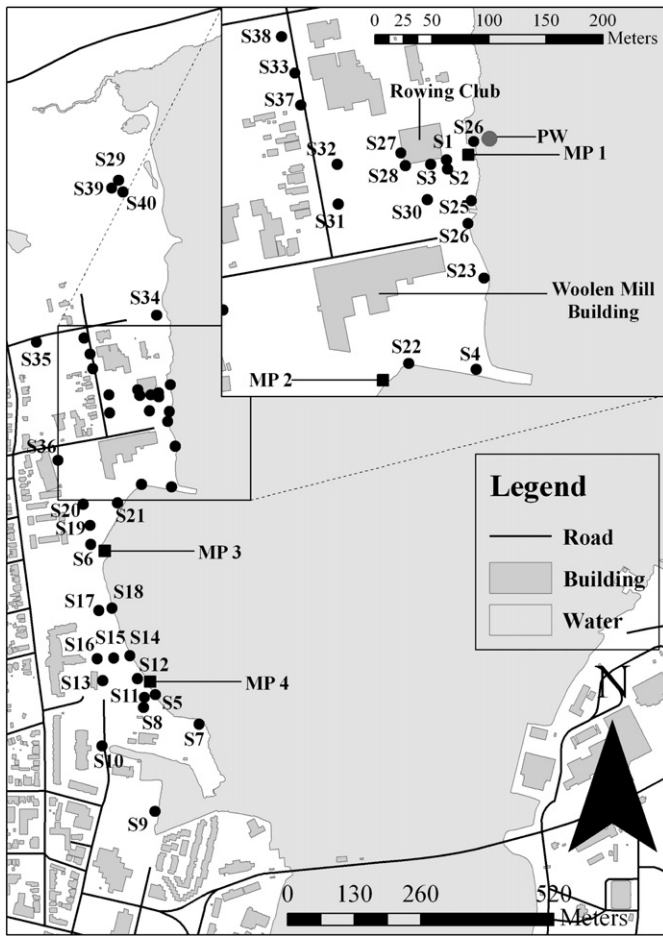
Fig. 3. Map of southwestern shoreline south of Belle Park indicating soil (S1–S40), storm or runoff water (MP 1–MP 4), and peizometer pore water (PW) sampling locations. Rowing Club and Woolen Mill Buildings are indicated on insert map.

2.7. THg in sediment and soils

Soil and sediment samples were analyzed for THg by cold vapour atomic absorption spectrophotometry (EPA Method 7473, United States Environmental Protection Agency, USEPA, 1998) at the Analytical Services Unit at Queen's University, using a Milestone Direct Mercury Analyzer (DMA-80) with a detection limit of 0.05 ng THg. Frozen sediment samples were thawed and oven dried at 35 °C prior to analysis in order to optimize Hg recovery during analysis
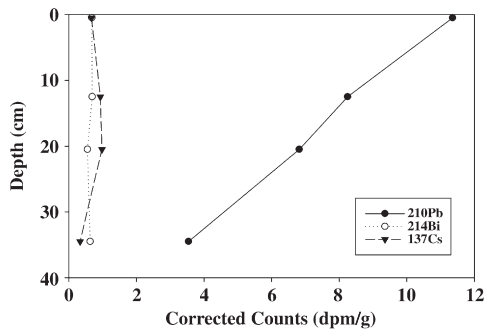

Fig. 4. Graph of corrected decay counts (dpm/g) recorded for ^{210}Pb, ^{214}Bi, and ^{137}Cs at four depths from core C3.

(Roos-Barraclough et al., 2002) and then ground with mortar and pestle, rinsing with 10% nitric acid between samples. Dried and ground samples were weighed and analyzed in acid-washed quartz boats. Each run of 15 samples included a duplicate, an aqueous QC (calibration check from separate Hg source), and duplicate samples of NCR Certified Reference Material MESS-3.

