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Monitoring metal and persistent organic contaminant trends through time using quagga mussels (*Dreissena bugensis*) collected from the Niagara River

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ABSTRACT

Historically, the Niagara River received the discharge of persistent bioaccumulative and toxic chemicals from municipal and industrial outfalls and hazardous waste landfills. American and Canadian governments have coordinated investigations of chemicals entering the river and initiated remedial measures and monitoring programs with a goal to reduce loadings of toxic chemicals to the river. This study, a component of the Ontario Ministry of Environment Mussel Biomonitoring Program, compares contaminant concentrations in quagga mussels (*Dreissena bugensis*) collected from nine locations in the Niagara River in 1995 and 2003 to assess anticipated changes in tissue concentrations of contaminants in response to ongoing remedial efforts by government agencies and local industries. The concentrations of persistent organic compounds (e.g., PCBs, hexachlorobenzene, hexachlorobutadiene, octachlorostyrene) in quagga mussels in 2003 were lower than concentrations measured in 1995, consistent with a decrease in reported mean annual concentrations of these compounds in water. Significant differences in total PCB concentrations in mussels between stations ($F=4.6$; $P<0.001$) suggested sources of PCBs on the American side of the upper Niagara River. In general, highest concentrations of persistent organic compounds were found downstream of the Occidental Chemical Corporation Buffalo Avenue facility suggesting local sources of these contaminants notwithstanding remedial efforts. In contrast, metal concentrations in quagga mussels in 2003 were similar to concentrations found in 1995 and to values reported in the literature for mussels collected from industrialized areas in the Great Lakes. Overall, our results suggest that remedial efforts to improve water quality in the Niagara River have been successful.

Introduction

The Niagara River flows 60 km from Lake Erie to Lake Ontario. It serves as a source of drinking water and recreation to millions of people as well as habitat for fish and wildlife and is an important resource for the generation of electricity. Historically, the river received the discharge of persistent bioaccumulative and toxic chemicals from municipal and industrial outfalls and hazardous waste landfills (Elder et al., 1981; Allan et al., 1983; Jaffe and Hites, 1984). In 1981, The Niagara River Toxics Committee (NRTC) coordinated a binational comprehensive investigation of toxic chemicals entering the Niagara River as a result of public concerns about the safety of drinking water drawn from the river and on ecosystem health (NRTC, 1984). This investigation led to the signing of the "Declaration of Intent" in 1987 by the four environmental government agencies in the United States and Canada, with the objective to reduce the concentration of toxic pollutants in the River. The Niagara River Toxics Management Plan (NRTMP) was implemented to achieve these reductions. In 1996 the goals of the NRTMP were revised to specifically target reducing toxic chemicals in the river by reducing inputs from sources along the river. Remedial actions at hazardous waste sites and point source discharges have been ongoing since the mid-1980s (Niagara River Secretariat, 2007). Recently decreases in mean annual loadings and concentrations in water of priority contaminants have been reported by the Niagara River Secretariat. Along with reduced inputs from Lake Erie, remedial actions within the River were hypothesized to have contributed to improved water and sediment quality (Marvin et al., 2003; Marvin et al., 2007), as well as decreases in Lake Ontario fish tissue contaminant concentrations (Karst-Riddoch et al., 2008).

As part of Ontario's commitment to the NRTMP, the Ontario Ministry of Environment (MOE) has used caged mussels (*Elliptio complanata*) transplanted from reference populations to detect the presence of bioaccumulative contaminants in the waters of the Niagara River, to identify contaminant sources, and to assess the success of remedial actions (Richman, 2006). Transplanted mussels were deployed close to shore upstream and downstream of point and non-point sources and within tributaries to investigate site specific conditions. In 1995, zebra

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and quagga mussels were incorporated into the mussel biomonitoring program to assess ambient contaminant tissue concentrations. This 1995 study produced a baseline dataset to be used to assess river wide long-term contaminant changes during future monitoring surveys. Zebra and quagga mussels were more appropriate ambient biomonitors than the caged mussels since they were resident and integrated contaminant exposure over a longer time than the transplanted biomonitors, which were only deployed for 21 days. Additionally, quagga mussels could be collected from greater depths farther from shore-based sources so their tissue concentrations could potentially provide a better measure of ambient contaminant availability rather than short term presence/absence data (Comba et al., 1996; Robertson and Laurenstein, 1998; Bervoets et al., 2004). Accordingly, zebra and quagga mussels were collected from nine stations located throughout the Niagara River in 1995 and were analysed for trace metals, organochlorine pesticides, PCBs and chlorinated benzenes (Richman and Somers, 2005). Our subsequent 2003 study was conducted to determine whether observed improvements in water quality (Niagara River Secretariat, 2007) were reflected in reduced contaminant tissue concentrations relative to our 1995 results.

In this study we evaluate the results of a second biomonitoring assessment of ambient tissue concentrations of metal and persistent organic contaminants in quagga mussels collected from nine sites in the Niagara River. Our results from 2003 are compared to results from 1995 to examine temporal trends over an eight-year period. Our goals are to determine (1) if temporal changes have occurred; (2) if observed changes are consistent across all 9 sites; and (3), whether changes in metal and persistent organic contaminant concentrations are consistent with recent water quality improvements and remedial actions.

Methods

Sampling sites

In 1995 (September–October), zebra and quagga mussels were collected by SCUBA divers from nine sites located between the head and mouth of the river (Richman and Somers, 2005) (Fig. 1). From October 30 to November 5, 2003, divers returned to the same locations; however, sites were originally identified using a GPS without differential corrections so the level of precision (±100m) affected our ability to return to the exact location. As well, some mussel colonies had changed position between 1995 and 2003; consequently, updated coordinates for the location of the mussel beds and sample sites have been provided (Table 1). As in Richman and Somers (2005), one upstream reference site was used to monitor the uptake of contaminants entering the river from Lake Erie (i.e., Fort Erie). In the river proper, there were four upper river stations: one on the Canadian side in the Chippawa Channel, 50 m downstream of Ushers Creek which drained primarily agricultural land, and three stations were located on the American side of the river in the Tonawanda Channel: one site was upstream of the south Grand Island Bridge herein referred to as the Tonawanda Channel site, downstream of the mouth of Cayuga Creek and downstream of an outfall from the Occidental Chemical Corporation (sewer 003), herein referred to as the Occidental 003 site. The Tonawanda Channel mussels were expected to reflect contaminants from the Buffalo River and from the local industrial (primarily associated with the steel industry), and municipal facilities and waste sites. The Cayuga Creek site was located further downstream within an area considered to be the focal point for the chemical industry, as well as numerous hazardous waste sites

