Current Status and Trends of Aquatic Wildlife in the Niagara River (Ontario) Area of Concern

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Executive Summary

As one of five binational Areas of Concern (AOC) on the Great Lakes, the Niagara River AOC was identified as a problem area in 1985 largely as a result of historical localized industrial activities which degraded water and sediment quality and impaired a number of beneficial uses of the aquatic system including the health of fish and wildlife populations. Over the last twenty years the development and implementation of the Niagara River (Ontario) Remedial Action Plan (RAP) has worked to address major environmental issues within the AOC and restore these beneficial use impairments. The purpose of this report is to examine the current status and trends of aquatic wildlife which feed predominately within the Niagara River AOC and which are also sensitive to the toxic effects of contaminants in the aquatic environment. These Great Lakes sentinel species, studied extensively by the Canadian Wildlife Service (CWS), include snapping turtles (*Chelydra serpentina*), herring gulls (*Larus argentatus*), and mink (*Mustela vison*).

Of all contaminants examined, PCBs were found in the highest concentrations in aquatic wildlife studied in the Niagara River (Ontario) AOC. As an indicator of local sources of contaminants, snapping turtles were effective in detecting elevated levels of PCBs in eggs collected from 2001 to 2004 from Lyons Creek East where earlier environmental assessments had identified PCBs as compounds of concern. Sum PCB levels were significantly higher in eggs from this location compared to reference sites and toxic equivalent concentrations based on levels of coplanar PCBs with dioxin-like effects were also elevated compared to levels found at other Great Lakes AOCs. While overall hepatic levels of sum PCBs in liver of 15 mink trapped within the Niagara River AOC were statistically similar to levels at reference sites, one individual trapped at Lyons Creek East in 2004 had an hepatic PCB concentration (5,419 µg/kg) which greatly exceeded thresholds associated with impaired kit growth and kit mortality. Herring gulls, as indicators of regional contaminant conditions on the Niagara River, showed large and significant declines in levels of contaminants in eggs collected from an Annual Monitor Colony (AMC) on the Niagara River from 1979 to 2007, consistent with significant reductions in discharges of toxic pollutants to the River during this period. Levels of sum PCBs in herring gull eggs collected from 2003 to 2007 from this AMC were statistically similar to levels in eggs from the upstream Lake Erie reference AMC and overall were lower relative to many other Great Lakes AMCs. In addition, organchlorine pesticides in eggs of herring gulls as well as snapping turtles were statistically similar to concentrations found at respective reference sites. Hepatic levels of pesticides including mirex and HCB were significantly higher in mink from the Niagara River AOC compared to inland Ontario, but not significantly different from the upstream reference site in eastern Lake Erie. Polybrominated diphenyl ether flame retardants, as a new class of

compounds of recent concern, were detected all three wildlife species. In the case of herring gulls, levels of sum PBDEs in eggs from the Niagara River AOC were significantly higher than levels in eggs from the upstream reference colony. Temporal trend analysis of PBDEs in herring gull eggs from the Niagara River AMC showed no significant change in levels from 2000 to 2007, similar to the trend found at the reference colony. Levels of metals, including mercury, in wildlife tissues were generally similar between AOC and reference locations and were found below lowest effect levels where thresholds are available. Arsenic was noted as one exception where levels in turtle eggs from Lyons Creek East were significantly higher than reference sites, but within the range found at other Great Lakes AOCs.

Overall, large population-level effects associated with contaminant exposure were not found in aquatic wildlife feeding in the Niagara River (Ontario) AOC. Three species of colonial waterbirds, the herring gull, the ring billed gull (*Larus delawarensis*) and the black-crowned night-heron (*Nycticorax nycticorax*), currently nest on the Canadian side of the Niagara River. Dramatic declines in levels of contaminants in herring gull eggs from the Niagara River from 1979 to 2007 and an abundance of colonial waterbirds nesting in this portion of the River (as well as the U.S. side of the River and upstream in the eastern basin of Lake Erie) suggest that contaminants do not appear to be a limiting factor for nesting populations feeding in and around the AOC. Declines in nest numbers reported for herring gulls in the Ontario portion of the AOC are likely due to lack of suitable habitat in this turbulent/high flow area of the River where gulls nest. Biological endpoints associated with impaired reproduction, growth and development examined in this study (i.e., decreased hatching success and high deformity rates in snapping turtles and changes in organ size in mink) were generally not significantly different for wildlife species found within the Niagara River (Ontario) AOC versus those from non-AOC reference locations. While population-level effects of contaminants were not apparent in this study, increased exposure to some contaminants (e.g., PCBs, arsenic, PBDEs, HCB) was evident in some aquatic-feeding individuals foraging in the Niagara River (Ontario) AOC. For these individuals, current levels may be sufficient to elicit subtle physiological as well as biochemical effects, the overall health effects of which are not known or assessed in this study.

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Acknowledgments

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Introduction

The Niagara River is an important and major waterway in the Great Lakes interconnecting Lake Erie and Lake Ontario. Approximately 58 kilometres in length, the Niagara River is fast-moving with an annual average flow of 5,700 cubic metres per second and a drop in elevation of approximately 100 metres along its course, half of which occurs at the majestic and world-renowned Niagara Falls (Niagara River Toxics Committee 1984). The Niagara River provides a source of power generation, drinking water, recreation and tourism as well as provides a source of water to (and receives effluent from) a heavily industrialized area of steel, petrochemical and chemical manufacturing industries and municipal facilities. Following significant discharge of pollutants from many of these sources which degraded water quality and impacted full use of the river's resources, the Niagara River was identified as one of 43 Great Lakes Areas of Concern in 1985. The Niagara River (Ontario) Area of Concern (AOC) encompasses the entire stretch of the Niagara River on the Canadian side and includes the Welland River watershed which comprises approximately 81% of the Ontario portion of the AOC (Niagara Peninsula Conservation Authority 1999). Water quality issues pertaining to the Welland River as well its tributaries, including Lyons Creek, were identified as part of the AOC (Niagara River Remedial Action Plan 1995). The Welland River drainage basin contributes only a small portion of the total flow to the Niagara River (i.e., less than 0.1%) since the vast majority of the water of the Niagara River comes from the four upstream Great Lakes and their respective basins (Niagara River Remedial Action Plan 1993). The Niagara River AOC is one of five AOCs jointly shared by both Canada and the United States and, as such, Remedial Action Plans (RAPs) have been developed independently by Canadian and U.S. partners to address different concerns that are specific to the Ontario and New York portions of the River, respectively.

Historical industrial and municipal discharges and surrounding waste disposal and landfill sites have greatly impaired the water quality of the Niagara River and created a legacy of environmental degradation (Allan *et al.* 1983). Toxic chemical pollutants introduced into the Niagara River from these point and non-point sources include PCBs, dioxins (notably 2,3,7,8-tetrachlorodibenzo-*p*-dioxin), mercury and organochlorine pesticides such as hexachlorobenzene and mirex. Once discharged into the water column, these persistent contaminants may settle into the sediment or be carried by the current downstream to Lake Ontario where, in either instance, they may become available to biota and biomagnify through the food web. The large majority of point source loadings are from the U.S. side of the Niagara River (where industries and waste disposal sites are more heavily concentrated) while most of the environmental issues on the Canadian side of the River are associated with non-point sources within the rural watersheds of the Niagara-Welland basin and which have impaired water quality (e.g., high turbidity and phosphorus, low oxygen; Niagara River Toxics Committee 1984; Niagara River Remedial Action Plan 1993). Numerous exceedences of water quality objectives, sediment screening criteria and fish consumption guidelines for metals, PCBs and/or some pesticides were reported in the Niagara River and tributaries in the 1970s to 1990s (Niagara River Toxics Committee 1984; Niagara River Remedial Action Plan 1993; Scheider *et al.* 1998; Karst-Riddoch *et al.* 2008). Moderately high levels of PCBs found in muscle of snapping turtle (*Chelydra serpentina*) from the Welland River in 1988/89 also raised concerns about consumption of turtles in the area (Hebert *et al.* 1993). Early studies in the 1970s to 1990s have documented elevated levels of contaminants, low reproductive success, elevated deformity rates, and biochemical impairments for some measures of health in aquatic-feeding wildlife from some Great Lakes AOCs (Bishop *et al.* 1998; de Solla *et al.* 2001; Fox *et al.* 1998, 2002, 2007).

Since 1985, significant progress has been made toward the development and implementation of a Remedial Action Plan (RAP) to address major environmental issues of concern in the Niagara River (Ontario) AOC. Stage 1 (problem definition) and Stage 2 (goals, objectives, remedial actions and implementation plan) reports have been completed and numerous restoration activities have been successfully implemented (Niagara River Remedial Action Plan 1993, 1995; Niagara Peninsula Conservation Authority 1999, 2000). Largely a cooperative process, these restoration initiatives involve partnerships among numerous governmental agencies, local industries, academia and community groups utilizing information from a number of plans/programs (e.g., Niagara River Toxics Management Plan and the Welland River Watershed Strategy) with a common overall goal, i.e., improving the water quality and overall environmental health of the AOC. An update to the Stage 2 RAP report has been completed and provides information on the current status of beneficial use impairments as defined by the Great Lakes Water Quality Agreement, reports on monitoring activities and highlights remaining priorities to restore beneficial use impairments within the Ontario portion of the AOC (Niagara River Remedial Action Plan 2009). Throughout the RAP process, specific delisting criteria have been developed, reviewed and further refined for the Niagara River (Ontario) AOC through extensive rounds of consultations with assorted governmental and non-governmental agencies, technical experts, a public advisory committee and other interest groups (Niagara River Remedial Action Plan 1995; Environment Canada 2007; Niagara River Remedial Action Plan 2009). Remedial actions have focused on addressing these criteria which represent the environmental target or “yardstick” by which the results of monitoring activities are measured. They are satisfied when targets have been met and the beneficial use impairment is no longer impaired. When all beneficial uses have been restored at an AOC, it has been successfully remediated and is delisted as an Area of Concern.

This report will focus on the current status of aquatic wildlife, specifically those species monitored by the Canadian Wildlife Service (CWS), which feed predominately from the aquatic ecosystem in the Niagara River AOC. Colonial waterbirds, which historically have been affected by high levels of contaminants in the Great Lakes (Weseloh *et al.* 1983), provide information on nesting populations of birds which rely on fish from the River and which still may be impacted by high levels of contaminants. The herring gull (*Larus argentatus*), a well-studied, non-migratory species on the Great Lakes, forages in the AOC and provides important information on possible health effects as a result of contaminant exposure from local sources. The common snapping turtle, a long-lived and widespread species with a predominately fish-based diet and with a relatively small home range, is another useful indicator of local sources of contaminants (Bishop *et al.* 1998; de Solla *et al*. 2007). As a high trophic-level, fish-eating mammal, mink (*Mustela vison*) are sensitive to the effects of PCBs and mercury and can accumulate appreciably high levels of these contaminants (Basu *et al.* 2007). Much of the current data provided are based on the results of the Fish and Wildlife Health Effects and Exposure Study, initiated in 2001 by Environment Canada, to systematically assess Canadian AOCs for the occurrence of fish and wildlife health effects that are associated with contaminants in the aquatic environment. These findings also have direct relevance to delisting criteria for some of the wildlife-related beneficial use impairments (BUIs) and results reported here have been used to assess the current status of these BUIs in the Niagara River (Ontario) AOC.

Methods

Herring Gulls (*Larus argentatus*) and Other Colonial Waterbirds

Population Surveys – Nest Counts

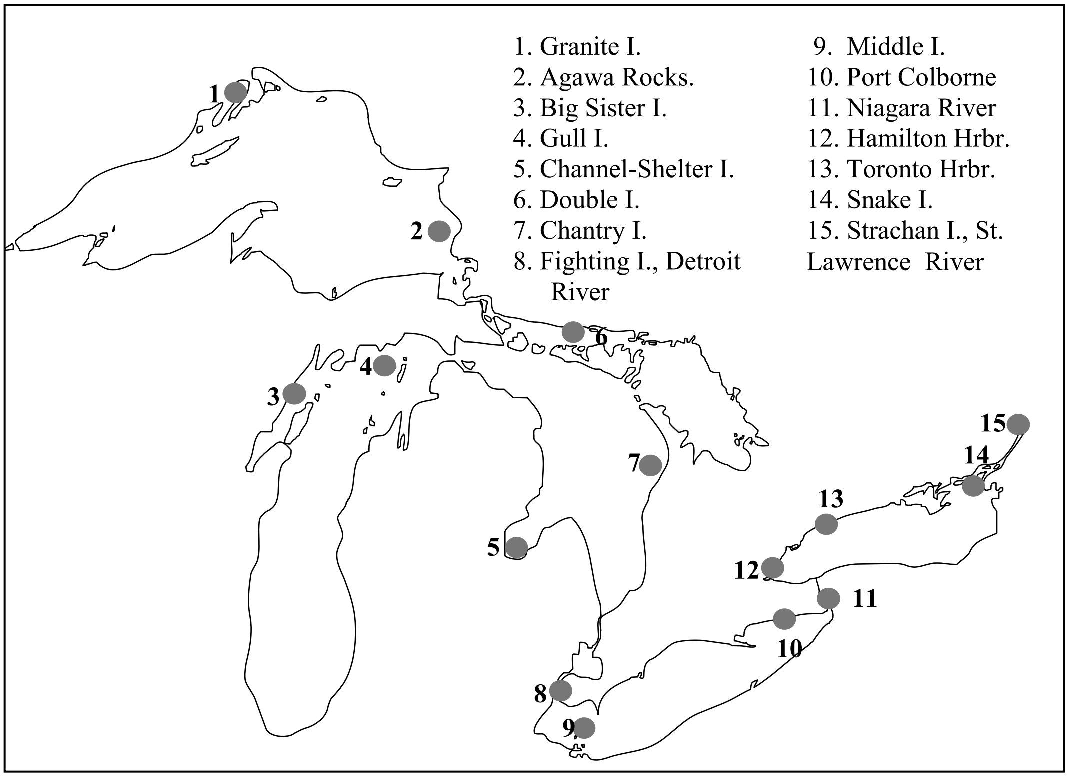
Since the 1970s, Canadian Wildlife Service (CWS) biologists have performed four decadal surveys of colonial waterbirds nesting on the Canadian side of the Great Lakes including connecting channels such as the Niagara River. The most recent decadal survey of nesting colonial waterbirds on the Niagara River (i.e. 4th survey) was conducted in 2007. The results of earlier surveys performed in 1977 (1st survey), 1990/91 (2nd survey), 1999 (3rd survey) are valuable for providing information on population trends of nesting birds in the region (Blokpoel and McKeating 1978; Blokpoel and Tessier 1996, 1998; CWS unpublished). During these surveys, all nests of colonial waterbirds were counted individually using the total count methods of Blokpoel and Tessier (1996). The results of CWS decadal surveys of colonial waterbird nests upstream on Lake Erie have also been provided and serve as a comparison to population trends of birds nesting on the Niagara River. Comprehensive surveys of the U.S. portions of the Niagara River and Lake Erie have also been conducted by U.S. Fish and Wildlife Service biologists as a part of the Great Lakes Colonial Waterbird Census during similar time periods (Scharf and Shugart 1998; Cuthbert *et al.* 2001; Cuthbert and Wires 2008) and using similar nest counting methods as reported in

Cuthbert *et al.* (2001). While surveys have been completed for the last U.S. decadal survey of the Niagara River and Lake Erie conducted in 2007/08, not all data have been submitted at this time; therefore, data reported for these regions are incomplete (Cuthbert and Wires 2008). Furthermore, it is important to note that estimates of nest numbers provided in the progress report by Cuthbert and Wires (2008) are subject to change as estimates may be revised.

Contaminants in Herring Gull Eggs

The Great Lakes Herring Gull Monitoring Program provides important spatial and temporal information on contaminant exposure of herring gulls feeding in the Great Lakes using eggs collected from 15 herring gull nesting sites known as Annual Monitor Colonies (AMCs) (Figure 1). Annual collections at many AMCs have been ongoing since the mid 1970s. On the Niagara River, herring gull eggs have been collected annually since 1979 from an unnamed island located approximately 300 metres above Niagara Falls. Collections followed the methods outlined by Mineau *et al.* (1984), Hebert *et al.* (1999) and Pekarik and Weseloh (1998). Chemical analytical methods have been described by Simon and Wakeford (2000), Neugebauer *et al.* (2000) and Won *et al.* (2001). For most collection years, chemical analyses have been performed using a pooled sample of eggs of 10 to 13 eggs. Overall spatial trends for contaminants among AMCs were examined using mean contaminant levels in eggs from 2003 to 2007, as per Weseloh *et al.* (2006). Data were ln transformed where appropriate to meet conditions of homogeneity of variances and Tukey's HSD test was used for all multiple-site comparisons. Mean concentrations of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF) were determined using data for years 2001 to 2005 since data for these compounds were not available for years 2006 and 2007. A single overall rank of contaminantion was calculated for each of the Great Lakes AMCs using herring gull eggs from 2003 to 2007 based on the mean weighted ranks for nine contaminants relative to fish flesh criteria for the protection of piscivorous wildlife and using the methods of Weseloh *et al.* (2006). Contaminants for which there are guidelines and which are included in the analysis include: 7 pesticides (sum DDT, dieldrin, HCB, HE, sum mirex, sum chlordane, and OCS), sum PCBs and 2,3,7,8-TCDD (dioxin data includes years 2003-2005 only). To assess the influence of upstream sources of contaminants relative to those within the Niagara River AOC, statistical comparisons of contaminants were performed using eggs from an upstream AMC site in the eastern basin of Lake Erie (i.e. Port Colborne Lighthouse, which is not in an Area of Concern) as well as with an AMC site typically used as a reference site on Lake Huron (i.e. Chantry Island). Temporal trends were assessed at $p<0.05$.

Figure 1. Location of the 15 herring gull Annual Monitor Colonies (AMCs) on the Great Lakes.



While health effects associated with contaminant exposure have been examined in herring gulls from other Great Lakes AOCs, unfortunately this could not be done for herring gulls nesting on the Niagara River due to the difficulty in accessing the Niagara River colony which is located immediately upstream of Niagara Falls.

Mink (*Mustela vison*)

Contaminants Levels in Liver and Somatic Indices

To assess contaminant burdens, collections of mink were focussed in areas within 7 kilometres of the Niagara River AOC shoreline. In total, 15 mink were collected from within the AOC from 2002 to 2006 in the Regional Municipality of Niagara including the City of Niagara Falls (43° 00' N, 79° 07' W), Town of Fort Erie (42° 57' N, 79° 00' W), City of Thorold (43° 02’ N, 79° 11' W), and the City of Welland (42° 58' N, 79° 12' W) (Figure 2). As a non-AOC reference site for comparison purposes, mink were collected upstream from eastern Lake Erie in Haldimand Norfolk Regional Municipality in Dunn Township, Ontario (42° 52' N, 79° 33' W) and also within 7 kilometres of the Lake Erie shoreline (Figure 3). Finally, mink were collected from inland Ontario reference sites (i.e., more than 10 km from the eastern Lake Erie, Lake Ontario, Lake St. Clair and St. Lawrence River shorelines) which included Lancaster

Township north of Cornwall, Storrington Township north of Kingston, Dover Township west of Lake St. Clair, North Cayuga Township east of Simcoe, Howard Township south of Chatham and Flamborough Township north of Hamilton. Overall, collection years of mink at reference sites ranged from 1999 to 2004. There is a substantial body of literature on the health effects of PCBs on experimentally exposed mink in ranch situations. Effect levels have been linked with liver concentrations of exposed animals. The number of animals with PCB concentrations exceeding thresholds for reproductive endpoints was calculated and compared among sites.

Mink carcasses were pelted by trappers, wrapped in tinfoil and held at -20°C until collection by CWS personnel. The location where the animal was captured as well as the date of capture were collected by trappers and verified by CWS personnel. Mink carcasses were brought to the Ontario Veterinary Collage of Ontario in Guelph and necropsied under the supervision of a veterinary pathologist. All organs were removed, weighed and examined for lesions and sex was noted. Livers were excised with hexane cleaned instruments and stored in chemically cleaned containers. Livers were stored at -20°C prior to chemical analysis. The baculum, or penis bone, was removed from adult male mink, dried and then cleaned by a colony of dermestid beetles at the Ontario Veterinary College and at the Royal Ontario Museum in Toronto. The baculum were then washed and dried in a drying oven at 80°C for 10 hours to remove excess water and until they had attained a stable weight. Baculum were weighed and the length measured using Vernier calipers.

Livers were sent to the National Wildlife Research Centre in Hull Québec for analyses of chlorinated organic contaminants and metals. Quantitative analysis of organochlorine pesticides and PCBs was performed using capillary gas chromatography, coupled with a mass selective detector operated in selected ion monitoring mode and according to the methods of Norstrom *et al.* (1988). Total mercury in liver was measured using an Advanced Mercury Analyzer (AMA-254). For twelve mink trapped within the Niagara River AOC, organic (methyl) mercury concentrations were determined by first extracting the organic mercury component from the liver and then analyzing the extracts on the AMA-254. Selenium, arsenic, cadmium and lead concentrations in liver were determined either by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or by graphite furnace atomic absorption spectrometry (GFAAS).