2.8. THg in water samples

Water sampled from 2005 to February 2006 was analyzed for THg by the Analytical Services Group, RMC, Kingston, Ontario. Analysis was performed using cold vapour generated mercury hydride-atomic absorption spectrophotometry (wavelength 253.7 nm), with a detection limit of 0.04 ug/L. The remaining water samples were analyzed for THg by cold vapour atomic fluorescence spectroscopy (CVAFS) at the RPC Research in New Brunswick, with a detection limit of 0.001 ug/L.

2.9. MeHg in sediment

The same core sediment intervals selected for THg analyses were also used for MeHg analysis so that the mobility of Hg in pore water could be compared to the degree of methylation measured in sediment Hg. A subsample of each selected core interval was placed in acid-washed amber vials with Teflon lids, frozen and analyzed for MeHg at Flett Research in Winnipeg, Manitoba using a modified EPA Method 1630. Samples were analyzed wet and treated as aqueous samples, with MeHg extracted using potassium bromate and analyzed by ethylation, followed by purge and trap/GC separation and detection by cold vapour atomic fluorescence spectroscopy (CVAFS) with a detection limit of 0.06 ng/g.

2.10. Total organic carbon in sediment by loss on ignition (LOI)

Subsamples from cores C1, C3, C5, C6, C7, C9, C12 and C14 were analyzed for approximate total organic carbon (TOC) by loss on ignition (LOI) at the ASU at Queen's University. Samples were air dried for 24 h and then ground with a mortar and pestle. Approximately 2 g of wet soil was weighed into a 50-mL beaker and placed into an oven at 105 °C for 24 h and after cooling, weighed again. The sample was then placed in a preheated muffle furnace at 420 °C for 16 h and after cooling, weighed again. The three weights were used to calculate % organic matter (%OM) as LOI.
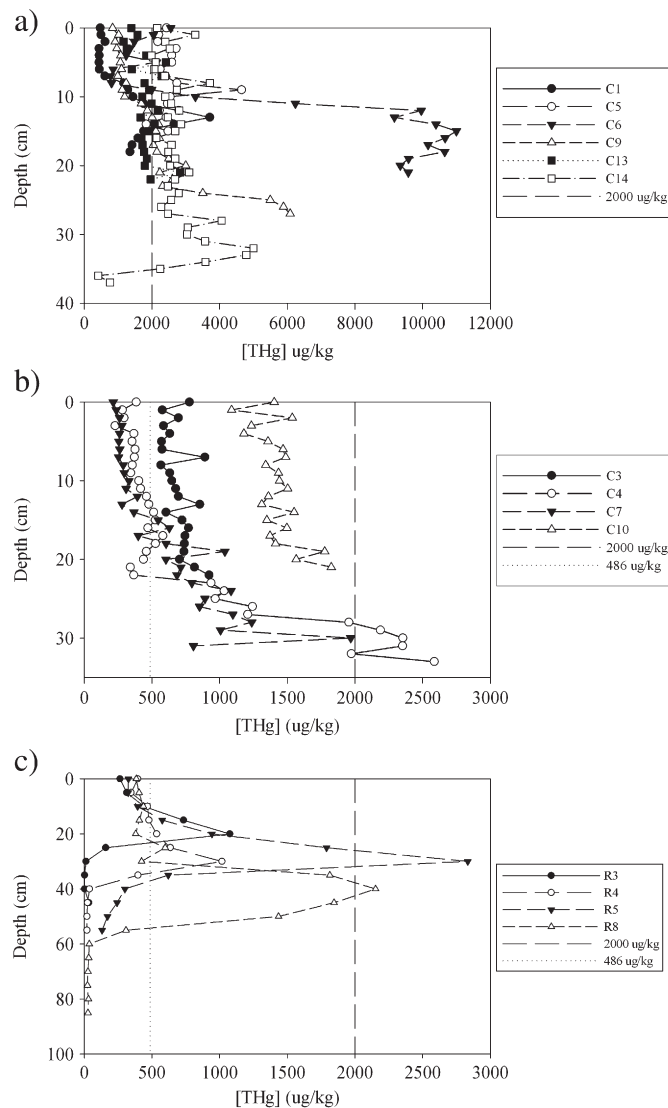
2.11. Spatial trend analyses

