

Spatial distributions and temporal trends in pollutants in the Great Lakes 1968–2008

Debbie Burniston, Paul Klawunn, Sean Backus, Brad Hill, Alice Dove, Jasmine Waltho, Violeta Richardson, John Struger, Lisa Bradley, Daryl McGoldrick and Chris Marvin

ABSTRACT

The Great Lakes have been the focus of intensive long-term research and monitoring programmes for the past 40 years. Spatial distributions and temporal trends have been determined for a range of environmental compartments, including surface water, sediment and fish. In general, there have been dramatic reductions in contamination by legacy pollutants including polychlorinated biphenyls (PCBs), organochlorine pesticides and metals. Concentrations of PCBs and lead in surface water at the mouth of the Niagara River have decreased by 58 and 54%, respectively, over the period 1986–2007. Correspondingly, concentrations of PCBs and lead in offshore sediments of Lake Ontario have decreased by 37 and 45%, respectively, since peak accumulations in the 1970s. Temporal trends for more modern chemicals, including polybrominated diphenylethers and perfluoroalkyl compounds, showed increases up until 2000 when management actions and heightened stakeholder awareness resulted in a levelling off or decline in the subsequent time period. While legacy issues are largely associated with areas of historical industrial activity, the presence of newer chemicals is generally associated with modern urban/industrial areas that act as diffuse sources.

Key words | Great Lakes, mercury, perfluoroalkyl compounds, pesticides, polybrominated diphenylethers, polychlorinated biphenyls

Debbie Burniston
Paul Klawunn
Sean Backus
Brad Hill
Alice Dove
Jasmine Waltho
Violeta Richardson
John Struger
Lisa Bradley
Daryl McGoldrick
Chris Marvin (corresponding author)
Water Science and Technology Directorate,
Environment Canada,
867 Lakeshore Road,
Burlington, ON,
Canada
E-mail: Chris.Marvin@ec.gc.ca

INTRODUCTION

The presence of persistent pollutants can adversely impact Great Lakes wildlife, biodiversity and aquatic ecosystems. Agricultural, industrial and municipal activities, both within the Great Lakes basin and in upwind regions, have resulted in pollution by a variety of contaminants and subsequent degradation of ecosystem health. Accumulation of pollutants in sediments, tissues of benthic invertebrates and fish is the result of both historical and contemporary inputs and sources. Information on the occurrence and spatial distribution of toxic substances in the Great Lakes furthers understanding of the role human activities play in discharging these chemicals to the environment, and can also serve as a benchmark in assessing contaminant discharge reduction strategies.

There is a considerable body of literature documenting the accumulation of persistent contaminants in the Great Lakes since the period of the late 1960s through the mid 1970s. Intensive lake-wide sediment surveys detected the presence of compounds including polychlorinated biphenyls (PCBs) (Frank *et al.* 1977, 1979), organochlorine pesticides (Frank *et al.* 1977; Van Hove Holdrinet *et al.* 1978) and mercury (Thomas 1972, 1974; Kemp & Thomas 1976; Thomas & Jaquet 1976; Cahill 1981) in lake sediments of all of the Laurentian Great Lakes at elevated concentrations due to the influence of anthropogenic activities. However, these studies pre-dated binational strategies to mitigate deleterious environmental impacts due to persistent toxics, including the banning of PCBs and the phasing-out of leaded gasoline.

Studies using sediment cores have concluded that deposition rates for a number of persistent organic pollutants (POPs) in the Great Lakes generally peaked during the period 1960–1980, with rates decreasing after this time (Wong *et al.* 1995; Pearson *et al.* 1997; Schneider *et al.* 2001).

Environment Canada, together with collaborating agencies, conducts multi-media long-term research and monitoring (Table 1) to measure the occurrence and spatial distribution of environmental contaminants in order to further understand the role human activities play in releasing toxic substances to the environment, for determination of temporal trends in contamination and to provide information for devising effective mitigation strategies. In addition, these programmes now enable early identification

of emerging contaminant issues. Water and sediment contaminant monitoring programmes were initiated in the late 1970s through to the mid 1980s, and are ongoing in the open waters and interconnecting channels of the Great Lakes.

Although each programme has associated reporting obligations, we have not previously attempted to present an all-encompassing overview of the results of all of our Great Lakes research and monitoring. In this paper, we present a review of selected observations from our Great Lakes studies, and assess the concurrence, or lack thereof, in general trends in environmental quality as it relates to toxic chemicals across the breadth of the basin in a range of environmental compartments. This review is far from

Table 1 | Listing and description of Environment Canada programmes for research and monitoring of contaminants in the Great Lakes basin. Collaborating agencies are denoted as follows: OMOE – Ontario Ministry of the Environment; USEPA – United States Environmental Protection Agency; NYSDEC – New York State Department of Environmental Conservation; DFO – Department of Fisheries and Oceans Canada

Programme	Description	Chemicals monitored	Collaborating agencies
Great Lakes surface water surveillance	Assess Great Lakes surface water quality to measure compliance with water quality objectives, evaluate spatial distributions and temporal trends and identify emerging issues. Two lakes annually surveyed on a rotational basis.	Nutrients, major ions, metals, organic contaminants, PAHs, atrazine, metolachlor PCBs, PBDEs (subset)	
Great Lakes tributary screening and trackdown	Screening level programme designed to assess quality of sediment entering lakes from tributaries and identification of sources of contamination within watersheds.	Organic contaminants, PCBs, PAHs, PBDEs (subset), PFCs (subset), dioxins and furans (subset)	OMOE, USEPA
Connecting channels monitoring	Assess surface water quality in Great Lakes connecting channels. Programmes for Niagara River (upstream/downstream), St. Clair River, Detroit River and Wolfe Island provide information on contaminant concentrations and temporal trends used in assessment of efficacy of control measures.	Nutrients, major ions, metals, organic contaminants, atrazine, metolachlor PCBs, PBDEs (subset)	OMOE, USEPA, NYSDEC
Pesticides surveillance	Determination of occurrence, distribution and fate of legacy and current-use pesticides (CUPs) in Great Lakes watersheds.	Organic contaminants	
Great Lakes sediment assessment	Determination of occurrence, distribution and fate of persistent toxics in Great Lakes sediments. Comparison of contaminant levels with historical data, and use of dated sediment cores, allows assessment of temporal trends.	Metals, organic contaminants, PCBs, PAHs, PBDEs (subset), PFCs (subset), dioxins and furans (subset)	OMOE, DFO
Fish contaminant monitoring and surveillance	Determination of occurrence, temporal trends and biomagnification and bioaccumulation of pollutants in fish for assessment of risk to non-human consumers of fish. Fish collected annually.		