Since organ weights varied significantly with body size, organ somatic indices were determined by dividing organ weight by body weight. Analysis of variance tests were performed to examine for differences in mean contaminant concentrations and biological endpoints among sites followed by Tukey's HSD post-hoc tests where tests were significant. Data were transformed where necessary to

Figure 2. Mink collected by trappers in the Niagara River AOC from 2002-2006. Circles indicate the approximate locations of 15 mink captured within 7 km of the shoreline and which are coded as follows: filled red circles denote the location of one mink, green filled circles of two mink and yellow filled circles of three mink t
Lyons

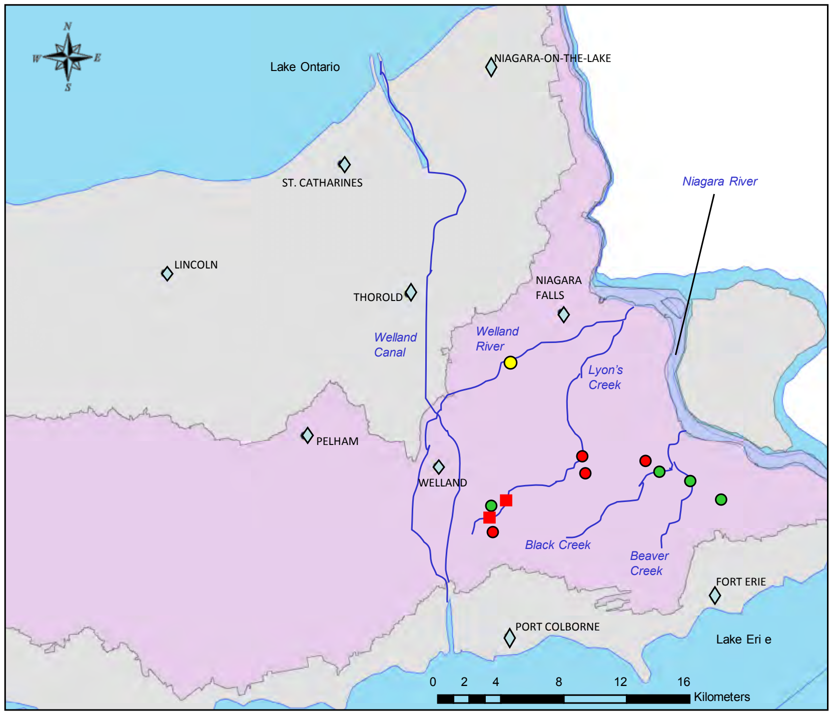
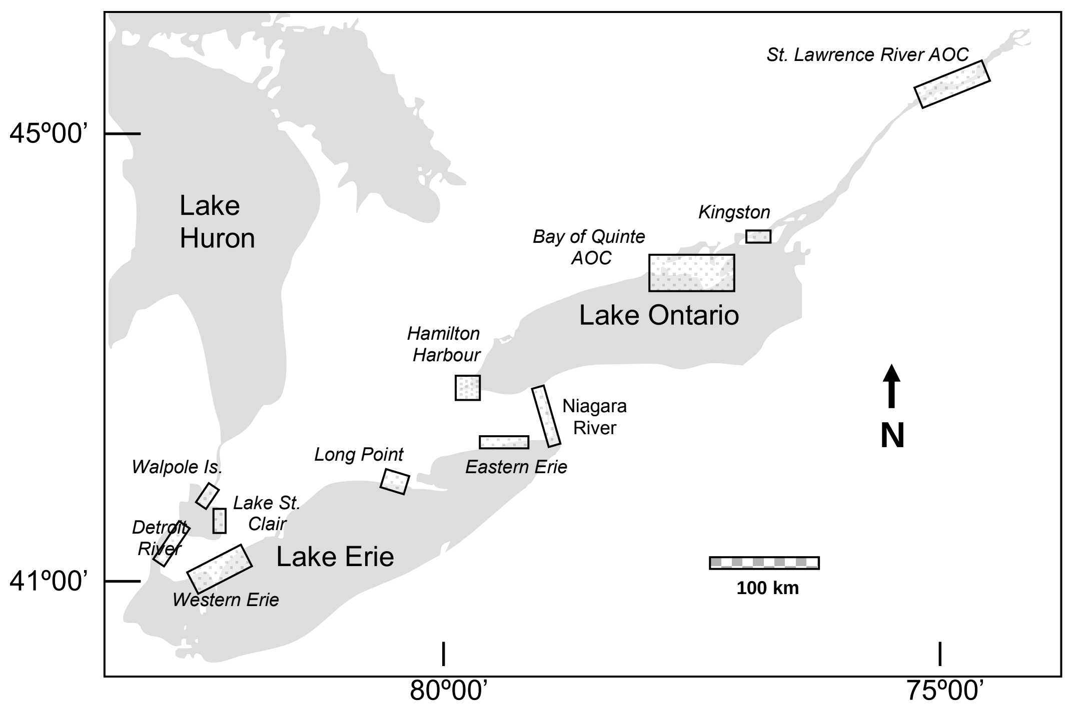


Figure 3. Great Lakes locations from which mink carcasses were obtained from commercial trappers in 1999-2006 including the eastern Lake Erie (non-AOC) reference site.



meet conditions of parametric testing. If data failed the assumption of equal variance (Levene's Test), comparisons were made using a Kruskal-Wallis one way Analysis of Variance (ANOVA) by ranks followed by non-parametric multiple contrast tests for unequal sample size (Zar 1984).

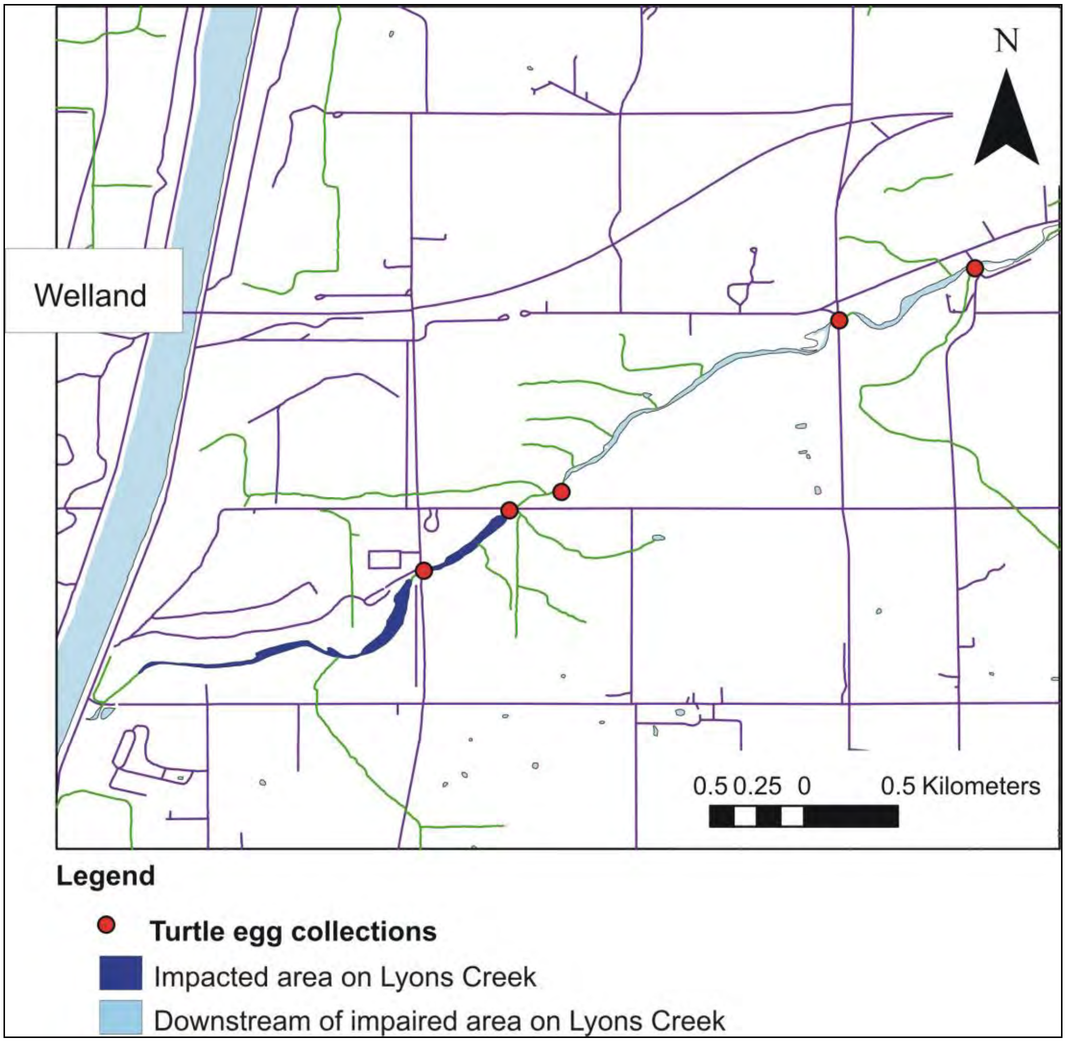
Snapping Turtles (*Chelydra serpentina*)

Contaminants in Snapping Turtle Eggs, Hatching Success and Hatchling Deformity Rates

From 2001 to 2004, as part of a Great Lakes basin-wide study, snapping turtle eggs were collected from wetlands at or near Areas of Concern (AOCs) in the Niagara River, Lake Erie, Lake Ontario, Detroit River, St. Lawrence River, and from two remote reference sites (Tiny Marsh and Algonquin Provincial Park). In the Niagara River AOC, turtle eggs were collected from Lyons Creek East (42° 58' N, 79° 12' W and 42° 59' N, 79° 11' W), a creek which flows from its headwaters in the Welland Canal and eastward to the Welland River where it discharges into the Niagara River. While only two collections sites are indicated in Figure 2 (due to the scale of the map), eggs were actually collected from five locations ranging between 1.8 to 5 kilometres along the Creek downstream from the Welland Canal (Figure 4). In Lake Erie, there is no immediate upstream non-AOC egg collection location which could serve as a suitable reference site for discerning between local effects specific to the Niagara River AOC and potential outside-of-the-AOC influences. Therefore for the purpose of this report, two references locations were selected for comparison purposes: one remote upstream site, Tiny Marsh, located near Elmvale on the shore of Lake Huron (44° 36' N, 79° 56' W) and a second non-AOC downstream location, the Upper Canada Bird Sanctuary on the St. Lawrence River (UCBS, 44° 59' N, 75° 01' W; 44° 59' N, 75° 02' W; 44° 58' N, 75° 02' W). These two sites represent the two closest non-AOC Great Lakes locations for which egg collection data are available and also provide a broad perspective of contaminant levels observed at Great Lakes sites outside of Canadian AOCs.

Entire clutches of eggs were collected within 48 h of oviposition. The eggs from each clutch were placed in plastic containers containing moistened vermiculite, then stored at approximately 18-24^{o}C. Eggs were incubated at the Canada Centre for Inland Waters in Burlington, Ontario. Within two weeks of collection, all eggs were placed in incubators under constant temperature conditions of 27.5 ± 1^{o}C. Water loss through evaporation was replaced every two to three days as required to maintain relatively constant moisture. Eggs were maintained under these conditions until hatching. Hatchling turtles were assessed for gross morphological deformities of the carapace scutes, eyes, head, limbs and tail. Adult snapping turtles were also trapped from Lyons Creek using baited hoop nets and examined for deformities.

Figure 4. Snapping turtle egg collection locations along Lyons Creek East relative to impacted area (as identified in Niagara River Remedial Action Plan 2009).



A subset of eggs, usually five, was selected for contaminant analysis from most clutches; if the clutch was small, fewer eggs were taken for contaminant analysis. Eggs were selected in a pseudo-randomly but stratified manner; eggs were ordered from the egg on top of the nest (last egg laid) to the egg on the bottom of the nest (first egg laid). Each clutch was divided into five groups of approximately equal size, and within each group an egg was selected haphazardly. Subsequently, the egg contents were pooled and frozen in hexane-cleaned amber glass jars at –20°C.

The frozen egg samples were shipped to GLIER (Great Lakes Institute of Environmental Research, University of Windsor) for the analysis of polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and organochlorine pesticides, which included *p*,*p*'-DDE (a breakdown product of

DDT), dieldrin, mirex, sum chlordane (sum of concentrations of oxychlordane, cis-chlordane, trans-chlordane, cis-nonachlor and trans-nonachlor), HE, HCB, and OCS. For PCBs, organochlorine pesticides and by-products, all of the eggs in 2001 and 2002 were quantified using gas chromatography-electron capture detection (GC-ECD) while eggs in 2003 and 2004 were analysed using gas chromatography-mass spectrometry (electron ionization) (GC-MSD (EI)). Sum PCB concentrations consist of all 34 congeners that were common to both GC-ECD and GC-MSD. For PBDEs, all egg samples were analysed using GC-mass spectrometry-electron capture negative ionization (GC-MS(ECNI)) and sum PBDEs reported are based on the sum of nine PBDE congeners which include BDE-28, -47, -99, -100, -138, -153, -154, -183, and -209. Contaminants were expressed on a wet weight basis. For PCBs and organochlorine pesticides, the method limit of quantification (MLOQ) ranged between 0.01 to 0.09 ng/g for the eggs samples analyzed by GC-ECD, 0.1 ng/g for the eggs analysed using GC-MSD, and 0.01 ng/g for PBDEs using GC-MS(ECNI). Further details of chemical analyses as well as quality assurance and quality control analyses are found in de Solla *et al.* (2007, 2008). Selenium, arsenic, cadmium and lead concentrations in eggs were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and total mercury in eggs was measured using the Advanced Mercury Analyzer (AMA-254).

Statistical analyses of organochlorine pesticide, PCB, PBDE and metal data were tested for homogeneity of variance using Levene's test and then ln transformed (where necessary) to meet conditions of parametric testing. Hatching success and deformities were calculated for each clutch as proportions of eggs incubated and eggs hatched, respectively, and then arcsine transformed prior to analysis. Analysis of variance tests were performed to examine differences among sites followed by Tukey's HSD test for all multiple comparisons. Organochlorine pesticides and PCB/PBDE congeners which were below detection limits were replaced with an estimate of the concentration using the method outlined in de Solla *et al.* (2008). All results were considered significant at $p<0.05$. Toxic equivalents were calculated using coplanar PCBs with dioxin-like effects (i.e., some non-*ortho* and mono-*ortho* congeners), dioxins and furans and based on toxic equivalency factors reported by van den Berg *et al.* (1998) for birds.

For this report, statistical analyses compared contaminants levels in eggs, hatching success and deformity rates in turtles from three study sites which included Lyons Creek East in the Niagara River AOC, and the two reference sites, Tiny Marsh (upstream) and UCBS (downstream). Given the relatively higher levels of some contaminants found in eggs from the downstream reference site at UCBS (see results below), similar analyses were also performed using only the Niagara River site and Tiny Marsh (i.e., excluding UCBS) to assess spatial similarities inside and outside of the Area of Concern. Data for Algonquin

Provincial Park are presented for comparative purposes only and were not included in any of the statistical analyses.

Results and Discussion

Herring Gulls (*Larus argentatus*) and Other Colonial Waterbirds

Population Surveys – Nest Counts

In 2007 as part of the 4th decadal CWS Great Lakes colonial waterbird survey, three species including the ring-billed gull (*Larus delawarensis*), herring gull (*Larus argentatus*) and black-crowned night-heron (*Nycticorax nycticorax*) were found nesting on the Canadian side of the Niagara River (CWS unpublished; Table 1A). In total, 915 nests (=breeding pairs) were counted at seven sites situated on natural habitat (i.e., small islands and rocks) and on artificial habitat (i.e., a gated control structure). Ring-billed gulls were the most abundant species with one large colony of 508 nests counted at Table Rock in 2007. Black-crowned night-heron were found at three nesting sites (378 nests) which included one large colony of 296 nests and one newly colonized site of 30 nests on an island where the birds had not been found during the 3rd survey. Twenty-nine herring gull nests were counted at five sites including three single nest sites in 2007. Numbers of ring-billed gull nests have remained high at over 300 nests over the four survey periods and over the last two surveys increased by 60% from 317 nests in 1999 to 508 nests in 2007, representing an annual rate of increase equal to 6.1% (Blokpoel and McKeating 1978; Blokpoel and Tessier 1996; CWS unpublished). Black-crowned night-heron nests which were relatively fewer in number during the 1st survey period in 1977 (65 nests) have at least tripled in number since that time and between the 3rd and 4th decadal surveys increased in number by 54% from 246 nests in 1999 to 378 nests in 2007 at an annual rate of increase equal to 5.5% (Blokpoel and McKeating 1978; Blokpoel and Tessier 1998; CWS unpublished). In contrast, herring gull nests reached a peak in number in 1990 to an estimated 104 nests at two sites and then declined dramatically by 67% from 88 nests in 1999 to 29 nests in 2007 at an annual rate of decline of -13.0% (Blokpoel and McKeating 1978; Blokpoel and Tessier 1996; CWS unpublished). One possible reason for the decline in herring gull nests may be related to habitat availability. Specifically at the largest herring gull nesting site situated above Niagara Falls (where 24 nests were counted in 2007), a qualitative assessment suggests that floating debris (e.g., tree branches) in this high-flow area may have reduced and compacted the total area of available ground nesting habitat for these gulls (D.V.C. Weseloh pers. obs.). No other ground-nesters (i.e., ring-billed gulls) were found at this site. While there have been reports of botulism poisoning in gulls nesting on Lake Ontario, there have been no such cases in Ontario gulls collected from the Niagara River in 2007 or 2008 and only a few cases in birds from the eastern basin of Lake Erie prior to that time (Canadian Cooperative Wildlife

Health Centre 2009). Overall, the total number of colonial waterbird nests on the Canadian side of the Niagara River increased from 651 nests in 1999 to 915 nests in 2007.

Table 1. Census data of colonial waterbird nests (=pairs) on the Canadian side of the Niagara River (A), the Canadian side of Lake Erie (B), and the eastern basin of the Canadian side of the Lake Erie (C) during the 1st (1977), 2nd (1990/91), 3rd (1997-2000) and 4th (2007) decadal surveys as part of the Great Lakes colonial waterbird surveys conducted by the Canadian Wildlife Service (Blokpoel and McKeating 1978; Blokpoel and Tessier 1996, 1998; CWS unpublished). Annual rates of change indicated are for the 3rd and 4th surveys. NC denotes rate cannot be calculated.

A) Niagara River (Canada)

Species	**Census Year**				**Annual Rate of Change**
	1977	**1990/91**	**1999**	**2007**	
Ring-billed Gull	400	400	317	508	+6.1%
Herring Gull	38	104	88	29	-13.0%
Black-crowned Night-Heron	65	426	246	378	+5.5%
Totals	**503**	**930**	**651**	**915**	**-**

B) Lake Erie (Canada)

Species	**Census Year**				**Annual Rate of Change**
	1977	**1990/91**	**1997-2000**	**2007**	
Ring-billed Gull	14,730	48,208	43,988	36,153	-2.4%
Double-crested Cormorant	57	1,956	7,434	12,186	+5.1%
Herring Gull	1,085	4,203	2,884	2,495	-1.8%
Great Black-backed Gull	0	0	1	0	-100%
Black-crowned Night-Heron	1,220	151	98*	65	-5.7%
Great Blue Heron	76	368	69	326	+21.4%
Great Egret	21	143	32**	61	+8.4%
Caspian Tern	0	0	0	300	NC
Common Tern	1,524	1,135	540	14	-33.4%
Totals	**18,713**	**56,164**	**55,046**	**51,600**	**-**

* Middle Sister Island and East Sister Island surveyed for black-crowned night-heron in 2003
** East Sister Island surveyed in 2001

C) Lake Erie (Canada) – Eastern Basin Only

Species	**Census Year**				**Annual Rate of Change**
	1977	**1990/91**	**1997-2000**	**2007**	
Ring-billed Gull	14,729	48,158	43,752	36,135	-2.4%
Double-crested Cormorant	0	2	3	1,825	+89.9%
Herring Gull	344	381	486	411	-2.1%
Great Black-backed Gull	0	0	1	0	-100%
Black-crowned Night-Heron	0	0	5	10	+10.4%
Caspian Tern	0	0	0	300	NC
Common Tern	1,500	935	540	14	-33.4%
Totals	**16,573**	**49,476**	**44,787**	**38,695**	**-**

Nests counts of all colonial waterbirds breeding on the Canadian side of Lake Erie were conducted during similar periods and serve as a comparison to trends observed on the Canadian side of the Niagara River. Nearly 52,000 nests of eight species at 12 different nesting locations were counted in the 4th decadal CWS Great Lakes colonial waterbird survey (Table 1B; CWS unpublished). Three of the 12 nesting sites were located in the eastern basin of Lake Erie near Dunnville and Port Colborne while the remaining nine nesting sites were localized in the western basin of Lake Erie and west of Point Pelee. Ring-billed gulls were the most abundant species on Canadian Lake Erie (comprising 70% of all nests found) with nest numbers declining by 18% from 1999 to 2007 at an average rate of decline of -2.4% per year. Similar to the trend in the Niagara River, a decline in herring gull nests was also evident in Canadian Lake Erie where numbers dropped by 13% from 2,884 nests in 1999 to 2,495 nests in 2007 but at a relatively lower rate of decline equal to -1.8% per year. Black-crowned night-heron, which nested in relatively fewer numbers on Canadian Lake Erie compared to the Niagara River, dropped by 34% from 98 nests in the 3rd survey to 65 nests in the 4th survey (-5.7% per year). Common terns (*Sterna hirundo*) nested at one colony on the Port Colborne Breakwall on the north shore of Lake Erie where a dramatic decline in nest numbers was found between the last two surveys, from 540 nests in 1998 to 14 nests in 2007 (-33.4% per year). By 2009, no common terns were found nesting on the Port Colborne Breakwall. Despite ongoing conservation efforts, the eventual abandonment of the colony was attributed to egg predation by ring-billed gulls and/or mammalian predators as well as lack of suitable nesting substrate (Morris 2009; R.D. Morris pers. comm.). A single great black-backed gull (*Larus marinus*) nest was found during the 3rd census in 1999 but was not found in 2007. Double-crested cormorant (*Phalacrocorax auritus)* was the second most abundant species on Canadian Lake Erie with nest numbers increasing by 64% from 7,434 nests in 1997 to over 12,000 nests in 2007 (5.1% per year). Current evidence based on annual surveys of double-crested cormorants nesting lake-wide on Lake Erie indicate however that numbers of cormorant nests reached a peak in 2004 (to over 19,000 nests) and have then steadily declined to approximately 16,600 nests counted in 2007 (CWS and New York State Department of Environmental Conservation (NYSDEC) unpublished). While preliminary, this suggests that numbers of nesting cormorants on Lake Erie may be declining or have stabilized. There was also evidence of illegal destruction of cormorant nests and killing of young at Mohawk Island in 2007 (CWS unpublished). Rates of increase in nest numbers were apparent for the great blue heron (*Ardea herodias*) (21.4% per year) and great egret (*Ardea alba*) (8.4% per year) in Canadian Lake Erie between the 3rd and 4th CWS decadal surveys. Caspian tern (*Sterna caspia*) also recently colonized Canadian Lake Erie where 300 nests were found at Mohawk Island in the eastern basin in 2007. These birds were found nesting on rows of dead zebra and quagga mussel shells which were deposited on the Island and which appeared to provide them with a suitable substrate on which to nest (D.V.C. Weseloh pers. obs.).

Population trends of colonial waterbirds nesting at the three Canadian nesting sites in the eastern basin of Lake Erie and immediately upstream of the Niagara River are provided in Table 1C. Overall, the eastern basin of Lake Erie represents a significant proportion of the total Canadian nesting population since most of the ring-billed gulls (99.9%) and all nesting common terns and Caspian terns were found at this end of the Lake in 2007 (compare to Table 1B). No nesting great blue herons or great egrets however were found in this part of Lake Erie. While fewer in number relative to all of Canadian Lake Erie, herring gulls in the eastern basin showed a similar rate of decline in nest numbers relative to the entire Lake (-2.1% per year). Unlike the trend for Canadian Lake Erie but similar to the trend found in the Niagara River, an increase in black-crowned night heron nests was found in the eastern basin between the 3rd and 4th surveys (10.4% per year). Finally, while the eastern basin represents a relatively small proportion (15%) of nesting cormorants on Canadian Lake Erie, a dramatic increase in nest numbers was also found between the 3rd and 4th surveys at the only two sites where they were found nesting in 2007 (i.e., Mohawk Island and Port Colborne Breakwall; 89.9% per year).

During the 4th decadal colonial waterbird survey by the U.S. Fish and Wildlife Service (USFWS) on the U.S. side of the Niagara River in 2007, over 13,700 nests of seven colonial waterbird species were reported at six different sites on the River (Table 2A; Cuthbert and Wires 2008). These included four nesting species, double-crested cormorant, great blue heron, great egret and common tern, which were not found on the Canadian side of the River. Overall, the U.S. side supports a much higher proportion of nesting birds due to a greater availability of suitable habitat on many large islands (e.g., Strawberry Island and Motor Island) compared to nesting sites on the Canadian side of the River which consist of small islands and rocky outcrops and which are relatively much smaller in size. It is difficult to report on U.S. population trends between the 3rd and 4th surveys since nest count data for this side of the River at this time are incomplete. Nonetheless, ring-billed gulls have always been the most abundant species found nesting on this side of the River, representing during the first three decadal surveys between 88-98% of all nests of colonial waterbirds counted. Numbers of nesting double-crested cormorants have increased since 1992 when they first colonized the U.S. side of the River at Buckhorn Weir (seven nests). Annual counts of double-crested cormorants on the U.S. side of the River indicate that nest numbers gradually increased over the next thirteen year period to a peak of 705 nests at five sites in 2005 and then subsequently declined to 552 nests at four sites in 2007 (CWS and NYSDEC unpublished).