Since the cores collected by RMC (cores RC1 to RC8) were extruded at 5 cm intervals, Hg concentrations between could not be compared directly to our 1 cm intervals during the spatial interpolation process. Thus, kriging estimations of Hg concentrations in sediment used a mean of every 5 cm in the 1-cm cores to create prediction maps (0–5, 5–10, and 10–15 cm). The deepest depth used for kriging is 15 cm, as it is the last depth interval for which a THg value is available for every core sampled. Histogram plots of the core Hg data for the 0–5 cm, 5–10 cm, and 10–15 cm core intervals showed an asymmetrical distribution towards many low concentrations, so a natural-log transformation of each data set was performed prior to spatial modelling. Using the geostatistical analyst tool in ArcMap©, the spherical kriging method was found to create the lowest standardized error for each of the prediction maps, and since the semivariogram models indicated a directional dependence along a southeastern direction for all three kriging depths, so an anisotropic spherical model was used to create the experimental variograms. Cross validation standardized errors between the experimental and predicted values were below the acceptable threshold (<-2.5) indicating the model was valid.

3. Results and discussion

Sediment cores ranged from 15 to 105 cm long and had uniform, brownish-black silty loam profiles with some clay, usually increasing with depth. Cores C3, C11, C13, and C14 from around Belle Island and Rowing Club site had large wood chip pieces throughout the core, with the size and density of wood chips increasing with depth. In addition, traces of oil and hydrocarbons were noticeable both visually and aromatically in cores C1, C7, C8, C9, C10, C13 and C14 from around Anglin Bay and the Rowing Club sites, with intensity increasing with depth. Sediment from Anglin Bay, which was adjacent to both a coal gasification plant and a fuel depot, has shown evidence of deposits of coal tar in an unpublished report by R. Jaagumagi (1991), which may be contributing factors.
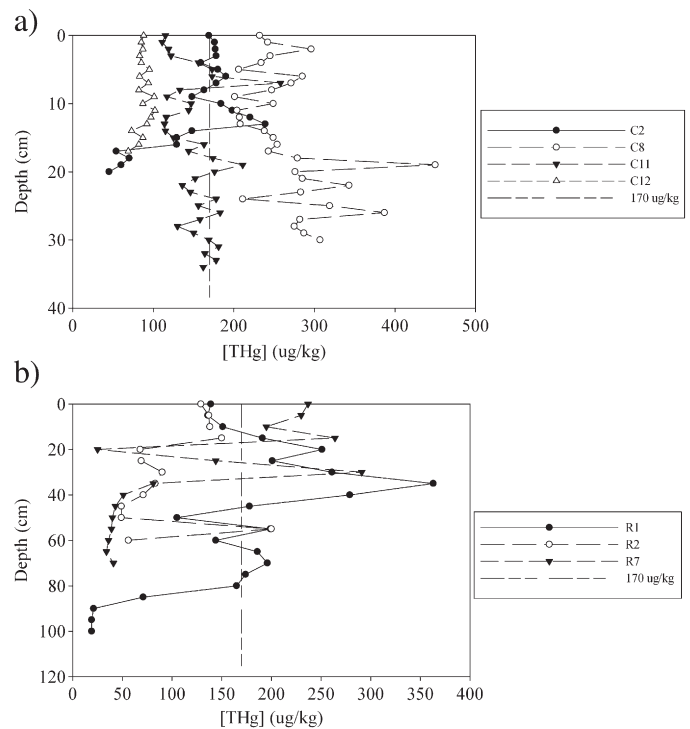
3.1. Core profiles