comprehensive, and focuses on legacy and new chemicals for which we have the most complete data sets. However, in a general sense the contaminant classes discussed serve as proxies for other pollutants with similar production and usage patterns. Spatial distributions and temporal trends are assessed and show the response in the ambient environment to toxic reduction initiatives at local, regional and continental scales. For example, depositional sediments from Great Lakes tributaries can screen watersheds for potential upstream sources of toxics, sediment cores and archived sediment samples can hind-cast trends, while fish levels demonstrate the level of bioaccumulation in the food chain. We also describe the evolution of programmes to include information on the presence of contaminants of new and emerging concern in the basin, in addition to continuing to maintain a high level of vigilance with respect to legacy compounds that are still considered priority pollutants in some jurisdictions. Specific objectives of the review are as follows:

- Determine general occurrence and spatial distributions of toxics in the Great Lakes, including the latest generation of contaminants associated with consumer products (per-fluorinated compounds and brominated flame retardants (BFRs)).
- Measure temporal trends of contaminants and assess against production and usage, and assess the efficacy of binational initiatives to reduce discharges of legacy toxics.
- Assess primary sources of contaminants.

METHODS

Sample collection

Detailed descriptions of field methods are provided in various publications (Table 2).

Surface water

Connecting channel samples were collected from January through December each year. Niagara River water (26 samples annually/site) was collected using a large-volume

Table 2 | References for field methods

Media	Location	Reference
Surficial sediment	Lakes Erie, Ontario, Superior and St. Clair	Marvin <i>et al.</i> (2002a)
Surficial sediment	Lake Michigan	Rossmann (2002)
Surficial sediment	Great Lake tributaries	Dove <i>et al.</i> (2003)
Suspended sediment	St. Clair R., Detroit R.	Marvin <i>et al.</i> (2004b)
Water	Great Lakes	Dove <i>et al.</i> (2009)
Water	Niagara River, St. Clair R., Wolfe Island	NRAP (1992); Harrison & Klawunn (2006)
Water (pesticide analysis)	Selected streams/ rivers in Great Lakes basin	Struger <i>et al.</i> (2007)
Fish	Great Lakes	McGoldrick <i>et al.</i> (2010)

24 h time integrated dissolved/particulate phase sampling protocol under the auspices of the Niagara River Upstream/Downstream Program. The St. Clair River (26 samples annually/site), St. Lawrence River and Wolfe Island (13 samples/site) connecting channel programmes have similar protocols. Whole water was collected from a submersible pump into Teflon bottles for mercury analyses, and into plastic bottles for metals analyses. Suspended particulates were collected by passing water through a Westfalia continuous centrifuge and analysed for trace metals, mercury and organic contaminants. Centrifuged (dissolved phase) water was extracted in dichloromethane using a large-volume continuous-flow Goulden extractor (Goulden & Anthony 1985) and subsequently analysed by gas chromatography-mass spectrometry. Whole water samples for mercury analysis were collected from April through November, 16 samples per site just below the water surface using isomet technology.

Open-lake surface water samples (1 sample/site/survey) were collected aboard the CCGS Limnos in spring of the sampling year for organic pollutants using the PoPCart, a clean sample collection system designed to collect, filter and dispense water into glass bottles without exposing the sample to air and other sources of contamination. Samples for metal analysis were collected during the spring cruise

using the isomet, which fills glass bottles with whole water using clean methodologies. Water samples for pesticide analysis (approximately 10/site/year) were collected in rivers or streams (15 sites) near areas of application. Pesticide-free 1 L amber bottles with Teflon lids were affixed to a fibreglass sampling pole. Bottles were rinsed twice in sample water prior to collection. Samples were collected from mid-stream, 10–15 cm below the surface where possible. Samples were preserved in the field if required and were stored in coolers with ice packs for transport to the lab where they were refrigerated until extraction or analysis.

Sediments

Surficial sediment samples from Lakes Erie, Ontario, Superior and St. Clair (1 sample/site) were collected beginning in 1999 aboard the CCGS Limnos using a mini box core sampling procedure. Lake Michigan surficial sediments were collected aboard the Guardian using either a box corer or a Ponar dredge. The top 3 cm of the sediment was subsampled for analysis. The top 2 cm of recently deposited bottom sediment (collected fall 2001–2006) from tributaries to the Great Lakes (1 sample/site) was collected in shallow areas using a stainless steel spoon or petite Ponar dredge and sieved through a 2 mm stainless steel sieve. Sediment deposition zones were sought near the mouths of the tributaries such that they were likely downstream from potential contaminant sources yet sufficiently far upstream not to be influenced by the water body into which it drains. Suspended sediments (6 monthly samples/site) in the St. Clair-Detroit River corridor were collected from May to October beginning in 1999 using single-point sediment trap moorings. The moorings were refurbished monthly and accumulated material deposited in the traps was removed, transferred to Nalgene® containers, refrigerated and then frozen until analysis.

Fish

Fish specimens were collected annually from 10 stations on the four Great Lakes that border Canada from a total network consisting of 12 permanent monitoring stations. Each year, specimens were collected from four stations on Lake Ontario and two stations on Lake Erie. Two of the three stations located on each of Lake Huron and Lake

Superior were visited annually on a rotating basis. Fish collection methods varied depending on the target species and water body. Generally, the objective was to collect 50 piscivorous fish such as lake trout (*Salvelinus namaycush*) and walleye (*Sander vitreus*) from each station with bottom set gillnets and 100 to 200 of each dominant forage fish species with a bottom trawl. After capture, fish were immediately frozen and transported to the laboratory where they were partially thawed, weighed, measured and sexed. Scales, fin rays and/or otoliths were removed for ageing. All remaining portions of the fish, including internal organs, were then homogenized by passing through a meat grinder five times. Piscivorous species were processed as individuals and forage species were grouped by size and pooled (five pooled samples per site) prior to homogenization. Homogenized tissues from individual piscivorous or forage species were split into 5–15 sub-samples of ~20 g each.

Sample analyses

References to detailed descriptions of analytical methods are summarized in Table 3. Water samples for analysis of neutral herbicides (NHs) including atrazine, phenoxy acids (PAs), organophosphorus insecticides (OPs) and organochlorine pesticides (OCs) including dieldrin were extracted with dichloromethane. OP, NH and OC analysis was done by fractionation on 10% deactivated silica and analysed by dual capillary column gas chromatography using nitrogen-phosphorus detection (GC/NPD) for OP analysis and electron capture detection (GC/ECD) for NH and OC analysis. The PA extract was allowed to go to dryness, reconstituted with acetone, esterified using pentafluorobenzylbromide and eluted through 5% deactivated silica. PA analysis was done using dual column GC/ECD.