Table 2. Census data of colonial waterbird nests (=pairs) on the U.S. side of the Niagara River (A), the U.S. side of Lake Erie (B) and the eastern basin of the U.S. side of the Lake Erie (C) during the 1st (1977), 2nd (1989-1991), 3rd (1997-1999) and 4th (2007/08) decadal surveys as part of the Great Lakes colonial waterbirds surveys conducted by the U.S. Fish and Wildlife Service (Scharf and Shugart 1998; Cuthbert *et al.* 2001; Cuthbert and Wires 2008). Data presented for the U.S. sides of the Niagara River and Lake Erie for the 4th survey are incomplete and hence no annual rates of change have been calculated.

A) Niagara River (U.S.)

Species	Census Year			
	1977	**1989-1991**	**1997-1999**	**2007***
Ring-billed Gull	4,809	11,427	16,859	12,917
Double-crested Cormorant	0	0	49	552
Herring Gull	110	156	24	12
Black-crowned Night-Heron	0	0	38	98
Great Blue Heron	0	0	40	61
Great Egret	0	0	7	20
Common Tern	518	160	113	89
Totals	**5,437**	**11,743**	**17,130**	**13,749**

* Data for 4th survey are incomplete (i.e., counts not yet available for two sites).

B) Lake Erie (U.S.)

Species	Census Year			
	1977	**1989-1991**	**1997-1999**	**2007/08***
Ring-billed Gull	583	17,555	24,099	24,490
Double-crested Cormorant	0	0	1,823	4,414
Herring Gull	1,208	6,512	6,074	1,193
Black-crowned Night-Heron	3,000	1,568	460	767
Great Blue Heron	2,538	2,546	2,122	1,528
Little Blue Heron	0	1	0	1
Great Egret	200	1,425	884	948
Snowy Egret	0	1	13	12
Cattle Egret	0	11	30	16
Common Tern	263	644	909	1,424
Totals	**7,792**	**30,263**	**36,414**	**34,793**

* Data for 4th survey are incomplete

C) Lake Erie (U.S.) – Eastern Basin Only

Species	Census Year			
	1977	**1989-1991**	**1997-1999**	**2007/08***
Ring-billed Gull	524	10,879	7,137	24,490
Double-crested Cormorant	0	0	46	277
Herring Gull	0	23	114	160
Common Tern	0	581	790	1,237
Totals	**524**	**11,483**	**8,087**	**26,164**

* Data for 4th survey are complete but may be subject to change.

During the 4th decadal survey of the U.S. side of Lake Erie in 2007/08, over 34,700 nests of ten colonial waterbird species were counted (Table 2B; Cuthbert and Wires 2008). Three species nesting on the U.S. side of the Lake Erie but not on the Canadian side in the last survey included the snowy egret (*Egretta thula*), cattle egret (*Bubulcus ibis*) and the rare little blue heron (*Egretta caerulea*). Within the eastern basin of U.S. Lake Erie, four species were found nesting at seven sites and preliminary results show large increases in nest numbers of all species in this part of the Lake between the 3rd and 4th surveys (Table 2C).

Recent efforts to increase common tern habitat on the U.S. side of Lake Erie in Buffalo may have contributed to the 57% increase in nest numbers of common terns (from 790 to 1,237 nests) between surveys in this region. It is possible that many of these birds may have previously nested at the Port Colborne Breakwall in eastern Canadian Lake Erie where a decline in nest numbers was reported between survey periods at this colony (see Table 1B; Morris 2009).

Spatial Trends of Contaminants in Herring Gull Eggs

As non-migratory species, herring gulls are excellent biomonitors of regional contaminant conditions in the Great Lakes. Herring gulls eggs were collected in 2006 and 2007 from an unnamed island on the Niagara River, Port Colborne Lighthouse, an upstream Annual Monitor Colony (AMC) on Lake Erie, and Chantry Island, the reference site in Lake Huron and analyzed for contaminants. Mean contaminant concentrations for 11 compounds (i.e., organochloirine pesticides, PCBs, polybrominated diphenyl ethers (sum PBDEs) and mercury) for these two years in pooled eggs are provided in Table 3. For all three AMCs, PCBs (both 1:1 and sum) in herring gull eggs were found at the highest concentrations of all compounds. Concentrations of sum PBDEs and *p*,*p*'-DDE in eggs from the Niagara River ranked second and third highest of all compounds, respectively. Conversely in eggs from Port Colborne Lighthouse and Chantry Island, *p*,*p*'-DDE levels were ranked second followed by sum PBDEs which were roughly one-half of *p*,*p*'-DDE levels. Mercury concentrations were ranked fourth highest at all three AMCs. For the remaining compounds, mean concentrations in herring gull eggs were below 0.10 μg/g. Overall among the three AMCs, eggs from Niagara River were the most contaminated for two of 11 compounds, hexachlorobenzene (HCB) and sum PBDEs, and were never the least contaminanted for any compounds. Eggs from Port Colborne Lighthouse were the least contaminated for eight of 11 compounds (*p*,*p*'-DDE, dieldrin, HCB, heptachlor epoxide (HE), mirex, octachlorostyrene (OCS), sum chlordane and sum PBDEs) and were the most contaminated for the remaining compounds which included PCBs (1:1 and sum) and mercury. Eggs from Chantry Island were the least contaminated for PCBs (1:1 and sum) and mercury but were the most contaminated for six of 11 compounds (i.e., pesticides including *p*,*p*'-DDE, dieldrin, HE, mirex, OCS, sum chlordane). No statistical tests were possible on only two years of pooled data. No dioxin or furan data are available for these two years.

Significant differences in mean contaminants levels were found among the 15 Great Lakes AMCs for nine of 13 compounds from 2003 to 2007 ($p<0.05$, Figure 5). These compounds include: *p*,*p*'-DDE, PCBs (1:1 and sum), mirex, HE, OCS, 2,3,7,8-TCDD (data for 2001 to 2005), sum PBDEs (no data available for 2004), and mercury. No significant differences in mean contaminant concentrations were found among Great Lakes AMCs for dieldrin, sum chlordane, HCB, and 2,3,7,8-TCDF (data for 2001 to 2005). Figure 5 provides additional details with regard to significant differences in contaminant levels in eggs from the Niagara River AMC relative to other AMCs on the Great Lakes. For all compounds, the Niagara River AMC was generally ranked as intermediate-low of all AMCs, with the exception of HCB and mirex where this AMC was ranked first and fifth of 15, respectively. Mercury concentrations in herring gull eggs from Niagara River from 2003 to 2007 did not approach the threshold level of 0.5 ug/g typically associated with adverse reproductive effects in birds (range=0.07 to 0.17 μg/g; Thompson 1996).

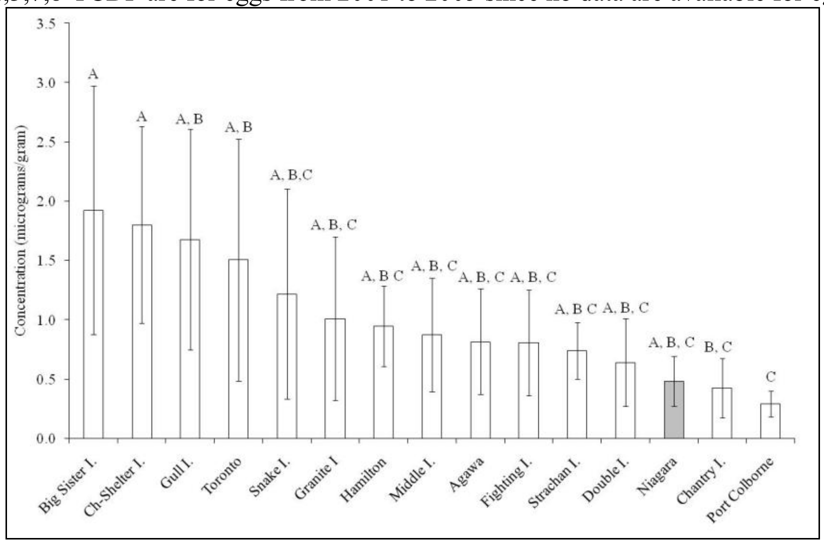
Two-site comparisons of contaminants in eggs from 2003 to 2007 at the Niagara River AMC relative to the Port Colborne Lighthouse AMC on Lake Erie showed no significant differences in mean concentrations for 12 of the 13 compounds. Sum PBDEs were the one exception where levels were significantly higher in eggs from the Niagara River AMC compared to Port Colborne Lighthouse ($t_{(6)}=4.51$, $p=0.0041$). Levels of mirex were also marginally significantly higher in eggs from Niagara River compared to Port Colborne Lighthouse ($t_{(8)}=2.16$, $p=0.063$). Comparisons of mean contaminant concentrations at Niagara River, Port Colborne Lighthouse and Chantry Island showed no significant differences among the three AMCs for any compounds with the exception of: 1) PCBs (both 1:1 and sum) where means were not significantly different between either Niagara River and Port Colborne Lighthouse and Niagara River and Chantry Island but where eggs from Port Colborne Lighthouse had significantly higher mean PCB levels than Chantry Island ($F_{(2,12)}>4.53$, $p<0.034$), and; 2) PBDEs where levels were significantly higher in eggs from the Niagara River compared to Port Colborne Lighthouse but where means were not significantly different between either Niagara River and Chantry Island and Chantry Island and Port Colborne Lighthouse ($F_{(2,9)}=5.22$, $p=0.031$). There is limited knowledge on the effects of PBDEs exposure in humans and animals but their structural similarity and toxicity tests suggest their toxicity may be somewhat similar to PCBs (Darnerud *et al*. 2001).

Table 3. Two-year mean (SD) concentrations of organochlorine pesticides, PCB 1:1, sum PCBs, and mercury (µg/g, wet weight) in herring gull eggs from the Niagara River AMC, Port Colborne Lighthouse AMC (upstream herring gull colony on Lake Erie), and Chantry Island AMC on Lake Huron in 2006 and 2007. Mean sum PBDE concentrations in eggs during this period are also shown (µg/kg, wet weight). Results are based on the analyses of a single pooled egg sample of 10-13 eggs per site. No dioxin or furan data are available for these years.

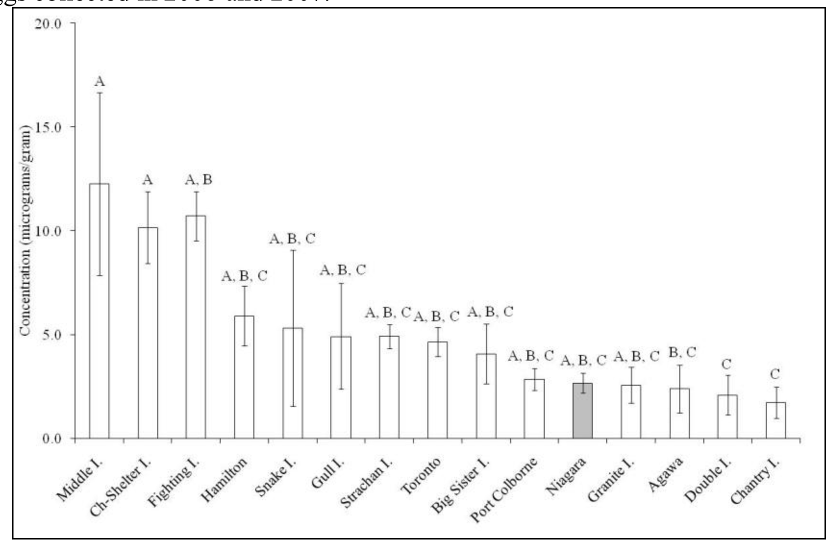
AMC	Year	*p,p'*-DDE	Dieldrin	HCB	HE	Mirex	OCS	Sum Chlordane	PCB 1:1[1]	Sum PCBs[2]	Mercury	Sum PBDEs[3]
Niagara River	2006	0.410	0.020	0.083	0.008	0.036	0.002	0.029	4.996	2.824	0.139	308.460
Niagara River	2007	0.501	0.009	0.011	0.008	0.057	0.002	0.033	3.875	2.181	0.115	691.760
	Mean	**0.455**	**0.014**	**0.047**	**0.008**	**0.047**	**0.002**	**0.031**	**4.436**	**2.503**	**0.127**	**500.110**
	SD	0.064	0.008	0.051	0.000	0.015	0.000	0.003	0.792	0.455	0.017	271.034
Port Colborne Lighthouse	2006	0.284	0.000	0.008	0.002	0.001	0.000	0.006	4.966	2.881	0.139	156.530
Port Colborne Lighthouse	2007	0.348	0.017	0.005	0.008	0.018	0.001	0.029	4.709	2.558	0.129	138.488
	Mean	**0.316**	**0.009**	**0.007**	**0.005**	**0.010**	**0.001**	**0.017**	**4.837**	**2.720**	**0.134**	**147.509**
	SD	0.045	0.012	0.002	0.005	0.012	0.001	0.016	0.181	0.229	0.007	12.758
Chantry I.	2006	0.804	0.056	0.014	0.023	0.083	0.005	0.086	2.866	1.695	0.088	192.160
Chantry I.	2007	0.343	0.015	0.006	0.009	0.017	0.001	0.029	3.220	1.815	0.080	277.352
	Mean	**0.573**	**0.036**	**0.010**	**0.016**	**0.050**	**0.003**	**0.058**	**3.043**	**1.755**	**0.084**	**234.756**
	SD	0.327	0.029	0.006	0.010	0.046	0.003	0.041	0.250	0.085	0.005	60.240

[1] Based on 1:1 ratio of Aroclor 1254:1260
[2] Based on the sum of 59 PCB congeners
[3] Based on the sum of 25 PBDE congeners

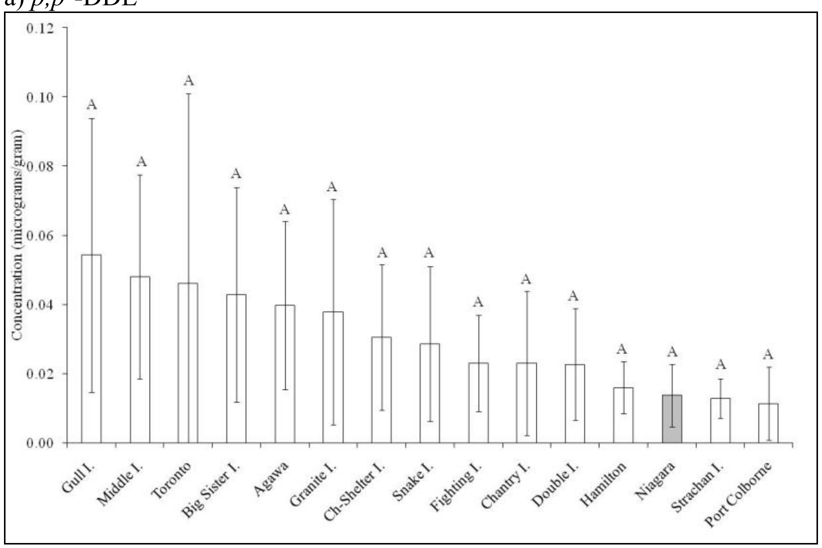
Figure 5. Mean (SD) contaminant levels in herring gull eggs from 15 Annual Monitor Colonies (AMCs) on the Great Lakes from 2003-2007. The shaded bar indicates the Niagara River AMC. No contaminants data were available for Fighting Island in 2006 or sum PBDEs in 2004. Means for 2,3,7,8–TCDD and 2,3,7,8-TCDF are for eggs from 2001 to 2005 since no data are available for eggs collected in 2006 and 2007.



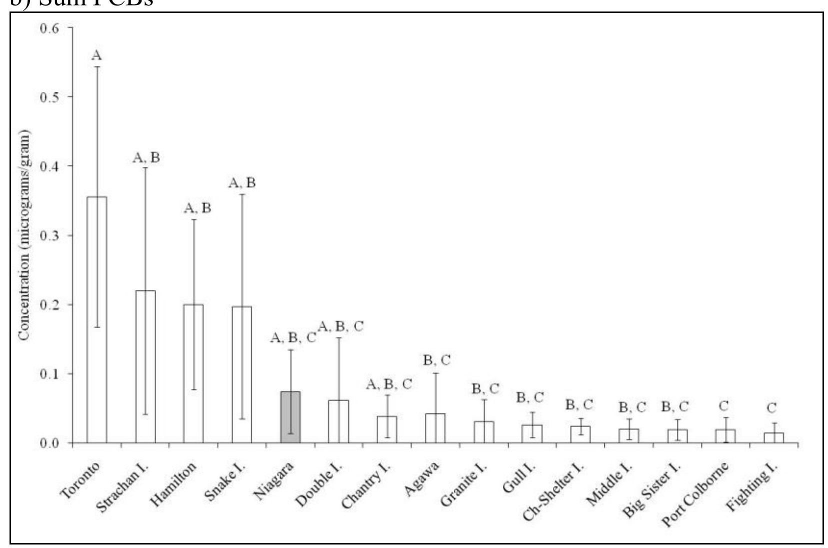
a) *p,p'*-DDE



b) Sum PCBs

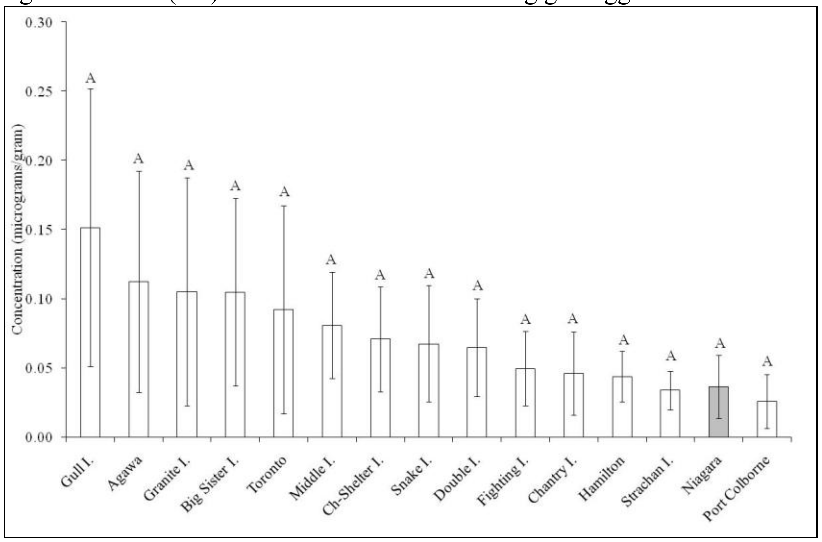


c) Dieldrin

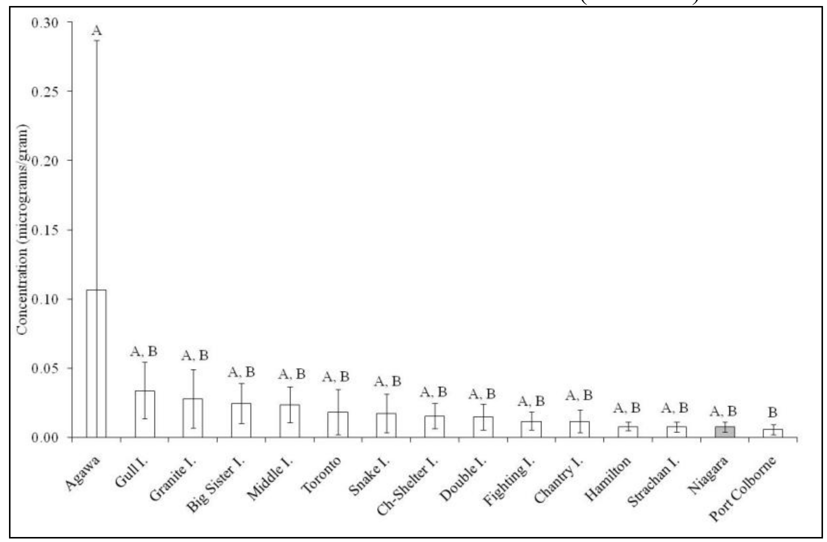


d) Mirex

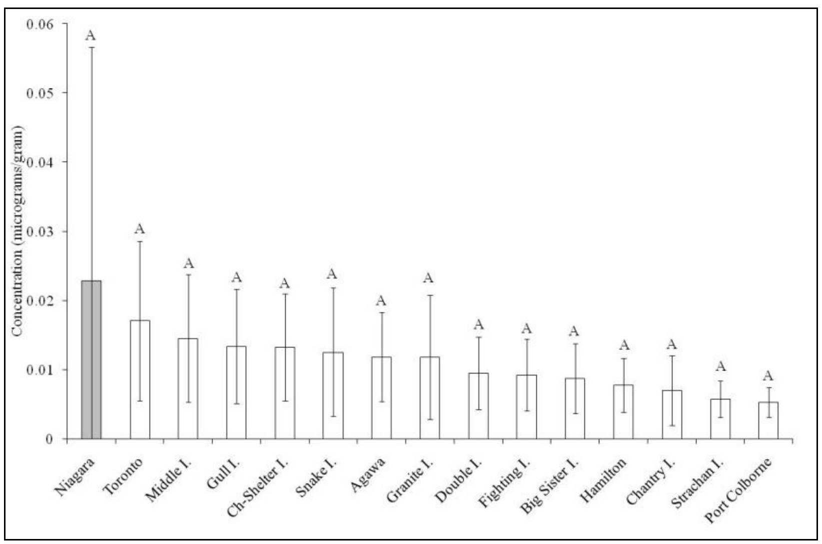
Figure 5. Mean (SD) contaminant levels in herring gull eggs from 15 Annual Monitor Colonies on the Great Lakes from 2003-2007 (continued).



