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The Niagara River mussel biomonitoring program (*Elliptio complanata*): 1983–2009

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ABSTRACT

The Ontario Ministry of the Environment has monitored the concentrations of contaminants in mussel (*Elliptio complanata*) tissue and bottom sediments at sites in the Niagara River since 1983 to describe the general contamination of the river and identify contaminant sources. More recently, the data have been used to document the effectiveness of remedial actions implemented at identified sources along the river. Results from Canadian sites and five U.S. sites at which remedial actions have been implemented [Bloody Run Creek (Hyde Park Hazardous Waste Site); Gill Creek; Occidental Chemical Company (Buffalo Avenue Plant); 102nd Street Hazardous Waste Site; and Pettit Flume Cove] are discussed. p,p′-DDE, PCBs and dioxins were the only contaminants detected at Canadian sites at concentrations probably representative of background. Results from the five sites showed the effectiveness of implemented remedial actions in reducing the flow of contaminants to the river ranged between very effective (Gill Creek: PCBs; and 102nd Street, CBs) to no effect (Bloody Run Creek: PCBs, CBs, and dioxins). Remedial actions at the Pettit Flume Cove (for dioxins/furans) initially appeared to be effective, but were subsequently shown to have missed a source to the cove. The effectiveness of the actions taken at these sites in improving contaminant conditions in the Niagara River since the 1980s as demonstrated by our mussel and sediment results is corroborated by the data from other fish and water quality monitoring programs. Additional remedial efforts are still required at these sites and other known sources of contaminants to the river.

Introduction

The Niagara River flows 60 km (37 mi) connecting Lake Erie and Lake Ontario. Numerous water quality problems have been identified over the years since the first investigation of the river by the International Joint Commission (IJC) in 1912 as part of its larger study of the pollution of the Great Lakes boundary waters between Canada and the United States (IJC, 1918). Issues have included excessive concentrations of bacteria, oil, chloride and mercury to name a few. The most recent concern is the contamination of the river by a variety of toxic chemicals, many of which are both persistent and bioaccumulative. Examples include chlorobenzenes (CBs), organochlorine pesticides, polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), octachlorostyrene (OCS), Mirex and dioxins and furans. Most were entering the river via municipal and industrial outfalls (e.g., steel and petrochemical and chemical manufacturing industries), hazardous waste landfills and other non-point sources (e.g., surface run-off). Some, however, were also entering from Lake Erie and areas upstream. The words "Love Canal", perhaps, best highlight the seriousness of the issue.

Between 1981 and 1983, the four environmental agencies in Canada and the United States [Environment Canada (EC), Ontario Ministry of the Environment (OMOE), New York State Department of Environmental Conservation (NYSDEC), and the United States Environmental Protection Agency Region II (USEPA II)] conducted a major study to identify the specific sources of toxic chemicals to the river and document the environmental conditions in river water, sediment and biota (NRTC, 1984). The study was initiated because of the findings of earlier reports by EC and the OMOE (COA, 1979, 1981), and the IJC (1981), which highlighted the contamination in the river. In 1983, the *Journal of Great Lakes Research* published a special issue on the pollution of the Niagara River (JGLR, 1983). These reported findings and recommendations of the Niagara River Toxics Committee (NRTC) ultimately led to the signing of the Niagara River Declaration of Intent (DOI) by the heads of the same four environmental agencies in February, 1987. The DOI, along with an annually revised work plan, became the Niagara River Toxics Management Plan (NRTMP). The work plan was directed toward identifying and quantifying the loads

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of toxic chemicals to the river from point and non-point sources, the conditions in the river and, in particular, the changes in these in response to implemented remedial actions. The overall goal was to reduce the concentrations of toxic chemicals by reducing inputs from sources along the river.

Recent improvements in the extent of contamination of the river have been well documented in the numerous reports of the NRTMP secretariat, in several agency reports, as well as in the published literature (e.g., Niagara River Secretariat, 2007; Richman and Somers, 2010; Williams et al., 2000; Williams et al., 2003a). Some of the improvements (e.g., reductions in the concentrations of dieldrin) have been due to reduced inputs from areas upstream of the river. For many other chemicals (e.g., chlorinated benzenes and PCBs), improvements have been due, specifically, to the success of programs initiated by the Canadian and the United States governments to remediate hazardous waste sites and to control discharges from point and non-point sources (Niagara River Secretariat, 2007).

We provide this brief synopsis to highlight the intensity of ongoing activities undertaken by both Canada and the U.S. on the Niagara River over almost the last 30 years. An important component of these activities, since the early 1980s, has been the freshwater mussel (*Elliptio complanata*) biomonitoring program conducted by the Ontario Ministry of the Environment. The emphasis of the program since its inception has been to determine the presence/absence of contaminants at various sampling locations along the Niagara River (i.e., problem site identification) rather than quantitative monitoring. While the latter approach uses mussel data to back calculate water concentrations with the help of laboratory modeling which determined toxicokinetic parameters (Gewurtz et al., 2003; Raeside et al., 2009), additional long-term (up to 15 weeks) deployments in the Niagara River with staggered retrievals confirmed that the mussels were responding to chemical changes in their environment. Furthermore, significant differences in contaminant tissue concentrations between survey years within a site, and spatially between sites, suggested that the data could be used for more than simply reporting the presence and absence of the individual compounds particularly since ongoing remedial actions anticipated a change in contaminant loadings to the river and local improvements in water quality. Initially, the mussel biomonitoring program contributed to documenting the state of toxic substance contamination in biota. Subsequently, as a key component of the NRTMP Work Plan, it has been instrumental in documenting the effectiveness of remedial programs implemented at identified sources along the river. The length of the data set (26 years) and consistency of the approach used over this time frame have been the major factors which have enabled us to demonstrate the latter.

Since 1983, the program has selectively monitored sixty-two sites on the Canadian and U.S. sides of the river for the presence of toxic chemicals (Table 1). Between 1983 and 1997, surveys were conducted every two years. More recently, they have been scheduled every three years. Typically, at least 30 stations have been monitored on each survey. Stations at the head and mouth of the Niagara River have been monitored consistently. Similarly, stations at sites known to be significant sources of contaminants to the river, all of which, perhaps, not surprisingly given the results of numerous earlier studies, were on the U.S. side, have also been monitored consistently. Other river sites have been assessed only once or twice. We now have a comprehensive data base at many of these stations over the last two and a half decades. In addition to a brief description of data for mussels deployed at sites on the Canadian side of the river, we focus, in this paper, on five sites: Bloody Run Creek (Hyde Park Hazardous Waste Site); Gill Creek; Occidental Chemical Company (Buffalo Avenue Plant); 102nd Street Hazardous Waste Site; and Pettit Flume Cove (Fig. 1), where our data clearly demonstrate the success (or lack thereof) of implemented remedial actions, or that no remedial action has been taken. Some sites showed a demonstrable, lasting reduction in chemical contaminant concentrations in the mussel tissue. Chemical concentrations in mussel tissue at other sites, while exhibiting a decrease immediately after the completion of planned remedial actions, subsequently started to increase again, suggesting that the remedial actions taken had not entirely ameliorated the problem. This prompted further investigation of possible sources and, often, the implementation of additional remedial measures. We discuss these three situations in this paper.

Methods

The principle behind the mussel biomonitoring program is to take organisms from a relatively uncontaminated site and place them in an environment that was known or suspected of being contaminated with persistent, bioaccumulative toxic substances. Mussels are abundant, easily collected and transported and sedentary. They are responsive to their surrounding environment meaning mussel tissue concentrations can often reflect short-term fluctuations in contaminant concentrations which may not be detected by routine water quality monitoring (Kauss and Hamdy, 1991; Lobel et al., 1991; Metcalfe and Charlton, 1990; Muncaster et al., 1989). *E. complanata* is a filter feeder, feeding on plankton and organic detritus and will accumulate contaminants directly from both the water column and the particulate matter (Pennak, 1978). This makes it a good biomonitor since contaminants often partition between the dissolved and particulate phases.

Field sampling

Mussels

Mussels of approximately the same size (6.5 to 7.2 cm), to reduce variability due to tissue weight and mussel age were collected by divers from Balsam Lake, a relatively uncontaminated lake located in Victoria County, Ontario. They were placed in buckets lined with clean bioassay (food-grade) polyethylene bags partially filled with lake water and then sealed with trapped air inside for transportation back to the laboratory. Rapid temperature fluctuations were avoided. Three to five, randomly selected mussels per collection, were submitted for analysis to determine initial tissue contaminant concentrations. These mussels are referred to as the Balsam Lake control mussels.

At each field sampling station along the Niagara River (Table 1), at least five mussels were placed in 30×45 cm envelope-shaped cages constructed of 1.25 cm galvanized mesh poultry netting. At times, additional mussels were added to the cages dependent on the yearly study objectives and analytical requirements beyond the routine analysis. A nylon rope was attached to the cages, which were then anchored to the river bottom using a cement block, pegs or rocks. Sometimes they were attached to a shoreline structure. Cages were usually located within two to three meters from shore since the study was designed to investigate the impact of shore based sources on water quality rather than ambient river conditions.

Mussels were consistently deployed in July and retrieved after 21 days in August. Using a consistent sampling time frame reduced the possible variation in contaminant uptake resulting from seasonal physiological changes in the mussels (e.g., spawning; Lobel et al., 1991), or seasonal changes in water column contaminant concentrations. With regard to the latter, in designing the program, we suspected that the response of the mussels to the uptake of the contaminants would be more dictated by their external environment. This has subsequently been shown to be the case (Muncaster et al., 1989). With the mussels having been deployed in known or suspected source areas, contaminant uptake would probably be more related to the possibly episodic nature of the inputs than to seasonality in environmental concentrations. The latter could be expected if the mussels were placed in the open river, for example, where water column contaminant concentrations are known to vary seasonally (Williams et al., 2003a).