Trace metal and mercury analyses for surficial sediment surveys, with the exception of Lake Michigan and Detroit River suspended sediment, were determined by a hot aqua-regia extraction with measurement by ICP-AES. Total mercury was determined by digestion with hot nitric acid and hydrochloric acid followed with measurement by cold vapour atomic absorption spectrometer. Lake Michigan sediments were extracted by automated digestion, or microwave digestion, and subsequently analysed using an automated mercury analysis system. The automated mercury analysis

Table 3 | References for analytical methods

Medium	Location	Analysis	Reference/laboratory
Surficial sediment	Great Lakes tributaries, L. Erie, Ontario, Superior and St. Clair	Organic contaminants, metals, mercury	Caduceon Laboratories, Ottawa, ON
Surficial sediment	St. Clair R., Lake St. Clair, Detroit R.	PBDEs	AXYS Analytical, Sidney, BC
Surficial sediment	Lake Michigan	Organic contaminants, metals, mercury	Rossmann (2002); Van Hoof & Hseih (1997a, b)
Surficial sediment	Great Lakes tributaries	Organic contaminants	Maxxam Analytical, Mississauga, ON
Suspended sediment	St. Clair R., Detroit R.	Organic contaminants	Backus <i>et al.</i> (2008) (SOP 05-5002)
Water	Great Lakes	Organic contaminants, pesticides	Backus <i>et al.</i> (2007) (SOP 05-5000)
Water	Great Lakes	Trace metals	Environment Canada (1997)
Water	Niagara River, St. Clair R., Wolfe Island	Organic contaminants	Environment Canada (1997)
Water (suspended sediment fraction)	Niagara River, St. Clair R., Wolfe Island	Trace metals	Environment Canada (1997)
Water (suspended sediment fraction)	Niagara River	PBDEs	Marvin <i>et al.</i> (2007)
Water	Selected streams/ivers in Great Lakes basin	Pesticides	Environment Canada (1997) (SOP 05-5000)
Fish	Great Lakes	Organic contaminants	University of Guelph, Guelph, ON

system was based on cold vapour atomic absorption spectrometry. Analyses of trace metals in Lake Michigan sediments were performed by inductively coupled plasma-mass spectrometry (ICP/MS) after microwave digestion in 10% v/v nitric acid. This latter method for trace metals, and a similar method for mercury, was used for analysis of suspended sediments for the connecting channel programmes.

Tributary surficial sediment analysis included an accelerated solvent extraction, and organochlorines were analysed by gas chromatography/dual column electron capture detector (GC/ECD). Polycyclic aromatic hydrocarbon (PAH) samples were extracted by sonication, and the extracts concentrated and analysed by GC/MS. For polybrominated diphenyl ether (PBDE) analysis, samples were spiked with isotopically labelled surrogate standards and solvent extracted and cleaned up on a series of chromatographic columns including layered acid/base silica, florisil and alumina columns. The final extract was spiked with isotopically labelled standards prior to instrumental analysis. Analysis of the extract was performed using HRGC (DB-5HT, 30 m, 0.25 mm i.d., 0.10 µm film thickness) coupled with HRMS. For perfluorinated compound (PFC) analysis,

samples were spiked with surrogate standards, acidified with dilute acetic acid and shaken twice with a methanolic ammonia solution. The supernatant was collected after each agitation. The combined supernatants were shaken with ultra pure carbon powder then extracted by solid phase extraction (SPE) using a weak anion exchange sorbent. Eluates were spiked with recovery standards and analysed by LC/MS/MS.

Wet surficial sediments (20–40 g) were dried with sodium sulfate and extracted with dichloromethane. Extracts were cleaned up using columns containing 3% deactivated silica gel overlaid with 10% deactivated alumina and analysed by GC/ECD. Total PCBs for sediments in Lakes Erie and Ontario were based on the sum total of 103 individual congeners and were not corrected for blanks or surrogate recoveries. Total PCBs for Lake Michigan sediments were based on the sum total of 110 individual congeners; total PCB concentrations less than 4 ng/g were blank-corrected.

For organochlorine/PCB analysis of fish samples, fish homogenates were mixed with sodium sulfate until free flowing and extracted with 1:1 dichloromethane hexane.

Thirty per cent of the extract is used for lipid determination. The remainder of the extract was cleaned up using a series of chromatographic columns starting with gel permeation chromatography and followed by partially deactivated florisil. Final extracts were analysed using GC/ECD.

Data analyses

Surface water

Whole water open lake data are individually compared spatially to other sites on the same lake as well as a lake-wide comparison to the other Great Lakes. These data are also compared to connecting channel whole water data for Lakes Huron, Erie and Ontario, which is a more robust value, representing a mean value of 23 samples. Interconnecting channel data are reported as annual mean concentrations and, while not reported here for clarity, their 90% confidence limits. These data are reported elsewhere (Chan *et al.* 2007; Hill & Klawunn 2010). Annual means and confidence limits were calculated by applying the maximum likelihood estimate (MLE) method only to chemicals having three or more 'trace' (>practical detection limit) values. Whole water mercury data are the geomean of 16 samples.

Sediment

Suspended sediment samples are reported as either a mean value of five monthly samples (mercury) or as a single monthly sample (PBDE). While not included here mercury mean values including standard deviations are reported in Jia *et al.* (2010). All surface sediment data are individual samples compared spatially to other sites on the same lake as well as a lake-wide comparison to the other Great Lakes.

Fish

PCBs (arochlors) are analysed both spatially and temporally across the Great Lakes. Median values ($N = 5-50$) were calculated on an annual basis per lake with each data point shown. The interquartile range (IQR) is shown as calculated. Annual mean concentrations are calculated for mercury on a lake-wide basis based on species of fish. The slope and

r -squared value of the regression was also calculated and reported. For mercury, annual means and standard errors represent 50 fish for Lakes Superior, Huron and Erie, and 100 fish for Lake Ontario per year.

RESULTS AND DISCUSSION

Surface water

Surface water monitoring now focuses on two lakes annually (except for Lake Michigan) by conducting one spring cruise and optional summer and/or autumn cruises. The most recent results (2004–2007) generally indicate contaminant concentrations are low. No exceedences of Canadian federal water quality guidelines (CCME 2007) were observed in open waters of the Great Lakes. Of the organochlorines, α -HCH, γ -HCH (lindane), heptachlor epoxide, dieldrin, hexachlorobenzene (HCB), p/p-DDE and pentachlorobenzene (PeCB) are widely detected. Many PAHs (e.g. 1- and 2-methyl-naphthalene, fluoranthene, chrysene, phenanthrene, fluorine, pyrene and acenaphthene) were detected in nearly all samples.