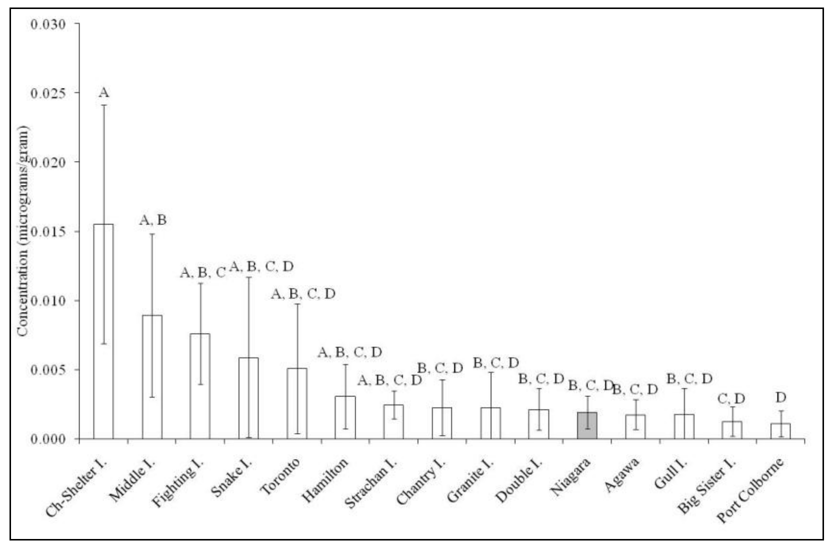
e) Sum Chlordane



f) Heptachlor Epoxide (HE)

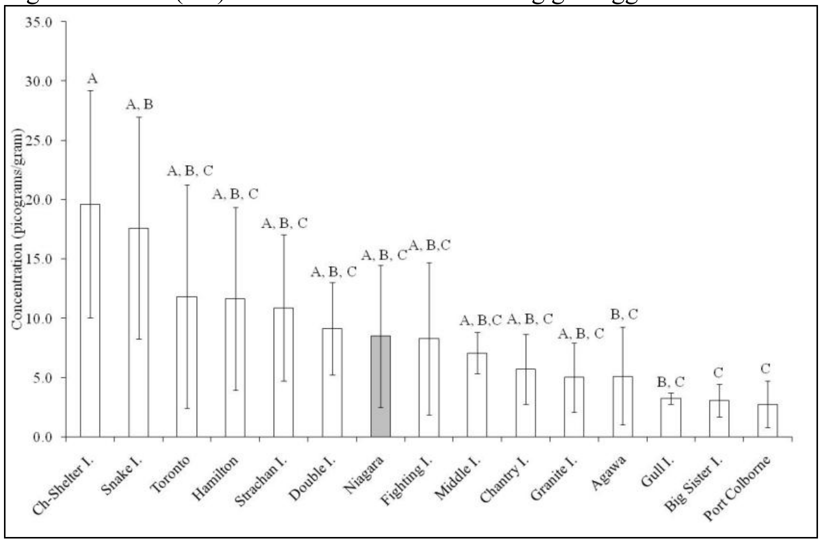


g) Hexachlorobenzene (HCB)

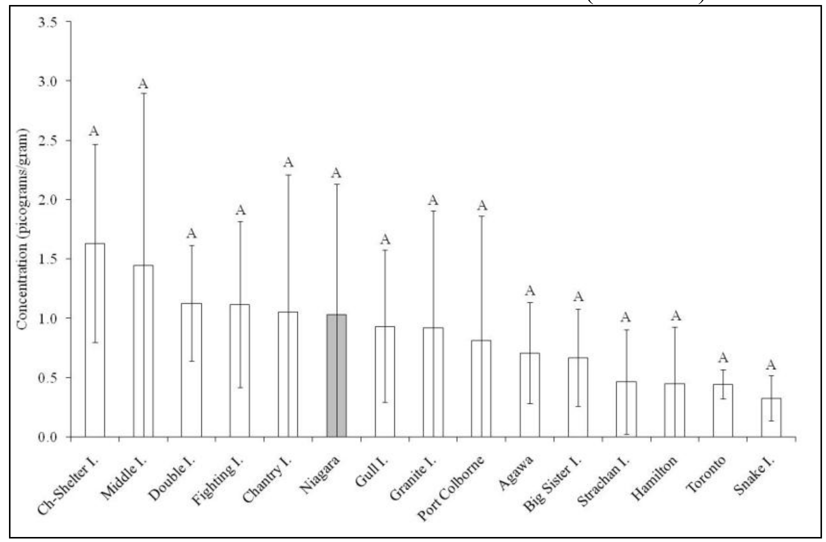


h) Octachlorostyrene (OCS)

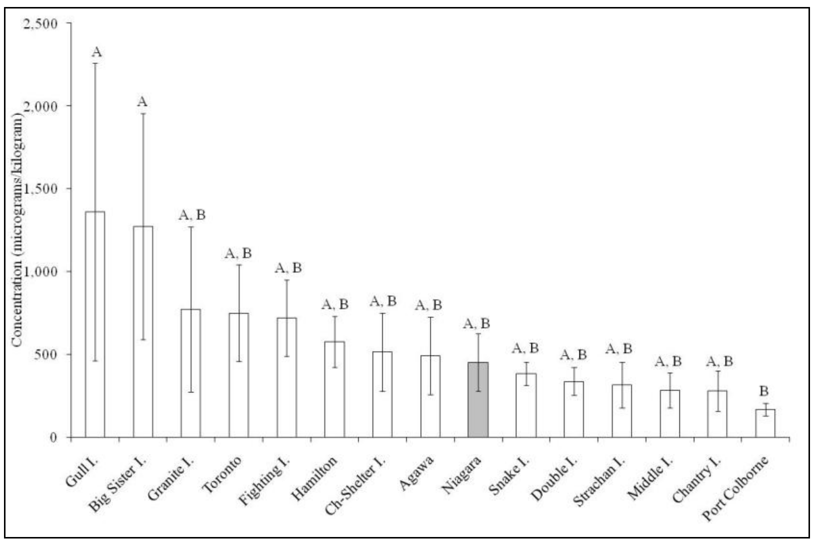
Figure 5. Mean (SD) contaminant levels in herring gull eggs from 15 Annual Monitor Colonies on the Great Lakes from 2003-2007 (continued).



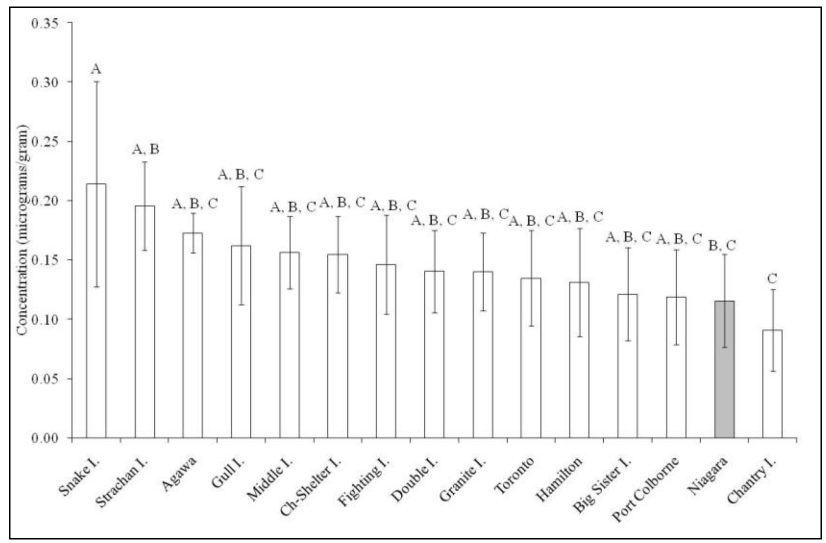
i) 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD)



j) 2,3,7,8-tetrachlorodibenzofuran (TCDF)



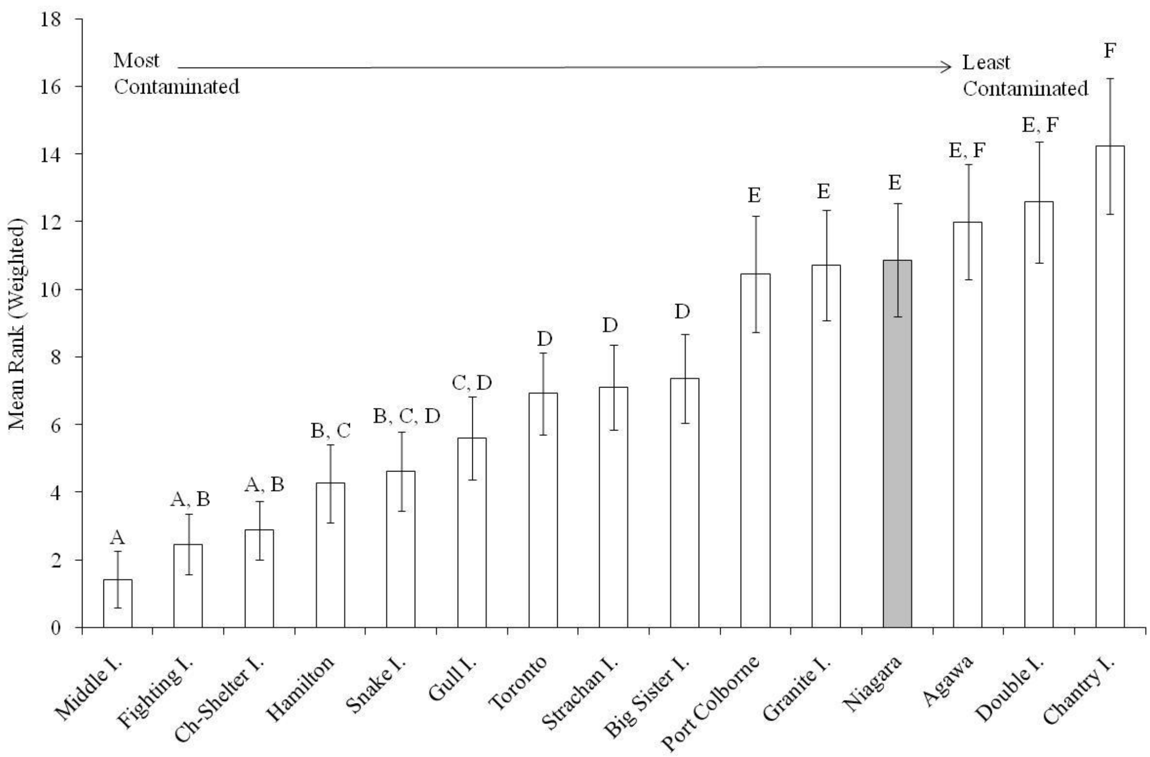
k) sum PBDEs



l) Mercury

A single overall rank of contamination in herring gulls eggs for each of the Great Lakes AMCs from 2003 to 2007 was calculated using mean weighted ranks for nine contaminants relative to fish flesh criteria for the protection of piscivorous wildlife (see Weseloh *et al.* 2006 for methods; Figure 6). Among Great Lakes AMCs, there were significant differences in the overall ranks ($F_{(14,120)}$=36.08, p<0.00001). Eggs from Niagara River were signficantly different from the nine most contaminated AMCs (from Middle Island in western Lake Erie to Toronto) and fell into an intermediate range with a ranking equal to twelfth of the 15 Great Lakes AMCs in terms of overall mean contamination. Sum PCBs, sum DDT, and TCDD contributed the most to the rankings of the sites (83.5%. 9.5% and 5.0%, respectively). As such, marginally higher levels of PCBs found in eggs from Port Colborne relative to eggs from the Niagara River AOC (seen in Figure 5b) contributed to the higher overall ranking of contamination determined for the Port Colborne AMC.

Figure 6. Mean weighted rank for nine contaminants in herring gull eggs from each AMC from 2003 to 2007 based on contaminant toxicity using fish flesh criteria guidelines. Values are based upon least squares following an ANOVA and bounded by 95% confidence intervals. Sites are arranged from most contaminated (lowest values) to least contaminated (largest values).



Temporal Trends of Contaminants in Herring Gull Eggs

Large declines in levels of 11 of 12 compounds were evident in herring gull eggs from the Niagara River AMC from the first year of chemical analysis between 1979-1987 (depending on the compound or in

2000 for sum PBDEs) to the last year of analysis which was in 2007 (with the exception of TCDD and TCDF which were last analyzed in 2005; Figure 7). Mercury (Hg) showed the smallest decline equal to 50.5% relative to the concentration in 1979 while dieldrin showed the largest decline equal to 95.6%. In contrast, sum PBDEs in eggs from the Niagara River increased by 60.1% from 432.0 µg/kg in 2000 to 691.8 µg/kg in 2007. During similar time periods at the Port Colborne Lighthouse AMC upstream in Lake Erie, similar large declines of these compounds (with the exception of sum PBDEs) were apparent ranging from 48.9% of the original concentration for mercury to 97.6% for 2,3,7,8-TCDD (Figure 8). In actuality, declines for many of these compounds measured at Port Colborne Lighthouse were larger than shown here since egg collections at this AMC have been ongoing since 1974 (see Figure 9 below). In contrast to that observed at the Niagara River AMC, levels of sum PBDEs in eggs from Port Colborne Lighthouse declined by 28.0% from 192.4 µg/kg in 2000 to 138.5 µg/kg in 2007.

Figure 7. Percent decline in the concentrations of 11 contaminants in herring gull eggs from the Niagara River AMC from the first year of analysis (i.e., depending on compound from 1979-1987) to the last year of analysis (i.e., 2007 for all except for TCDD and TCDF where 2005). Concentrations of sum PBDEs are not shown here since concentrations increased 60.1% from 2000 to 2007 at this AMC.

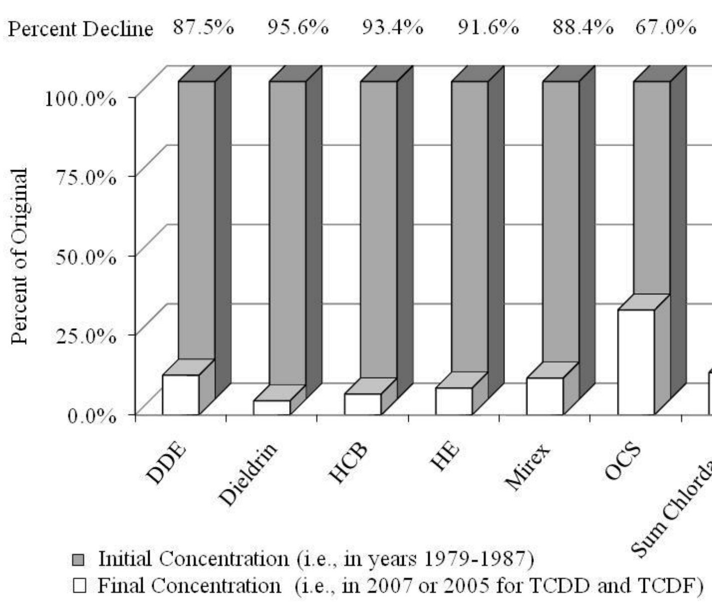
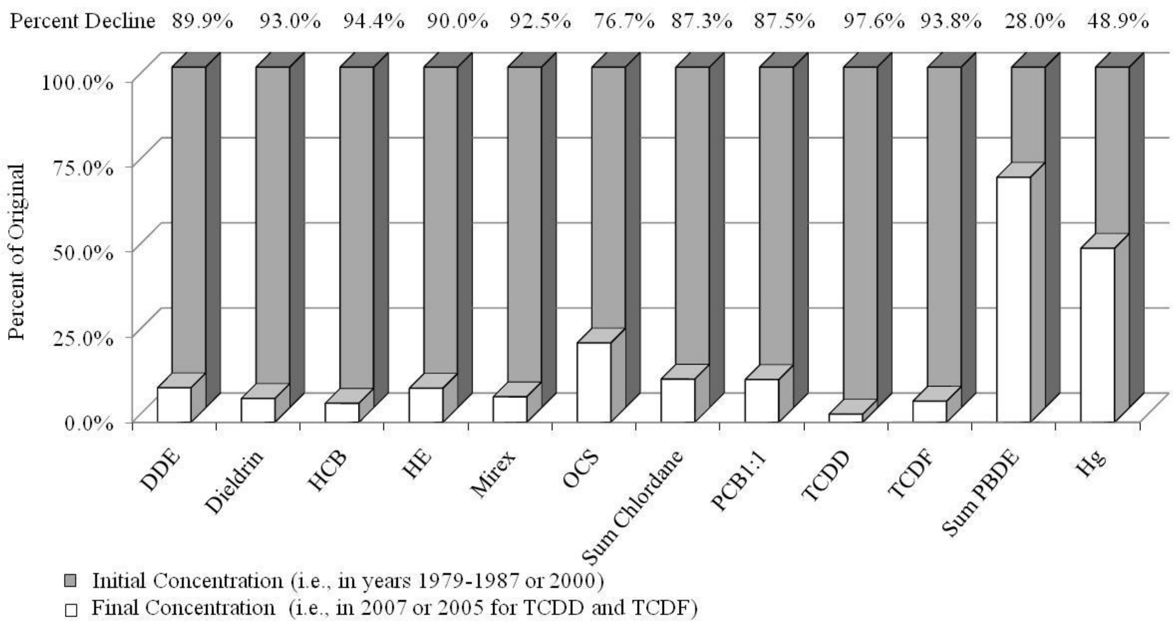
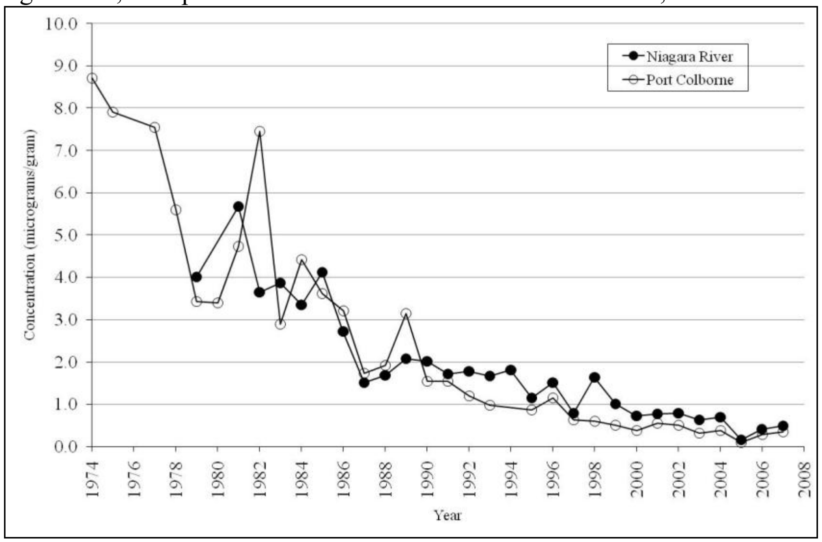


Figure 8. Percent decline in the concentrations of 12 contaminants in herring gull eggs from the Port Colborne Lighthouse AMC during a similar time period as Niagara River AMC egg collections from the first year of analysis (i.e., depending on compound from 1979-1987 or 2000 for sum PBDEs) to the last year of analysis (i.e., 2007 for all except for TCDD and TCDF where 2005).

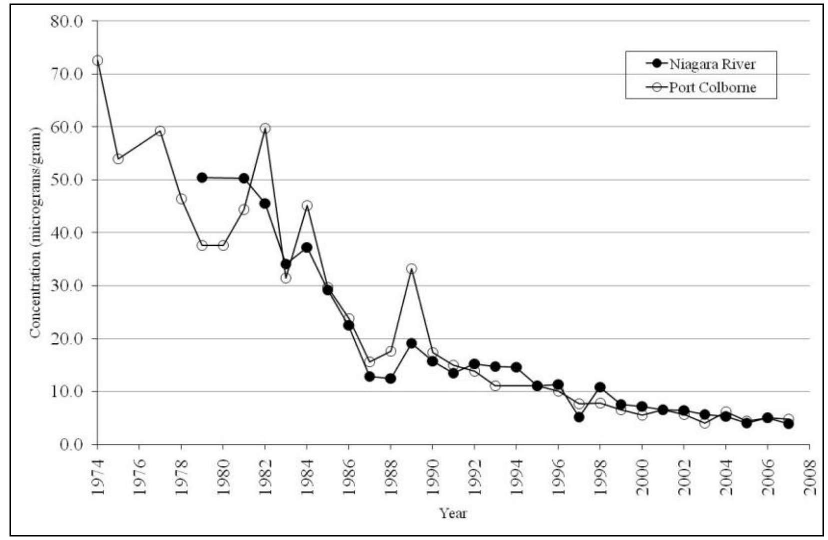


Long term changes in contaminant levels are further illustrated in Figure 9 which shows the annual contaminant concentrations in eggs from both AMCs since initiation of the monitoring program at the Niagara River AMC in 1979 and the Port Colborne Lighthouse AMC in 1974. Linear regressions of ln transformed data show significant declines in concentrations of all compounds at both AMCs ($r>0.54$; $p<0.01$) with a few exceptions. While an increase in sum PBDEs was found in Niagara River eggs when initial and final-year comparisons of concentrations were examined (as reported above), overall no significant change in levels of sum PBDEs was found in eggs from this AMC from 2000 to 2007 ($r=0.30$, $p=0.62$). Similarly, no significant change in levels of sum PBDEs was found in eggs from Port Colborne Lighthouse during the same time period ($r=0.42$, $p=0.48$).

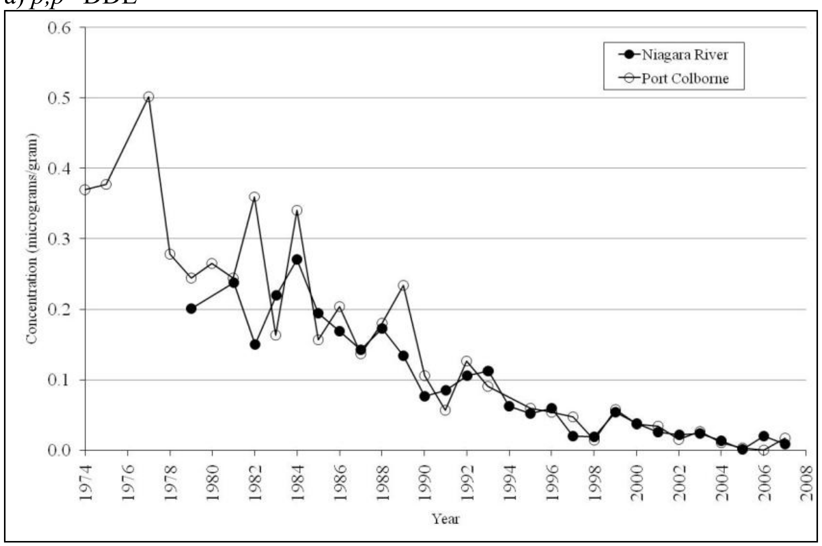
Figure 9. Temporal trends in levels of contaminants in herring gull eggs collected from the Niagara River AMC from 1979-2007 and from Port Colborne Lighthouse, the upstream AMC on Lake Erie from 1974-2007, where available.