E. complanata can readily monitor environmental gradients of biologically available compounds within exposure periods as short as two days (Kauss et al., 1983); however, longer periods could be required for certain compounds (Muncaster et al., 1989). These results were confirmed in 1997 and 2000 when mussels were deployed for up to 105 days at various Niagara River sites with retrievals after exposure for 1, 2, 3, 7, 14, 21, 42, 63, 84 and 105 days (15 weeks). Additionally, there were staggered deployments throughout to compare short term accumulation with the long term deployment (Richman, 1992–2006). The results from these studies suggested that the 21 day survey was sufficient to provide an indication of the presence of bioavailable contaminants (organochlorine pesticides,

Table 1
Mussel sampling locations, survey years and presence (√) of specific contaminants in mussel tissue. NR — mussels deployed along the Niagara River shoreline. U/S and D/S refer to upstream and downstream of a specific site, respectively.

Sampling station	Survey year(s)	pp′-DDE	Total PCBs	HCH[a]	Chlordanes	Mirex	OCS	HCBD	TriCB	TetraCB	PentaCB	HCB	TCT
Canadian sites													
NR — Fort Erie at Robertson St.	1983/1987–2009	√											
NR — Chippawa Channel	1983/1987–2009	√	√										
Frenchman's Creek	1987–1995	√											
Frenchman's Creek at Durez	1987/1989/2003	√											
Miller Creek	1987/1995/2009	√											
Baker Creek	1987/2009	√											
Black Creek	1987/1997	√											
Boyer's Creek	1987/2000/2009	√											
Ussher's Creek	1987/2006	√											
Chippawa Creek	1987												
NR — Maid of the Mist Pool	1987												
NR — Whirlpool	1991	√											
NR — Queenston	1991	√											
NR — Lewiston	1991	√											
NR — Niagara-on-the-Lake (NOTL)	1983/1987–2009	√											
American sites													
Buffalo River	1987–2003	√	√										
Black Rock Canal	1995–1997	√									√		√
Scajaquada Creek	2009		√										
NR — Tonawanda Channel (outfall)	1997/2000												
NR — Tonawanda Channel	1995–2009	√	√								√		
Two Mile Creek (mouth)	1987–2009	√	√		√						√	√	
Two Mile Creek (U/S in the Creek)	2006	√	√										
Rattlesnake Creek	2009		√				√						
NR — near Booth Oil	1993	√	√										
Ellicott Creek	1997/2000	√	√										
Holiday Park (U/S Exolon)	2003	√								√			√
Holiday Park (D/S Exolon)	2003	√								√			
Pettit Flume (U/S)	1983/1991–2009	√	√										
Pettit Flume (site A)	1983–1985/1989–93	√	√		√		√	√	√	√	√	√	√
Pettit Flume (site B)	1987–2009	√	√		√		√	√	√	√	√	√	√
Pettit Flume (D/S)	1983/1991–2009	√	√					√	√	√	√	√	√
NR — Wheatfield	1987–1997	√	√								√	√	
NR — Gratwick/Riverside Park(U/S)	1997–2003	√	√									√	√
NR — Gratwick/Riverside Park(D/S)	1987–2003	√	√							√	√	√	√
NR — sewer D/S of Superior Lubricant	1997/2003	√	√										
NR — 102nd Street (U/S)	1983/1995–2009	√	√				√				√	√	
NR — 102nd Street	1983/1987–2000	√	√	√	√	√	√	√	√	√	√	√	√
NR — 102nd Street (outfall)	2003	√									√		
Little Niagara River (D/S 102nd St.)	2006–2009	√	√			√	√		√	√	√	√	
Cayuga Creek (in the Ck)	1995–2009	√	√	√						√	√	√	√
Little Niagara River (D/S Cayuga Ck)	2006–2009		√							√	√	√	
NR — 60th Street Sewer	1989									√	√		
NR — U/S Occidental Chemical Corp.	2006–2009	√	√							√	√		
NR — U/S OCC. Sewer A	1997–2009		√							√			
NR — OCC. Sewer A	1997–2009	√	√							√		√	
NR — OCC. Sewer B	1997–2009		√							√	√	√	√
NR — between OCC. Sewer B and C	1997–2009		√										
NR — OCC. Sewer C	1997–2009		√							√	√	√	
NR — between OCC. Sewer C and 003	1983/1991–2009	√	√	√		√	√	√	√	√	√	√	
NR — Occidental 003	1983/1987–2009	√	√	√	√	√	√	√	√	√	√	√	√
NR — OCC. Storm Sewer (S&N area)	1983/1991–2009	√	√			√	√	√	√	√	√	√	√
NR — Occidental 002	1991–1995	√	√			√		√	√	√	√	√	√
NR — OCC. S&N area near wall	1983/1991–2000	√	√			√		√	√	√	√	√	√
NR — D/S Occidental Chemical Corp.	2006–2009	√									√		√
NR — at Dupont	2006	√											√
NR — 75 m U/S Gill Creek	2006	√											√
Gill Creek mouth	1983/1987–2009	√	√	√			√	√	√	√	√	√	√
Gill Creek (U/S in the ck)	1993–2006	√	√	√						√		√	√
NR — Falls St. Tunnel	1987	√					√				√		
NR — Bloody Run Creek (U/S)	1997–2009	√	√					√			√	√	√
NR — Bloody Run Creek	1987–2009	√	√	√		√	√	√	√	√	√	√	√
NR — Bloody Run Creek (D/S)	2000–2009	√	√					√		√	√	√	

[a] HCH (α, β, and/or γ); Chlordane (α and/or γ); HCBD: hexachlorobutadiene; HCB: hexachlorobenzene; CB: chlorobenzenes; TCT: trichlorotoluenes.

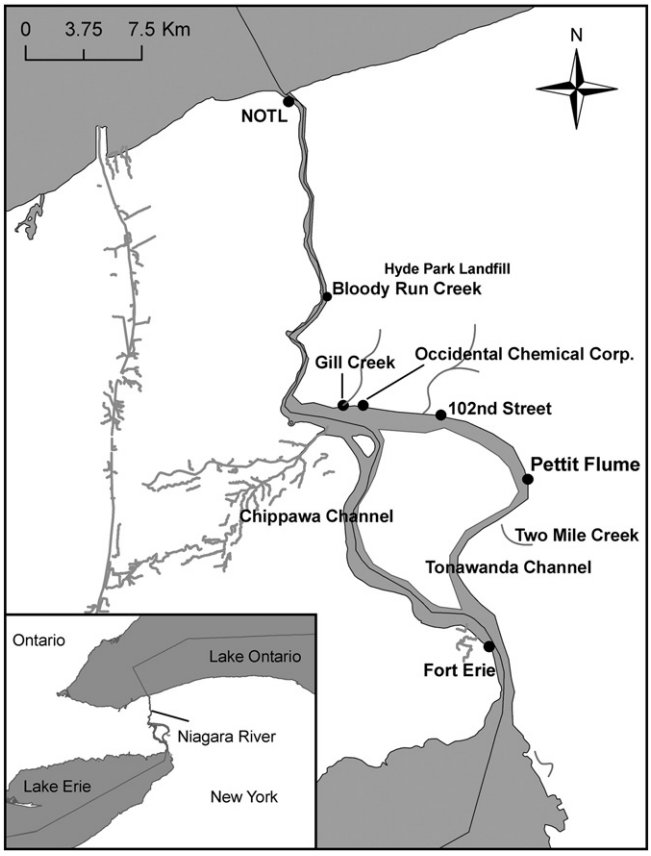

Fig. 1. Map of the Niagara River and mussel sampling sites. Only selected stations with long-term data records are shown in the figure (NOTL: Niagara-on-the-Lake).

CBs and total PCBs). There were no assumptions made about whether the mussels had reached steady state, and tissue concentrations changed through time likely in response to changes in contaminant exposure due to external forces such as storm events or fluctuations in contaminant loadings from local sources.

Upon retrieval, mussels were immediately shucked, excess water drained and the soft tissues weighed, individually wrapped in hexane-rinsed aluminum foil, placed in plastic bags and frozen until analyzed. Typically, three individual mussels from each station were analyzed for percent lipid, and a variety of contaminants including organochlorine pesticides, total PCBs, and chlorinated benzenes (Table 2). PCDDs and PCDFs were analyzed only at selected stations using a sample composite of four mussels. PAHs were only occasionally analyzed in mussel tissue. In 2006, congener specific PCBs were analyzed using three composites of 12 mussels per station, that were freeze dried prior to analysis.

Sediment

Surficial sediment samples (top 3 cm) were collected from selected stations using a hexane rinsed stainless steel spatula and placed in amber glass jars which were kept on ice in the field, and refrigerated at 4 °C in the dark until analysis. Samples were analyzed for particle size, total organic carbon (TOC) and PCDDs and PCDFs. In 2003 and 2006, samples were analyzed for both total and congener specific PCBs.

Analytical

The analysis of contaminants in mussels and sediment, and sediment particle size from the 1980s to the early 1990s used standard methods documented in OMOE (1983). Since then, there have been several changes in analytical methods to incorporate new technology which can be found in Richman and Somers (2005, 2010),

Table 2
Parameter list.