Many contaminants show spatial distributions indicating a trend toward higher concentrations in the lower Great Lakes. These compounds include those with sources predominantly located in the more highly agricultural, urbanized or industrialized watersheds of the lower lakes, and compounds that are less susceptible to atmospheric transport. Some are legacy compounds that are no longer in commercial use. Compounds with elevated concentrations in waters of Lakes Erie and Ontario include the trichlorobenzenes, PeCB, hexachlorobutadiene (HCBd), hexachlorocyclopentadiene (HCCPD, in Lake Erie), HCB (Lake Ontario), α -chlordane, p/p-DDE (Lake Ontario), total PCBs, mercury and most PAHs.

Some compounds were found at higher concentrations in the upper lakes, compared with the lower lakes. These compounds were generally legacy compounds that have few or no current sources; also the large surface area, colder waters and longer retention times of the upper Great Lakes make them more susceptible to accumulation of contaminants as a result of atmospheric transport. Compounds with elevated concentrations in Lake Superior

included α -HCH, lindane, γ -chlordane, α -endosulfan, endrin and β -endosulfan, although the latter is only found in trace quantities. Heptachlor epoxide and α -chlordane were found at highest concentrations in Lake Michigan.

An example of the contemporary spatial distribution of a legacy organic contaminant (dieldrin) is shown in Figure 1. Despite its status as a legacy pollutant (banned in North America in the 1970s), dieldrin remains ubiquitous in the Great Lakes. However, concentrations continue to decline over time (Figure 1). Open-lake dissolved-phase concentrations are primarily influenced by atmospheric deposition. Concentrations are similar throughout the lakes (Lake Superior 2005 lake-wide average 0.102 ng/L; Lake Huron 2007 lake-wide average 0.071 ng/L; Lake Erie and Lake Ontario 2006 lake-wide averages of 0.096 ng/L) with the exception of Lake Michigan, where concentrations were higher (2006 lake-wide average 0.183 ng/L) due to heavy historical agricultural usage in the watershed. Localized areas of higher dieldrin concentrations were also found near some urban areas and tributary inputs and presumably reflect historical usage in the watersheds.

Other contaminants also show intra-lake distributions that indicate higher concentrations in the nearshore,

compared to the open lake. These spatial distributions were indicative of watershed sources. Contributing sources may be historic, but historically contaminated resuspended sediment may be continuing to contribute loadings to the lakes. Contaminants exhibiting elevated nearshore concentrations include PCBs, mercury, PAHs and some chlorobenzenes.

The distribution and temporal trend of the current-use pesticide (CUP) atrazine is shown in Figure 2. Atrazine is a current-use broad-leaf herbicide that is heavily used, primarily in agriculture. The temporal trends shown for the interconnecting channels in Figure 2 indicate that concentrations are not declining over time. The spatial distribution shows that concentrations in the upper Great Lakes (Lake Superior 2005 lake-wide average 5.4 ng/L and Lake Huron 2002 lake-wide average 9.48 ng/L) are much lower than those found in the lower Great Lakes (Lake Erie, Lake Ontario and Lake Michigan 2006 lake-wide averages of 59.4, 72.6 and 56.3 ng/L, respectively). Concentrations primarily reflect current agricultural and possibly urban use in the lakes' watersheds; loadings are correspondingly lower in the upper Great Lakes as a result of lower usage.

Over time, focus has shifted from exclusively legacy pesticides such as organochlorine pesticides to CUPs, and from

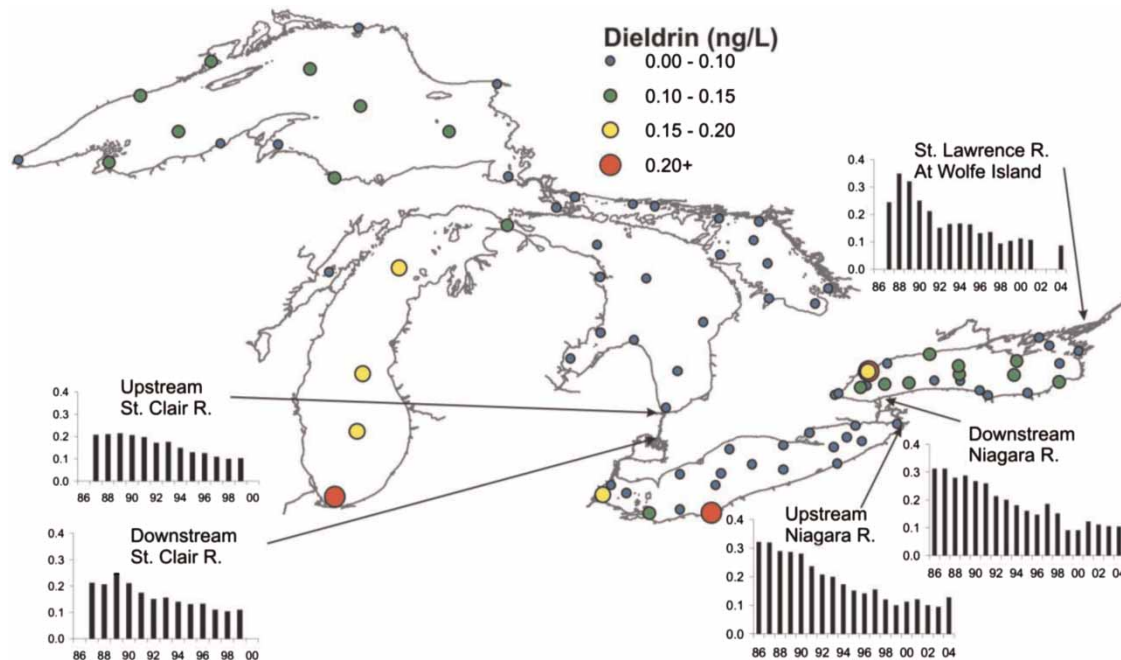


Figure 1 | Distribution of dieldrin in surface water (dissolved phase), and annual mean concentrations in the connecting channels from 1986 to 2004 (whole water). Lake Superior 2005, Lake Huron 2009, Lake Michigan 2006, Lake Erie 2006, Lake Ontario 2006.