Depth profiles of THg concentrations from gravity cores with the highest mean surface concentrations (0–5 cm) are shown in Fig. 5. The six cores that contained the highest concentrations were all from sites nearest the southwestern shoreline and downstream from the Rowing Club and former Woollen Mill, where surface sediment was above the SEL guideline (2000 ug/kg; Fig. 5a). Those cores also contain the highest concentration of THg at depth, with C6 by the Rowing Club reaching a maximum value of 11,000 ug/kg between 10 and 20 cm, suggesting one or more severe contamination events at some point in recent history. The cores with the lowest mean THg concentrations (Fig. 6) were found upstream of Belle Island (C11 and C12; Fig. 6a) or to the east of the navigation channel (R1 and R2; Fig. 6b), and were all below the PEL guideline (486 ug/kg). The mean surface THg concentrations (0–10 cm) from near the former Woollen Mill (C6, C5, C10, and C14) are significantly higher than those from locations upstream (C11 and C12) and to the east of the navigation channel (C1 and C2; Tukey test; $p < 0.01$) suggesting a local point source near the western shoreline around the Kingston Rowing Club and the Woollen Mill.

The core C7 from Anglin bay (Fig. 5b) exhibits higher THg concentrations around 30 cm. The increased THg concentrations at 30 cm and below in C7 could be a result of upward Hg migration from deposited coal tar or other buried wastes containing Hg, or from deposition of disturbed contaminated sediment, as a consulting report places coal tar 30–100 cm below overlying sediment (CH2M Hill Engineering Ltd, 1991). The surface sediments (0–10 cm) and deeper sediments (15–20 cm) from core C3 at the mouth of the Davis Tannery Creek had significantly greater (ANOVA; $p < 0.01$; Tukey test; $p < 0.01$) THg concentrations compared with those in nearby cores (C4, Fig. 5b; C2, C8, and R7 in Fig. 6). Since the creek drains the marsh once used by the Davis Tannery for effluent discharges (Ontario Ministry of the Environment, OME, 1978), processes and wastes from the former industries on the Tannery property may be responsible for the elevated Hg concentrations. While the Tannery Creek may be a point source of Hg loading to river sediments, there are significantly greater concentrations of Hg in sediment near the vicinity of the Rowing Club (ANOVA; $p < 0.01$; Tukey test; $p < 0.01$).

Fig. 5. Sediment depth profiles of THg concentrations in the cores with the highest concentrations of THg. The PEL (>486 ug/kg) sediment guideline is indicated by the dotted line and the SEL (>2000 ug/kg) is indicated by the dashed line in each graph. Note the difference in scales between the three graphs both in depth and THg concentration.

Fig. 6. Sediment depth profiles of cores that contained the lowest concentrations of THg. Vertical reference lines for the ISQG (>170 ug/kg) sediment guideline are indicated by the dashed line. Note the difference in scales between the two graphs both in depth and THg concentration.

The spatial distribution of Hg in surface sediment (0–5 cm) from core data estimated using kriging (Fig. 7a) suggests that the surface sediments with the higher concentrations of Hg (>2000 ug/kg) are immediately adjacent to the shoreline near the Rowing Club and the Woollen Mill. The THg contamination plume points southeast, following the river flow pattern, and decreases with distance from the shoreline (Fig. 7), which is consistent with known spatial trends of other metals such as copper and lead (Bennett, 2003). THg concentrations in sediments both at the surface and at the depth (Fig. 7b, c) decrease with distance from the western shoreline between the LaSalle Causeway and Belle Park. The distribution of THg is isolated primarily to the west of the navigation channel, south of Belle Park. Sedimentation is high in this area as water from Lake Ontario mixes with water from upstream, creating an estuary-like environment (Crysler and Latham Ltd., 1977). The area of the Hg plume increases with depth (Fig. 7b, c), suggesting that Hg loading to sediments may have been higher in the past. Furthermore, the Hg plume is consistently associated with the southwestern shoreline by the Rowing Club and the Woollen Mill rather than from upstream sources or the eastern shoreline.