Organochlorinated pesticides, industrial chemicals and chlorinated benzenes	Polycyclic aromatic hydrocarbons	PCB congener number		Dioxins and furans dioxin-like PCBs
Hexachloroethane	Naphthalene	18	153	2,3,7,8-Tetrachlorofuran
1,3,5-Trichlorobenzene	Acenaphthylene	19	155	1,2,3,7,8-Pentachlorofuran
1,2,4-Trichlorobenzene	Acenaphthene	22	158	2,3,4,7,8-Pentachlorofuran
1,2,3-Trichlorobenzene	Fluorene	28	168	1,2,3,4,7,8-Hexachlorofuran
Hexachlorobutadiene (HCBD)	Phenanthrene	33	170	1,2,3,6,7,8-Hexachlorofuran
2,4,5-Trichlorotoluene	Anthracene	44	171	1,2,3,7,8,9-Hexachlorofuran
2,3,6-Trichlorotoluene	Fluoranthene	49	177	2,3,4,6,7,8-Hexachlorofuran
1,2,3,5-Tetrachlorobenzene	Pyrene	52	178	1,2,3,4,6,7,8-Heptachlorofuran
1,2,4,5-Tetrachlorobenzene	Benz[a]anthracene	54	180	1,2,3,4,7,8,9-Heptachlorofuran
1,2,3,4-Tetrachlorobenzene (1,2,3,4-tetraCB)	Chrysene	70	183	Octachlorofuran
Pentachlorobenzene (pentaCB)	Benzo[b]fluoranthene	74	187	2,3,7,8-Tetrachlorodioxin
Hexachlorobenzene (HCB)	Benzo[k]fluoranthene	87	188	1,2,3,7,8-Pentachlorodioxin
Heptachlor	Benzo[a]pyrene	95	191	1,2,3,4,7,8-Hexachlorodioxin
Aldrin	Indeno[1,2,3-cd]pyrene	99	194	1,2,3,6,7,8-Hexachlorodioxin
p,p′-DDE	Dibenz[ah]anthracene	101	199	1,2,3,7,8,9-Hexachlorodioxin
α-BHC	Benzo[ghi]perylene	104	201	1,2,3,4,6,7,8-Heptachlorodioxin
β-BHC		110	202	Octachlorodioxin
γ-BHC (lindane)		119	205	PCB081
α-Chlordane		128	206	PCB077
γ-Chlordane		138	208	PCB123
Oxychlordane		149	209	PCB118
cis Chlordane		151		PCB114
trans Chlordane				PCB105
o,p′-DDT				PCB126
p,p′-DDD				PCB167
p,p′-DDT				PCB156
Mirex				PCB157
Photo-Mirex				PCB169
PCB (total)				PCB189
Toxaphene				
Octachlorostyrene				

Richman and Milani (2010) and OMOE (2008a,b). Long term data comparability was considered when methods were changed and, results over the duration of the program are comparable. Contaminant results for mussels are reported on a wet weight basis with the exception of congener specific PCBs which are reported on a dry weight basis because analyses were done on freeze dried samples. These results were converted to wet weight by determining the ratio of wet to dry weight for each individual sample submitted for analysis so the data could be compared with our historical PCB data. The water content of the mussel tissue ranged from 87 to 91%. Both sets of results are included in Table 3. Results for sediment are reported on a dry weight basis.

Total-PCB, congener PCBs and OC pesticides

Mussel samples were analyzed for total-PCB using the OMOE method E3136 and sediment samples were analyzed using OMOE method 3270 (Richman and Somers, 2010; Richman and Milani, 2010). Briefly, tissue samples (5 g) were digested with hydrochloric acid and extracted with hexane/dichloromethane. Sediment samples (5 g) were extracted with acetone/hexane using an Accelerated Solvent Extractor (Dionex, Salt Lake City, UT). Both sediment and biota extracts were reduced in volume, cleaned up using dry packed Florisil®. Total-PCBs were determined 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). A blank and a spiked blank matrix sample were processed with each set of samples (20 to 30). PCB congeners (OMOE method 3411 — biota and 3412 — sediments; OMOE, 2008a,b) listed in Table 2 were analyzed using an HP 6890 GC and Ni^{63} electron capture detector (ECD) equipped with DB-1701 and DB-5 GC columns (20 m × 0.1 mm i.d. × 0.1 μm film thickness, J&W Scientific, Folsom, CA, USA). The performance of all methods was monitored through laboratory intercalibration studies (the Northern Contaminants Program — NCP, and the Quality Assurance of Information for Marine Environmental Monitoring in Europe — QUASIMEME).

The OC pesticides were analyzed (OMOE, 2008b: OMOE method 3136 — biota and 3270 — sediments) using HP 6890 GC and Ni^{63} electron capture detector (ECD) equipped with Rtx-CLPesticides-I and Rtx-CLPesticides-2 (20 m × 0.18 mm i.d. × 0.14 μm film thickness, Restek Corporation, Bellefonte, PA, USA).

Dioxins/furans

All biological tissues and sediments were analyzed for the seventeen 2,3,7,8-substituted toxic PCDD/Fs and homologue totals using the OMOE method DFPCB-E3418 (Richman and Somers, 2005). Briefly, homogenized samples were fortified with $^{13}C_{12}$-labeled surrogates for each of the 2,3,7,8-substituted PCDD/Fs and twelve dioxin-like PCBs (DL-PCBs) (Wellington Laboratories, Guelph, ON, Canada). Mussel samples (5 g) were digested with hydrochloric acid and extracted with hexane. Dried sediment samples (5–10 g) were Soxhlet-extracted with toluene. Sample extracts were processed using a 3 stage modified silica, alumina, and Amoco PX21 carbon-activated silica column procedure (see OMOE, 2008a for details), resulting in 2 fractions for analysis; Fraction A (mono-*ortho*-PCBs) and Fraction B (PCDD/Fs and non-*ortho*-PCBs) were analyzed in separate gas chromatography–high resolution mass spectrometry (GC–HRMS) runs. Both fractions (A and B) were analyzed using a Waters Autospec HRMS (Waters Corporation, Manchester, UK) at a resolving power of 10,000 coupled to a Hewlett-Packard HP 6890 gas chromatograph (Agilent Technologies, Santa Barbara, CA, USA) on a 40 m DB-5 column (0.18 mm i.d., 0.18 μm film thickness; J&W Scientific, Folsom, CA, USA). All PCDD/F and DL-PCB data were corrected for surrogate standard recoveries.

Data analysis

Since the data set is large, individual tissue contaminant data were summarized as the mean +/− standard error (SE) at each station, for each survey. Data for all surveys can be obtained from the corresponding author upon request. Typically, means were based on three individual mussels for each station. When sample sizes differed in a survey, usually due to additional study objectives unique to that survey year, they were noted in the figures. Concentrations below the detection limit were treated as zero in calculating the means. To

Table 3
Total PCB concentrations (sum of 55 congeners) in caged mussels (2006) and surface (0–3 cm) sediment (2003 and 2006) collected from the Niagara River. Mussel data is the mean of 3 replicate samples +/− standard error (SE). Each replicate is a composite of 12 mussels. Data for mussels reported as dry wt. and wet wt. Percent lipid analyzed on freeze dried samples. Sediment data (n = 1) is reported as dry wt.

	Mussels (2006)		Mussels	% Lipid	Sediment (2003)	TOC	Sediment (2006)		TOC	
	Total PCB ± SE		Total PCB ± SE		Total PCB		Total PCB			
	ng/g dry wt.		ng/g wet wt.		ng/g dry wt.	mg/g dry wt.	ng/g dry wt.		mg/g dry wt.	
	n = 3				n = 1		n = 1			
Canadian sites										
Balsam Lake (control)	17 ± 8.1	<T	2 ± 1	3.7 ± 0.35			4		3	<T
Fort Erie at Robertson Street	27 ± 5.1[a]	<T	3 ± 1	1 ± 0.06			5	<W	11	
Chippawa Channel	33 ± 9.3	<T	3 ± 2	1.1 ± 0	19	7	190		6	
Niagara-on-the-Lake	32 ± 3.8	<T	4 ± 1	5.2 ± 0.96	38	7	14	<T	9	
Lyons Creek					87	28				
American sites										
Tonawanda Channel — U/S Two Mile Creek	129 ± 18	<T	13 ± 2	6 ± 0.6						
Two Mile Creek — mouth	580 ± 17	<T	66 ± 4	6.5 ± 0.27	690	65	1200		34	
Two Mile Creek — U/S in Creek	103 ± 9.1	<T	10 ± 1	6.3 ± 0.17						
Niagara River — U/S Gill Creek	43 ± 21	<T	4 ± 4	1 ± 0.06						
Gill Creek — mouth	227 ± 15	<T	25 ± 3	1.2 ± 0.07	3400	7				
Gill Creek — U/S in Creek	230 ± 12	<T	29 ± 1	6.1 ± 0.2	150	17	120		8	
Niagara River — U/S Bloody Run Creek	57 ± 11	<T	6 ± 2	6 ± 0.13			220		12	
Niagara River — Bloody Run Creek	83 ± 8.1	<T	9 ± 2	5.6 ± 0.2	7900	22	440		14	
Niagara River at Occidental sewer 003					8800	8				

<W no measurable response.
<T measurable trace amount.
[a] n = 2.

assess the success of remediation at a site the overall mean contaminant concentration for years of data pre-remediation (i.e., the mean of yearly means) was compared with the overall mean concentrations for years post remediation using a two-sample Student's *T*-test (Microsoft Excel™).

Toxicity Equivalency Factors (TEFs) have been used to express the toxicity of different dioxins and furans and dioxin-like PCBs (DL-PCBs) on a common basis. The World Health Organization (WHO) TEFs for the protection of fish were used for the calculations for both sediment and mussels (van den Berg et al., 1998). When concentrations of individual isomers are converted to toxicity equivalents of 2,3,7,8-T4CDD they are then summed to yield a total toxic equivalent (TEQ). TEQs were calculated to facilitate comparisons of mussel tissue and sediment dioxin/furan concentrations among stations and through time. Although not directly applicable to mussels, TEFs for the protection of fish were used since invertebrate TEFs were not available.

Only the caged mussel data for individual dioxin and furan isomers, which became available *post*-1990, are discussed in this paper. The earlier data (1985–1989), based on total homologue concentrations, are available upon request.

Statistical analysis on the congener specific PCB data was performed using STATISTICA™ and SigmaStat™. To compare total PCB concentrations between stations a one-way analysis of covariance (ANCOVA) was used with percent lipid as the covariate. If significant differences were found, we used the Tukey HSD test for multiple comparisons to determine which stations differed.