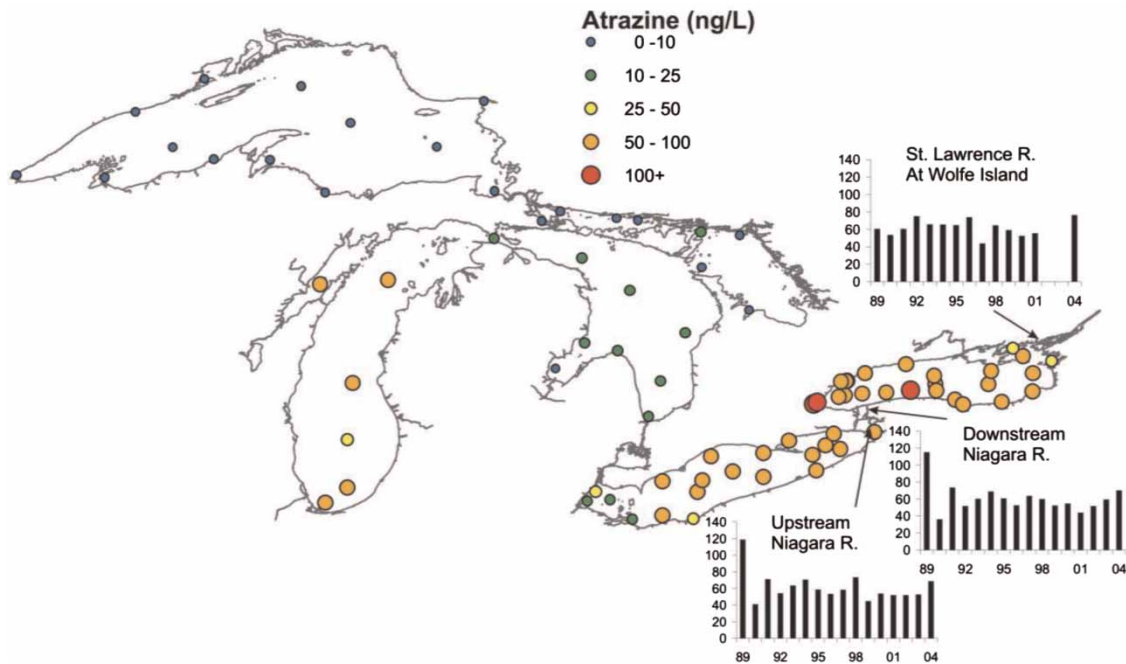


Figure 2 | Distribution of atrazine, in surface water (dissolved phase), and annual mean concentrations in connecting channels from 1986 to 2000 (whole water). Lake Superior 2009, Lake Huron 2002, Lake Michigan 2006, Lake Erie 2006, Lake Ontario 2006.

open waters to small streams in proximity to areas of application in agricultural and urban settings. *Struger et al. (2004)* have reported on spatial trends in CUPs in the Great Lakes from 1994 to 2000 including triazine herbicides and metolachlor, acid herbicides and organophosphorous insecticides. The programme also monitors CUPs in connecting channels and small agricultural and urban streams throughout the Ontario portion of the basin. In 2004, the most frequently detected pesticides in Great Lakes basin streams from Ontario were atrazine (93%), dicamba (83%), 2,4-D (81%), mecoprop (73%), metolachlor (58%) and MCPA (56%). Exceedances of CCME aquatic life guidelines (*CCME 2007*) or Ontario provincial water quality objectives (PWQO) occurred much less frequently, but were observed for atrazine, dicamba, 2,4-D, mecoprop, diazinon, chlorpyrifos and malathion.

In addition, the programme addresses specific issues such as the occurrence of the larvacide methoprene used to control mosquitoes and applied to prevent the spread of the West Nile virus. Where applied, methoprene was frequently detected in storm sewers throughout the late spring and summer, but methoprene and its metabolites were rarely found in receiving waters in southern Ontario

(*Struger et al. 2007*). Time-integrated sampling during rain events showed that methoprene was rapidly flushed from storm sewers and subsequently rapidly diluted in the downstream water courses. In response to changing herbicide usage in agricultural row crop production in Ontario, sampling was expanded to include monitoring for glyphosate and AMPA in small streams and wetlands in agricultural and urban areas throughout Ontario (*Struger et al. 2008*). Glyphosate was found in a variety of agricultural and urban water bodies throughout southern Ontario, although it did not exceed the *CCME 2007* Canadian Water Quality guideline for the protection of aquatic life (65 µg/L). *Struger & Fletcher (2007)* reported the occurrence of 11 lawn care and agricultural pesticides in two urbanized Lake Ontario watersheds. Four pesticides (diazinon, atrazine, carbofuran and chlorpyrifos) exceeded federal or provincial water quality guidelines (*CCME 2007*) or objectives and diazinon exceeded the PWQO in 28% of samples (*OMOE 1994*).

The Niagara River Upstream/Downstream (U/D) Program was initiated in 1986, although water quality monitoring has been conducted in the river since 1975 at the Niagara-On-The-Lake (NOTL) station. The purpose of

Table 4 | Percent change in whole water concentrations in the Niagara River from 1986/87–2006/07 based on modelled annual maximum likelihood estimates. The 2007 concentrations also presented in brackets. $N = 24/\text{year}/\text{site}$

Chemical	Period of record	% Change in whole water; () current concentration ng/L	
		Fort Erie	Niagara-on-the-Lake
Hexachlorobenzene	1986–2007	–61.8 (0.015)	–78.9 (0.049)
α -chlordane	1986–2007	–77.7 (0.0092)	–63.4 (0.011)
γ -chlordane	1986–2007	–89.4 (0.0020)	–87.5 (0.0034)
p,p'-DDT ^a	1986–2007	–91.5 (0.021)	–63.7 (0.028)
o,p'-DDT	1986–2006	–93.7 (0.0025)	–83.1 (0.0037)
p,p'-DDD	1986–2007	–82.6 (0.032)	–51.1 (0.031)
p,p'-DDE	1986–2007	–85.3 (0.055)	–37.2 (0.048)
Dieldrin	1986–2007	–73.5 (0.089)	–68.3 (0.10)
Mirex	1986–2007	ND	–80.2 (0.0028)
PCBs ^a	1986–2007	–68.1 (0.28)	–58 (0.52)
Benz(a)anthracene	1986–2007	–43.7 (0.94)	–7.2 (2.3)
Benzo(a)pyrene	1986–2007	245 (1.3)	80.6 (2.6)
Benzo(b/k)fluoranthene	1986–2007	148 (2.7)	74.3 (5.2)
Chrysene-triphenylene	1986–2007	–37.1 (1.5)	7.6 (3.4)
Octachlorostyrene	1986–2007	ND	–87.1 (0.0019)
<i>Trace metals in whole water ($\mu\text{g}/\text{L}$)</i>			
Lead	1986–2007	–46.3 (0.73)	–54.4 (0.74)
Arsenic	1986–2007	81.8 (0.11)	49.0 (1.1)

ND = not detected.

^a = sediment fraction ONLY.

ocs-NOTL start year = 88/89.