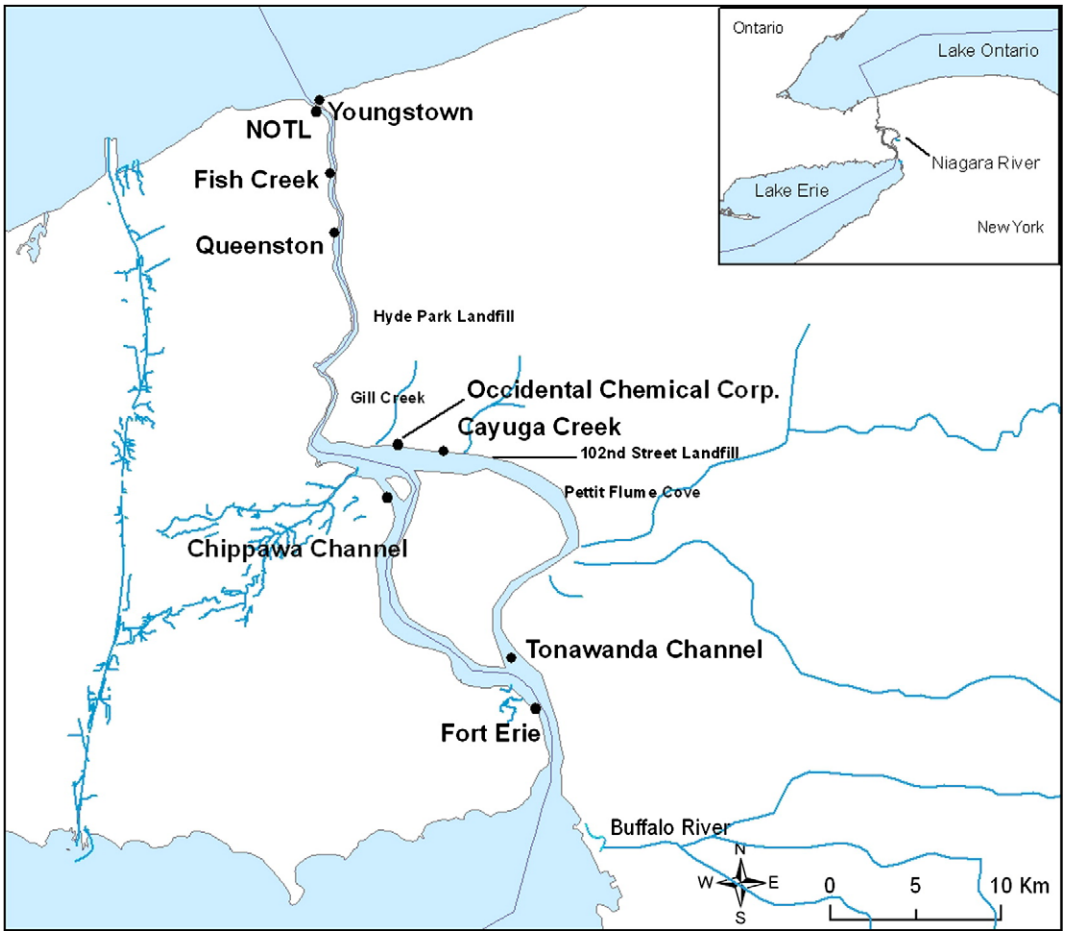

Fig. 1. Map of the Niagara River and mussel sampling sites.

Table 1
Quagga mussel sampling stations, Niagara River 2003.

Station description	1995		Revised - 2003		Sample depth (m)	Collection area (m^2)	Distance from shore (m)	Mussel size (mm)
	Latitude	Longitude	Latitude	Longitude				
Canadian sites								
Fort Erie (downstream of Buffalo River - midchannel)	42° 53.08′	78° 54.91′	42° 53.083′	78° 54.909′	3.1	20	1000	20–25
Chippawa Channel (50 m downstream of Ushers Creek)	43° 03.29′	79° 01.38′	43° 03.29′	79° 01.380′	5.4	40	90	15–20
Queenston (Canadian side of river - south of Queenston Heights)	43° 11.01′	79° 03.37′	43° 11.010′	79° 03.370′	8	60	80	10–15
Downstream of Fish Creek (site located on the Canadian side)	43° 12.61′	79° 03.51′	43° 12.61′	79° 03.510′	7	95	50	10–15
Niagara on the Lake	43° 15.94′	79° 04.04′	43° 15.9826′	79° 04.0458′	10	75	380 off U.S. shore	15–20
American sites								
Tonawanda Channel (downstream of South Grand Island Bridge)	42° 57.85′	78° 55.41′	43° 0.522′	78° 55.181′	7.7	100	250 off U.S. shore	10–15
Downstream of mouth of Cayuga Creek	43° 04.41′	78° 58.85′	43° 04.290′	78° 58.848′	4.8	60	150 off U.S. shore	15–20
Occidental Sewer 003 (Occidental Chemical Corp. facility)	43° 04.60′	79° 00.49′	43° 04.545′	79° 00.599′	8	35	20 off U.S. shore	15–20
Youngstown (U.S. side of river)	43° 15.32′	79° 03.13′	43° 14.959′	79° 03.075′	5.6	40	2 off U.S. shore	10–15

suspected of being significant non-point sources of persistent organic contaminants (e.g., the Pettit Flume, Gratwick Riverside Park, 102nd Street, Love Canal, etc.) (Allan et al., 1983). The Occidental 003 site was in proximity to the Occidental Chemical Corporation outfalls and nine associated landfills. There were also four stations in the lower Niagara River: These lower river stations included one on the U.S. side, and three on the Canadian side, of which one was at Niagara-on-the-Lake at the mouth of the river where it enters Lake Ontario. The lower river stations were located downstream of known significant sources of contaminants (e.g., Hyde Park waste site) and were expected to reflect the integration and mixing of contaminants from all sources in the upper river (El-Shaarawi et al., 1985).

Quagga mussel collections and sample processing

Divers collected three replicate samples of mussels from each station with each replicate comprising a composite sample ranging from 125 to 590 mussels. Mussels were placed in hexane rinsed stainless steel pans containing river water for inspection and species identification. Once sufficient numbers of mussels were collected from a site mussels were placed in Whirl-Pak bags and frozen on dry ice in the field and kept frozen (-20 C) until sample processing. Mussels collected from all stations ranged from 10 to 20 mm in length with the exception of the Fort Erie site where mussels were slightly larger at 20–25 mm.