Results and discussion

Balsam Lake control mussels

No organochlorine pesticides, total PCBs or chlorinated benzenes were detected in Balsam Lake mussels since collections began in 1983, with the exception of trace concentrations of α-HCH (hexachlorocyclohexane), 1,2,3-trichlorobenzene and PCBs in three separate mussel samples collected on separate occasions. This is consistent with the low (at or below detection) concentrations found in Balsam Lake mussels reported previously (Curry, 1977/78; Kauss et al., 1981; Kauss and Hamdy, 1985; Suns et al., 1980). As noted above, in 2006, we also analyzed mussel and sediment samples for total congener specific PCBs (sum of 55 congeners) in addition to total PCBs using the Aroclor method. Detection limits for this methodology are much more sensitive than for total PCBs (0.1 to 2 ng/g dependent on the congener vs. 20 ng/g). Concentrations in three composite samples of 12 mussels each from Balsam Lake ranged between 0.6 and 3.4 ng/g wet weight. The corresponding concentration in sediment was 4 ng/g dry weight (Table 3). The low concentrations and high percentage (42%) of trichlorobiphenyls present in the samples relative to the other homologues suggested atmospheric deposition as the likely PCB source (Fig. 2a; Johnson et al., 2005; MacDonald and Metcalfe, 1991).

No dioxins or furans were ever detected in Balsam Lake mussels or sediments. The total TEQ in mussels of 0.4 pg/g in 2004, for example, was due entirely to the presences of DL-PCBs.

Canadian sites

Since the first survey in 1983, mussels deployed at Canadian sites did not accumulate detectable concentrations of organochlorine pesticides nor industrial organic compounds with the exception of p,p′-DDE and trace concentrations of total PCBs and dioxins (Anderson et al., 1991; Kauss and Angelow, 1988; Richman, 1992–2006). These results probably represent background concentrations. Concentrations of p,p′-DDE were typically less than 10 ng/g at most stations. In general, the p,p′-DDE data were consistent with results from mussels deployed at American sites and suggested that this compound was ubiquitous on both sides of the river at low

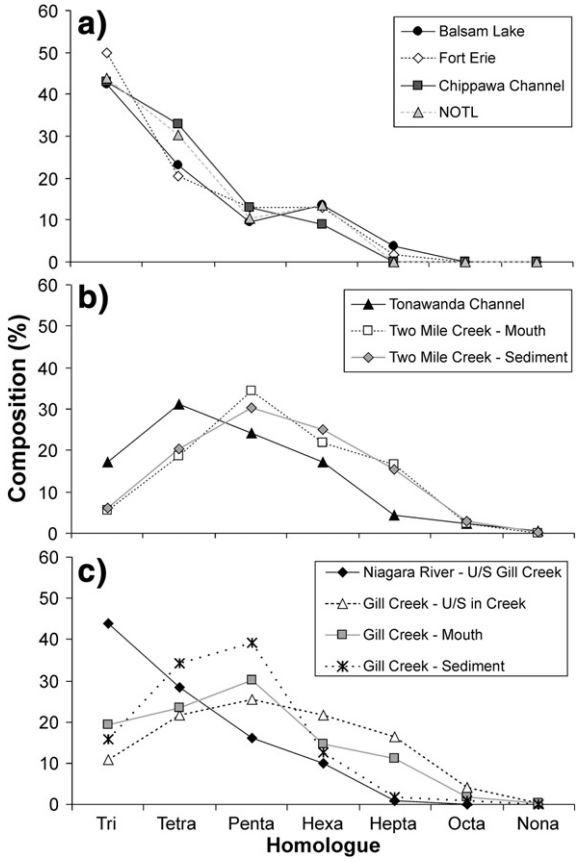

Fig. 2. PCB homologue distribution patterns in caged mussels deployed at various locations in the Niagara River, 2006. a) Canadian sites and Balsam Lake control mussels; and b and c) American sites (U/S: upstream).

concentrations. The most recent juvenile fish data collected by OMOE (e.g., spottail shiners: 2000–2006 unpublished data: Biomonitoring Section, Environmental Monitoring and Reporting Branch) from stations in the upper and the lower river also had detectable concentrations of p,p′-DDE confirming the caged mussel results. Concentrations were all below the IJC wildlife criterion of 200 ng/g for DDT (IJC, 1988). Environment Canada's Niagara River Upstream/Downstream Program measures the concentrations of organic contaminants in water and suspended sediments at the head (Fort Erie; FE) and mouth (Niagara-on-the-Lake; NOTL) of the river. Results have shown a statistically significant ($p<0.05$) downward trend in the concentrations of total DDT and its metabolites between 1986 and 2005 (Hill and Klawunn, 2009). This is consistent with a similar significant decrease in the reservoir sediment concentrations at the Sir Adam Beck Canadian power plant when a comparison was made between 1983 and 1998 results (Williams et al., 2003b).

The PCB homologue patterns observed in mussels deployed on the Canadian side of the river in 2006 were distinctly different from those observed in mussels from the American sites. Homologue and congener patterns observed in the mussels from the Canadian sites were similar to those seen in the Balsam Lake mussels, which as we noted above are indicative of an atmospheric source (Fig. 2a). There were also significant differences in the total PCB (sum of 55 congeners) concentrations among the stations (ANCOVA; $F=140$; $p<0.001$) with concentrations being significantly greater ($p<0.001$) in mussels from American sites. Percent lipid did not explain a significant amount of the variability ($F=1.6$; $p<0.22$; $r^2=0.07$). The Tukey HSD test for multiple comparisons showed that the total PCB concentrations in mussels deployed on the Canadian side of the river were not significantly different from those observed in Balsam Lake mussels ($p<0.999$). In contrast, mussel biomonitoring at American

sites over the last 26 years has shown that PCBs were bioavailable at a number of these sites suggesting local sources to tributaries and the Niagara River (e.g., Gill Creek, Two Mile Creek, and Rattlesnake Creek; Table 3, Fig. 3). These results are consistent with those from EC's Upstream/Downstream Program which showed that not only are PCBs entering the river from Lake Erie and upstream, but also from sources along the Niagara River (Hill and Klawunn, 2009).

Dioxins and furans in sediment collected from Canadian sites were typically low between 1993 and 2003 (Table 4). Total TEQ concentrations ranged from less than 1 pg/g to 14 pg/g. Dioxin-like PCBs were also low and contributed less than 4% to the total TEQ. Mussel dioxin/furan concentrations were below the detection limit at these sites and DL-PCBs were less than 1 pg TEQ/g. The earlier studies from 1985 to 1989 which only provided data for total homologue groups (accordingly the data are not included in Table 4), also showed low concentrations in mussels at the Canadian sites and were typically below the detection limits. In contrast, data for sediment and mussels from many sites on the American side of the river showed, at times, significant contamination and unique isomer patterns that identified specific sources. Some of these sites are discussed in detail in the following section.

American sites

Hyde Park Hazardous Waste Site

Hyde Park, a 6.1 hectare hazardous waste disposal site, was operated by the Hooker Chemical Co. (now Occidental Chemical Co.; OCC) from 1953 to 1975 (NRTC, 1984). Approximately 55,000 t of halogenated wastes including chlorinated benzenes, toluenes and phenols, to name but a few, was buried at this site (Interagency Task Force on Hazardous Waste, 1979). The 2,4,5-trichloropenol wastes contained significant amounts of 2,3,7,8-TCDD. Bloody Run Creek (BRC), which runs adjacent to the waste site, drains storm water run-off and overburden leachate overflow from the site and discharges it into the lower Niagara River (Fig. 1). The Creek is divided into upper and lower sections by a roadway which runs up the Niagara River gorge face. Seeps, which run down the face, were also contaminated with toxic chemicals from this site. The Hyde Park site was specifically identified as a major source of contaminants to the Niagara River and, subsequently, to Lake Ontario (Jaffe and Hites, 1985, 1986). Remediation of this site and the upper part of Bloody Run Creek began in the late 1980s and continued throughout the 90s until 1997 (remediation of the upper part of Bloody Run Creek was completed in 1993). In effect, remediation is still on-going since the long-term remediation strategy included the continuing requirement to pump and treat contaminated groundwater. Remediation of the upper Creek involved the removal of 22,000 m^3 of contaminated sediment and relining the Creek with clean gravel. According to the US EPA and NYSDEC (2004) the most significant contamination from the site has now been controlled.

In contrast, the lower section of the Creek and the Niagara River shoreline have never been remediated due to the steepness and wooded nature of the gorge face below the roadway making it difficult, if not impossible, to get equipment in to do the necessary remedial work. In addition, the location of the shoreline changes as the water levels rise and fall with control of the Niagara River for electric power generation (Williams et al., 2003b). Bloody Run Creek, therefore, continues to be a source of contaminants to the Niagara River, despite the remediation at the Hyde Park site and the upper section of the Creek. This is substantiated in Fig. 4a, which shows the concentrations of pentachlorobenzene (pentaCB) and hexachlorobenzene (HCB) in mussels collected from the Creek site since 1987. We have no definitive explanation for the anonymously high concentrations for these two contaminants in 1993. We speculate that this may have been due to the unusually high rainfall during the period of mussel deployment. Rainfall in 1993 was the highest recorded (100 mm) compared to the other deployment periods (range 14 to 85.5 mm, Environment Canada data). This could have resulted in increased surface run-off from the Hyde Park site which, in turn, would have increased the off-site migration of contaminants.