F.E. benzo(a)pyrene start year = 87/88.

op-DDT = most recent value is 2005/06 as 2006/07 is ND for FE and NOTL.

the programme is to measure concentrations and statistical loads of contaminants and report on trends in the river, specifically in relation to implemented control measures. Table 4 shows the change in whole water concentration of the priority toxics (mercury data not available) from the base year (1986/1987) to the most recent reported year (2006/2007) along the Niagara River. These results are based on a ratio of modelled data annual MLEs and should not be considered an analysis of trend. However, results indicate significant decreases (>70%) in concentrations for most toxics. Notable exceptions were arsenic, benzo(a)pyrene and the benzo(b/k)fluoranthene; concentrations suggest an increase at both the Fort Erie and NOTL stations. The increases in concentrations of these PAHs are presumably linked to increases in vehicular emissions. The interconnecting channel programmes in the Niagara, St. Clair and St. Lawrence (at Wolfe Island)

Rivers provide the most comprehensive information on temporal trends for dieldrin. The annual mean whole water concentrations of dieldrin at both Fort Erie and NOTL showed a downward trend over the period 1986–2007; concentrations declined by roughly 70% over this period (Table 4). Data from the U/D stations in the St. Clair River and a monitoring station at Wolfe Island in the St. Lawrence River showed a similar trend (Merriman 1998; Chan *et al.* 2007). Most legacy contaminants have decreased in concentration over time; these reductions were typically in the 50–90% range (Table 4).

Sediment

Sediments in the Great Lakes generally represent a primary sink for contaminants (Schneider *et al.* 2001), and can act as a source to benthic invertebrates through direct contact, or

through resuspension and subsequent redistribution within lakes. Surficial sediments, defined as the top 1–3 cm in open waters, represent the bulk of material available for resuspension. However, burial in sediments also represents a primary mechanism by which contaminants are sequestered and prevented from re-entering the water column.

Marvin *et al.* (2003a and 2004a) have reported on spatial distributions and temporal trends of both legacy and current-use persistent toxic substances in water and sediment using information from Environment Canada and USEPA programmes encompassing the breadth of the Great Lakes. Results of bottom sediment surveys conducted during the periods 1968–1974 and 1997–2002 illustrate the spatial distribution of contaminants, the impacts of local historical sources and, in concert with sediment cores, provide information on temporal trends and responses to management initiatives. Comparisons of surficial sediment contaminant concentrations with sub-surface maximum concentrations indicated that contaminant concentrations have generally decreased by more than 35% and, in some cases, by as much as 80% (Table 5). Table 5 presents percentage reductions in contaminant concentrations (surface vs. sub-surface) in Lakes Ontario, Erie, Huron, Superior and St. Clair estimated using sediment core data.

We have selected mercury as a focal point for discussion of spatial distributions and temporal trends in sediment contamination throughout the Great Lakes, which are related in

turn to sources, sedimentology and bathymetry, and circulation patterns in the individual lakes. In addition, spatial distributions in mercury contamination generally represent those of other toxics, both other metals and organics such as PCBs, as accumulation of a broad range of contaminants on a lake-by-lake basis can be the result of common sources, e.g. chlor-alkali production (Thomas 1972; Mudroch & Hill 1989). The scope and resolution of data are shown in Figure 3 as reported previously in Marvin *et al.* (2003a, 2004a, c). The highest concentrations of mercury in sediments of Lakes Michigan, St. Clair, Erie and Ontario were observed in offshore depositional areas characterized by fine-grained sediments. The spatial distribution of mercury across the Great Lakes was generally representative of the distributions of the other metals, with the exception of lead, where the degree of contamination in Lake Michigan was similar to Lake Ontario. Contaminant concentrations were generally correlated with particle size; therefore the distribution of mercury is a function not only of loadings and proximity to sources, but also of the influence of substrate type and bathymetry. The association of mercury with sediment type in Lakes Erie, Ontario and Michigan was previously reported (Thomas 1972; Thomas & Jaquet 1976; Rossmann 2002; Marvin *et al.* 2004c); concentrations of mercury increased from shallow nearshore coarser sediments outward into deep-water depositional basin sediments composed of silts and clays. There was an apparent spatial distribution in

Table 5 | Percentage reductions in contaminant concentrations in the Great Lakes estimated from sediment cores. Contemporary 75th percentile surficial sediment concentrations in offshore waters are given in brackets. Concentrations for PCBs and total DDT are given in ng/g; concentrations for dioxins are given in pg/g TEQs; concentrations for lead and mercury are given in µg/g

Parameter	Ontario % reduction	Erie % reduction	St. Clair % reduction	Huron % reduction	Superior % reduction
Mercury	73 (0.79)	37 (0.65) ^w (0.09) ^e	89 (0.27)	82 (0.05)	0 (0.09)
PCBs	37 (140)	40 (102) ^w (26) ^e	49 (10.3)	45 (25)	15 (4.4)
Dioxins	70 (180)	NA	NA (1.6)	NA	NA
HCB	38	72	49	NA	NA
Total DDT	60	42 (33) ^w (2) ^e	78 (3.6)	93 (53)	NA (0.45)
Lead	45 (110)	50 (57) ^w (32) ^e	74 (11)	43 (44)	10 (66)

NA denotes not available.

^w = denotes western basin of Lake Erie.

^e = denotes eastern basin of Lake Erie.

Lake Ontario data from Marvin *et al.* (2003a).

Lake Erie data from Painter *et al.* (2001).

Lake St. Clair data from Gewurtz *et al.* (2007).

Lake Superior and Lake Huron data from Gewurtz *et al.* (2008).

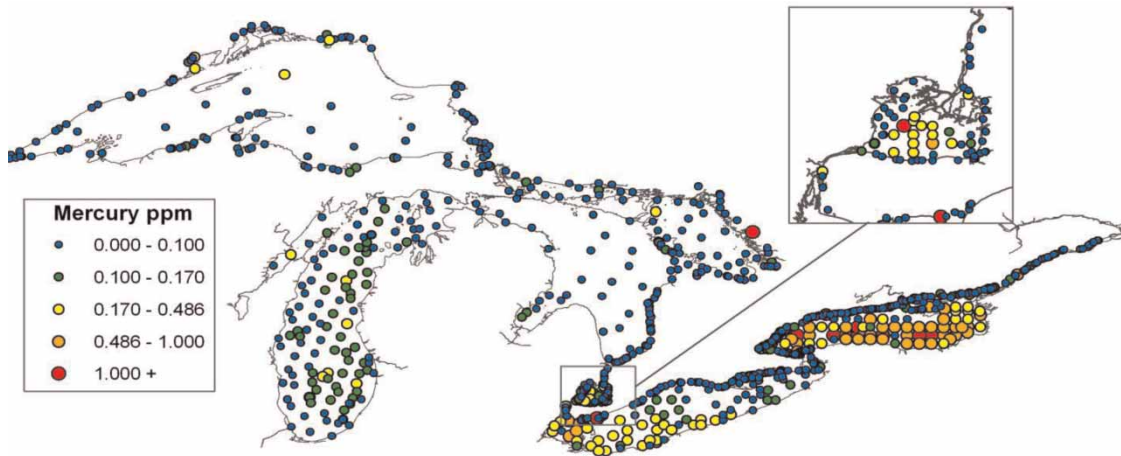


Figure 3 | Concentrations of mercury ($\mu\text{g/g}$) in Great Lakes open-lake and tributary sediments.