Prior to contaminant analysis, mussels were freeze dried for 24 h and then shucked. Whole mussel frozen weight, whole mussel freeze dried weight, freeze dried tissue weight and shell weight for each composite sample were recorded and subsequently used to calculate percentage of wet and dry weight after removing the shells. Samples were submitted for analysis of trace metals, organochlorine pesticides, total PCBs, and chlorinated benzenes.

Contaminant analysis

Trace metals (i.e., cadmium (Cd), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn)) were analysed in mussel tissue using Atomic Absorption Spectrophotometry (Varian Spectraa-400). For each sample, 2–3 g of tissue was digested overnight at 130 °C with 7 mL of concentrated nitric acid (reagent grade), 1.5 mL percloric acid and 100 μL hydrogen peroxide . Digested samples were diluted to 25 mL with distilled water passed though a reverse osmosis (RO) system. Complete laboratory details are provided in OMOE (2004). Mercury was analysed by cold vapour atomic absorption spectrophotometry (OMOE 2009). For the mercury analyses, tissue samples (0.2–0.35 g) were digested using a sulphuric: nitric acid mixture (4:1) for 16 h at 215–235 °C and then diluted to 25 mL with distilled water prior to analysis.

For all analyses each sample run (generally 12–25 samples) was compared against a prepared standard and included the determination of low level detection limits, method blanks and recovery checks using spikes. An independent control standard was used to monitor accuracy and stability, duplicate samples were used to evaluate within run precision and calibration standards were used for a drift check. Details of QA/QC evaluations are provided in the method manuals listed above. The method detection limits were as follows: Hg (0.01 μg/g); Cd (0.005 μg/g); Cu (0.01 μg/g); Pb (0.02 μg/g); Mn (0.05 μg/g); Ni (0.02 μg/g); Zn (0.1 μg/g). All data were reported as dry weight.

Samples were analyzed for total PCBs, chlorinated benzenes (CBs) and organochlorine pesticides (OC) using standard methods (i.e., OMOE method E3136; OMOE 2008). Samples were weighed, spiked with decachlorobiphenyl and 1,3,5-tribromobenzene, and acid digested with concentrated HCl (reagent grade) and solvent extracted with a mixture of 25% methylene chloride in hexane solution. Extracts were reduced in volume and cleaned using dry packed Florisil® columns. Samples were collected in two fractions.

Fraction 1 was analyzed for Total-PCB on an Agilent 6890 GC and Ni^{63} electron capture detector (ECD) equipped with DB-17 GC column (30 m × 0.53 mm i.d. × 0.1 μm film thickness, J&W Scientific, Folsom, CA, USA). Quantification of total PCBs was determined using a 4:1 mixture of Aroclors 1254:1260. The chromatography was detuned to resemble classical packed column chromatography for classical Aroclor matching analysis. The 23 largest "Aroclor" peaks obtained in the pseudo packed column technique were used for quantification. Positive identification required a minimum of 11 peaks. The areas of the peaks detected were summed and compared to the summed areas of the 4:1 mixture of Aroclor 1254:1260. The method detection limit (MDL) was 8 ng/g (dry wt). Congener specific PCB analysis was not used in this study since data from this method were unreliable in 1995 and data between the two surveys would not have been comparable.

The OC pesticides were analyzed using fraction 2 (OMOE method 3136) using an HP 6890 GC and Ni^{63} electron capture detector (ECD) equipped with Rtx-CLPesticides-I and Rtx-CLPesticdes-2 (20 m × 0.18 mm i.d. × 0.14 μm film thickness, Restek Corporation, Bellefonte, PA, USA). The method detection limit (MDL) ranged from 0.4 to 2 ng/g (dry wt.) per congener and 19 ng/g (dry wt.) for total

toxaphene. Quantification for total PCBs and OCs using a 5-point calibration curve was verified by single point continuing calibration. Method blanks and matrix spikes were processed with each set of 20–30 samples. Laboratory inter-calibration studies (the Northern Contaminants Program (NCP) and QUASIMEME) were used to monitor method performance.

For each composite sample, the lipid content (%lipid) was determined gravimetrically. A 20 mL aliquot of the final extract was added to a preweighed 50 mL beaker and air dried in a fume hood. The weight of the residue was calculated and used to calculate the percentage of lipid.

Data analysis

The Kolmogorov–Smirnov test in SigmaStat™ was used to test for normality and the variances were also tested for homogeneity. Metal tissue concentrations were compared among stations using one-way analysis of variance (ANOVA). If significant differences were found, we used the Holm–Sidak test for pair-wise multiple comparisons to determine which stations differed. Variances associated with the Mn and Pb data were heterogeneous, so a Kruskal–Wallis one way analysis of variance on ranks was used for those metals, followed by Dunn's multiple range test.

Multifactor analysis of variance was used to compare tissue metal concentrations among the nine stations and between sampling years (1995 vs. 2003) using rank-transformed data since tests for normality and/or homogeneity of variance indicated significance several times (Conover and Iman, 1981).

To assess the effect of year and station on total PCB concentrations, a two-way analysis of covariance (ANCOVA) was used with percentage of lipid as the covariate (STATISTICA™). Total PCB tissue concentrations were compared among stations using one-way analysis of covariance (ANCOVA). If significant differences were found, we used the Tukey HSD test for multiple comparisons to determine which stations differed. Between station and year statistical comparisons for other persistent organic compounds were not attempted due to the high frequency of non-detect data.

Results

Metals

In 1995 there were no significant differences in quagga mussel tissue concentrations among stations ($P>0.05$) for Pb, Zn, Hg and Ni although significantly higher concentrations of Cu, Cd and Mn were present at some stations (Richman and Somers, 2005). In contrast, in 2003 we found significant differences in metal concentrations (with the exception of Mn), in quagga mussel tissue among several sampling locations (Table 2; Figs. 2 and 3). These differences suggested that the bioavailability of metals varied spatially which could be an indication of a possible local source (e.g., Cd at Fort Erie, Ni at Chippawa Channel, Hg and Zn at the Occidental site, Pb at Youngstown). However, stations with elevated concentrations of metals were not consistent between 1995 and 2003 (with the exception of Cd in mussels collected from Fort Erie).