In 1994, there was a rockslide on the lower gorge face burying the location of the Creek mouth. Notwithstanding this occurrence, we continued to place the cages in the same location as previously until 2003, when cages were also placed at additional stations along the shoreline. In 2003, we did a reconnaissance of the lower gorge face in preparation for these additional monitoring stations for dioxins and furans in mussels. We found DNAPL (dense, non-aqueous phase

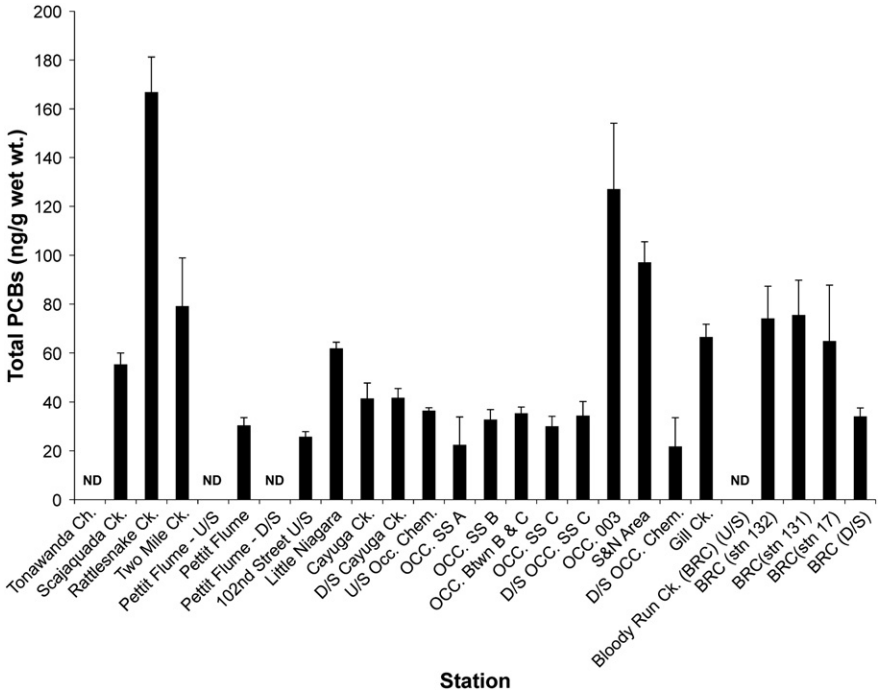

Fig. 3. Total PCBs (mean +/− SE) in cage mussels deployed at American sites along the Niagara River shoreline, 2009 (ND: concentrations were below the detection limit of 20 ng/g total PCB. U/S: upstream; and D/S: downstream; OCC SS: Occidental Storm Sewer).

Table 4
Total TEQ pg/g[a] and TEQ for dioxin-like (DL) PCBs (pg/g)[b] in caged mussels (wet wt.) and sediment (dry wt.) collected from the Niagara River. NR — Niagara River; and ND — below the detection limit.

Station	Year	Mussels		Sediment		TOC (mg/g)
		Total TEQ	DL-PCB TEQ	Total TEQ	DL-PCB TEQ	
Canadian sites						
NR — Fort Erie	1995	ND		0.9		
	1997			10		20
	2000	0.01	0.01	2	0.01	9
NR — Chippawa Channel	2000	ND	ND	0.01	0.01	5
Niagara-on-the-Lake	1993	ND		13		
	1995	ND		14		
	1997	ND				
	2000	0.01	0.01			
	2003			8	0.05	7
American sites						
Two Mile Creek	2000			30	3.3	39
	2003			52	1.4	65
Exalon (upstream) in Erie Canal	2003	0.04	0.04	77	0.2	33
NR — Gratwick/Riverside Park	1991	15				
NR — Wheatfield	1987	ND				
Little Niagara River (downstream 102nd St.)	2006	16		300	2.1	43
Cayuga Creek	1995	18		18		
	2003	0.16	0.05	59	0.3	82
Little Niagara River (downstream Cayuga Ck.)	2006	8		140	0.6	110
Occidental sewer 003	1991	ND				
Gill Creek (upstream in Creek)	2000			71	0.8	14
	2003	0.44	0.08	88	1.0	17
	2006	1		28	0.3	8
NR — 102nd Street	1991	70				
	1993	96		230		
	1995	130		500		
	1997	1		ND		ND
Pettit Flume (upstream)	1991	5				
	1993	ND		26		
	2000	ND	0.05	13	0.3	23
	2003	ND	ND	37	0.3	34
	2006	0.03		15		
Pettit Flume Cove (site A)	1991	960				
	1993	200		48,000		
Pettit Flume Cove (site B)	1997	46		20,000		110
	2000	74	ND	30,000	2.6	120
	2003	60	0.05	11,000	1.4	120
	2006	190		15,000		
Pettit Flume (downstream)	2000	3	0.03	490	0.2	33
	2003	0.36	0.01	2000	0.3	20
	2006	5		680		
NR — Bloody Run Creek (upstream)	2000	ND	ND	43	0.3	5
	2003			180	0.4	5
	2004	0.01	0.01			
	2006	2		36		12
NR — Bloody Run Creek	1993	270		120,000		
	1994	56				
	1995	120		61,000		
	1997	84		52,000		29
	2000	23	0.04	3300		7
	2003			110,000	6.2	22
	2004	46	0.06			
	2006	45		4200		14
Bloody Run Creek (downstream)	2004	9	0.02			
	2006	6		220		7

[a] Dioxin, furan and dioxin-like PCB concentrations were multiplied by the WHO *Toxicity Equivalency Factors (TEF) for protection of fish to express their respective toxicity* on a common basis and then summed to yield a total toxic equivalent (TEQ).
[b] Analysis for dioxin-like PCBs was not available prior to 2000.

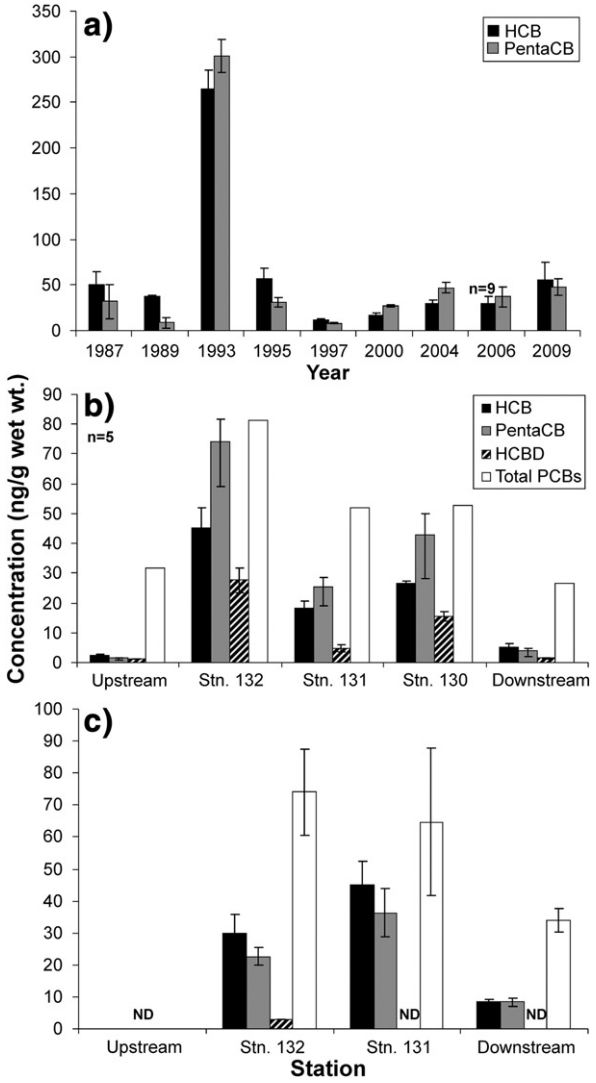

Fig. 4. Concentrations (mean +/− SE) of chlorinated compounds in caged mussels deployed at: a) Bloody Run Creek (BRC) long-term monitoring station (1987–2009); and b) additional stations positioned along the shoreline and upstream and downstream of the creek: 2004 data; and for c) 2009 data. The long-term monitoring station in 4 a is located 25 m downstream of station 133, 22 m downstream of station 131 and 12 m downstream of station 130 shown in b and c, respectively.

pollutants) – a dark black tar like material – adhering to the rocks suggesting the Creek and surrounding soil was probably contaminated. In addition, at the shoreline, we found water running all along the area which we suspected was near the Creek mouth, perhaps due to an extension of the seeps above the roadway. The 2003 samples went missing, either by vandalism or just being swept away. As a result, we re-sampled in 2004 (an "off" year as per the schedule noted in the Introduction) and placed the mussel cages again at the long-term BRC station (Fig. 4a), the upstream station (about 70 m upstream), a downstream station (about 150 m downstream), and three additional stations lined up with the running seeps. The results for the upstream, downstream and additional stations are shown in Figs. 4b and c for 2004 and 2009, respectively (station 130 was dropped in 2009 because we had sufficient information from the other two stations). They showed little or no contamination upstream, increases in the vicinity of the Creek mouth, and probably residual contamination downstream as the River current carries along the water mass from the area of the Creek mouth. Accordingly, the results still showed that the Creek was a source of contaminants to the River, whether this was from un-remediated lower Creek conditions or continued inputs from the Hyde Park site.

Sediment collected from the shoreline of the Niagara River in the vicinity of Bloody Run Creek between 1993 and 2006 had consistently

high concentrations of dioxins and furans with total TEQ concentrations ranging from 3300 pg/g to as high as 120,000 pg/g. The sediment sample from 2003 showed that the contribution of DL-PCBs to the total was negligible (Table 4). Since the sediment has not been remediated and the location of the shoreline changes as the water levels fluctuate in response to power production needs, the range in concentrations probably reflected the patchiness and variability in shoreline sediment contamination. The dioxin and isomer patterns found in Bloody Run Creek sediments are distinct from those seen at other sites in the Niagara River with lower concentrations of octadioxin relative to the 1,2,3,4,6,7,8 heptadioxin. Furthermore, all the tetra dioxin was in the form of 2,3,7,8 TCDD (the most toxic form of dioxin; Fig. 5a).