While it is possible that Hg may be migrating at depth, analysis of pore water from sediment cores indicated that the mobility of Hg between sediments is limited, because only the 20–22 cm interval from C3 near the Davis Tannery Creek had detectable THg in pore water (0.01 ug/L; det. limit = 0.01 ug/L). The large-volume surface pore water samples from drive-point piezometers also had low concentrations of THg (0.0035 to 0.014 ug/L). None of the pore waters measured were above the Canadian Water Quality Guideline (CWQG) for inorganic Hg (0.026 ug/L) and THg in surface waters of the inner harbour and upstream along the river have were all below detection limits (0.4 ug/L). The high pH measured in both surface and depth waters of this study (8.54–9.55 pH) and in previous studies (7.58–9.8;

Bennett, 2003) of the inner harbour may be partially responsible for the low pore water THg concentrations, despite the high THg concentrations observed in surface sediment. The affinity of Hg for acid-binding sites on organic matter in sediment is known to increase under more basic conditions (Ravichandran, 2004). The high pH of the inner harbour is likely influenced by the limestone bedrock geology, as well as an abundance of dissolved nutrients from wave action, particularly along the western shoreline where plant productivity is high.

3.2. Organic matter

The only significant correlation between organic matter, as indicated by % LOI and THg concentration in sediment cores, was found in the C3 core ($r^2 = 0.95$; $p < 0.0001$) at the mouth of the Tannery Creek (Table 2). Strong correlations between DOM and Hg are frequently observed in waterways draining wetlands (Ravichandran, 2004). Since the Tannery Creek drains the marsh once used as a discharge site for effluent from the Davis Tannery, it is possible that the Hg observed in sediment from C3 was transported via organic matter during times of high hydrologic flow from the marsh. However, the lack of significant correlations for organic matter and THg in all of the other cores from the Inner Harbour region suggests that other hydrological characteristics may be more dominant than organic carbon in the Hg biogeochemical cycle, which is similar to other studies that have examined organic content and THg in organic-rich sediments (He et al., 2007; Mason et al., 2006).

3.3. Methylmercury in sediment

In all cores, MeHg concentrations consistently decreased with depth, and there was a positive but insignificant correlation between
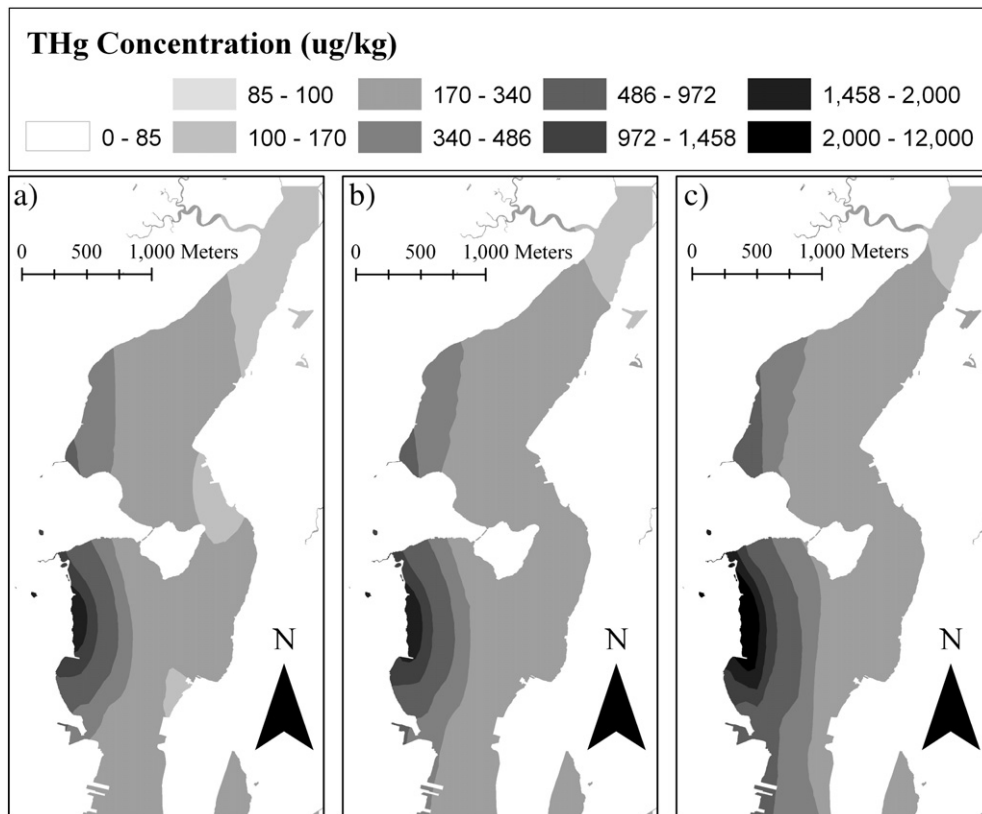