contamination in Lake Erie with decreasing concentrations from the western basin to the eastern basin, and from the southern area to the northern area of the central basin (Figure 3). The spatial pattern in Lake Erie was influenced by industrial activities in the watersheds of major tributaries, including the Detroit River, and areas along the southern shoreline (Painter *et al.* 2001). The most recent sediment surveys were not conducted to the same degree of spatial resolution as surveys conducted over the period 1968–1972; however, the majority of stations sampled in Lakes Ontario, Erie, St. Clair and Huron during 1997–2002 were stations sampled by Environment Canada over the period 1968–1972. The sampling strategy in the historical surveys was based on grid intersections to avoid site-selection biases. The majority of samples from our recent surveys were comprised of fine-grained silts and clays, as we specifically targeted deeper-water depositional sediments. Therefore, the reductions in contaminant concentrations shown in Table 5 generally represent contamination in offshore depositional areas.

Surveys conducted in Lake Erie in 1997 (Painter *et al.* 2001) and Lake Ontario in 1998 (Marvin *et al.* 2002b) showed that surficial sediment PCB concentrations have declined roughly three-fold and six-fold, respectively, in the last 30 years. Concentrations of mercury and lead in Lake Ontario surficial sediments declined from 0.79 $\mu\text{g/g}$ and 125 $\mu\text{g/g}$, respectively, in 1968–0.59 $\mu\text{g/g}$ and 69 $\mu\text{g/g}$, respectively, in 1998 (Marvin *et al.* 2002b). In 1971, the Lake Erie surficial sediment 75th percentiles for mercury

in the western, central and eastern basins were 1.72 $\mu\text{g/g}$, 0.58 $\mu\text{g/g}$ and 0.65 $\mu\text{g/g}$, respectively, while the corresponding values in 1997 were 0.65 $\mu\text{g/g}$, 0.25 $\mu\text{g/g}$ and 0.09 $\mu\text{g/g}$. However, sediments in Lake Ontario were more contaminated, compared to Lake Erie, and continued to exceed sediment quality guideline values for a number of contaminant classes (Marvin *et al.* 2002b). It should be noted that differences in analytical methods between historical and modern studies can confound comparisons of these data sets. For example, PCB values reported for studies conducted in the 1960s and 1970s were generated using packed-column gas chromatography that lacks the resolving power of modern capillary methods. As a result, direct comparisons of these data sets may not reflect known PCB production and usage trends, and therefore should be interpreted with caution (Gewurtz *et al.* 2007).

The determination of spatial distributions and temporal trends in sediment contamination also can assist in identification and assessment of contributions of sources. Metals in sediments in Lakes Michigan and Superior generally exhibited low levels of contamination, with the exception of lead in sediments of Lake Michigan (lake-wide average of 141 $\mu\text{g/g}$), which exhibited roughly the same degree of contamination as the western basin of Lake Erie (average of 161 $\mu\text{g/g}$). There appeared to be no significant transport to Lake Huron from Lakes Michigan and Superior, as evidenced by most concentrations of metals in surficial sediments being similar to estimated background levels or geochemical norms. Sources and loadings of mercury to

Lake Huron appear to have been reduced to the point that no apparent spatial pattern exists. Historical studies had indicated that mercury contamination in Saginaw Bay and Georgian Bay were sources of mercury to southern Lake Huron and Lake St. Clair (Thomas 1974). Our most recent studies indicate these source areas are no longer significant. As in the historical studies, elevated concentrations of mercury were found in the central and east-central areas of Lake St. Clair (2000), the western basin of Lake Erie (1997–1998) and the three major depositional basins of Lake Ontario (1998). The current degree of contamination in these areas is substantially lower than peak levels that occurred in the mid 1950s through the early 1970s. However, the similarity in spatial patterns between recent and historical surveys indicates significant sources within the individual lake basins continue to influence contaminant distributions over large areas. Areas of the major connecting channels including the Niagara, Detroit and St. Clair rivers are all associated with historical mercury cell chlor-alkali production; these areas were also intensively industrialized and were primary sources of a variety of persistent toxins to the open lakes, including PCBs. Localized areas of highly contaminated sediment, and/or hazardous waste sites associated with these industrial historical sources, may continue to act as sources of these contaminants and influence their spatial distributions. Conversely, these local sources may no longer be predominant, and the spatial patterns observed in our most recent surveys may reflect resuspension, intra-lake mixing and deposition of existing sediment inventories. In this case, further declines would be expected as these contaminants are ultimately deposited and buried in the sedimentary record. In Lakes Superior and Ontario, atmospheric sources of mercury are now predominant (Pirrone *et al.* 1998).

Surficial sediment concentrations were not only compared with historical levels, but were also assessed against guideline values established for the protection of aquatic biota. We have selected the Canadian Sediment Quality Guidelines Probable Effect Level (PEL) (CCME 2007) as a benchmark. These guidelines can be applied as screening tools in the assessment of potential risk, and for the determination of relative sediment quality concerns. For metals and PCBs, PEL guideline exceedances were frequent in Lake Ontario for lead, cadmium and zinc. Guideline exceedances

were rare in all of the other lakes, with the exception of lead in Lake Michigan where the PEL (91.3 µg/g) was exceeded at over half of the sites. There were no PEL (277 ng/g total PCBs) guideline exceedances for PCBs in any of the Great Lakes sediments included in our data set. We have also developed a sediment quality index (SQI) that produces a numerical score based on the frequency and magnitude of sediment guideline exceedances and the number of contaminants combined in the calculation. Relative sediment quality scores for Lakes Erie and Ontario reflected the general spatial distributions shown for the mercury (Figure 3) and dieldrin (not shown); Lake Ontario exhibited relatively poorer SQI scores, compared to Lake Erie (Marvin *et al.* 2003b). The poorer SQI scores in Lake Ontario were attributed to generally higher levels of contamination for a broad range of compounds.