Sediment collected from a shoreline station about 70 m upstream of the Creek had relatively low concentrations of dioxins and furans in 2000 and 2006 (total TEQs of 43 and 36, respectively) and isomer patterns similar to those seen at other Niagara River sites. In contrast, concentrations were higher in 2003 (total TEQ 180; Table 4) and the isomer patterns were similar to those seen in Creek sediments. The sediment sampling sites vary year to year since, due to reasons noted above, the water levels fluctuate. The relatively high concentrations in the upstream sediment in 2003 may have been due to the collection of sediment further downstream than previous collections and it is possible that a wider area of sediment is contaminated than anticipated based on the location of Bloody Run Creek (i.e. there may be additional seeps along the gorge upstream of the BRC sample area). Sediment collected in 2006 from a station about 150 m downstream of Bloody Run Creek had higher concentrations of dioxins and furans (total TEQ of 220 pg/g; Table 4) than those seen at the station upstream of the Creek. The isomer patterns were identical to those seen in Creek sediments suggesting that some of the Creek sediments had migrated downstream (Fig. 5a).

The total TEQ concentrations in caged mussels deployed in the vicinity of Bloody Run Creek from 1993 to 2006 ranged between 23 and 270 pg/g with isomer patterns the same as that seen in Creek sediment. Also, consistent with the pattern in sediments, the total TEQ was almost exclusively due to the high concentrations of 2,3,7,8-TCDD (>98% of the total TEQ) and the contribution of DL-PCBs to the total was negligible. The same was true for mussels deployed at the station 150 m downstream of the Creek in 2004 and 2006. Total TEQ concentrations in these mussels (9 and 6 pg/g for 2004 and 2006, respectively; Table 4) were also higher than those seen in the mussels deployed 70 m upstream of the Creek. The variability in mussel tissue concentrations between survey years from 1993 to 2006 may have been due to the episodic nature of run-off from the Hyde Park site, or the uncertainty in positioning the cages with respect to the Creek mouth as a result of the 1994 rockslide noted above.

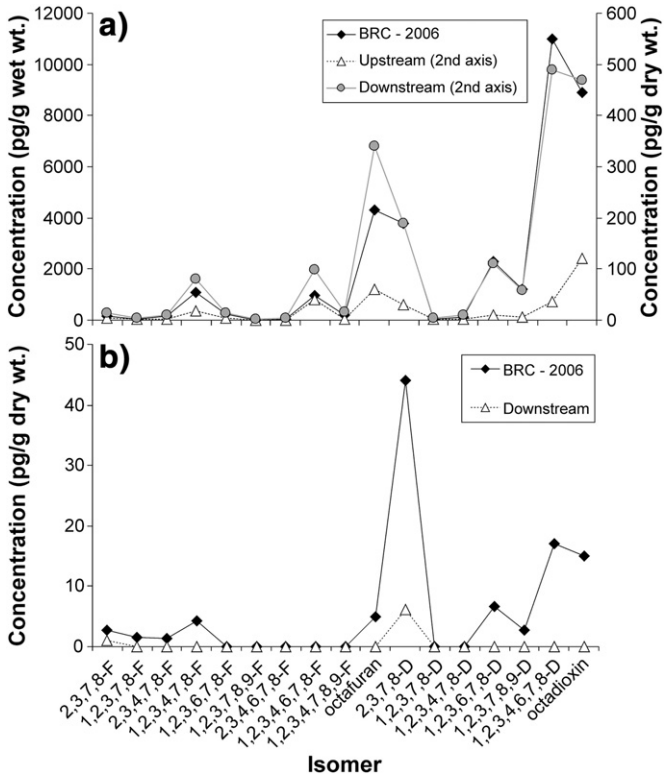

Fig. 5. a) Dioxin and furan isomer patterns in sediment collected in 2006 from the Niagara River at Bloody Run Creek; and b) dioxin and furan isomer patterns in mussels deployed in the Niagara River at Bloody Run Creek, 2006.

Gill Creek

Gill Creek discharges into the Niagara River just above Niagara Falls on the U.S. side. It received contaminants from the Olin Chemical Corporation (Buffalo Avenue Plant) and the E. I. Dupont Company. These two plants had three and six hazardous waste sites on their properties, respectively. Historically, Olin used the site for the production of chlorine and caustic soda from rock salt (sodium chloride) using various modifications of the mercury-cell/chlor-alkali process. From the early 1950s until 1956, Olin also manufactured organic chemicals, including trichlorobenzene, trichlorophenol, and hexachlorocyclohexane (HCH) (NRTC, 1984). Several waste products were disposed of onsite including the use of brine sludge containing mercury and PCBs as fill material. Chemicals disposed of at the Dupont waste sites included carbon tetrachloride, chloroform, di-, tri- and tetrachloroethylene and PCBs as well as other organic and inorganic chemicals (US EPA and NYSDEC, 2004).

Gill creek was a major contributor of PCBs to the Niagara River; estimated to have contributed as much as 20% of the total PCB load (US EPA and NYSDEC, 1994). Comparison of the PCB homologue pattern seen in mussels deployed at Gill Creek (Fig. 2c) with those seen in mussels from Balsam Lake and those from Canadian sites (Fig. 2a) shows very distinct differences confirming a local source of PCBs in the Creek. The pattern seen in Creek mussels is corroborated by that seen in Creek sediment. The higher concentrations of tetra-, penta- and hexachlorobiphenyls suggested a mixture of Aroclors 1254 and 1260 (Frame et al., 1996; Johnson et al., 2005).

Major remediation of PCB contaminated sediment in Gill Creek upstream of the mouth was completed in 1992. Additional sediment remediation was completed further upstream in 1998 after high PCB concentrations were reported in caged mussels and juvenile fish at this location (Preddice et al., 2002; Richman, 1992–2006). Mean PCB concentrations measured post-remediation in mussels deployed at the stream mouth as well as further upstream were consistently, significantly lower than those seen prior to remediation at both sites ($t = 3.37$, $p < 0.005$; and $t = 5.37$, $p < 0.006$, respectively; Figs. 6a and b). In addition the S.E.s were much smaller. Although the additional remediation in 1998 upstream within the Creek reduced the bioavailability of PCBs locally it did not appear to further reduce concentrations of PCBs in mussels deployed at the mouth. When referring to the figures note that there are no data for 1995 at the mouth of Gill Creek and for 1997 upstream within the Creek. In both cases cages were either vandalized or had moved downstream into the Niagara River.

The sediment remediation projects in the Creek have likely contributed to a reduction in PCB loadings to the Niagara River and Lake Ontario (Marvin et al., 2003, 2007). PCB concentrations and estimated annual loads at both Lake Erie and within the Niagara River have decreased over the period 1986 to 2005 as shown by the results from Environment Canada's Upstream/Downstream Niagara River Program (Hill and Klawunn, 2009). More specifically, the within river loads (termed the "differential loads") calculated over this period show, coincidentally, substantial decreases in 1992/93 and again in

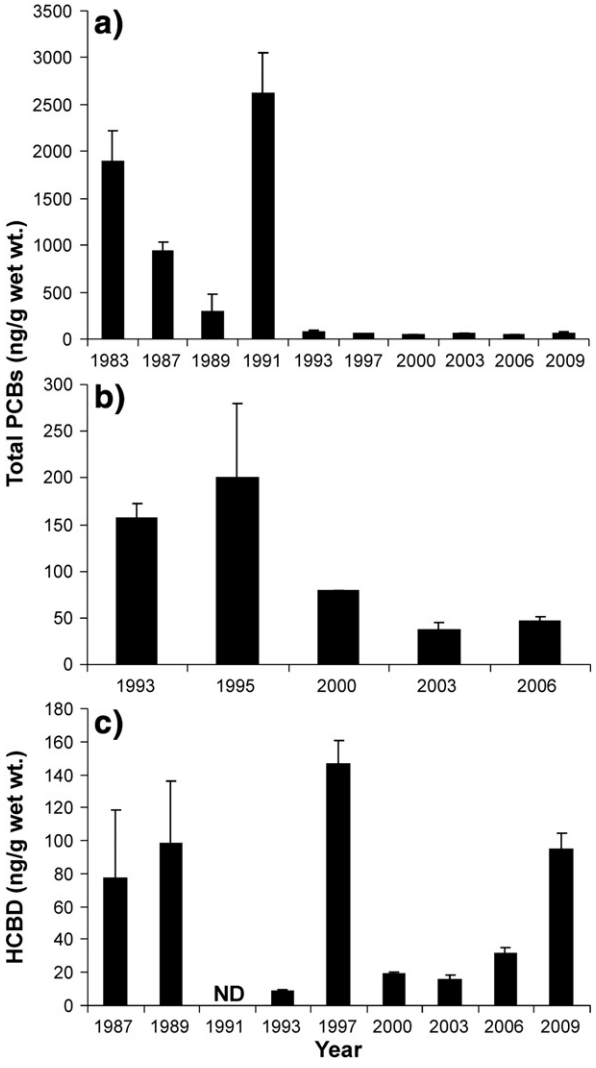

Fig. 6. a) Total PCBs (mean +/− SE) in cage mussels deployed at the mouth of Gill Creek (1983–2009); b) total PCBs (mean +/− SE) in cage mussels deployed upstream (U/S) within the Creek (1993–2006) and c) HCBD concentrations (mean +/− SE) in mussels deployed at the mouth of Gill Creek (1987–2009). ND: concentrations were below the detection limit of 1 ng/g HCBD.

1998/99 (Environment Canada, Science and Technology Branch, unpublished data). The differential load is calculated by subtracting the load estimated at Fort Erie (FE) from that estimated for Niagara-on-the-Lake (NOTL). We suggest that these differences are due, at least in part, to the remediation work at Gill Creek given the percentage contribution of the Gill Creek PCB load to the River noted above. A review of MOE sport fish data for the lower Niagara River has also shown a statistically significant decrease in total PCB concentrations in lake and rainbow trout between 1984 and 2002 and 2004, consistent with ongoing remedial action to reduce loads of PCBs to the river (Karst-Riddoch et al., 2008).