Fig. 7. Kriging estimation maps for core data sets from left to right: 0–5 cm (a), 5–10 cm (b) and 10–15 cm (c). Contour intervals were chosen based on the sediment quality guidelines (ISQG>170 ug/kg; PEL>486 ug/kg; SEL>1000 ug/kg).

Table 2
Mean %OM and standard deviation (Std dev) of each of the eight cores analyzed for TOC by LOI. The regression analysis between THg concentration and %OM by LOI is also indicated along with each corresponding r^2 and p value of the correlation.

Core	%OM as LOI	Std dev	THg $= m(\%OM) + b$	r^2	p
C2	11	1.3	$m = 9.3; b = 0.01$	0.23	0.029
C3	26	12.4	$m = 5.1; b = 0.02$	0.95	<0.0001
C5	5.4	1.6	$m = 5.3; b = 4.5 \times 10^{-5}$	0.0003	0.95
C6	12	6.4	$m = 7.0; b = 0.09 \times 10^{-2}$	0.36	0.003
C7	16	6.3	$m = 12.4; b = 0.06 \times 10^{-1}$	0.14	0.038
C9	18	1.9	$m = 16.2; b = 0.69 \times 10^{-3}$	0.26	0.006
C12	33	2.5	$m = 33.6; b = -0.42 \times 10^{-2}$	0.00015	0.97
C14	16	2.3	$m = 15.2; b = 0.49 \times 10^{-3}$	0.03	0.33

MeHg and THg concentrations in all core intervals ($r^2 = 0.21$; $p = 0.13$). If only the top 5 cm of sediment in each core is considered though, then correlations between THg and MeHg become significant ($r^2 = 0.81$; $p < 0.01$). Whether or not the distribution of MeHg is in any way related to loading at that location remains unknown though, as Rydberg et al. (2008) have shown that methylmercury in surface sediment can be an artifact of diagenetic processes, or net methylation from deeper sediments.

The highest amount of % MeHg:THg at all four depth intervals was found to be in C12 by the Cataraqui Marsh compared to those for C3 and C14 (Table 3). The higher proportion of THg as MeHg observed in C12 at the 0–1 cm layer (1.04%) suggests that spatial differences in methylation within the harbour may exist, perhaps a result of favourable processes originating from the Marsh, as wetlands and marshes have been shown extensively to contribute to increased methylation in sediments (Gustin et al., 2006; Galloway and Branfireun, 2004).