Metal concentrations in mussel tissue were similar between years at some stations although the interaction term for station and year was statistically significant (Cd, Ni $P<0.03$; Mn, Cu $P<0.001$), requiring a closer look at the data (Figs. 2 and 3). Quagga mussel tissue concentrations for most metals were larger in 1995 than in 2003, although these differences were not always significant. The two-way ANOVA on ranks found that between-year differences were significant ($P<0.001$) for Hg, but not for Pb and Zn. Between-station differences were also significant for most metals ($P<0.001$) with the exception of Pb and Hg.

Concentrations of Cd, Zn, Pb and Mn were generally larger in 1995 compared to concentrations in 2003 at some stations (Figs. 2a and 3a–c). At stations where there were statistically significant differences between years, for example Cd (Queenston $t=2.4$, $P<0.05$ and Fish Creek $t=4.6$, $P<0.001$) and Mn (Queenston, $t=4.9$, $P<0.001$, Fish Creek, $t=4.8$, $P<0.001$ and Fort Erie $t=3.5$, $P<0.01$), concentrations were also consistently greater in 1995 than 2003. However, within-station variability for Pb and Zn was greater in 1995, suggesting little change in concentrations overall for these two metals between sampling years.

Table 2
Mean (± standard error) metal tissue concentrations (μg/g dry wt.) in three composite samples of quagga mussels collected from the Niagara River, 2003. Significant differences in concentration between stations are designated by letters (Holm–Sidak test and Dunn's multiple range test: $P<0.05$).

Station description	Cadmium		Copper		Mercury		Manganese		Nickel		Lead		Zinc	
	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
Fort Erie upstream of Buffalo R - Mid Channel	6.9 ^{A}	0.35	16 ^{B}	1.5	ND		64	2.0	11 ^{C}	0.33	1.3 ^{B}	0.17	57 ^{D}	0.88
Chipawa channel - 50 m downstream of Ushers Creek	3.1 ^{B}	0.13	27 ^{AB}	1.5	0.03 ^{B}	0.003	130	10	16 ^{A}	0.67	2.1 ^{B}	0.29	64 ^{CD}	0.88
Tonawanda Channel upstream of S Grand Is. Bridge[a]	2.5 ^{BC}	0.10	15 ^{B}	0.5	0.03 ^{B}	0.01	120	30	11 ^{C}	0.51	2.1 ^{B}	0.20	63 ^{CD}	0.00
Downstream of the mouth of Cayuga Creek	1.4 ^{C}	0.12	29 ^{AB}	5.4	ND[b]		260	87	11 ^{C}	1.0	2.9 ^{B}	0.59	84 ^{B}	3.8
Occidental Sewer 003	1.7 ^{C}	0.12	20 ^{B}	0.3	0.06 ^{A}	0.01	150	13	12 ^{BC}	0.58	3.6 ^{B}	0.20	102 ^{A}	4.4
Queenston: S of Queenston Heights CA Side	2.5 ^{BC}	0.09	30 ^{AB}	1.8	0.04 ^{AB}	0.01	130	22	13 ^{BC}	0.67	2.6 ^{B}	0.12	68 ^{CD}	5.3
Downstream of Fish Creek: CA Side	2.1 ^{BC}	0.30	27 ^{AB}	1.2	0.03 ^{B}	0.003	90	1.9	10 ^{C}	0.75	2.1 ^{B}	0.15	58 ^{D}	5.1
Youngstown: US Side	2.1 ^{BC}	0.32	60 ^{A}	19	0.05 ^{AB}	0.003	210	51	15 ^{AB}	0.00	6.2 ^{A}	0.96	76 ^{BC}	0.88
Niagara-On-The-Lake	3.0 ^{B}	0.29	14 ^{B}	0.7	0.04 ^{AB}	0.003	200	55	11 ^{BC}	1.0	1.8 ^{B}	0.13	64 ^{CD}	1.5

Historical data	Cadmium	Copper	Mercury	Manganese	Nickel	Lead	Zinc
	Range	Range	Range	Range	Range	Range	Range
Lake Ontario (zebra mussels - 1991)[c]	0.6	6	0.07	105	7	1.8	124
Lake Ontario (zebra/quagga mussels - 1992)[d]	3–6.4	5–15	0.08–0.35	29–102	7–13	1.9–5.9	71–236
Lake Erie (quagga mussels - 1997)[e]	2.5–4.4	21–61	0.15–0.22	50–109	8–15	2.5–4.8	63–92
Lake Ontario (quagga mussels - 1997)[e]	8.5	25	0.11	119	12	2.5	134
Lake Erie (zebra/quagga mussels - 2004–2005)[f]	3–5	9–23	0.03–0.04		11–18	3–4	56–84
Lake Ontario (zebra/quagga mussels - 2004–2005)[f]	1–2	24–41	0.05–0.06		11–18	3–4	56–84

[a] $n=2$.
[b] Not detected.
[c] Secor et al., 1993.
[d] Mills et al., 1993.
[e] Rutzke et al., 2000.
[f] Kimbrough et al., 2008.