Despite the remediation of PCB-contaminated Creek sediments, residual contamination remains in the Creek since other contaminants continue to be detected in caged mussels deployed at this site with no observed, consistent decreases in concentration. Compounds such as hexachlorobutadiene (HCBD), HCH and chlorinated benzenes have been routinely detected in mussels from this site. HCBD, for example, was stored in waste sites which were known to be leaching contaminants into the Creek. The HCBD concentrations measured in mussels deployed at the Creek mouth over the period 1987 to 2009 are shown in Fig. 6c. Concentrations have remained highly variable over this period with no significant decrease ($t = 0.14$: $p = 0.45$) in concentration evident post the 1992 PCB remediation. Indeed, the highest mean concentration of HCBD observed in all the mussels deployed at Niagara River sites in 2009 was in the Gill Creek mussels (mean 95 ng/g; S.E. 10 ng/g). The next highest concentration (75 ng/g; S.E. 3 ng/g) was seen in mussels deployed at OCC's Buffalo Avenue site (see below), with concentrations in all other mussels deployed at Niagara River sites in that year being less than 9 ng/g. No HCBD was detected in mussels deployed along the Niagara River shoreline 325 m, 220 m and 65 m upstream of the Creek indicating that the source was the Creek itself.

102nd Street Hazardous Waste Site

The 102nd Street Hazardous Waste Site located in the city of Niagara Falls on the bank of the Niagara River was used by OCC and Olin Chemical Corporation between the early 1940s and 1971 for the disposal of an estimated 150,000 t of waste including demolition wastes, flyash, organic and inorganic phosphates and a variety of organic compounds including tri-, tetra-, penta- and hexachlorobenzene (HCB), and hexachlorocyclohexane (NRTC, 1984; US EPA and NYSDEC, 2004).This was a U.S. National Priority List site and a joint USEPA/NYSDEC lead Superfund site. Remedial actions including the on-site containment of contaminants, implementing a program for the long-term pump and treatment of contaminated groundwater, and the removal of contaminated sediments from the Niagara River were completed in 1999. Actual sediment remediation was completed in 1996. The concentrations of penta- and HCB found in mussels deployed at this site over the period 1983 to 2003 are shown in Fig. 7a (the 2006 and 2009 data are discussed further below). The results clearly showed the pre- and post remediation difference — from high concentration pre-remediation to NDs after contaminated sediment removal. Similarly, the dioxin/furan concentrations seen in mussels and sediment from the 102nd Street site over the period 1991 to 1997 are shown in Table 4. Again, the differences in concentrations in both mussels and sediment post remediation compared to those prior to remediation are striking. The consistency of the results in both mussels and sediment is self-reinforcing, both illustrating the efficacy of the sediment remediation activity.

In 2006 and 2009, mussels were deployed in the Little Niagara River which branches off from the Niagara about 240 m downstream of the location where the sediment was removed. The Little Niagara travels a short distance around an island and then rejoins the main river downstream. Organic contaminants historically detected in mussels deployed adjacent to the 102nd Street site were also bioavailable at this downstream location. These included, for example, 1,2,3,4-tetraCB (range 17–25 ng/g), pentaCB (range 16–95 ng/g), HCB (range ND — 28 ng/g), and dioxins/furans (TEQ 16 pg/g; Table 4) in addition to the presence of trace concentrations of Mirex in 2006 (range 6–16 ng/g). Mirex was also detected by MOE in 2006 in juvenile fish collected from the area (mean 8 ng/g; SE 0) (MOE unpublished data: Biomonitoring Section, Environmental Monitoring and Reporting Branch). The presence of Mirex was not surprising given that the waste site was used by Occidental and they were the sole producer of Mirex until 1976 when its use was restricted by both Canadian and U.S. legislation (Apeti and Lauenstein, 2006; Interagency Task Force on Hazardous Waste, 1979).

Although concentrations of these organic compounds were lower than those seen previously in mussels deployed adjacent to the 102nd Street waste site (for example, compared to highest concentrations for pentaCB and HCB seen in Fig. 7a), they suggested that contaminated sediment had likely migrated downstream into the Little Niagara River prior to sediment removal in 1996. Indeed, the dioxin/furan concentrations measured in Little River sediments in 2006 (TEQ 300 pg/g; Table 4) were within the range of concentrations measured at the 102nd Street site in 1993 and 1995 (TEQ 230–500 pg/g).

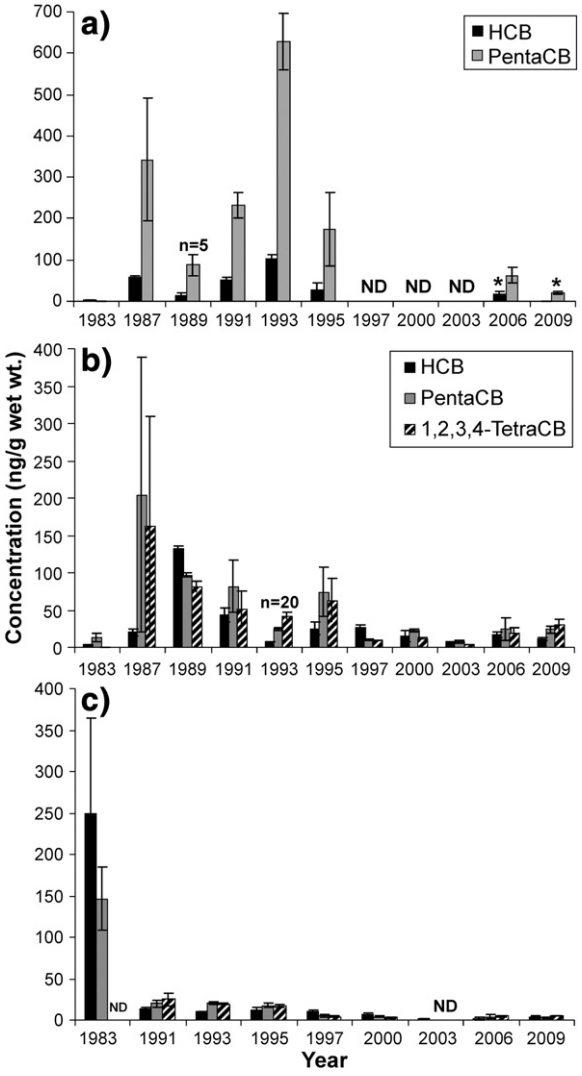

Fig. 7. Concentrations (mean +/− SE) of chlorinated benzenes in caged mussels deployed at: a) the 102nd St. Hazardous Waste Site (1983–2009), * mussels deployed downstream of 102nd St. in the Little Niagara River; b) the Occidental sewer 003 (1983–2009); and c) a storm sewer (S&N area) located downstream of sewer 003 (1983–2009). Note change in the y axis scale.

Occidental Chemical Company, Buffalo Avenue Plant, Niagara Falls, New York

OCC's Buffalo Avenue Plant is located adjacent to the Niagara River upstream of Gill Creek (Fig. 1). Persistent, bioaccumulative contaminants have entered the Niagara River along the waterfront of this site via sewers and contaminated groundwater (NRTC, 1984). The facility has manufactured over 250 chemical products including halogenated benzenes, toluenes, phenols and aliphatics. In addition to the 10 hazardous waste sites located on the property, including the well-known "S-area", which have contributed to the groundwater contamination, chemical raw materials, products and wastes have also been burned, or spilled, on the plant site. Throughout the 1990s, there have been extensive remediation efforts at various locations on the property including removing and capping of contaminated soils, long-term pump and treatment of contaminated groundwater, installation of a sheet piling along the Niagara waterfront to contain and reverse the flow of contaminated groundwater away from the river, and the repairing and replacement of pipes of the industrial sewer system (US EPA and NYSDEC, 2004). At one time, groundwater infiltration into the on-site industrial waste sewer system was a significant source of contamination to the river. OCC has had an ongoing program for replacing and repairing pipes since the 1980s. In particular, an investigation into the infiltration into the Plant's Outfall Sewer System was completed by OCC in June 1996 and measures to eliminate infiltration points were implemented from the Fall of 1996 to the Spring of 1997 (US EPA and NYSDEC, 1999).

In the 1980s, in addition to high concentrations of PCBs (not shown), high concentrations of 1,2,3,4-tetraCB, pentaCB and HCB were also observed in caged mussels deployed near the sewer outfalls along the OCC property adjacent to the Niagara River. The data for the New York State SPEDS (State Pollution Elimination Discharge System) permitted outfall, sewer 003, and a storm sewer located near the S&N area (hazardous waste sites) are shown in Figs. 7b and c. We are not certain of the reason for the low concentrations observed at sewer 003 in 1983 (Fig. 7b), but the fact that the discharge of contaminants is controlled by OCC may be part of the explanation. Sewer 003 is currently the only one that is operational (i.e., being actively used).

The pattern seen in the mussel concentration data shown in Fig. 7c appears to be consistent with the remedial activities taken to reduce contaminated groundwater infiltration into the on-site industrial waste sewer system. There is a significant reduction in concentrations from the early 1980s to the 1990s. Also, tissue concentrations post 1997 were less than those observed in the early 1990s. This coincides with the completion of eliminating the infiltration points in the spring of 1997 noted above. Even the permitted sewer 003 was probably subjected to groundwater infiltration. A similar pattern in mussel concentrations is seen in mussels deployed at this site (Fig. 7b). 1,2,3,4-tetraCB, pentaCB and HCB (Fig. 7b) and PCBs (Fig. 3) continued to be detected in the tissue of mussels deployed at sewer 003 in 2009 indicating that this outfall is still a source of these contaminants to the Niagara River. Although the remaining sewers along the OCC Buffalo Avenue Plant water front have been inactive for many years, various chlorinated compounds including PCBs, HCBD and Mirex were sporadically measured at trace concentrations in deployed mussels. We speculate that this may be due to run-off from the surrounding area during rain events, residual contamination in the sewer lines or possibly groundwater infiltration.