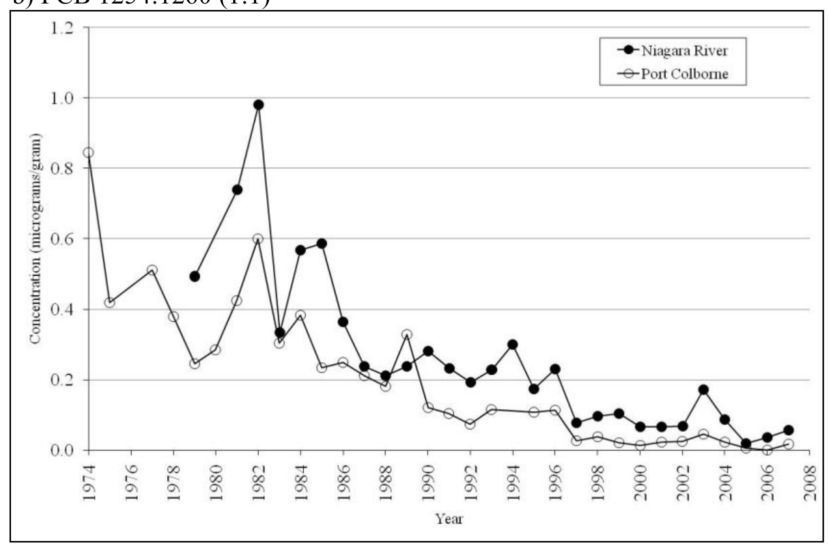
a) *p,p'*-DDE



b) PCB 1254:1260 (1:1)

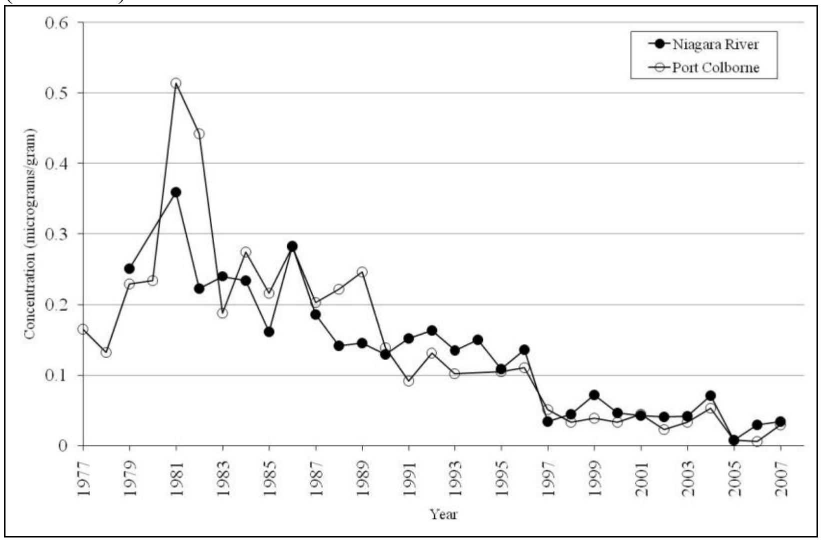


c) Dieldrin

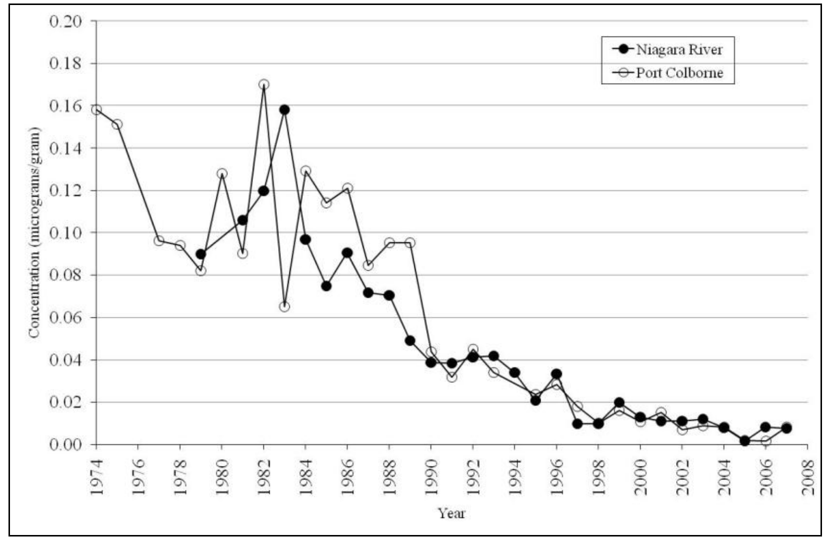


d) Mirex

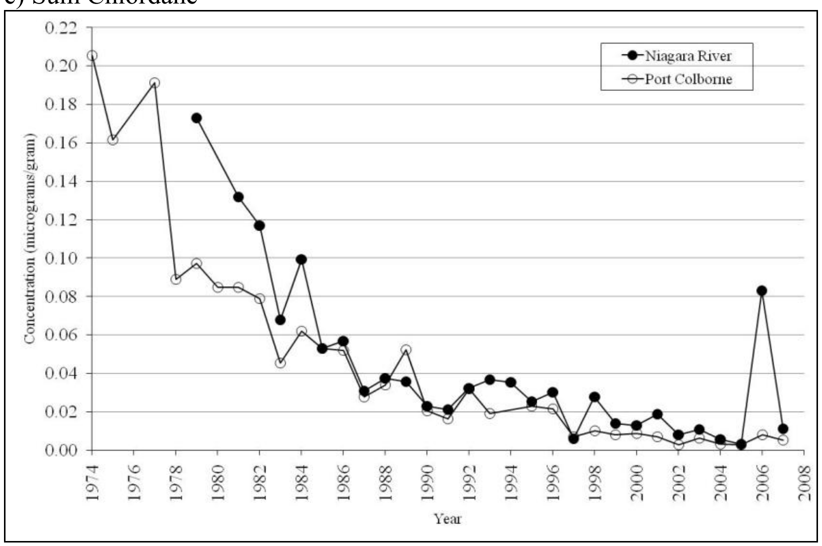
Figure 9. Temporal trends in levels of contaminants in herring gull eggs collected from the Niagara River AMC and Port Colborne Lighthouse AMC (continued).



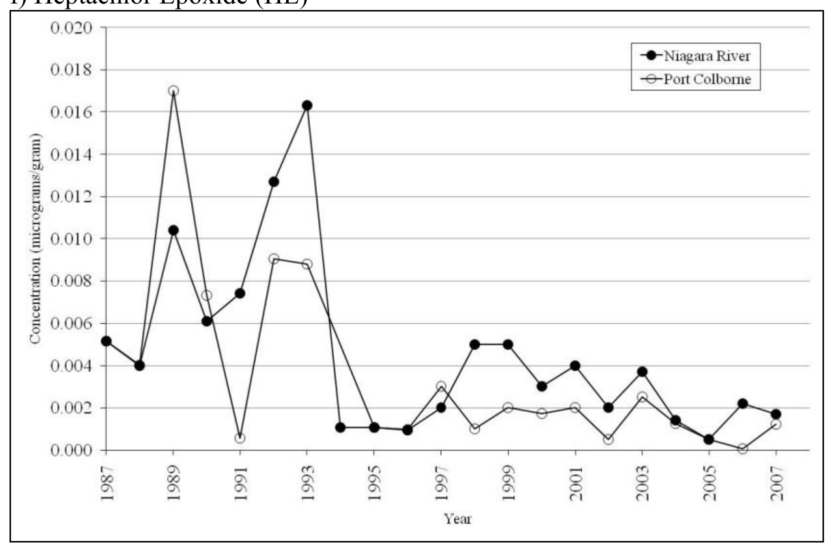
e) Sum Chlordane



f) Heptachlor Epoxide (HE)

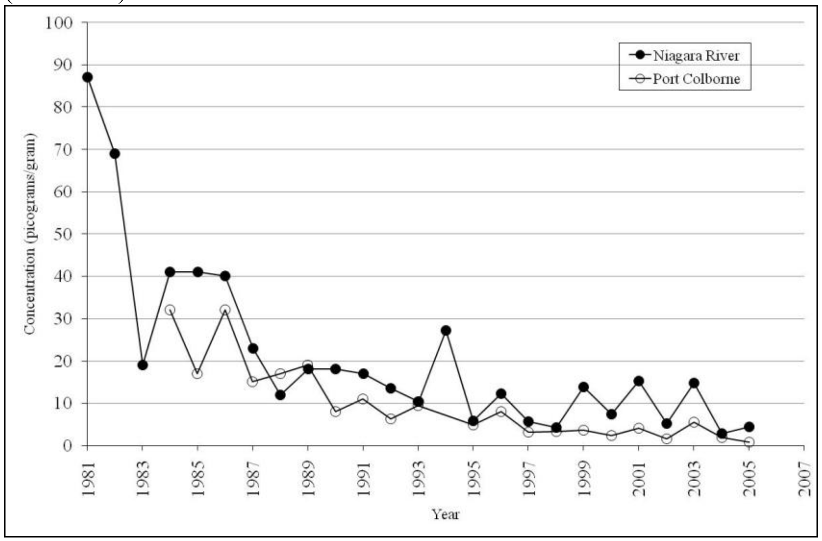


g) Hexachlorobenzene (HCB)

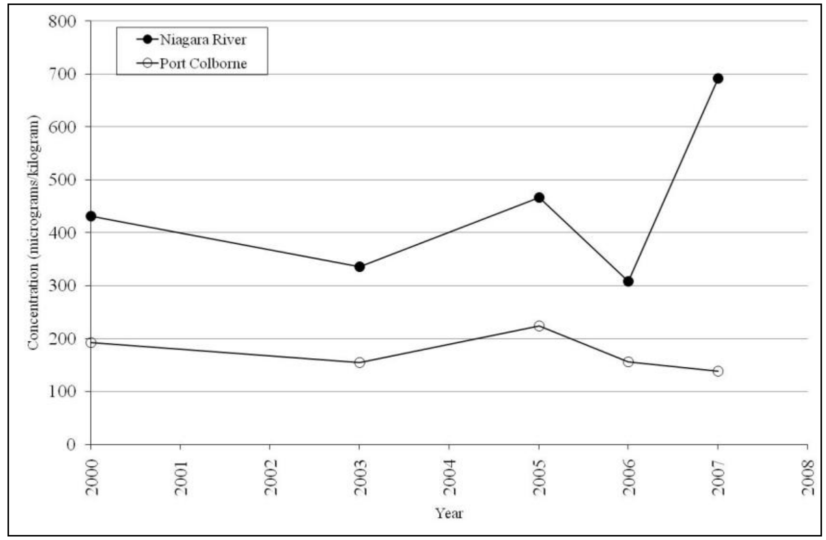


h) Octachlorostyrene (OCS)

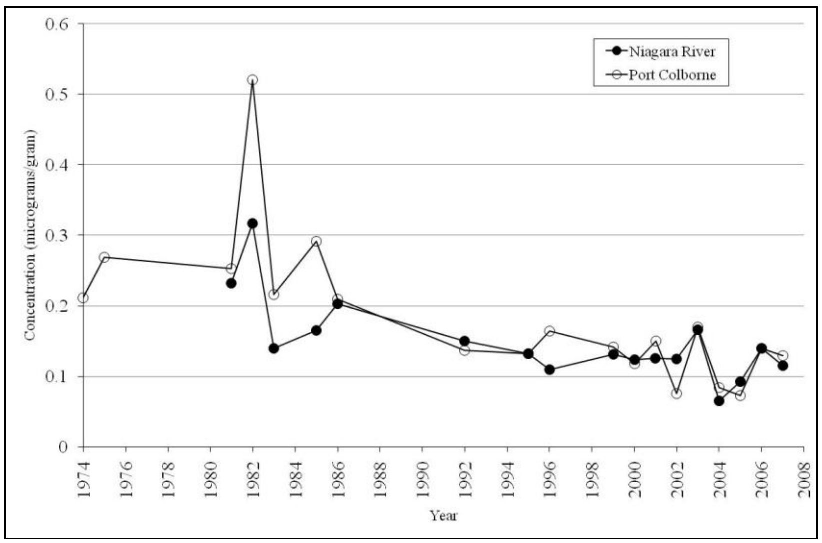
Figure 9. Temporal trends in levels of contaminants in herring gull eggs collected from the Niagara River AMC and Port Colborne Lighthouse AMC (continued).



i) 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD)



j) Sum PDBEs



k) Mercury

Mink (*Mustela vison*)

Spatial Trends of Contaminants in Mink Liver

Mean hepatic sum PCB (±SE) concentrations ranged from 71 (±13) µg/kg ww in mink from inland Ontario to 456 (±336) µg/kg ww in mink from the Niagara River AOC (Table 4). Overall, there was a marginally significant difference in mean sum PCB concentrations among mink trapped in the Niagara River AOC, eastern Lake Erie (non-AOC) and inland Ontario reference sites ($F_{(2,49)}$=2.96, p=0.06). The mean sum PCB burden in mink from the Niagara River AOC was high relative to most other Great Lakes sites although it was approximately only one-quarter of the mean PCB concentration of the most contaminated site found on the shoreline of western Lake Erie (Figure 10a). In one individual of 15 mink trapped within the Niagara River AOC, the hepatic sum PCBs concentration was extremely high (5,419 µg/kg) and greatly exceeded thresholds associated with impaired kit growth (980 µg/kg ww) and kit mortality (2,200 µg/kg ww; Heaton *et al.* 1995; Restum *et al.* 1998). This 12-month old individual trapped in 2004 was one of the three mink trapped at Lyons Creek East near Highway 140. The two other mink trapped nearby this location in 2005 and 2006 had relatively lower hepatic concentrations of sum PCBs (equal to 42 µg/kg and 187 µg/kg). Finally, two additional Lyons Creek mink were also trapped further downstream near Montrose Road in 2003 and 2005 and these individuals also had relatively lower hepatic sum PCB levels (equal to 12 µg/kg and 390 µg/kg). Overall, with the exception of the one mink with elevated PCB levels, none of the remaining 14 Niagara River mink had hepatic PCB levels which were above threshold values. No mink from inland Ontario exceeded threshold values and one mink from eastern Lake Erie with a sum PCB concentration of 995 µg/kg ww exceeded the threshold associated with impaired kit growth. While high levels of PCBs in sediment and biota have been associated with an historical industrial source of PCBs in Lyons Creek East (Milani and Fletcher 2005; Golder Associates Ltd. and Dillon Consulting Ltd. 2008), overall, there was no significant difference in mean hepatic PCBs levels in the five mink trapped along Lyons Creek East compared to mink trapped elsewhere within the AOC (t_{13}=0.82, p=0.42).

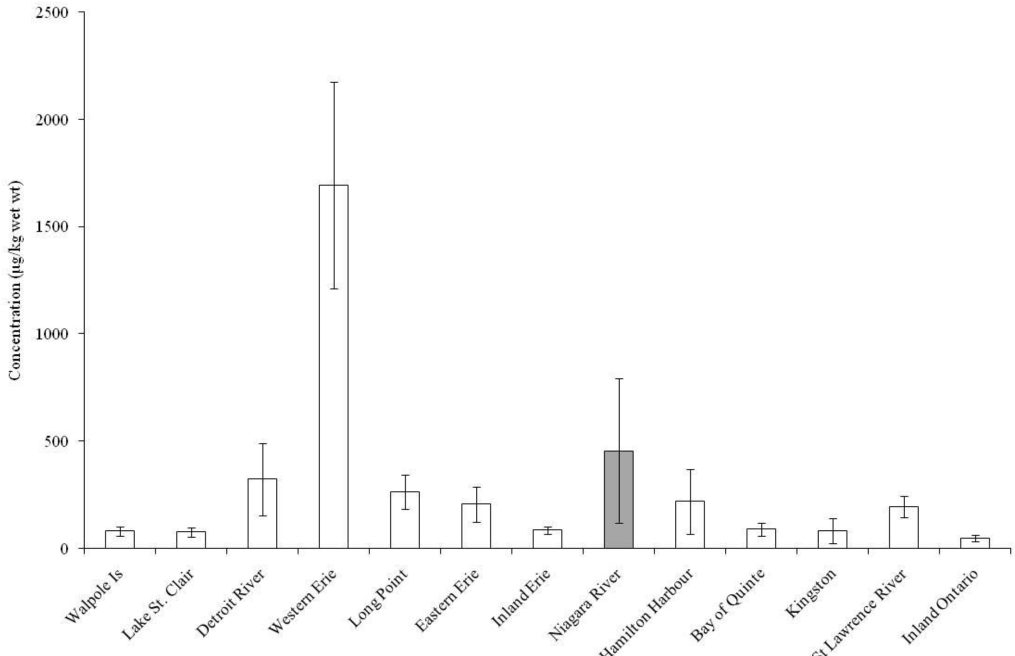
While hepatic *p,p'*-DDE levels in mink from the Niagara River AOC were high relative to the other two study sites, mean concentrations were not significantly different among the three sites ($F_{(2,33)}$= 2.48, p=0.10; Table 4). Overall, *p,p'*-DDE concentrations were within the range of means reported for other Great Lakes sites although relatively higher (and more variable among individuals) compared to some sites (Figure 10b). Mean mirex concentrations were significantly higher in mink from the Niagara River AOC than at inland Ontario sites (where it was found at below the level of detection) but were not significantly different from levels in mink upstream from eastern Lake Erie ($H_{(2,36)}$=7.60, p=0.02; Table 4). Mirex levels in mink from the AOC were high relative to some other Great Lakes study sites although

Table 4. Mean (SE) and maximum concentrations of organochlorine pesticides, PCBs and sum PBDEs in livers of mink trapped in the Niagara River AOC, eastern Lake Ontario and inland Ontario sites from 1999–2006. Contaminant concentrations are shown on a lipid basis (mg/kg) and a wet weight basis (µg/kg). N denotes the number of individuals collected and analyzed for all contaminants where the N values in brackets denotes numbers analyzed for sum PCBs only. ND denotes below the level of detection.

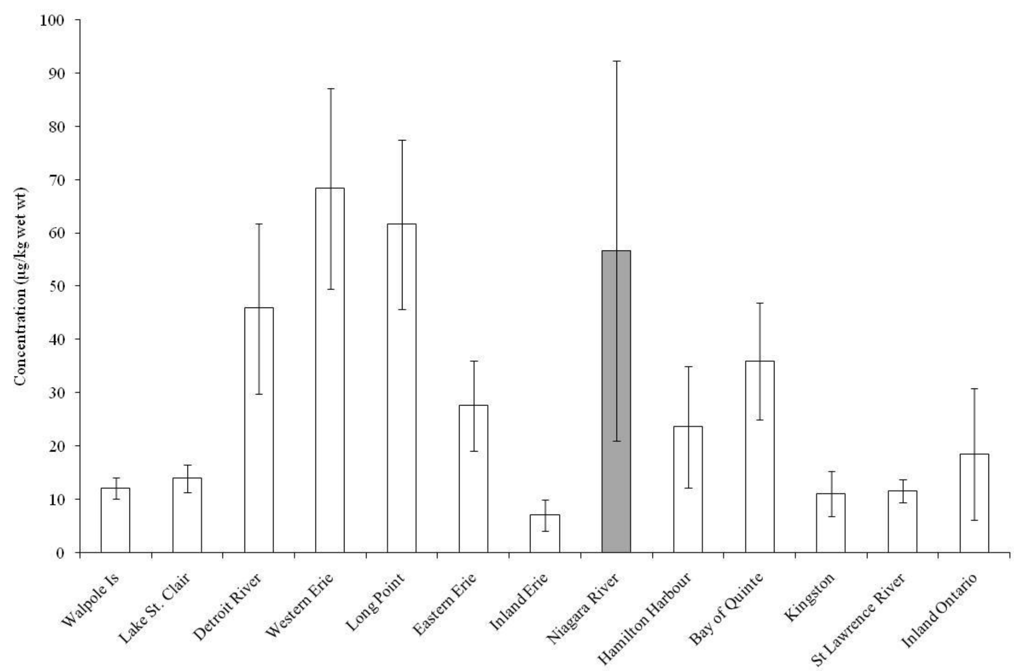
Compound		**Site**			**Statistic**[3]
		Niagara River AOC[1]	**Eastern Lake Erie**[1]	**Inland Ontario**[2]	
	N	15 (15)	9 (13)	12 (24)	
Sum PCB	lipid	19.74 (13.09) 201.13	11.26 (5.83) 77.10	2.51 (0.37) 6.03	F = 2.96
	wet	456 (336) 5,149	207 (83) 995	71 (13) 298	p = 0.06
PCB 1260	lipid	32.49 (23.70) 362.6	26.04 (17.82) 166.5	3.12 (0.95) 9.60	F = 3.29
	wet	766 (610) 9,283	393 (230) 2,148	54 (19) 230	p = 0.05
PCB1254:1260	lipid	54.13 (37.04) 567.0	32.00 (17.71) 160.1	4.50 (1.36) 14.83	F = 3.11
	wet	1,252 (950) 14,515	535 (266) 2,065	72 (18) 168	p = 0.06
p,p'-DDE	lipid	3.12 (1.71) 25.84	1.52 (0.47) 3.80	0.67 (0.36) 4.56	F = 2.48
	wet	57 (36) 548	28 (8) 83	15 (8) 103	p = 0.10
p,p'-DDD	lipid	0.036 (0.008) 0.096	0.013 (0.005) 0.041	0.013 (0.005) 0.051	F = 2.3
	wet	0.62 (0.14) 1.48	0.35 (0.16) 1.32	0.25 (0.10) 1.14	p = 0.11
p,p'-DDT	lipid	0.13 (0.04) 0.29 **B**	0.57 (0.13) 1.32 **A**	0.35 (0.18) 1.88 **AB**	H = 8.0
	wet	2.2 (0.7) 5.7	12.5 (3.6) 38.8	7.5 (4.3) 45.0	p = 0.02
OCS	lipid	0.005 (0.001) 0.017	0.039 (0.036) 0.325	ND	F = 0.99
	wet	0.11 (0.03) 0.45	0.95 (0.88) 8.00	ND	p = 0.41
Oxychlordane	lipid	0.82 (0.23) 2.88 **A**	0.90 (0.35) 3.38 **A**	0.53 (0.40) 4.83 **B**	F = 4.80
	wet	15.3 (4.0) 46.5	22.6 (9.7) 90.5	11.3 (8.9) 108.6	p = 0.01
HE	lipid	0.027 (0.010) 0.128	0.025 (0.011) 0.081	0.011 (0.004) 0.050	F = 0.67
	wet	0.50 (0.20) 2.72	0.43 (0.22) 2.00	0.18 (0.06) 0.57	p = 0.52
HCB	lipid	0.014 (0.003) 0.04 **A**	0.008 (0.004) 0.04 **AB**	0.006 (0.002) 0.03 **B**	F = 6.11
	wet	0.27 (0.06) 0.80	0.13 (0.04) 0.40	0.11 (0.05) 0.60	p = 0.01
Dieldrin	lipid	0.178 (0.070) 0.724	0.076 (0.30) 0.244	0.058 (0.04) 0.456	H = 0.65
	wet	3.1 (1.1) 14.1	2.2 (0.8) 6.0	1.4 (0.9) 10.3	p = 0.73
Mirex	lipid	0.08 (0.02) 0.24 **A**	0.02 (0.01) 0.09 **AB**	ND **B**	H = 7.60
	wet	1.3 (0.3) 4.4	0.6 (0.4) 3.3	ND	p = 0.02
Sum PBDEs	N	8	NM	2[4]	t = 1.12
	lipid	0.23 (0.06) 0.53		0.08 (0.01) 0.10	p = 0.30
	wet	3.83 (0.87) 7.69		2.11 (0.05) 2.16	

[1] Animals trapped within 7 km of Niagara River or eastern Lake Erie shorelines
[2] Animals trapped 8-40 km of the eastern Lake Erie, Lake St. Clair, St. Lawrence River or Lake Ontario shorelines.
[3] Based on analyses of lipid weight values where means followed by differing uppercase letters were significantly different ($p<0.05$); "F" and "H" statistics denote results of parametric ANOVA and non-parametric Kruskal-Wallis ANOVA tests, respectively, and "t" statistic denotes result of parametric two sample t-test.
[4] Two Ontario mink trapped inland from Hamilton Harbour in East Flamborough

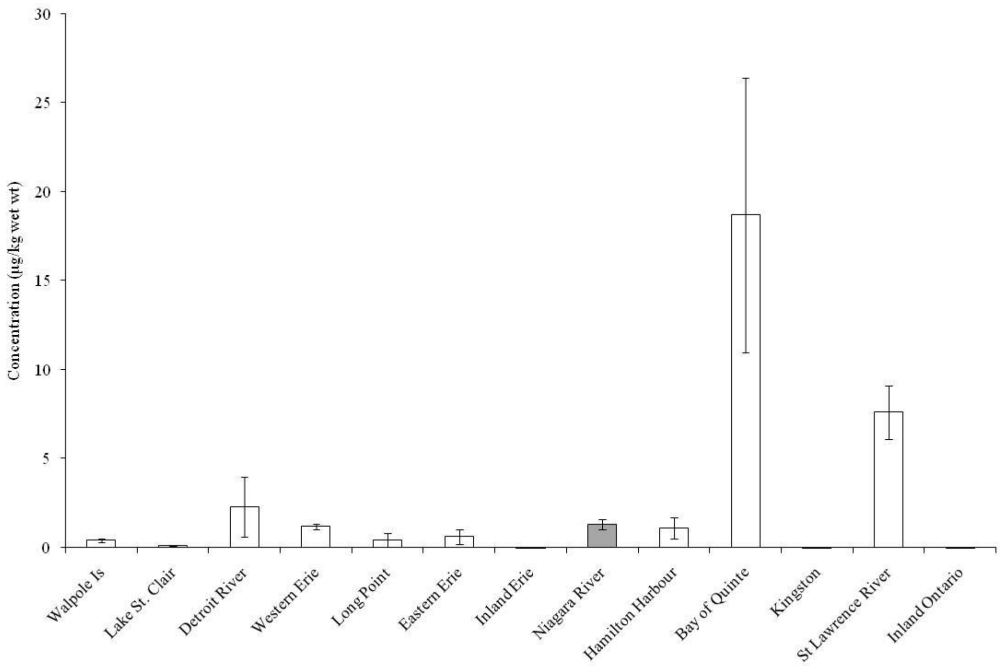
Figure 10. Mean (SE) concentrations of sum PCBs (A), *p,p'*-DDE (B) and mirex (C) in livers of mink collected from sites in the Great Lakes (µg/kg, wet weight). Shaded bar denotes mean concentration in mink from the Niagara River AOC. Mean concentrations in mink from non-AOC sites including eastern Lake Erie and other inland Ontario sites, shown separately as inland Lake Ontario and inland Lake Erie sites, are also provided.