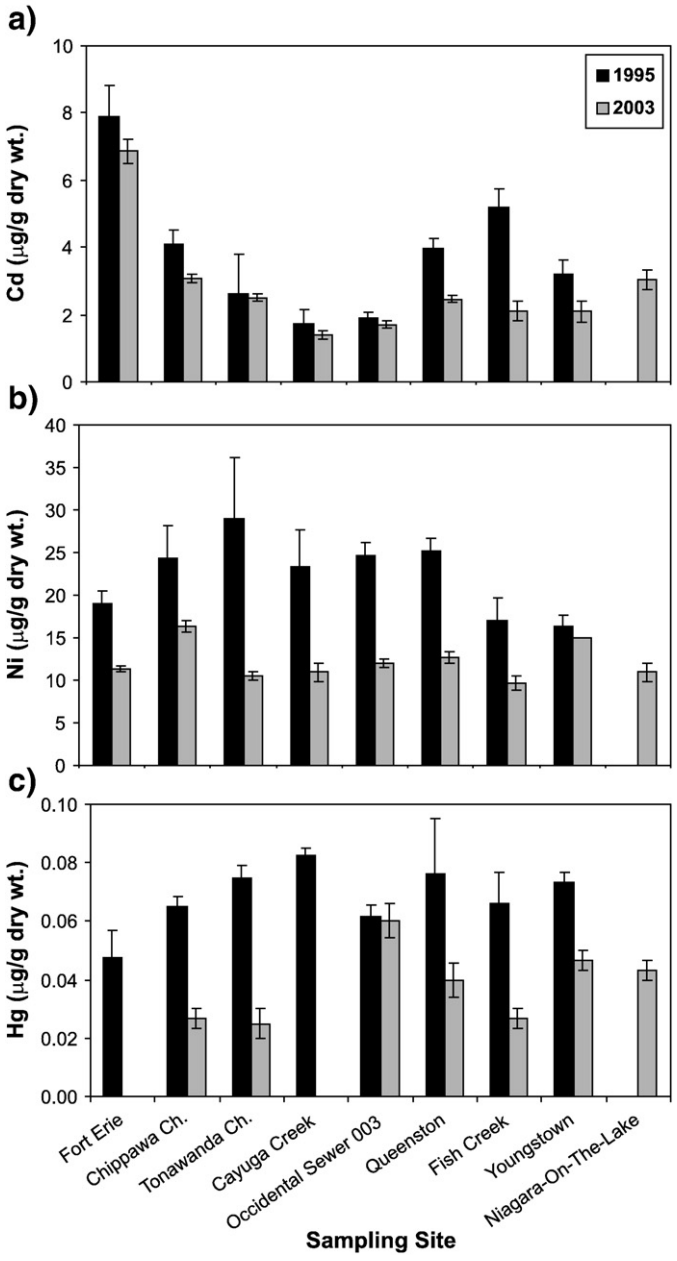

Fig. 2. Mean (± SE) of (a) cadmium, (b) nickel, and (c) mercury concentrations in quagga mussels collected from the Niagara River, 1995 and 2003.

Tissue concentrations of Ni and Hg were significantly larger in 1995 than 2003 at most stations ($P<0.05$; Fig. 2b and c). In contrast, Cu concentrations were similar between years at some stations (e.g., Tonawanda Channel and Occidental 003), but at half of these stations concentrations tended to be larger in 2003 than 1995 (Fig. 3d).

Organics

In 1995, DDT, p'p-DDE and 2,3,6-trichlorotoluene and 2,4,5-trichlorotoluene were not detected in quagga mussels. In contrast, in 2003, DDT and p'p-DDE were found at trace concentrations at most stations (i.e., <6 ng/g dry wt.; Table 3) and 2,3,6-trichlorotoluene and 2,4,5-trichlorotoluene were present at trace concentrations in mussels from all stations, suggesting no specific source areas for these compounds within the river.

The highest concentrations of total PCBs, hexachlorobutadiene (HCBD), hexachlorobenzene (HCB), pentachlorobenzene (pentaCB)

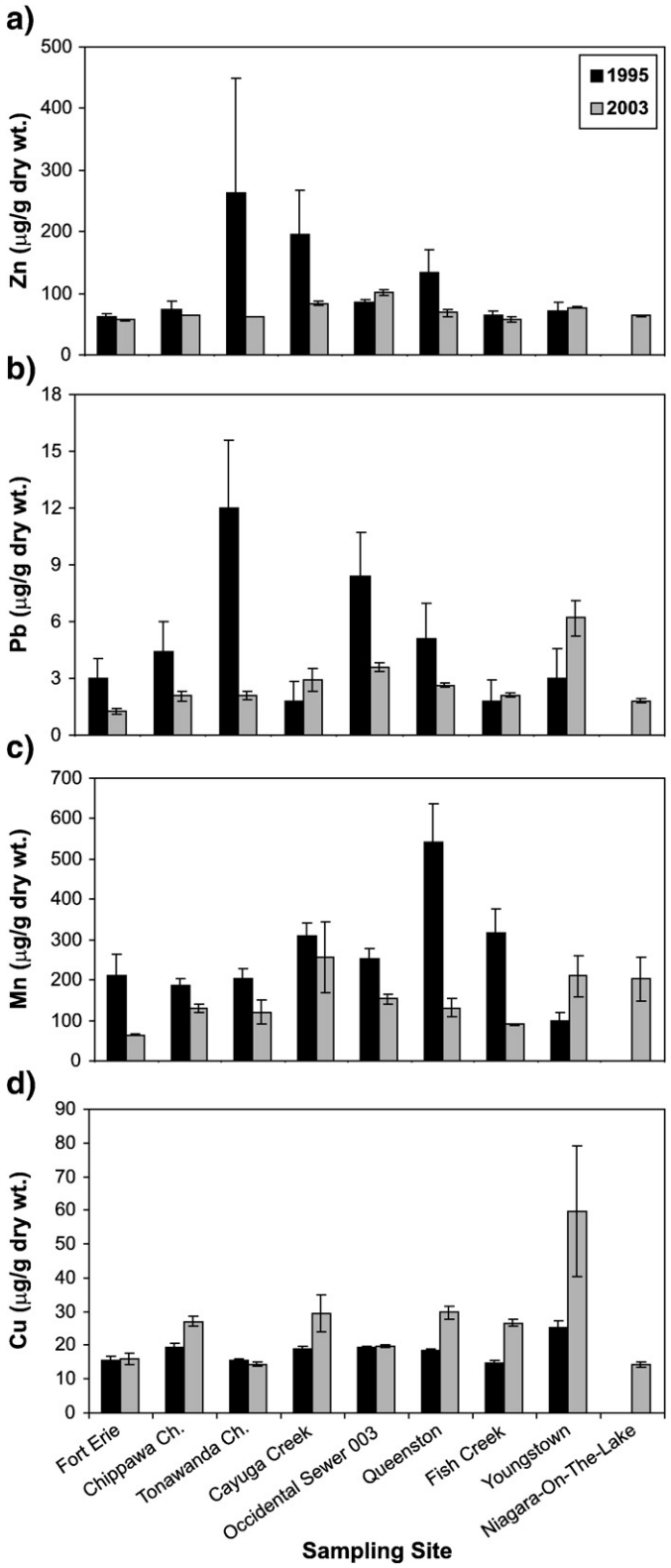

Fig. 3. Mean (± SE) of (a) zinc, (b) lead, (c) manganese, and (d) copper concentrations in quagga mussels collected from the Niagara River, 1995 and 2003.

and mirex were found in mussels downstream of the Occidental 003 sewer on the American side of the river in both 1995 (Richman and Somers, 2005) and 2003 (Table 3). In mussels collected from other stations upstream in the Tonawanda Channel, on the Canadian side of the river and in the lower Niagara River, these parameters (with

the exception of PCBs) were either not detected or only found at trace levels. This pattern of contamination, consistent in both surveys, was suggestive of a local source(s) of PCBs, HCBD, HCB, pentaCB and mirex in the vicinity of the Occidental 003 sampling site. There was only sufficient data for total PCBs to assess between-station differences. Just like the 1995 data, there were significant differences in total PCB tissue concentrations between stations ($F=4.6$; $P<0.0004$). These differences suggested sources of PCBs on the American side of the upper Niagara River (Fig. 4) because Grand Island, located in the upper Niagara, precludes any mixing of river water between the American and Canadian channels until the water passes over the falls.