Mirex has been detected in caged mussels deployed at Niagara River sites adjacent to OCC's Buffalo Avenue Plant property and sporadically near hazardous waste sites used by OCC to store waste materials (e.g., downstream of the 102nd Street site and Bloody Run Creek). The highest concentrations (mean 167 ng/g; S.E. 35 ng/g) were observed in mussels deployed in 1987 at OCC's sewer 003. Its detection in caged mussels in the 1980s, and periodically at trace concentrations (<20 ng/g) at locations along the OCC water front throughout the 1990s to the present, showed that residues of Mirex were continuing to enter the Niagara River. The bioavailability of Mirex was confirmed by data collected from quagga mussels. *Dreissena bugensis* collected throughout the Niagara River in 1995 and 2003 had detectable concentrations of Mirex (range 90–140 ng/g dry weight) in mussels collected near OCC's sewer 003 in both years, with little difference between years. No Mirex was detected in mussels collected from the River upstream of this site. In contrast, while Mirex was detected only at this site in 1995, it was also detected in quagga mussels collected from the lower river (~10 ng/g dry weight) in 2003 (Richman and Somers, 2010). Mirex has also only been detected in sports fish (lake and rainbow trout) collected from the lower Niagara River while not present in fish collected from the upper river or Lake Erie. Concentrations in fish tissue in the 1990s and 2004 were statistically significantly lower than those measured in the 1980s (Karst Riddoch et al., 2008). The Mirex data from Environment Canada's Upstream/Downstream Niagara River program clearly show that concentrations have decreased between 1987 and 2005 (Hill and Klawunn, 2009). However, they still exceed the most stringent agency criterion (NYSDEC; 0.001 ng/L). These results corroborate our mussel data. Implementation of remedial actions at those sites associated

with OCC is the probable reason for the decreases seen in all the above media.

Pettit Flume Cove

The Pettit Flume is a storm sewer in North Tonawanda that received waste water from the OCC's Durez Division and surrounding hazardous waste sites (Geologic Testing Consultants Ltd., 1984). The site was designated as a Superfund site on the U.S. National Priority List. Remediation of the site from 1990 to 1995 included on-site containment of contaminants, cleaning out the sewer lines, and sediment removal from the cove. Specifically, 11,500 m^3 of contaminated sediment was removed from the cove in 1995. The sediments were contaminated with a variety of inorganic and organic wastes including chlorinated phenols, chlorotoluene, dioxins and furans and phenol tar containing chlorinated benzenes to name just a few (Interagency Task Force on Hazardous Waste, 1979; US EPA and NYSDEC, 2004).

Prior to sediment remediation, mussels deployed in the cove had high tissue concentrations of 1,2,3,4 tetraCB, pentaCB and HCB (Fig. 8a). We speculate that the anonymously high concentrations for these contaminants in 1991 may have resulted from the ongoing remediation of the North Tonawanda sewer system which involved the removal of contaminated sediment from within the sewers and DNAPL found under the sewer lines. Cleaning and flushing of the sewers may have influenced the contaminant loadings to the cove. While concentrations of these contaminants continued to be detected in mussel tissue post sediment remediation, they were significantly lower than those seen prior to sediment removal attesting to the success of the remedial effort for chlorobenzenes. This was confirmed by tests on the difference in concentrations between these two periods: 1987–1993 vs. 1995–2009 (HCB: $t = 2.5$, $p < 0.02$; pentaCB: $t = 2.2$, $p < 0.03$; and tetraCB: $t = 2.9$, $p < 0.01$). Their continued presence in the cove was likely due to residual contamination in the flume that was flushed into the cove during storm events.

In contrast to the reductions seen in the post remediation data for chlorinated benzenes, high concentrations of dioxins and furans continued to be detected in both mussels and sediment suggesting the presence of a source that had eluded the remediation (Table 4). Originally, in the 1980s there were two monitoring sites (site A and site B) in the cove. Throughout the 1990s until the present, monitoring was reduced to one site since the two sites produced comparable data. The dioxin and furan isomer patterns seen in mussels and sediments from the cove were similar (Figs. 8b and c) and unique to the cove itself. Sediment collected in 2006 from the cove was extremely contaminated with dioxins and furans with a TEQ of 15,000 pg/g. For comparison, sediment collected from a site immediately upstream of the cove had a TEQ of 15 pg/g (Table 4). Furthermore, the isomer pattern in this sediment sample did not match the unique Pettit Flume profile, but rather was similar to patterns detected in sediment collected at other sites in the Niagara River (for example, see the pattern for the upstream Bloody Run Creek station in Fig. 5a). The total TEQ for caged mussels deployed in the cove in 2006 was 190 pg/g, while that for mussels deployed immediately upstream was only 0.03 pg/g (Table 4). The isomer patterns were also different. The high dioxin/furan concentrations seen in cove mussel tissue suggested that these compounds were still bioavailable. Since fish, other aquatic biota and waterfowl move freely in and out of the cove to feed, the cove continues to be a source of dioxins and furans to indigenous biota.

High concentrations of dioxins and furans (total TEQs ranging between 490 and 2000 pg/g; Table 4) and isomer patterns consistent with those seen in cove sediments were also seen in sediment collected from a station downstream of the cove. This showed that contaminated sediment has migrated out of the cove into the Niagara River and downstream. However, the total TEQ concentrations in mussels deployed at this site have been low (range 0.36 to 5 pg/g) suggesting low bioavailability although isomer patterns were consistent with mussels deployed in the cove. Occidental Chemical Corporation is currently investigating the recontamination of the cove.

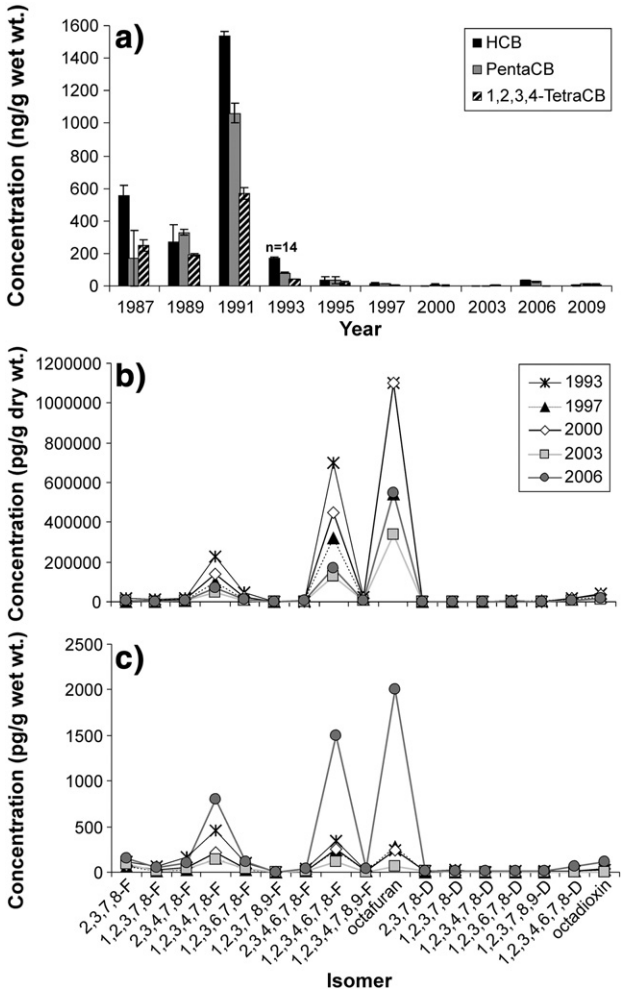

Fig. 8. a) Concentrations (mean +/− SE) of chlorinated benzenes in caged mussels deployed at the Pettit Flume Cove (1987–2009). b) Dioxin and furan isomer patterns in sediment collected from 1993 to 2006 from the Petit Flume Cove; and c) dioxin and furan isomer patterns in mussels deployed in the Pettit Flume Cove (1993–2006).

Conclusions

Since 1983, the Ontario Ministry of the Environment has sampled numerous sites along the Niagara River as part of its freshwater mussel (*E. companata*) biomonitoring program. The original objective of the program was to determine the presence/absence of contaminants at these sites (i.e., problem site identification). The length of the data set (26 years) and consistency of approach used over this time frame, however, have made the program an instrumental contributor to documenting the effectiveness (or lack thereof) of remedial programs implemented at sources along the River. Five sites have been discussed in this paper with respect to documenting the effectiveness of implemented remedial actions in reducing the flow of contaminants from these sites to the Niagara River. Results have ranged from being very effective (PCBs: Gill Creek; and CBs: Pettit Flume) to no effect (Hyde Park–Bloody Run Creek: PCBs, CBs, and dioxins) due to the unremediated lower Creek. Additionally, there have been occasions where the implemented remedial actions, while first appearing to be effective, have subsequently been shown by additional mussel data to have apparently missed a source (dioxins/

furans: Pettit Flume). While the remedial actions taken have not, in most cases, entirely reduced the input of contaminants to the River from these sites, they have, without doubt, reduced the magnitude of the inputs, in some cases, significantly as shown by the decreases in the mussel tissue concentrations over the period of collection. Contaminant data for juvenile fish and sport fish generated by Ontario and the State of New York also show decreasing trends from the 1980s to the present. Similarly, the data from Environment Canada's Upstream/Downstream Niagara River program have exhibited decreasing trends for many of these contaminants including HCB, other chlorinated benzenes, pesticides, Mirex and industrial chemicals such as HCBD between 1986 and 2005 (Hill and Klawunn, 2009). Combined, these data sets independently corroborate the improving water quality conditions in the Niagara River with respect to the concentrations of organic contaminants. Much of this improvement has been due to implemented remedial actions at known sources to the river. Many of these were identified by the mussel biomonitoring program. The program will continue to be a critical component of the Niagara River Toxic Management Plan (NRTMP).

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