3.4. Terrestrial water and soils

Elevated THg was detected in the storm sewer water samples from the Woollen Mill sewer outlet and the runoff waters from the Rowing Club in all sampling events (Table 4). Runoff THg concentrations observed at Douglas Park (MP 3) south of the Rowing Club were significantly lower (Table 4; ANOVA, $p < 0.01$). Even so, the amount of THg observed in water runoff in one of the two samples from Douglas Park was above the CWQG of 0.026 ug/L for water bodies, while the average THg concentrations in the runoff samples from the Rowing Club (31.97 ug/L) was over 1000 times higher than the CWQG guideline. When the last Rowing Club overland flow sample was filtered and analyzed, the THg concentration in the water sample was reduced from 11.1 ug/L (unfiltered) to 0.19 ug/L (filtered). In addition, a snow sample from the Rowing Club runoff location (MP 1) was measured at 0.009 ug/L, while runoff from melting snow carrying soil particulates was measured at 11.1 ug/L. Since concentrations of Hg were not detected in storm sewer waters, and unfiltered runoff water contains up to 1000 times more Hg than filtered water and snow, the potential sources of Hg seems to be associated with soil and particulate

Table 4
THg concentration (ug/L) measured in soil runoff, snow and/or storm sewer water.

Sampling location	Sample type	2-Sept-06 (ug/L)	11-Mar-07 (ug/L)	03-June-07 (ug/L)
MP 1	Runoff	61	22.5; 25.6 (d)	11.1
	Snow	–	0.009	–
MP 2	Storm sewer	–	0.071; 0.035 (d)	0.01
MP 3	Runoff	<0.4; <0.4 (d)	–	<0.01; <0.01 (d)
	Storm sewer	<0.4	–	<0.01
MP 4	Storm sewer	–	–	<0.01
	Snow	–	0.008	–

(d) − indicates field duplicate sample.

matter. As a result, Hg-contaminated soil along the western shoreline between the Rowing Club and the Woollen Mill is very likely an ongoing source of Hg to Cataraqui River.

The THg concentrations for surface soil samples from along the Cataraqui River varied widely depending on location, ranging from 9 ug/kg to 4380 ug/kg (Fig. 8). However, the ten highest THg concentrations were all located north of the Woollen Mill site, near the Rowing Club (Fig. 3). The highest concentration (4390 ug/kg) was observed at the southeast corner of the Rowing Club building, also where the runoff water sample with highest THg concentration was sampled. Six of the ten samples on and around the Rowing Club property are above the MOE guidelines of 230 ug/kg for soils within 30 m of a surface water body (Environmental Protection Act, 2004). The five highest concentrations in soil around the Rowing Club (S1, S2, S25, S26, and S24) are all in an east or southeast direction from the Rowing Club building, and are significantly higher than the samples from the adjacent Emma Martin Park, or along the south part of the Woollen Mill property (Tukey; $p < 0.01$).

The elevated Hg concentrations in soils, and by association, the runoff and nearby sediments around the Kingston Rowing Club property may be a result of buried wastes or other materials on the site, likely from industrial activities years before the construction of the Rowing Club building. In a study done by Water and Earth Science Associates Ltd. (1988), eight test pits (TP1–TP8) were studied on the property over an area where a proposed addition (since completed) was planned. Elevated concentrations of Hg were found (4–4600 ug/g) along with other contaminants (including arsenic and nickel) at various depths within the test pits. In the report, it advised that subsurface wastes could be entombed to prevent the movement of contaminants rather than excavating them, since there was clay underlying some of the wastes, and clay could be added to the top of

Table 3
MeHg concentrations (ng/g) and % MeHg:THg measured in sediment core samples.