For almost all organic compounds analysed in this study, tissue concentrations in mussels collected in 1995 were higher than in 2003. Hexachlorocyclohexane (in particular α-HCH and γ-HCH), 1,2,3-trichlorobenzene, and 1,2,4-trichlorobenzene were present at detectable concentrations in mussels collected from all stations in 1995 (Richman and Somers, 2005). Concentrations of α-HCH and γ-HCH ranged from 31 to 48 ng/g and 15 to 34 ng/g, respectively, and 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene ranged from 76 to 160 ng/g and 88 to 200 ng/g respectively. Concentrations were not significantly different among stations suggesting that these values represented background conditions for the Niagara River rather than individual point sources (much like p'p-DDE and 2,3,6 and 2,4,5-trichlorotoluene). However, α-HCH and γ-HCH were not detected in 2003 and 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene were only found in mussels collected from the Occidental 003 site and the Queenston site farther downstream at concentrations that were lower than those measured anywhere in the river in 1995 (Table 3). Similarly, the highest concentrations of octachlorostyrene (OCS) in 1995 were found in quagga mussels collected from the Tonawanda Channel (9–23 ng/g), whereas OCS was not detected in any mussels in 2003. Total PCB concentrations in 1995 were also significantly greater than concentrations in 2003 ($F=27.2$; $P<0.0001$; Fig. 4). Although the decrease in total PCB tissue concentrations between 1995 and 2003 differed among the stations, the interaction term in the two-way ANCOVA was also significant ($F=3.2$; $P<0.006$). Results from the ANCOVA showed that the covariate: % lipid, did not account for a significant amount of the variation ($F=0.31$; $P=0.58$; $r^2=0.007$).

Due to the high variability of the data for both 1995 and 2003 the between year differences in tissue concentrations of contaminants in mussels collected downstream of the Occidental 003 sewer (HCB, HCBD and PentaCB) were not statistically significant, but a trend towards lower concentrations in 2003 was apparent (Fig. 5). Mirex was an exception to this downward trend. Mirex was only detected at the Occidental 003 site in 1995 and was present in only two of the six replicates (e.g., 140 and 90 ng/g dry wt.). In 2003 the pattern was similar in that mirex was not detected upstream of the Occidental site indicating a source(s) within this area. However, mirex concentrations were not lower in 2003 when compared with the 1995 data unlike the other compounds (Table 3). Furthermore, mirex was detected in mussel samples collected from all stations in the lower Niagara River.

Discussion

Metals

Investigations of toxic chemicals (persistent organic compounds and metals) entering the Niagara River in 1981 identified 38 significant municipal and industrial point sources, and 61 non-point sources (hazardous waste sites) with significant potential for contributing contamination to the River (NTRC 1981). Accordingly, sources of metals assessed in this study have been previously identified. Additionally, as part of the Upstream/Downstream Niagara River Monitoring Program, Environment Canada (EC) reports mean annual concentrations and loads of metal and organic contaminants in water and suspended solids (organics only) for stations at Fort Erie and Niagara-on-the-Lake (NOTL). A comparison of annual mean metal loads at Fort Erie and NOTL for the metals in this study also suggested the contribution of Niagara River sources of metals to the NOTL loads (Williams et al., 2001; Hill and Klawunn, 2009). In both 1995 and 2003 there were statistically significant differences in tissue concentrations for some metals among stations thereby suggesting varying bioavailability and hence local sources within the River. However, with the exception of Cd at Fort Erie, stations with elevated concentrations of metals were not consistent between 1995 and 2003 making conclusions about potential sources difficult.

Concentrations of most metals in mussel tissue were generally larger in 1995 compared to concentrations in 2003. However, the data were not consistent for all stations, and for some metals the variability in tissue concentrations within a station was high. Water quality data were available for Cd, Cu, Ni, Pb and Zn to compare mean annual concentrations and loadings between 1995–1996 and 2003–2004 (Williams et al., 2001; Hill and Klawunn, 2009). In contrast to some mussel tissue results, the water quality data suggested little difference in mean annual metal concentrations between these two periods for Cu, Ni, Pb and Zn, although Cd concentrations and loadings were lower in 2003–2004 relative to 1995–1996 (Kuntz, 1997; Williams et al., 2001; Hill and Klawunn, 2009). The general absence of a significant difference in water-borne metal concentrations may explain the inconsistent results in some mussel tissue concentrations among

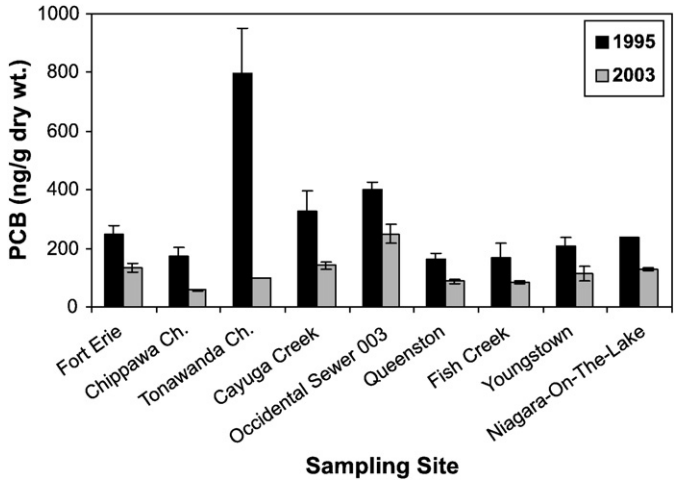

Fig. 4. Mean total PCB concentrations (± SE) in quagga mussels collected from the Niagara River, 1995 and 2003.

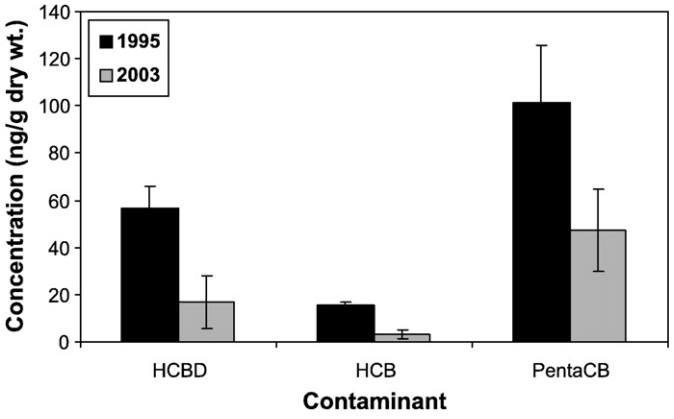

Fig. 5. Tissue concentrations (mean ± SE) of organic contaminants in quagga mussels collected from the Occidental 003 sewer site, Niagara River, 1995 and 2003.