A) sum PCBs



B) *p,p'*-DDE



C) Mirex

not nearly as high as levels found in mink from the Bay of Quinte AOC and the St. Lawrence River AOC at Cornwall (Figure 10c). Mean concentrations of oxychlordane and hexachlorobenzene (HCB) were significantly higher in mink from the Niagara River AOC compared to inland Ontario reference sites but not significantly different from levels in mink from the eastern Lake Erie ($F_{(2,33)}$=4.80, p=0.01 and $F_{(2,33)}$=6.11, p=0.006, respectively). Octachlorostyrene (OCS), heptachlor epoxide (HE) and dieldrin were also found in liver of mink from the Niagara River AOC but at levels not statistically different from the other two reference sites. Hepatic HE levels were far below the LOAEL concentration equal to 8.87 µg/g in mink (based on whole body concentrations, Crum *et al.* 1993). In the eight AOC mink for which PBDEs were measured in liver, sum PBDE levels were found at low and similar concentrations to levels found in two mink from inland Ontario and no mink exceeded the no adverse effect level for thyroid hormone disruption (Zhang *et al.* 2009).

Hepatic PCBs in mink from the Niagara River AOC from 2002-2006 were on average four times higher than levels measured in eight mink trapped in Wainfleet Township from 1988/89 where the mean total PCB level (±SE, measured as PCB 1254:1260) was 287 (±129) µg/kg ww (Haffner *et al.* 1998). In this study, mink from eastern Lake Erie in Dunn Township, situated west of Wainfleet Township, also had twice the PCB burden of mink from Wainfleet Township in the late 1980s. Furthermore, mean hepatic levels of pesticides including oxychlordane and dieldrin were at least three times higher in mink from the Niagara River AOC, eastern Lake Erie and inland Ontario sites compared to mink trapped in the early study. In contrast, the mean HCB concentration in the earlier study was approximately four times higher than that of Niagara River AOC mink while levels of mirex, heptachlor epoxide and *p,p'*-DDE were much more similar between mink from the Niagara River AOC and Wainfleet Township between the two time periods. While a portion of Wainfleet Township is located within the Niagara River AOC, it is not possible to speculate on temporal changes in exposure of mink trapped in the current study relative to levels reported in the study by Haffner *et al.* (1998) given the differences in trapping locations between the two studies. Apart from differences in relative exposure between the two time periods, exposure can also be influenced by differences in diet as well as age of mink trapped between the two studies.

Two metals, mercury and selenium, were consistently found at the highest concentrations in liver of mink from the Niagara River AOC, eastern Lake Erie and inland Ontario reference sites compared to levels of other metals (Table 5). No significant difference in mean total mercury concentrations was found among study sites ($F_{(2,32)}=0.61$, $p=0.55$). In mustelids which died of methylmercury intoxication in experimental studies or which were found dead or dying in the wild, total mercury concentrations in the liver have typically exceeded 25 µg/g wet weight (Wobeser and Swift 1976; Wobeser *et al.* 1976; Wolfe *et al.* 1998). In this study, all mink had hepatic mercury burdens which were well below this probable effect level with the maximum hepatic concentration in mink from the Niagara River equal to approximately one-tenth of this concentration. Unfortunately, little information is available on the effects of sub-lethal concentrations of mercury on mink. The mean organic (methyl) mercury concentration (±SE) was equal to 0.39 (±0.11) µg/g ww in twelve mink collected from 2002 to 2006 from the Niagara River AOC, which was not significantly different from organic mercury concentrations in inland Ontario mink. Expressed as percentage of total mercury in liver, the mean percentage of organic mercury (equal to 58%) was slightly higher than that found in mink collected in the mid 1980s from Ontario (53%, Wren *et al*. 1986). The mean hepatic mercury concentration in mink from the Niagara River AOC was within the range of means found in mink from other AOC and non-AOC locations on the Great Lakes (Figure 11a). Mink from the Niagara River AOC had approximately one-half of the total mercury concentration and one-third of the organic mercury concentration of mink trapped in south-central Ontario in 1994 (Evans *et al.* 2000).

Mean selenium concentrations were significantly different among study sites with significantly higher levels found in mink from the Niagara River AOC compared to inland Ontario sites but not significantly different from levels in mink from the eastern Lake Erie ($F_{(2,32)}=3.71$, $p=0.03$; Table 5). While selenium itself is toxic in higher concentrations, it also has an antagonistic effect on mercury toxicity, decreasing the toxic effects of mercury exposure (Cuvin-Aralar and Furness 1991). Selenium uptake in mammals is believed to be enhanced in response to tissue mercury concentrations so that the elevated levels of

Table 5. Mean (SE) and maximum concentrations of lead, selenium, cadmium, arsenic, total mercury (Hg) and organic mercury in livers of mink trapped in the Niagara River AOC, eastern Lake Erie and inland Ontario sites from 1999–2006. Metal concentrations (µg/g) are shown both on a dry weight basis and a wet weight basis. N denotes the number of individuals collected. Mean percentage of organic mercury (out of total mercury) in mink liver is also shown.

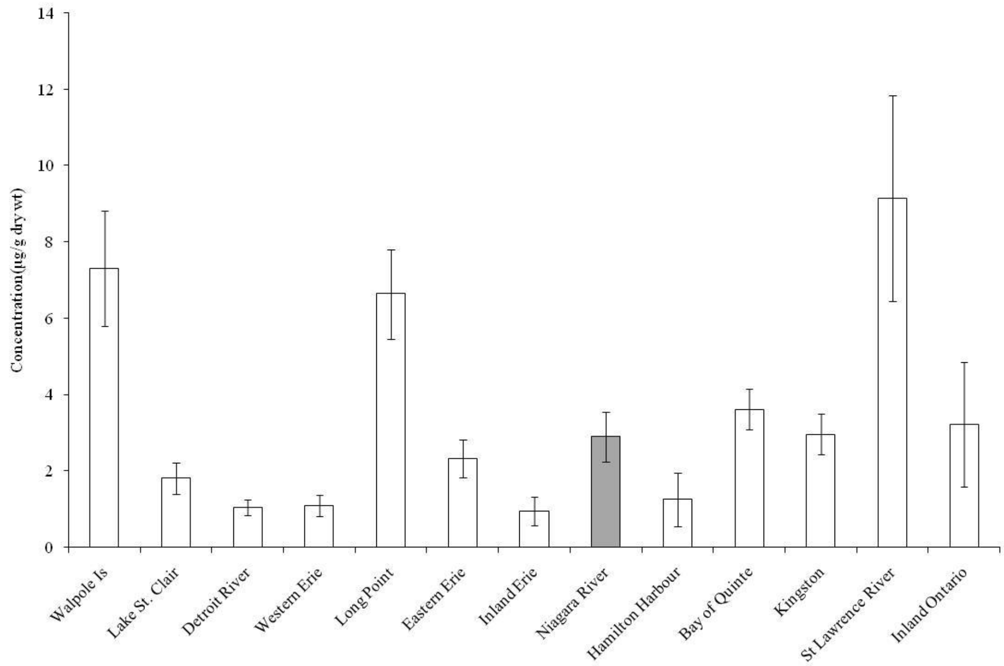
Compound		Site			Statistic[3]
		Niagara River AOC[1]	Eastern Lake Erie[1]	Inland Ontario[2]	
	N	14	9	12	
Lead	dry	0.35 (0.11) 1.34	0.44 (0.19) 1.92	0.24 (0.080 1.01	F = 0.60
	wet	0.10 (0.03) 0.36	0.12 (0.05) 0.54	0.07 (0.02) 0.28	p = 0.55
Selenium	dry	3.09 (0.28) 5.28 **A**	2.36 (0.19) 3.59 **AB**	2.29 (0.16) 3.25 **B**	F = 3.71
	wet	0.87 (0.08) 1.55	0.65 (0.05) 0.95	0.62 (0.04) 0.89	p = 0.03
Cadmium	dry	0.32 (0.08) 1.26	0.52 (0.29) 2.82	0.28 (0.07) 0.68	F = 0.42
	wet	0.09 (0.02) 0.37	0.14 (0.08) 0.78	0.08 (0.02) 0.19	p = 0.66
Arsenic	dry	0.17 (0.05) 0.60	0.14 (0.01) 0.20	0.15 (0.01) 0.20	H = 0.35
	wet	0.05 (0.01) 0.15	0.04 (0.002) 0.05	0.04 (0.003) 0.06	p = 0.84
Total Hg	dry	2.90 (0.66) 7.39	2.33 (0.49) 5.21	2.38 (1.12) 14.3	F = 0.61
	wet	0.82 (0.19) 2.11	0.64 (0.13) 1.38	0.62 (0.29) 3.71	p = 0.55
Organic Hg	N	12	0	2	
	dry	1.38 (0.37) 4.36		0.65 (0.21) 0.86	t = 0.77
	wet	0.39 (0.11) 1.24		0.20 (0.06) 0.26	p = 0.46
% Organic Hg		58.0 (3.9) 73.7		63.3 (1.4) 64.7	

[1] Animals trapped within 7 km of Niagara River or eastern Lake Erie shorelines.
[2] Animals trapped 8-40 km of the eastern Lake Erie, Lake St. Clair, St. Lawrence River or Lake Ontario shorelines.
[3] Based on analyses of dry weight values where differing uppercase letters were significantly different ($p<0.05$); "F" and "H" statistics denote results of parametric ANOVA and non-parametric Kruskal-Wallis ANOVA tests, respectively, and "t" statistic denotes result of parametric two sample t-test.

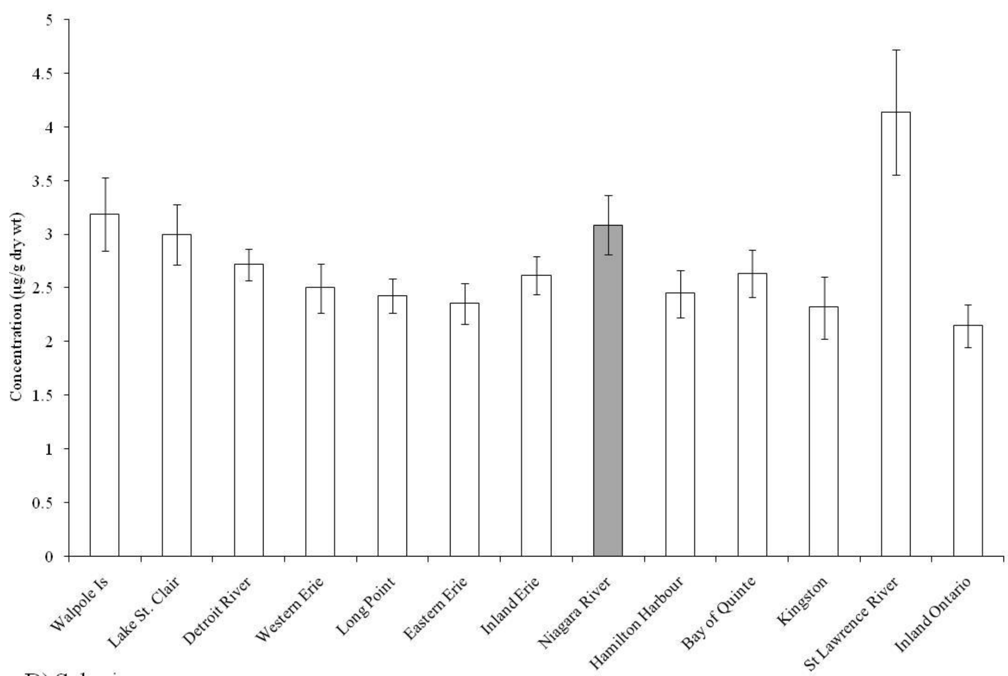
selenium in mink livers from the Niagara River AOC may be more of a reflection of higher mercury levels at this site (Wren 1986). Similar to mercury, the mean selenium concentration in mink from the Niagara River AOC was within the range of means found in mink from other AOC and non-AOC locations on the Great Lakes (Figure 11b).

Cadmium concentrations in mink liver did not vary significantly among sites and were at least two orders of magnitude lower than concentrations (100 – 200 µg/g ww) associated with kidney dysfunction (Scheuhammer 1991). Lead levels also did not vary among sites and were similarly below probable effect levels of greater than 10 µg/g (Buck *et al.* 1976). Finally arsenic, which was found at the lowest concentrations of all metals, did not differ among sites and concentrations in all mink were well below effect levels. In rats with an arsenic concentration of 53.7 µg/g in liver, no adverse effects associated with arsenic toxicity were seen (Siewicki 1980).

Figure 11. Mean (SE) concentrations of total mercury (A) and selenium (B) in livers of mink collected from sites in the Great Lakes (μg/g, dry weight). Shaded bar denotes mean concentration in mink from the Niagara River AOC. Mean concentrations in mink from non-AOC sites including eastern Lake Erie and other inland Ontario sites, shown separately as inland Lake Ontario and inland Lake Erie sites, are also provided.



A) Total Mercury



B) Selenium

Somatic Indices

Organ somatic indices, particularly liver and spleen, may be affected by contaminant burdens. While no significant difference among sites was found for the liver index, the mean spleen index was significantly greater in mink from the Niagara River AOC compared to that in mink from inland Ontario reference sites ($F_{(2,84)}$=4.98, p=0.01; Table 6). A closer examination of the data revealed that one mink from the Niagara River had a grossly enlarged spleen due to an undiagnosed massive thoracic infection. In addition, a second mink from inland Ontario was diagnosed with Aleutian disease, a viral infection, which enlarges the spleen and other organs. Removal of these two individuals from the analyses resulted in a marginally significant difference in the spleen index among the three sites ($F_{(2,82)}$=2.7, p=0.07). Overall these data suggest that enlarged spleens observed in some individuals may be indicative of a stimulated immune response associated with infection. Baculum weight and length were also compared among sites as some reports (e.g., Harding *et al.* 1999) suggest that these parameters may vary with contaminant burdens. Mean testes and baculum weights were significantly higher in mink from eastern Lake Erie compared to the inland Ontario reference site (Table 6). This finding can likely be attributed to differences in mink ages since male mink from the eastern Lake Erie were on average eight months older than those trapped in inland Ontario sites and would be expected to have greater development of reproductive organs.

Table 6. Mean weight (SE) of male and female mink and organ somatic indices (SE) for mink trapped in the Niagara River AOC, eastern Lake Erie and inland Ontario sites from 1999–2006. Organ indices are organ weights adjusted for body size of the animal. Mean (SE) testes and baculum weights and mean (SE) baculum lengths are also provided. N denotes the number of individuals collected.

Endpoint			**Sites**		**Statistic[3]**
		Niagara River AOC[1]	**Eastern Lake Erie[1]**	**Inland Ontario[2]**	
Weight	N	9	12	42	F = 0.44
Males (g)		992 (88) 1561	959 (55) 1334	919 (36) 1460	p = 0.65
Weight	N	4	4	20	F = 0.15
Females (g)		531 (47) 650	494 (27) 564	498 (27) 941	p = 0.86
Liver	N	12	15	61	F = 1.92
Index		0.063 (0.004) 0.082	0.063 (0.002) 0.081	0.0058 (0.002) 0.084	p = 0.31
Heart	N	12	16	60	F = 2.58
Index		0.012 (0.001) 0.021	0.014 (0.0006) 0.019	0.012 (0.0003) 0.018	p = 0.08
Lung	N	12	15	59	F = 1.15
Index		0.027 (0.002) 0.040	0.040 (0.012) 0.210	0.03 (0.001) 0.061	p = 0.32
Kidney	N	11	15	51	F = 1.36
Index		0.010 (0.001) 0.012	0.011 (0.001) 0.014	0.010 (0.0002) 0.015	p = 0.26
Spleen	N	12	15	60	F = 4.98
Index		0.006 (0.001) 0.021 **A**	0.005 (0.0002) 0.006 **AB**	0.004 (0.0001) 0.011 **B**	p = 0.01

Endpoint		Sites		Statistic[3]
	Niagara River AOC[1]	Eastern Lake Erie[1]	Inland Ontario[2]	
Omentum N	11	15	57	F = 3.07
Index	0.011 (0.002) 0.027	0.012 (0.002) 0.033	0.008 (0.0006) 0.037	p = 0.05
Pancreas N	11	15	59	F = 0.36
Index	0.005 (0.0004) 0.007	0.006 (0.0004) 0.008	0.005 (0.0002) 0.010	p = 0.70
Testes N	11	11	37	F = 5.0
Weight (g)	2.89 (0.42) 5.10 **AB**	4.36 (1.68) 20.40 **A**	1.75 (0.23) 4.78 **B**	p = 0.01
Baculum N	11	12	37	F = 2.25
Length (mm)	41.72 (0.79) 47.25	42.83 (0.49) 46.06	41.01 (0.47) 47.20	p = 0.11
Baculum N	7	12	38	F = 6.68
Weight (g)	0.29 (0.03) 0.40 **AB**	0.34 (0.02) 0.49 **A**	0.23 (0.02) 0.44 **B**	p = 0.003

[1] Animals trapped within 7 km of Niagara River or eastern Lake Erie shorelines.
[2] Animals trapped 8-40 km of the eastern Lake Erie, Lake St. Clair, St. Lawrence River or Lake Ontario shorelines.
[3] Differing uppercase letters were significantly different (p<0.05); "F" statistic denotes results of parametric ANOVA test.

Snapping Turtles (*Chelydra serpentina*)

Spatial Trends of Contaminants in Snapping Turtle Eggs

Of all compounds in snapping turtle eggs collected from 2001 to 2004, sum PCBs were found in the highest concentrations with means (±SD) ranging from 14.7 ± 9.5 ng/g (wet weight) at Algonquin Provincial Park to 1142.9 ± 773.44 ng/g at Lyons Creek East (Table 7). Concentrations of *p,p'*-DDE, mirex and sum chlordane were generally the highest of all organochlorine pesticide compounds. The mean concentration of *p,p'*-DDE in eggs from the Lyons Creek and Tiny Marsh collection locations did not exceed the total DDT tissue residue guideline for the protection of the wildlife consumers of aquatic biota equal to 14.0 ng/g (CCME 2001) while the downstream Great Lakes reference location, Upper Canada Bird Sanctuary (UCBS) on the St. Lawrence River, did exceed this threshold. Sum PBDEs were also high relative to some pesticides with mean concentrations in eggs ranging from 3.05 ± 1.97 ng/g at Lyons Creek to 6.37 ± 4.44 ng/g at UCBS.

Mean concentrations of sum PCBs and four of seven organochlorine pesticides in turtle eggs varied significantly among the Lyons Creek site and upstream and downstream Great Lakes reference sites, Tiny Marsh and UCBS (Table 7). Overall, sum PCB concentrations in eggs from Lyons Creek were elevated and significantly higher than levels in eggs from either of the two reference sites. In addition, mean levels of *p,p'*-DDE, sum chlordane, mirex and octochlorostyrene (OCS) in eggs from UCBS were significantly higher than levels in Tiny Marsh eggs. Levels of three of these compounds (i.e., *p,p'*-DDE, sum chlordane, and OCS) in eggs from Lyons Creek were of intermediate values and statistically similar to levels at both of the two reference sites while levels of mirex were similar to levels at Tiny Marsh and significantly lower than levels at UCBS. Sum PBDEs in eggs were not significantly different between Lyons Creek and UCBS. Generally with the exception of PCBs, levels of contaminants were highest at UCBS of the three sites, a finding likely due to downstream effects arising from its location on the St. Lawrence River and downstream of all of the Great Lakes. When the statistical analyses are performed on Lyons Creek and Tiny Marsh only (i.e, the UCBS sampling location is excluded from the analysis), the results are the same with only levels of PCBs significantly different between the two sites. While not included in the among-site statistical analyses, eggs from Algonquin Park, a remote reference site, generally had the lowest mean levels of contaminants.

Table 7. Mean (SD) organochlorine pesticide, sum PCB and sum PBDE concentrations (ng/g, wet weight) in snapping turtle eggs from Lyons Creek East in the Niagara River Area of Concern, Upper Canada Bird Sanctuary (UCBS, downstream reference site on the St. Lawrence River), Tiny Marsh (Great Lakes reference site) and Algonquin Provincial Park (remote area) from 2001-2004. N represents the number of clutches sampled. NM denotes contaminant not measured. With one exception, statistics reported are based on comparisons of mean concentrations in eggs from Lyons Creek, UCBS, and Tiny Marsh where similar uppercase letters are not significantly different; for sum PBDEs, comparisons are based on analyses of Lyons Creek and UCBS eggs only.

Compound	Lyons Creek	UCBS	Tiny Marsh	Algonquin	Statistic
Sum PCBs	1142.9 (773.4) **A**	112.9 (49.0) **B**	31.8 (33.7) **C**	14.7 (9.5)	$F = 46.71$ $p < 0.0001$
p,p'-DDE	6.73 (10.1) **AB**	16.8 (15.1) **A**	3.84 (2.18) **B**	3.76 (3.87)	$F = 3.48$ $p = 0.043$
Sum chlordane	2.31 (4.61) **AB**	4.65 (3.01) **A**	1.91 (1.24) **B**	1.35 (1.01)	$F = 4.95$ $p = 0.014$
Mirex	0.67 (5.05) **B**	11.6 (6.89) **A**	1.80 (3.39) **B**	0.32 (0.40)	$F = 15.17$ $p = 0.00003$
Dieldrin	0.68 (0.56)	0.49 (1.33)	0.43 (0.42)	0.22 (0.31)	$F = 0.28$ $p = 0.76$
HCB	0.23 (0.14)	0.36 (0.24)	0.20 (0.14)	0.17 (0.10)	$F = 1.76$ $p = 0.19$
Octachlorostyrene	0.10 (0.16) **AB**	0.42 (0.43) **A**	0.05 (0.03) **B**	0.05 (0.04)	$F = 5.80$ $p = 0.007$
N	9	11	14	15	
Sum PBDEs	3.05 (1.97)	6.37 (4.44)	NM	3.85 (4.44)	$F = 0.37$
N	6	5		9	$p = 0.56$
HE	0.25 (0.20)	0.25 (0.32)	0.22 (0.25)	0.21 (0.18)	$F = 0.13$
N	5	11	10	12	$p = 0.87$

Analyses of coplanar PCBs with dioxin-like effects, dioxins and furans in snapping turtles eggs from Lyons Creek East in 2002 (based on a pooled analysis of six clutches of eggs) revealed higher concentrations of dioxin-like PCBs relative to levels of dioxins and furans (Table 8). In addition, concentrations of three of the five coplanar PCBs shown were highest in eggs from Lyons Creek relative to levels in eggs from four other AOCs, which include Centennial Park (Bay of Quinte), Grindstone Creek (Hamilton Harbour), Turkey Creek (Detroit River) and Wheatley Provincial Park (near Wheatley Harbour). As a result, the toxic equivalent concentration (TEQ) derived from coplanar dioxin-like PCBs

Table 8. Coplanar PCBs with dioxin-like effects, dioxin and furan concentrations with associated total TEQs (pg/g wet weight) in pooled snapping turtle eggs from Lyons Creek East in the Niagara River AOC in 2002 and other AOCs including Centennial Park in the Bay of Quinte AOC, Turkey Creek in the Detroit River AOC, Wheatley Provincial Park near the Wheatley Harbour AOC, and Tiny Marsh and Algonquin Park (remote reference sites) in years as indicated. Similar data for snapping turtle eggs collected in 1999 from Walpole Island in the St. Clair River AOC have also been included (Ashpole *et al.* 2004); "NR" indicates data were not reported in the publication. "NM" denotes that concentration of congener was not measured. Concentrations indicated with a "<" are at or below the detection limit for the chemical analysis performed.