Core	Depth interval of sediment core (cm)	MeHg (ng/g)	% MeHg:THg
C3	0–1	1.6	0.24
C3	4–5	0.2	0.03
C3	9–10	0.4	0.07
C3	20–21	0.4×10	0.01
C12	0–1	0.9	1.04
C12	4–5	0.2	0.22
C12	9–10	0.3	0.36
C12	20–21	0.3	0.45
C14	0–1	4.3	0.16
C14	4–5	2.1	0.1
C14	9–10	0.4	0.02
C14	20–21	0.2	0.01
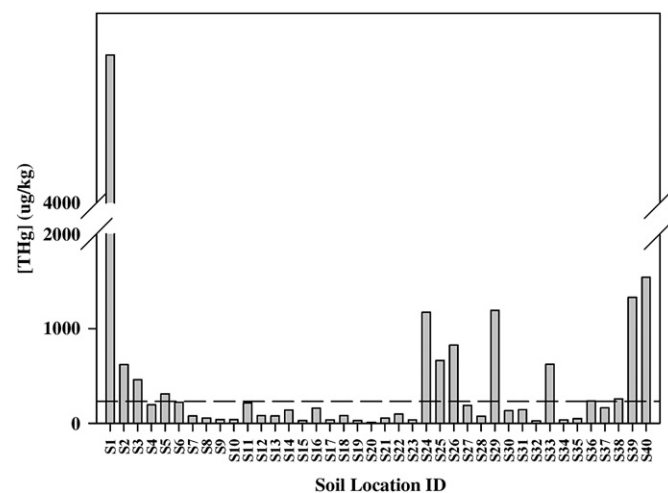
Fig. 8. [THg] (ug/kg) in soil samples taken along southwestern shoreline as indicated in Fig. 3. Dashed line indicates standard for mercury in non-agricultural soil (230 ug/kg) located within 30 m of a surface water body.

the soil and around the buildings, as it can act as an impermeable barrier to leaching wastes. Of the eight test pits though, three did not reach the 120 cm depth where clay was found and no test pits were sampled beyond the extent of the proposed addition. Since the extent of the test pits did not cover the entire property, it is possible that there are discontinuities in the clay layers believed to entomb wastes beneath the building, or there may be wastes that exist beyond the boundaries of the Rowing Club building. Since no reports are available that indicate what wastes are buried around the property, and hydrologic flow is unknown, it is unclear what barriers, if any, are preventing those wastes from migrating to the river. There is also potential for wastes to be transported to the surface soils, particularly during disturbance of soils during development.

4. Conclusions

The area of the inner harbour with surface sediment concentrations of THg above the probable effect level (PEL; >486 ug/kg), is predominantly along the southwestern shoreline, south of Belle Park. If sediment and water are constantly being directed towards the southwestern shoreline, it likely contributes to the isolation and concentration of contaminants in this area. The increasing THg concentration in surface sediments near the Rowing Club and Tannery property is of concern, but depth profiles of sediment in the more contaminated zones also indicate that buried concentrations of THg are higher, representing a classic management dilemma. By removing small portions of surface sediments for 'hot-spot' contaminant remediation (e.g. elevated PCBs or Hg in surface sediments), it may be possible to expose historically deposited Hg of greater concentrations. Since, preliminary analysis of THg in pore water suggests that movement of THg between sediment particles may be minimal, further analysis of the affinity of THg for sediments of the inner harbour is a potential first step in assessing the immediate threat and course of action for THg in sediment.

THg concentrations in soil adjacent to the Kingston Rowing Club are currently above the standards for soils located along a shoreline. Pre-existing wastes beneath the Rowing Club property are known to contain high concentrations of Hg, and are a likely source of the higher concentrations measured around its structure. The excavation and installation of a combined sewer overflow tank at Emma Martin park from 2004–2006 by the City, immediately to the West of the property, may have also contributed to the re-distribution of buried Hg wastes in the area to surface soils. Since the limits of buried wastes beneath the property are unknown, further work should be done to evaluate the full extent of Hg and other wastes, in order to establish whether removal or remediation of these soils are warranted to prevent further Hg loading to the river and ultimately Lake Ontario. Otherwise, removal and replacement of clean sediment will be in place to be contaminated by historical waste. The evidence that historically contaminated terrestrial soil may be contributing to ongoing Hg loading to river sediments though provides an impetus for urban brownfield development. If contaminated sites are left undeveloped due to contamination concerns, the failure to remediate the property until a development strategy is agreed upon, is done at the risk of allowing the property to continue to degrade environmental quality to its surroundings.

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