Table 3
Mean (± standard e rror) organic contaminant tissue concentrations (ng/g dry wt.) in three composite samples of quagga mussels collected from the Niagara River, 2003. Significant differences in total PCB concentrations between stations are designated by letters (Tukey HSD test $P<0.03$).

Station description	LIPID (%)		Total PCB[a]		p'p-DDE		DDT		Mirex	
	Mean	SE	Mean	SE	Mean[b]	SE	Mean	SE	Mean	SE
Fort Erie upstream of Buffalo R - Mid Channel	9	0.6	130 ^{C}	15	3	0	3.0	0	ND	
Chipawa channel - 50 m downstream of Ushers Creek	7	0.6	57 ^{BC}	4	ND[c] - 2		ND		ND	
Tonawanda Channel upstream of S Grand Is. Bridge[d]	8		100 ^{BC}		4		4.0		ND	
Downstream of the mouth of Cayuga Creek	7	0.7	140 ^{B}	12	5	0.3	5	0.3	ND	
Occidental Sewer 003	8	0.6	250 ^{A}	31	ND - 30		ND - 30		140	90.0
Queenston: S of Queenston Heights CA Side	6	0.4	87 ^{BC}	6	ND - 5		ND - 5		10	0.9
Downstream of Fish Creek: CA Side	5	0.4	83 ^{BC}	4	ND - 2		ND		10	0.6
Youngstown: US Side	7	0.3	120 ^{BC}	25	ND - 3		ND - 3		ND - 10	
Niagara-On-The-Lake	8	1.2	130 ^{BC}	6	ND - 3		ND - 3		11	1

[a] PCB resembled mixture of aroclor 1254 and 1260.
[b] If at least 1 value was below the detection limit the range is provided.
[c] Non detect.
[d] $n=1$.

stations. The changes in metal concentrations in quagga mussels between 1995 and 2003, and differences among the stations may be within the range of the variability to be expected in environmental data. Similar to the Niagara River mussel data, tissue results collected through the NOAA National Status and Trends Mussel Watch Program for Lake Erie and Lake Ontario did not show a significant change in concentrations for any of the metals between 1994 and 2004 (Kimbrough et al., 2008). Metal contaminant concentrations in Niagara River mussels were within the same range as the NOAA data and concentrations found in quagga mussels from industrialized areas in Lake Erie and Lake Ontario in the 1990s (Table 3) (Mills et al., 1993; Secor et al., 1993; Rutzke et al., 2000).

Organics

The absence of DDT and DDE and 2,3,6-trichlorotoluene and 2,4,5-trichlorotoluene in mussels collected from the Niagara River in 1995 was likely affected by the detection limits since these compounds were only present at trace concentrations in 2003. The presence of p, p'-DDE and DDT in mussels in 2003 at most stations was consistent with the historic use of DDT in the Lake Erie and Niagara River watersheds and suggested that these compounds were ubiquitous on both sides of the River at low concentrations. Water quality data identify both Lake Erie and the Niagara River as sources of DDT and metabolites and although concentrations and mean annual loadings have significantly decreased since 1986/1987, concentrations still exceed the strictest agency (United States and/or Canadian) water quality criteria for DDT and metabolites at Fort Erie and NOTL (Williams et al., 2001; Hill and Klawunn, 2009). The quagga mussel data was also consistent with recent and historical juvenile fish data collected by MOE and New York State (Suns et al., 1993; Niagara River Secretariat 2007) and the MOE caged mussel data: p'p-DDE has been detected sporadically, generally at trace concentrations throughout the Niagara River in all the caged mussel surveys since 1983 (Richman, 2006). DDT concentrations in zebra mussels collected from the western basin of Lake Erie and from Lake Ontario for the NOAA Mussel Watch Program ranged from 2 to 26 ng/g dry wt. With the exception of one station in Lake Ontario there were no reported changes in concentrations through time. The Niagara River quagga mussels fall within the low range of the NOAA mussels.

Based on the history of waste disposal and industrial activity along the Niagara River, and water quality data presented by Williams et al. (2001) and Hill and Klawunn (2009), sources of HCBD, HCB, pentaCB and mirex are predominately within the Niagara River not Lake Erie (Elder et al., 1981; Allan et al., 1983; Kuntz and Warry, 1983; Jaffe and Hites, 1984). Hazardous waste sites and industrial facilities near the river in the vicinity of the Occidental 003 site were also known to contain these compounds (Interagency Task Force on Hazardous Waste, 1979). The presence of these compounds in quagga mussels collected from this site and the absence of the compounds in mussels collected from sites upstream on the American side and on the Canadian side suggested that these contaminants were entering the river likely from these local sources and were bioavailable.

In the past, caged mussels have been useful in identifying site specific sources of PCBs, HCBD, HCB, pentaCB and mirex in the river, and in particular in the vicinity of the quagga mussel sampling area (i.e., the Occidental Chemical Corporation and associated waste sites) (Richman, 2006). Concentrations of these compounds in the caged mussels deployed at the 003 site ranged from 2 to 14 times greater than the quagga mussels likely because of the proximity of the caged mussels to this point source. The comparison of quagga mussel tissue concentrations measured in 1995 at the 003 site with those reported in 2003 for these compounds suggested a downward trend. This trend may be linked to the remedial activities in the late 1990s at the Occidental Chemical Corporation facility, associated waste sites and waterfront (US EPA/NYSDEC 2004). EC has reported that mean annual concentrations of HCB, HCBD and pentaCB in water and suspended solids and loadings for these compounds in 2003–2004 were also lower when compared with the 1995–1996 data from NOTL (Kuntz, 1997; Williams et al., 2001; Hill and Klawunn, 2009). These water quality improvements may be reflecting the remedial efforts at Occidental as well as the remediation of the 102nd Street hazardous waste site, Gratwick-Riverside Park, the Pettit Flume cove and other industrial, municipal and non-point sources of these compounds. Notwithstanding the downward trend in contaminant concentrations, this area is still an ongoing source of contaminants to the river noted by the elevated tissue contaminant concentrations. For example, total PCBs (mean 250 ng/g) were significantly greater than concentrations at other stations in this study and greater than concentrations reported in the NOAA Mussel Watch program for the eastern basin of Lake Erie and Lake Ontario (range 15–154 ng/g). As well, this area continues to be a source of mirex. A comparison of the data between years showed no change in tissue concentrations in contrast to the other parameters associated with this area. EC water quality data were also consistent with the quagga mussel data such that the concentrations of mirex at NOTL were similar in 1995 and 2003 at 0.004 and 0.002 ng/L, respectively. The NOAA Mussel Watch Program also identified the Niagara River as a source of mirex (Robertson and Laurenstein, 1998).