Compound	Lyons Creek 2002	Centennial Park 2006	Grindstone Creek 2002	Turkey Creek 2002	Wheatley Provincial Park 2002	Walpole Island, St. Clair River 1999	Tiny Marsh 2002	Algonquin Park 2002
PCB-37[a]	165	NM	8.85	10.1	1.79	2.5	1.24	0.982
PCB-77	311	80	93.3	125	37.1	19	6.45	2.74
PCB-126	588	490	543	402	198	71	30.6	17.9
PCB-169	19.2	22	53.4	34.6	24.1	6.1	5.05	3.48
PCB-189	1010	880	2360	1420	884	2	79.2	52.6
TEQ (dioxin-like PCBs)[b]	**74.38**	**53.03**	**59.04**	**46.50**	**21.69**	**8.06**	**3.39**	**1.93**
2378-TCDD	0.663	3.5	6.42	4.80	2.3	0.41	0.385	0.373
12378-PnCDD	0.949*	2.3	2.28	4.21	1.95	0.49	0.644	0.501
123478-HxCDD	0.273*	0.67	0.368	0.583	0.641	NR	0.201*	0.148*
123678-HxCDD	0.948	4.4	2.5	7.19	2.37	0.51	0.513	0.401
123789-HxCDD	0.296	<0.34	0.291*	1.16	0.422	NR	<0.100	0.146*
1234678-HpCDD	1.59	1.4	1.25	2.11	1.53	0.26	0.192	1.09
12346789-OCDD	2.43	3.9	2.49	2.91	8.19	0.77	0.231*	0.506*
2378-TCDF	0.385	<0.67	0.22	0.10*	0.272	NR	<0.100	0.106
12378-PnCDF	0.109	<0.51	0.187*	0.104	0.178	NR	<0.100	<0.100
23478-PnCDF	2.07	2.6	7.92	2.42	2.65	NR	0.762	0.638*
123478-HxCDF	<0.100	<0.26	0.263*	0.101*	<0.100	NR	<0.100	<0.100
123678-HxCDF	0.19	<0.7	0.622	0.353	0.226*	NR	<0.100	<0.100
234678-HxCDF	0.172	<0.17	0.329	0.193	0.127	NR	<0.100	<0.100
1234678-HpCDF	0.181*	<0.32	0.166*	0.314	<0.100	NR	<0.100	<0.100
TEQ (PCDD/Fs)	**4.17**	**8.48**	**17.06**	**11.83**	**7.32**	**NR**	**1.81**	**1.65**

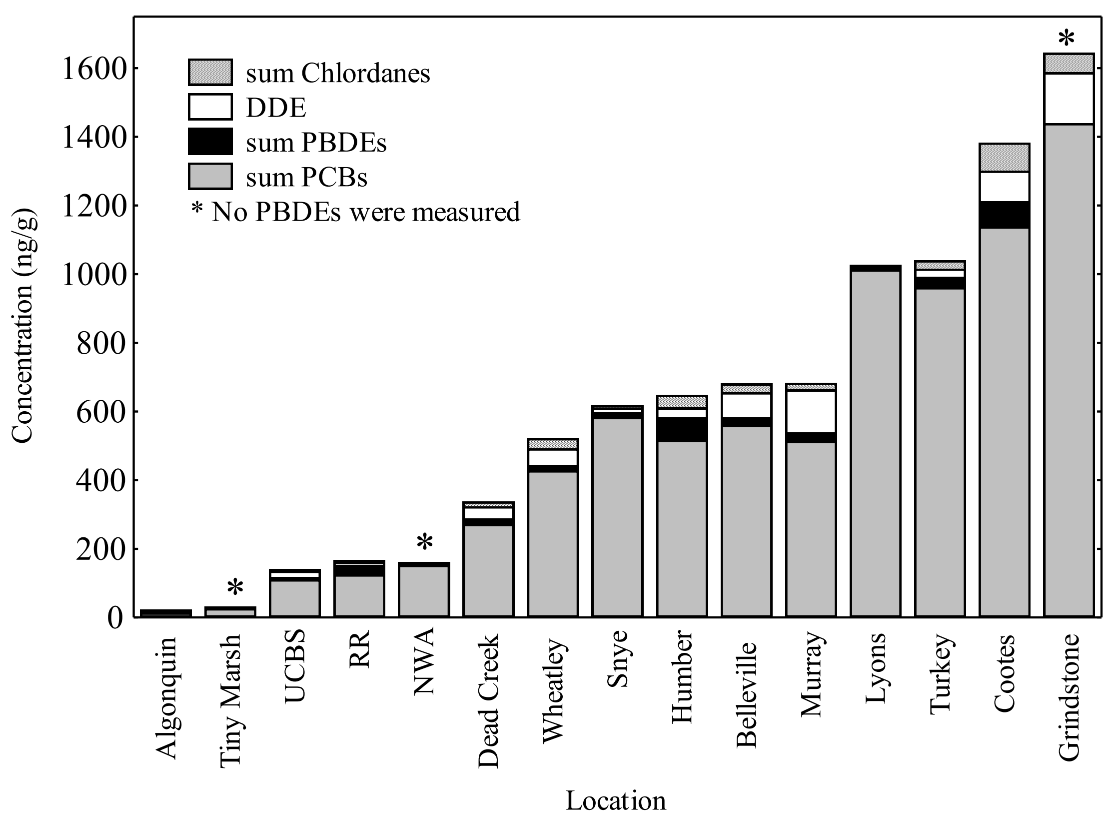
[a] Since no TEF for birds is available for PCB-37, this compound is not included in the calculation of the TEQ.

[b] TEQs are based on toxic equivalency factors developed by van den Berg *et al.* (1998) for birds. Asterisks (*) indicate concentrations were outside the 15% quality control limit around the theoretical ion abundance ratio and results should be viewed with caution. Concentrations denoted with a "<" were given a value of zero in the calculation of the TEQ.

in snapping turtle eggs from Lyons Creek was higher relative to TEQs found at other AOCs and were nearly twenty-two times the TEQ concentration in eggs from Tiny Marsh (Table 8). In contrast, the TEQ derived from dioxins and furans in eggs from Lyons Creek was low relative to other AOCs. The analysis of pooled samples of eggs precluded the ability to statistically test for differences in TEQs among AOCs.

A Great Lakes perspective of contaminants in snapping turtle eggs from 2001 to 2004 represented as cumulated totals of mean sum PCBs, sum PBDEs, *p*,*p*'-DDE and sum chlordanes is provided in Figure 12 (de Solla *et al.* 2008). Overall, eggs from Lyons Creek were more contaminated relative to many other Great Lakes locations largely as a result of high levels of PCBs with relatively minor contributions of PBDEs and pesticides to the cumulative contaminant total. PCB contamination in snapping turtle eggs has been associated with large urban centres where there is substantial industry (Ashpole *et al.* 2004; de Solla *et al.* 2007). Unlike the pattern observed at many of the Great Lakes location, the two pesticides, *p*,*p*'-DDE and sum chlordane, contributed very little to the overall measure of contamination found in eggs collected from this AOC.

Figure 12. Cumulated totals of mean sum PCB, sum PBDEs, *p,p'*-DDE and sum chlordane concentrations (ng/g, wet weight) in snapping turtle eggs in the Canadian Great Lakes collected from 2001–2004. Sites with an asterisk did not have PBDEs measured.



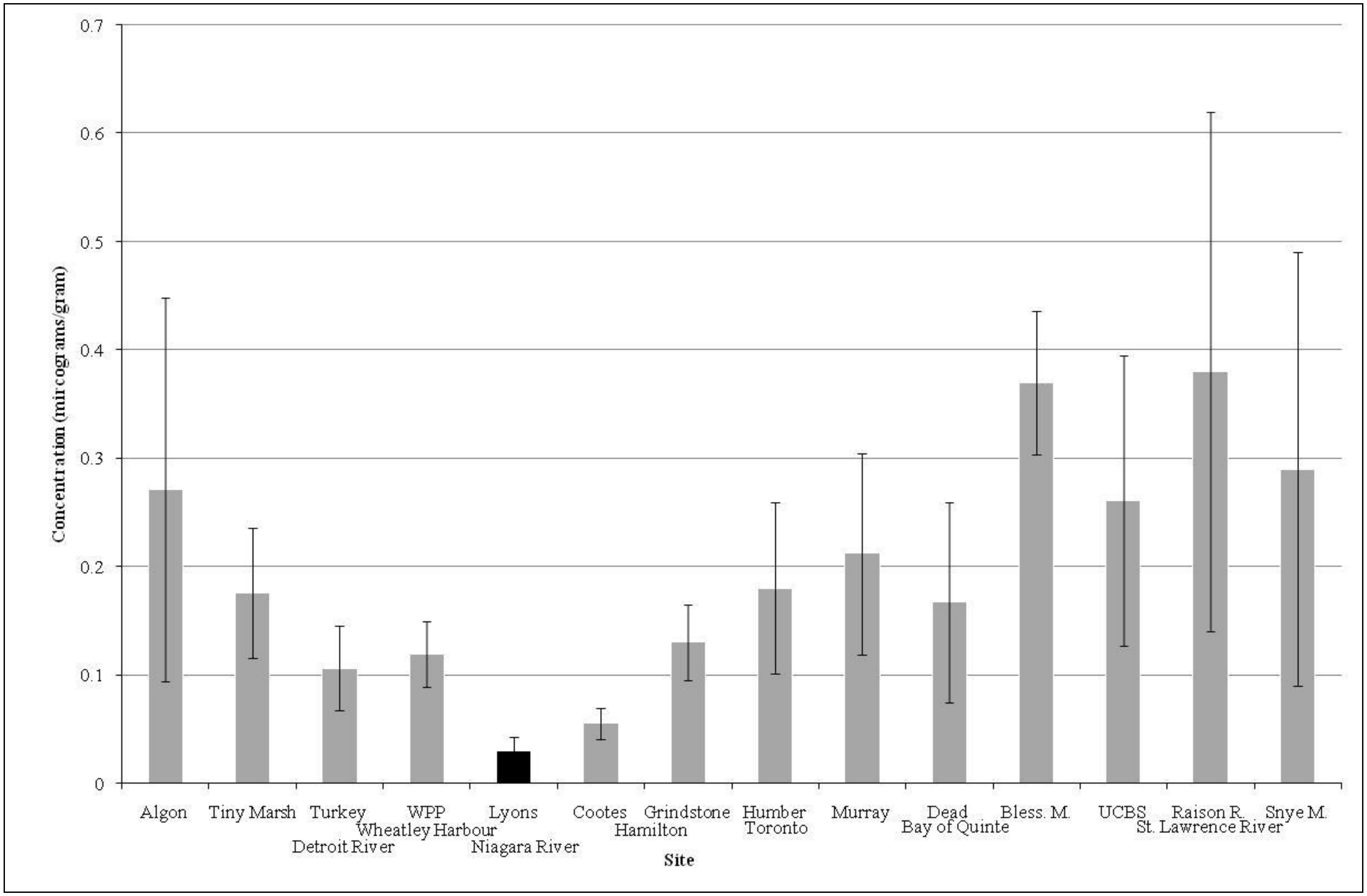
Of the five heavy metals measured in snapping turtle eggs collected from 2002 to 2004, selenium concentrations were the highest with means (±SD) ranging from 1.44 ± 0.28 µg/g (dry weight) in eggs from Upper Canada Bird Sanctuary (downstream Great Lakes reference site) to 2.05 ± 0.32 µg/g at Algonquin Provincial Park, the remote reference site, with levels in eggs from Lyons Creek East falling in between these two locations (Table 9). Arsenic concentrations ranked second highest in eggs from Lyons Creek (mean equal to 0.204 µg/g) while, at the other three locations, UCBS, Tiny Marsh and Algonquin, mercury levels in eggs ranked second highest (range in means=0.18-0.27 µg/g). Significant differences among sampling locations were found in eggs for both arsenic ($F_{(2,23)}$= 25.02, $p<0.00001$) and mercury ($F_{(2,23)}$= 51.12, $p<0.00001$). Mean arsenic concentrations were significantly higher in eggs from Lyons Creek than in eggs from the other two reference sites, where they were found at approximately one-half of the concentration of eggs from the AOC. Among Great Lakes AOCs, the mean arsenic level in eggs from Lyons Creek was within the range of mean concentrations (±SD) in eggs collected during the same time period from other southern Ontario AOCs, notably Wheatley Harbour (0.18 ± 0.05 µg/g), Hamilton Harbour (Cootes Paradise: 0.21± 0.05 µg/g and Grindstone Creek: 0.17 ± 0.02 µg/g) and the Detroit River (Turkey Creek: 0.20 ± 0.07 µg/g). In contrast, the mean mercury concentration in Lyons Creek eggs was significantly lower than mean concentrations in either of the two other reference sites, UCBS or Tiny Marsh. Lead and selenium concentrations in turtle eggs were not significantly different among the three study sites including the two reference sites. Similar statistical results were found when eggs from UBCS were not included in the analyses. Cadmium concentrations were the lowest of all metals and found at levels below the practical limit of detection (i.e., <0.015 µg/g) in all clutches of eggs at all sites.

Table 9. Mean (SD) heavy metal concentrations (µg/g, dry weight) in snapping turtle eggs from Lyons Creek East in the Niagara River AOC, Upper Canada Bird Sanctuary (UCBS, downstream reference site on the St. Lawrence River), Tiny Marsh (Great Lakes reference site) and Algonquin Provincial Park (remote area) from 2002-2004. N represents the number of clutches sampled. ND denotes concentration was below the limit of detection (i.e., below 0.015 µg/g for cadmium). With the exception of Cd, statistics reported are based on comparisons of mean concentrations in eggs from Lyons Creek, UCBS, and Tiny Marsh where similar uppercase are not significantly different.

Compound	**Lyons Creek**	**UCBS**	**Tiny Marsh**	**Algonquin**
Arsenic	0.204 (0.046) **A**	0.094 (0.023) **B**	0.091 (0.037) **B**	0.124 (0.058)
Cadmium	ND	ND	ND	ND
Selenium	1.65 (0.28)	1.44 (0.28)	1.63 (0.31)	2.05 (0.32)
Lead	0.035 (0.016)	0.038 (0.022)	0.036 (0.013)	0.045 (0.024)
Mercury	0.03 (0.01) **B**	0.26 (0.13) **A**	0.18 (0.06) **A**	0.27 (0.18) **A**
N	7	9	10	12

Mercury concentrations in snapping turtle eggs collected from Lyons Creek within the Niagara River AOC from 2002 to 2004 were among the lowest found at study sites in the Great Lakes basin including

Figure 13. Mean (SD) mercury concentrations (µg/g, dry weight) in snapping turtle eggs collected from Lyons Creek East in the Niagara River Area of Concern (dark shaded bar) and various sites in the Great Lakes basin including AOCs from 2002-2004. With the exception of Algonquin and Tiny Marsh, sites are ordered from west to east. Means are based on number of clutches collected at each site (range=4-14).



some AOCs (Figure 13). Overall, mercury concentrations varied significantly among these Great Lakes study sites ($F_{(13,110)}$=7.46, p<0.0001).

Hatching Success and Deformity Rates of Hatchlings and Adults

Mean hatching success (±SD) of snapping turtle clutches collected from 2002 to 2004 within the Niagara River AOC at Lyons Creek East was equal 91.0 ± 9.3% (N=19 clutches) and was overall high relative to some other Great Lakes sites (Figure 14). Mean hatching success was also statistically comparable to hatching success at Tiny Marsh, the upstream Great Lakes reference location (i.e., equal to 86.0 ± 20.2%, N=20 clutches; $F_{(1,37)}$= 0.31, p=0.58). Furthermore, no significant difference in mean hatching success was found among clutches from Lyons Creek, Tiny Marsh and the downstream reference site, Upper Canada Bird Sanctuary (i.e., 88.4 ± 13.6%, N=10 clutches; $F_{(2, 46)}$=0.16, p=0.85). Overall, hatching success of snapping turtle clutches varied significantly among the Great Lakes study sites ($F_{(13, 165)}$=2.71, p=0.0017; Figure 14; de Solla *et al.* 2008).

Within the Niagara River AOC, the mean hatchling deformity rate in snapping turtles was equal to 6.7 ± 9.4% (N=19 clutches) at Lyons Creek East. While the mean hatchling deformity rate at Tiny Marsh was higher relative to Lyons Creek (equal to 11.3 ± 12.5%, N=20 clutches), no significant difference in deformity rate was found between the two sites ($F_{(1,37)}$= 2.31, p=0.14). When UCBS was included for comparative purposes in the analysis (mean deformity rate=18.3 ± 10.0%, N=10 clutches), a significant difference in deformity rate was found in which the rate at Tiny Marsh was not significantly different from the rates at either Lyons Creek or UCBS but the rate at Lyons Creek was significantly lower than the rate found at UCBS ($F_{(2,46)}$=4.97, p=0.011). Deformity rates of hatchling snapping turtles also varied significantly among the Great Lakes study sites ($F_{(13, 165)}$=3.34, p=0.0001; Figure 15; de Solla *et al.* 2008).

In addition, of the 25 adult snapping turtles captured from Lyons Creek East, none were found to have deformities. Deformities recorded included missing or extra marginal, dorsal or lateral scutes. Lyons Creek was the only AOC in which no deformities were recorded in adult turtles examined (de Solla *et al.* 2008). Deformity rates at other AOCs ranged from 3.8% at Dead Creek in the Bay of Quinte to 21.1% at Raisin River in the St. Lawrence River AOC (de Solla *et al.* 2008). These estimates are conservative since all animals which exhibited evidence associated with a possible injury (e.g., missing nails, bent tail, etc.) were excluded from the assessment.

Figure 14. Mean hatching success rates (SD) of snapping turtle eggs collected from Lyons Creek East in the Niagara River Area of Concern (dark shaded bar) and various sites in the Great Lakes basin including other AOCs from 2002-2004. With the exception of Algonquin and Tiny Marsh, sites are ordered from west to east. Means are based on number of clutches collected at each site (range=4-31).

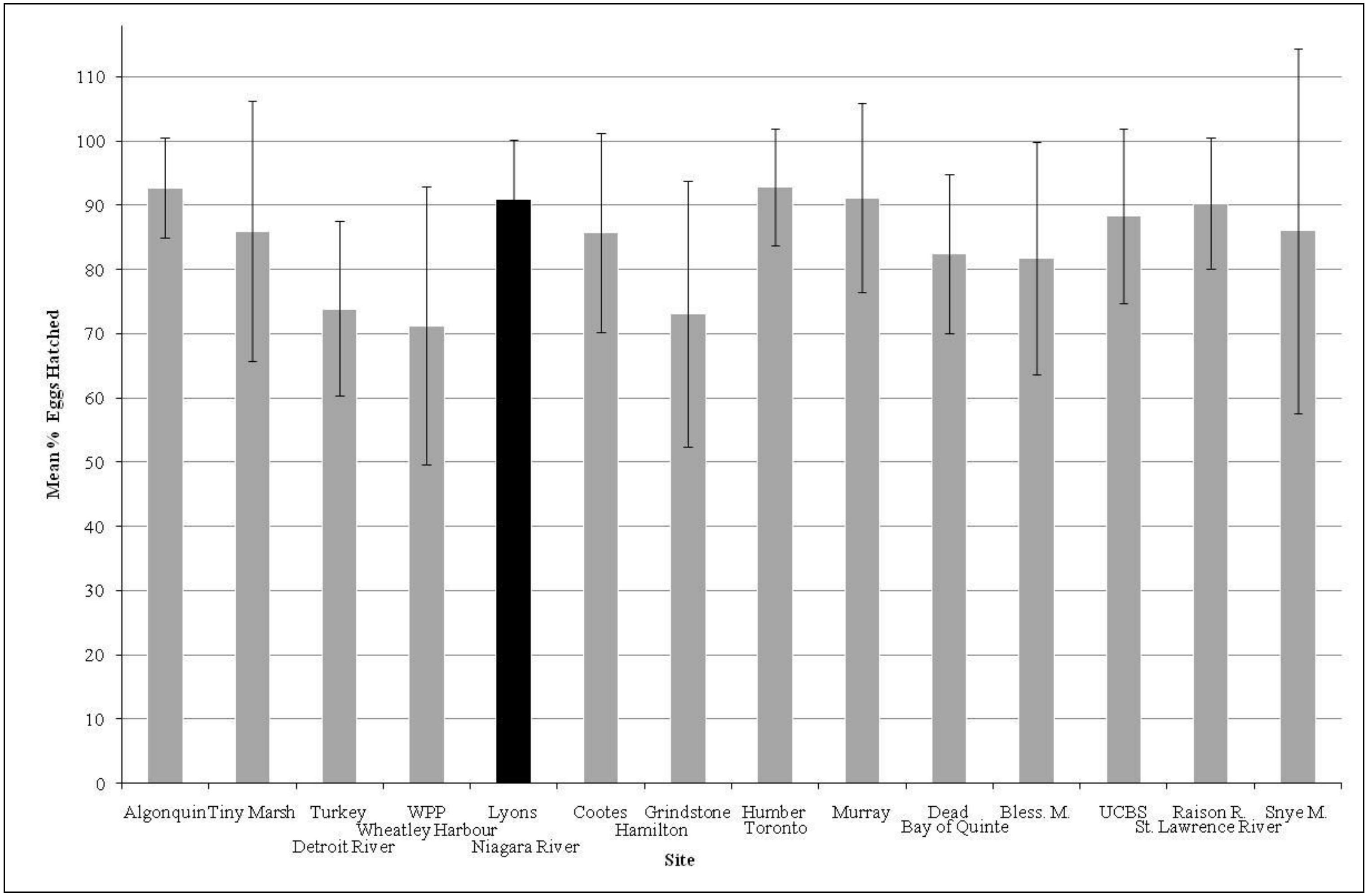
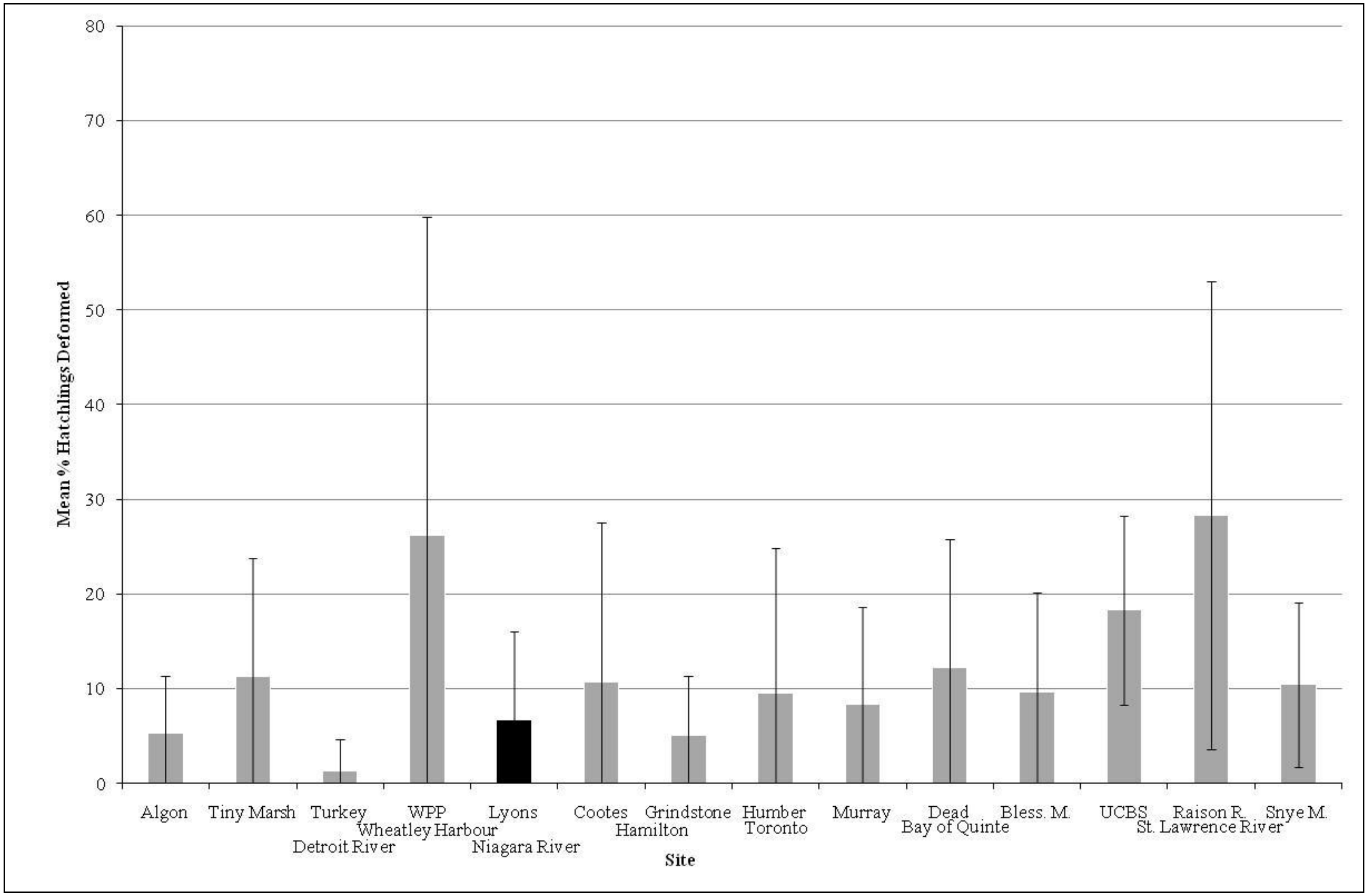


Figure 15. Mean deformity rate (SD) of hatchling snapping turtles collected from Lyons Creek East in the Niagara River Area of Concern (dark shaded bar) and various sites in the Great Lakes basin including other AOCs from 2002-2004. With the exception of Algonquin and Tiny Marsh, sites are ordered from west to east. Means are based on number of clutches collected at each site (range=4-31).



Conclusions

Following completion of the Welland Ship Canal Bypass in 1971, Lyons Creek was bisected into two sections, Lyons Creek East and Lyons Creek West, where subsequent environmental assessments in both sections identified polychlorinated biphenyl (PCBs) as compounds of concern. In Lyons Creek East, surficial sediment collected in the 1990s-2000s showed that PCBs, likely associated with a historical source, were highest in the upper reaches of the Creek (i.e., from the Welland Canal to Highway 140), after which concentrations progressively decreased with increasing distance downstream (Golder Associates Ltd. and Dillon Consulting Ltd. 2008). A similar downstream trend was also evident in snapping turtle eggs collected from 2001 to 2004 along Lyons Creek East downstream from the Welland Canal in which PCB congener patterns reflected a strong contribution from Aroclors 1248 and 1254 (Figure 4; de Solla *et al.* 2007). Other biota collected in 2002 and 2003, including benthic invertebrates, mussels and fish, also had the highest PCB levels in the upper reaches of the Creek (Milani and Fletcher 2005). In mink trapped within the Niagara River AOC, the most PCB-contaminated individual (5,419 μg/kg) was trapped at Lyons Creek at Highway 140 in 2004. Toxic equivalent concentrations for dioxin-like PCBs in forage fish collected in close proximity to this trapping location in 2002 and 2003 were found at levels associated with an increased risk to adverse effects in mammals, such as mink, consuming these fish (Milani and Fletcher 2005). Accordingly, this relatively young mink had a hepatic PCB concentration which greatly exceeded the thresholds associated with impaired kit growth (980 μg/kg ww) and kit mortality (2,200 μg/kg ww; Heaton *et al.* 1995; Restum *et al.* 1998). Some variability in exposure was evident as two other mink trapped nearby this location, as well as two additional mink trapped further downstream, had far lower hepatic PCB levels (i.e., less than 1/10 of this concentration) which did not approach thresholds associated with effects on growth or reproduction. Toxic equivalent concentrations based on levels of dioxin-like PCBs were also high in snapping turtle eggs from Lyons Creek East relative to levels in eggs collected from other Great Lakes Areas of Concern while levels of dioxins and furans in eggs were low and contributed far less to overall toxicity (Table 8). With regard to consumption of wildlife and associated risks to human health, the results of a local community survey indicated that there was no evidence of current or ongoing consumption of snapping turtles from Lyons Creek East and, therefore, the consumption of snapping turtle is not a concern in the Lyons Creek area (Dillon Consulting Ltd. 2007). Following an extensive risk assessment of PCBs to biota in Lyons Creek East (and Lyons Creek West), options for remediation have been developed and are currently being evaluated (Golder Associates Ltd. and Dillon Consulting Ltd. 2008).

Spatial differences in exposure to PCBs, as well as some other compounds, found among the three wildlife species highlight their utility as a diverse set of bioindicators reflecting conditions at varying geographic scales within the AOC. The use of snapping turtles as an indicator of local sources of contaminants was effective in assessing contaminant conditions in a tributary with a history of PCB contamination within the AOC where eggs collected from Lyons Creek had significantly higher PCB levels than eggs collected from either of the non-AOC reference sites (Tiny Marsh and Upper Canada Bird Sanctuary). For mink which were trapped over a much larger geographic area within the AOC, sum PCBs in liver were considered statistically similar (albeit marginally) among AOC and non-AOC locations (eastern Lake Erie and inland Ontario) and, while the sample size was low, no significant difference was found in levels of PCBs in mink trapped along Lyons Creek East compared to other locations (including other tributaries) within the AOC. Herring gulls usually feed within a few kilometres (up to 10 or 12) of their nesting colony and, as such, contaminant trends in eggs may be more reflective of regional conditions in the Niagara River proper. Significant declines in levels of PCBs, organochlorine pesticides, mercury, and 2,3,7,8-TCDD found in herring gulls eggs collected from the Niagara River from 1979 to 2007 (Figure 9) are consistent with long-term temporal trends observed for many of these persistent compounds in other top predators, including lake trout (*Salvelinus namaycush*) and rainbow trout (*Oncorhynchus mykiss*), collected from the lower Niagara River since the early to mid-1980s (Karst-Riddoch *et al.* 2008). Such large declines in the bioavailability of these contaminants can be attributed to production bans and restrictions of the use of chemicals, improved industrial practices, and the effectiveness of remedial activities in reducing chemical inputs into the Niagara River. For herring gull eggs collected from the Niagara River from 2003 to 2007, PCBs were found at low levels which were statistically similar to levels at the non-AOC sites (Port Colborne Lighthouse and Chantry Island), results of which largely contributed to the low-intermediate relative ranking of contamination determined for gulls at the Niagara River AMC relative to other Great Lakes sites (i.e., ranked as twelfth of 15 Great Lakes sites). For some Niagara River sport fish however levels of PCBs remain a concern and they were sufficiently elevated in 2002 and 2004 to exceed some Ontario Ministry of the Environment consumption restriction guidelines (Karst-Riddoch *et al.* 2008). As expected, the lowest contaminant levels were often found in wildlife from remote reference sites (e.g. Algonquin Park, Chantry Island and Tiny Marsh) which reflect background exposure.

With regard to organochlorine pesticides, the Niagara River has been identified as a significant source of mirex input to Lake Ontario as a result of the direct loss of mirex during the manufacturing process at the Hooker Chemical plant at Niagara Falls (Holdrinet *et al.* 1978; Thomas and Frank 1987). While mink from the Niagara River AOC had significantly higher levels of mirex relative to levels found in mink from inland Ontario, these levels were not significantly different from levels in mink trapped upstream from eastern Lake Erie sites. Furthermore, mirex levels in mink from the Niagara River AOC were not nearly as high as levels in mink trapped from downstream AOCs, namely the Bay of Quinte and the St. Lawrence River (Cornwall), where the influence of a second major source of mirex from the Oswego River in the eastern basin of Lake Ontario may be more prevalent (Holdrinet *et al.* 1978). In herring gull eggs collected from 1998-2002 in an earlier study, downstream AMCs on Lake Ontario and the St. Lawrence River had significantly higher concentrations of mirex compared to eggs from the Niagara River AMC (Weseloh *et al.* 2006). Such a trend was not evident in more recent 2003-2007 egg collections where, as a result of declines in levels of mirex at the downstream colonies since that early time period, statistically similar mirex levels were reported among Lake Ontario, St. Lawrence River and Niagara River AMCs (Figure 5). In addition, no significant difference in mean mirex levels (albeit a marginally significant one, p=0.06) was found in eggs from the Niagara River AMC compared to the upstream reference Port Colborne Lighthouse AMC. Mirex detected in eggs collected from colonies upstream from the Niagara River and on Lake Erie (Port Colborne and Middle Island) and Lake Huron (e.g., Double Island and Chantry Island) may be indicative of herring gull feeding on the Niagara River or Lake Ontario in the winter or pre-breeding and breeding periods (Weseloh *et al.* 1990; Ewins *et al.* 1992). Overall, low levels of pesticides, including mirex, sum chlordanes and *p,p*'-DDE, were found in snapping turtle eggs from Lyons Creek East, especially in relation to many other Great Lakes AOCs, including the upstream reference site at Tiny Marsh on Lake Huron (Table 7; Figure 12; de Solla *et al.* 2007).

In addition to PCBs and mirex, hexachlorobenzene (HCB) was also identified one of 18 priority toxic chemicals under the Niagara River Toxics Management Plan (NRTMP) since it exceeded the strictest agency criteria for water, sediment or biota in Lake Ontario and/or the Niagara River (DOI 1987). Mink trapped in the AOC had significantly higher hepatic HCB levels than mink trapped from inland Ontario but had HCB levels which were not significantly different from the eastern Lake Erie mink. This spatial pattern, also evident for oxychlordane (as well as mirex, as reported above), suggests that effects potentially attributable to Niagara River sources were not discernable from upstream Lake Erie/Great Lakes influences. In addition, while levels of HCB were elevated (and highly variable) in herring gulls eggs collected from the Niagara River AMC from 2003-2007, mean levels were overall not significantly different with other Great Lakes AMCs including the upstream Lake Erie reference site. Such upstream/downstream effects however were discernable for HCB and mirex using recent spatial data from the Niagara River Upstream/Downstream Program, a long-term water quality monitoring program and a component of the NRTMP. This program conducted by Environment Canada compares contaminant concentrations in water and suspended sediment at Fort Erie located upstream at the head of the Niagara River (which serves as a reference station) with concentrations downstream at the mouth of the River at Niagara-on-the-Lake to determine trends and loadings of chemicals to the River. Water quality data based on collections from these stations in 2004 and 2005 indicate that despite significant reductions in loadings of HCB and mirex to the Niagara River since the mid-1980s there are still inputs of these pesticides from Niagara River sources (Niagara River Secretariat 2007). Mink and herring gulls prey on locally available food sources and as a result they are exposed to varying degrees of contamination among prey and prey types. This likely contributed to the inability to discern between AOC and upstream effects for HCB and mirex and particularly at the low current levels reported in this study. For other contaminants such as dieldrin and PCBs, the influence of upstream sources was also indentified as an important contributor to contaminants loadings in the Niagara River (Niagara River Secretariat 2007).

Polybrominated diphenyl ether (PBDE) flame retardants which are used in a wide range of products including paints, plastics, textiles and electronics are a relatively new set of compounds of emerging concern in the Niagara River, Great Lakes and globally (WHO 1994; Norstrom *et al.* 2002; Niagara River Secretariat 2007). Their similarity in structure to PCBs and persistence and bioaccumulation in the environment and biota suggest that their effects may be detrimental to human and wildlife health. Toxicological studies of PBDE exposure in experimental animals reveal impacts on reproduction, neurological development, as well as immunotoxicity (Darnerud *et al.* 2001). In wildlife, evidence of altered thyroid function was found in the American kestrel (*Falco sparverius*) exposed to environmentally relevant levels of PBDEs (Fernie *et al.* 2005). Sum PBDE levels were significantly higher in herring gull eggs from Niagara River compared to the upstream Lake Erie reference site at Port Colborne Lighthouse which is indicative of PBDEs sources along the River. Marvin *et al.* (2007) also found higher concentrations of sum PBDEs in suspended sediment at the mouth of the River (Niagara-on-the-Lake) compared to concentrations at the upstream reference station (Fort Erie) from 2003-2004. Based on comparisons to global PBDE sediment concentrations, however, they suggest that the Niagara River watershed does not appear to be a significant local source of PBDEs to Lake Ontario and that the upstream/downstream effect is typical of a heavily industrialized and urbanized watershed especially relative to that of eastern Lake Erie. At sites on the U.S. side of the Niagara River and more specifically, Samara *et al.* (2006) found that PBDEs in sediment were highest in areas closest to discharge locations of municipal wastewater treatment plants and local industries. While significant increases in levels of PBDE congeners associated with the PentaBDE formulation were found in eggs collected from selected Great Lakes AMCs from 1981 to 2000 (Norstrom *et al.* 2002), increases were no longer evident in eggs from these AMCs from 2000 to 2006 likely in response to increased regulation and phasing out of production of PentaBDE and OctaBDE commercial mixtures (Gauthier *et al.* 2008). This may explain why no significant change in levels of sum PBDEs were found in eggs from either the Niagara River or Port Colborne Lighthouse from 2000 (when eggs were first analyzed for PBDEs) to 2007. However, changes in the levels and the composition of PBDEs specifically to more highly brominated diphenyl ether (BDEs) congeners in herring gull eggs have been reported at Great Lakes AMCs including the Niagara River post-2000 (Gauthier *et al.* 2008). Among these highly BDEs is the congener BDE-209 whose primary source is the DecaBDE commercial mixture for which there are currently no restrictions on production. Other current-use non-regulated flame retardants which may be the new replacements for phased-out flame retardant commercial mixtures have also been detected in eggs from the Niagara River and other Great Lakes AMCs (Gauthier *et al.* 2007). It is not known what health effects in herring gulls might be evident at current PBDEs levels in eggs from the Niagara River and little or no toxicological data are available for the new replacement flame retardants. PBDEs were also detected in snapping turtles and mink from the AOC. Levels of sum PBDEs in snapping turtle eggs from Lyons Creek were the lowest among southern Ontario AOCs and found at a mean concentration which was 1/20 of the most PBDE-contaminated and largest urbanized AOCs, namely Toronto and Hamilton (de Solla *et al.* 2007). Low levels of sum PBDEs were also found in mink from the AOC and at levels which were similar to the two reference inland Ontario mink.

Of the metals examined in this study, arsenic was found at significantly higher levels in snapping turtle eggs collected from Lyons Creek East in 2002-2004 than at both of the reference sites. Sediment and risk assessment studies have identified both arsenic and PCBs as compounds of concern in Lyons Creek West but not at Lyons Creek East where only PCBs were sufficiently elevated to pose a potential risk to biota (Golder Associates Ltd. and Dillon Consulting Ltd 2008). Snapping turtles and fish (as potential prey) from Lyons Creek East are unable to access Lyons Creek West due to the presence of the Welland Canal which acts as a physical barrier. Therefore, elevated arsenic exposure in snapping turtles from Lyons Creek East is somewhat surprising and further investigations may be required with respect to its (historic) source. Noteworthy is that one sediment sample collected from Lyons Creek East near the Welland Canal in 2002/3 exceeded the provincial sediment quality guideline (severe effect level) for arsenic and some other metals (Milani and Fletcher 2005). Overall however, arsenic levels in eggs were comparable to levels at some other Great Lakes AOCs and whether they are sufficiently elevated to generate adverse health effects in turtles is unclear. In the case of elevated arsenic levels found in sediment from Lyons Creek West and concerns of increased risk to biota, arsenic-contaminated sediment from Lyons Creek West was excavated in the summer of 2007 and placed in a secure landfill facility. In accordance with no known point sources of mercury in the watershed (Environment Canada 2007), mercury levels in snapping turtle eggs from Lyons Creek East were low overall and significantly lower than the reference sites. Another top predator, largemouth bass (*Micropterus salmoides*) collected from two Lyons Creek East sites was also found to have low levels of mercury (Environment Canada 2007). Hepatic concentrations of mercury, cadmium, lead and arsenic in mink from the Niagara River AOC were not significantly different from mink trapped from eastern Lake Erie or from inland Ontario references sites and were below lowest effect levels for metals where thresholds are available (Buck *et al.* 1976; Wobeser and Swift 1976; Wobeser *et al.* 1976; Siewicki 1980; Scheuhammer 1991; Wolfe *et al.* 1998). Levels of selenium were significantly higher in mink from the AOC compared to inland Ontario mink and were within concentrations reported from other Great Lakes sites. Similarly, mercury levels in herring gulls eggs from the Niagara River declined significantly from 1981-2007, were low overall from 2003 to 2007, and did not approach the threshold level typically associated with adverse reproductive effects in birds (Thompson 1996).

The Niagara River supports a large number of colonial waterbirds, the large majority of which are found nesting on the U.S. side of the River where large islands provide an abundance of suitable nesting habitat. During the 4th decadal CWS survey conducted in 2007, over 900 nests of three colonial waterbird species were counted on the Canadian side of the River. Compared to nest numbers counted during the 3rd decadal survey in 1999, nest numbers of ring-billed gulls and black-crowned night-heron increased in 2007 (at annual rates of growth equal to 6.1% and 5.5%, respectively). While an overall decline in herring gull nest numbers was found on Canadian Lake Erie, this decline was more pronounced for the relatively fewer number of herring gulls nesting on the Canadian side of the Niagara River during this period (-13.0% per year). This finding may be due to the loss of available nesting habitat at the largest colony where accumulation of floating debris in this high-flow area at the top of Niagara Falls may have reduced the size of the island. Overall, the large declines in contaminant levels in herring gull eggs from the Niagara River since the late 1970s and the relatively stable numbers of nesting species suggests that contaminant-induced effects do not appear to be limiting factors at the population level for birds feeding in the AOC. Bald eagles have recently returned to nest on the Niagara River at Navy Island and successfully fledged eaglets in 2005, 2006 and 2008 providing additional support for the improved health of aquatic-feeding birds in the AOC (Allair 2008). Finally, large snapping turtles visually observed from shore in Lyons Creek East as well as through capture in fyke nets set for short periods at Cooks Mill provide some qualitative evidence of an apparently abundant population (Dillon Consulting Ltd. 2007). Long term trends of black terns (*Chlidonias niger*) based on observation records reported to the Buffalo Ornithological Society (BOS) indicated a substantial decline in the average number of birds counted between the two periods 1940-1968/70 and 1969/71-2000/01 for both the one-day May counts and total annual counts at the headwaters of the Niagara River. The reason for the decline is unclear and may not be specific to the Niagara River but to other important staging areas in the southern Great Lakes (K. Jermyn-Gee and D.V.C. Weseloh, unpubl. data).

Endpoints associated with reproduction and development have been frequently used to assess the effects of contaminants on the health and survival of wildlife populations (Bishop *et al.* 1998; de Solla *et al.* 2007, 2008). While effects on reproductive success and development of snapping turtles have been found in some Canadian Great Lakes AOCs (de Solla *et al.* 2008), these were not evident in snapping turtles from Lyons Creek East where hatching success was high (91.0%), hatchling deformity rate was low (6.7%) and both were statistically similar to the upstream Tiny Marsh reference site. In addition, no deformities were found in 25 adult snapping turtles examined from this site in 2002. With regard to more subtle physiological effects, some differences in clinical chemistry parameters have been reported in snapping turtles from Lyons Creek compared to reference sites (Environment Canada 2007). There are no contaminant thresholds known however for the clinical chemical data in snapping turtles. In addition, the biological significance of these findings is unclear since it is difficult to link health effects observed as biochemical changes in the individual to subsequent alterations in growth, survival and reproduction (Fox 2001). Such alterations may be present (particularly for those individuals exposed to high PCB levels) but were not obviously apparent or among those measured in this study. Other potential physiological effects of contaminant exposure in wildlife include changes in organ size and while mink from the Niagara River AOC had a significantly larger spleen index relative to mink from inland Ontario, these effects may have been related to an infection. It is unclear to what extent the introduction of domesticated animals might influence the overall fitness and reproductive success of the breeding mink population in the Niagara River area since there is a known mink farm in the Municipality of Niagara from which domestic mink have escaped and mated with wild mink (Kidd *et al.* 2009). While health effects associated with contaminant exposure have been documented in recent studies of herring gulls foraging in other AOCs in the lower Great Lakes (Environment Canada 2003; Hughes *et al.* 2010), such effects in herring gulls from the Niagara River (Ontario) AOC could not be assessed due to inherent difficulties with accessing the colony for research purposes. While contaminant levels were generally low for gulls foraging within the AOC, for those compounds found at higher levels in some individuals (e.g. PBDEs, HCB), it is unclear to what extent subtle physiological effects might be prevalent.

In summary, this study has examined current data on spatial and temporal trends of toxic contaminants and potential health effects in aquatic wildlife in the Niagara River (Ontario) Area of Concern. Despite long-term significant declines reported for many persistent compounds since the 1970/80s in the Niagara River, elevated levels of some compounds, notably PCBs, were found in two of the three species (mink and snapping turtles) relative to levels at selected reference sites. While contaminant levels were not sufficiently elevated to elicit population-level effects in species foraging in the AOC, some subtle physiological health effects may be evident in some individuals. Of the 12 biological endpoints associated with impaired reproduction, growth and development and examined in the study, no effects of exposure were evident. However, the hepatic sum PCB concentration in one mink trapped in an area of known PCB contamination in the AOC was sufficiently high to exceed effect thresholds associated with impaired kit growth and mortality in mink.

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