For some compounds there was evidence of consistent changes in mussel tissue concentrations across all stations between 1995 and 2003. The absence of α-HCH, γ-HCH, OCS in quagga mussels collected in 2003, the low and/or infrequent detection of 1,2,3-trichlorobenzene and

HCBD		1,2,4,-TriCB		1,2,4,5-TetraCB		1,2,3-TriCB	HexaCB	PentaCB		2,3,6-Tri chlorotoluene		2,4,5-Tri chlorotoluene		2,6A-Tri chlorotoluene
Mean	SE	Mean	SE	Mean	SE	Mean	Mean	Mean	SE	Mean	SE	Mean	SE	Mean
ND		ND		ND		ND	ND	ND - 4		9	0.7	7	0.9	ND
ND		ND		ND		ND	ND	4	0.3	9	2	8	0.3	ND
ND		ND		ND		ND	ND	ND		ND		ND		ND
ND		ND		ND		ND	ND	ND - 2		9	0.6	7	0.9	ND - 2
17	11	10	0.9	7	3	ND - 5	ND - 6	47	17	9	0.6	7	0.6	ND - 3
ND - 10		18	10	ND - 12		ND - 4	ND - 2	4	0.9	9	0.7	8	0.3	ND
ND		ND - 5		ND		ND - 3	ND	3	0.6	8	1	9	1	ND - 2
ND		ND		ND		ND	ND	3	0.3	8	1	6	0.7	ND
ND		ND		ND		ND	ND	3	0.3	9	2	8	0.6	ND

1,2,4-trichlorobenzene, and the consistent decrease in total PCB concentrations at all stations may be reflecting the overall changes in concentrations for these compounds in the Niagara River and Lake Erie. A review of the EC Upstream/Downstream water quality data for 1995–1996 and 2003–2004 indicated that mean water concentrations and annual mean loadings of α-HCH, γ-HCH and OCS were lower in 2003–2004 at the Fort Erie and NOTL sampling stations. For example, the mean concentration of α-HCH at NOTL was 0.669 ng/L in 1995 vs. 0.139 ng/L in 2003; for 1,2,4-trichlorobenzene the mean concentration at NOTL in 1995 was 0.648 ng/L and in 2003 it was 0.249 ng/L; and for OCS in 1995-1996 the mean suspended solids equivalent water concentration was 0.007 ng/L whereas it was 0.0015 ng/L in 2003–2004 (Kuntz, 1997; Williams et al., 2001; Hill and Klawunn, 2009). The main source of α-HCH and γ-HCH is believed to be Lake Erie whereas there are numerous sources of OCS and 1,2,3- and 1,2,4-trichlorobenze within the Niagara River (Williams et al., 2001).

PCBs are known to originate from both Lake Erie as well as sites within the Niagara River (Williams et al., 2001; Samara et al., 2006). Although concentrations of total PCBs still exceed the strictest agency water quality criteria (NYSDEC: 0.001 ng/L) at both Fort Erie and NOTL, EC has reported a decrease in total PCB loadings from Lake Erie and within the Niagara River which was consistent with the lower total PCB concentrations found in quagga mussels in 2003 when compared with 1995 (Williams et al., 2001; Hill and Klawunn, 2009). Caged mussel data has identified site specific sources of total PCBs on the U.S. side (e.g., Occidental Chemical Corp., Pettit Flume, Two Mile Creek), as well as decreases in total PCB concentrations through time at sites that have been remediated (Richman, 2006). For example, major clean ups of PCB contaminated sediment in two locations in Gill Creek were completed in 1992 and 1998, effectively removing a significant source of PCBs to the Niagara River (US EPA/NYSDEC, 2004). The quagga mussel trend data were also consistent with PCB trends reported for bottom sediment, suspended sediment and sport fish (Marvin et al., 2003, 2007; Karst-Riddoch et al., 2008). Decreases in concentrations in all cases were attributed to the reduced loadings reported by EC.

Conclusions

Metal concentrations in quagga mussels collected from the Niagara River were similar to concentrations measured in mussels collected from Lake Erie and Lake Ontario (Mills et al., 1993; Secor et al., 1993; Rutzke et al., 2000; Kimbrough et al., 2008). In general, the concentrations of most metals (e.g., Cd, Mn, Ni and Hg) in quagga mussels in 2003 were lower than concentrations measured in 1995. However, changes in tissue concentrations over time were not always statistically significant or consistent at all stations which may reflect previous observations of no change in annual mean metal concentrations in water collected from Fort Erie and NOTL. Accordingly, trends in metal tissue concentrations in quagga mussels were inconclusive.

The concentrations of most organic compounds (e.g., total PCBs, HCB, HCBD, OCS, pentaCB, 1,2,3- and 1,2,4-trichlorobenzene, α-HCH and γ-HCH) in quagga mussels in 2003 were lower than concentrations measured in 1995. This decrease in contaminant levels could reflect reduced contaminant availability due to a decrease in waterborne concentrations suggesting that environmental conditions in the Niagara River are improving. These results were consistent with long-term monitoring trends for sediment in Lake Ontario (which receives some of its contaminant load from the Niagara River), as well as sport fish and juvenile fish collected from the Niagara River (Suns et al., 1993; Marvin et al., 2003, 2007; The Niagara River Secretariat, 2007; Karst-Riddoch et al., 2008). However, our results are based on only two sets of observations so we recognize that additional years of data are required to confirm these general conclusions. Although the 2007 Niagara River Toxics Management Plan Progress Report (The Niagara River Secretariat, 2007) attributed statistically significant reductions in concentrations and loadings of many "priority toxics" to the effectiveness of point and non-point source remediation along the Niagara River, we propose that trend results like those presented in this study, as well as data from ongoing government biomonitoring programs using caged mussels, juvenile fish and sport fish will assist in evaluating environmental improvements in the Niagara River.

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