A screening-level survey of recently deposited sediments was undertaken for Canadian Great Lakes tributaries over a five-year period from 2001 to 2005. The geographical scope of the programme was from the Quebec border on Lake Ontario in the east to the Canada/US border on Lake Superior in the northwest. A total of 433 tributaries were sampled and analysed for 52 organic compounds and 27 metals (Dove *et al.* 2002, 2003, 2004; Burniston *et al.* 2006a, 2007). The purpose of the sampling was to assess sediment quality in depositional zones in each tributary prior to discharge into the lake by integrating samples from different depositional zones at the mouth of the tributary. Sampling was done in the fall of each sampling year in an effort to capture current-year deposition. This programme was designed to identify sources of contaminants to the Great Lakes from the surrounding watersheds.

Screening for perfluoroalkyl compounds (PFCs) including perfluorooctane sulfonate (PFOS), a surfactant used in both industrial and commercial products, was one of the first agency programmes to analyse for this compound in sediment (Figure 4, Burniston *et al.* 2006b). While concentrations appeared low, elevated levels were found in highly urbanized/industrialized watersheds. Levels of PFOS in sediment from Lake Ontario watersheds were considerably lower than those deposited in the open lake (Stock *et al.* 2007); however, not all of the PFCs showed a similar spatial distribution, which may be due to different physical characteristics within the PFC class, or differences in sources. It is

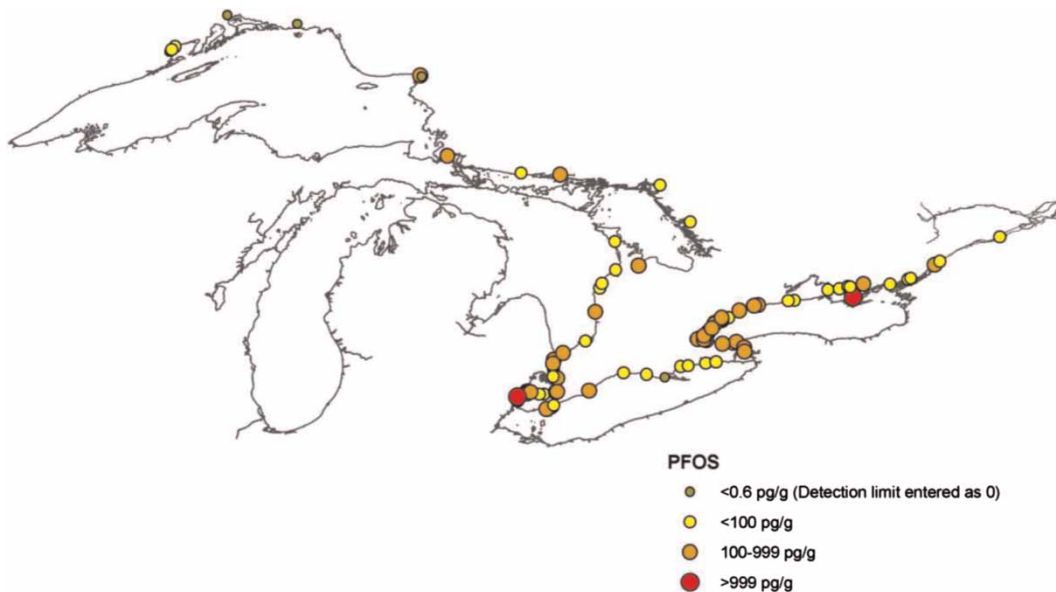


Figure 4 | Concentrations of perfluorooctane sulfonate (PFOS) in surficial sediment ($\mu\text{g/g}$) from Canadian tributaries to the Great Lakes 2001–2005.

important to note that the PFC compound class includes chemicals that were produced commercially and compounds that are precursors or breakdown products.

Analyses of newly deposited sediments in tributaries indicated that watersheds in general do not contribute highly contaminated sediment to the lakes. However, even moderate levels of contamination associated with sediment can have adverse impacts when watersheds deliver high sediment loadings to the receiving body. For example, the Niagara River is a source of mercury to Lake Ontario where higher concentrations were observed in the west, compared to the east. Tributary contaminant loadings may not always be apparent; fine-grained organic-rich material that may exhibit relatively higher contaminant burdens may impact concentrations in the open lake receiving environments. Conversely, these fine-grained sediments, when mixed with coarser material discharging into the lake, may result in a lowering of contaminant concentrations. Fine-grained sediment may be transported from watersheds and nearshore environments to deeper water areas as a result of physical processes; this phenomenon is referred to as sediment focusing. While screening for ongoing sources it was evident that larger industrial and urban locations tended to exhibit higher levels of contaminants, but relatively few tributaries contributed sediment

with concentrations of contaminant at levels of concern. This trend is also evident spatially across the Great Lakes as demonstrated by mercury in surficial sediments, which shows a definite west-to-east concentration gradient (Figure 3).

Many of the new compounds measured in the environment are produced for use in consumer products. The PBDEs are heavily produced flame retardants used in thermoplastics, polyurethane foams and textiles. Although the penta- and octa- formulations are no longer produced in North America, the fully substituted BDE 209 is still used and is typically the most predominant congener detected in sediments. A major vector for PBDEs to enter the aquatic environment is through the atmosphere. The semi-volatile compounds are released to the atmosphere from the products where they partition onto particulates. There is also evidence that the less volatile compounds like BDE 209 enter the atmosphere from weathering and abrasion of polymers from commercial products (Hale *et al.* 2002; Webster *et al.* 2009). Indoor air has been reported at levels 20–30 times higher than outdoor air, which is in turn vented to the outside environment (Hazrati & Harrad 2005). For many compounds associated with consumer products the bulk of the releases occur through weathering and through land filling at the end of the product life cycle. These

compounds are very persistent and do not degrade efficiently, or at all, in sewage treatment plants (STPs). Therefore, they may be directly released in treated effluent or via application of sewage sludges (Alaee *et al.* 2003). The occurrence and spatial distribution of PBDEs in suspended sediment for 2001 in the Detroit River/Lake St. Clair/St. Clair River corridor is shown in Figure 5. Background levels from Lake Huron were roughly 12 ng/g and did not change significantly downstream through the

St. Clair River, despite the presence of heavy industrialization. There was little change in these concentrations in 2006. Increased levels of PBDEs were observed in the upper reaches of the Detroit River, and subsequently increased downstream along the American side of the river. Cross-river differences in levels of total PBDEs at the mouth of the river indicate the majority of PBDE loadings are along the western shoreline (Burniston *et al.* 2010). The distribution of PBDEs in the Detroit River was similar to

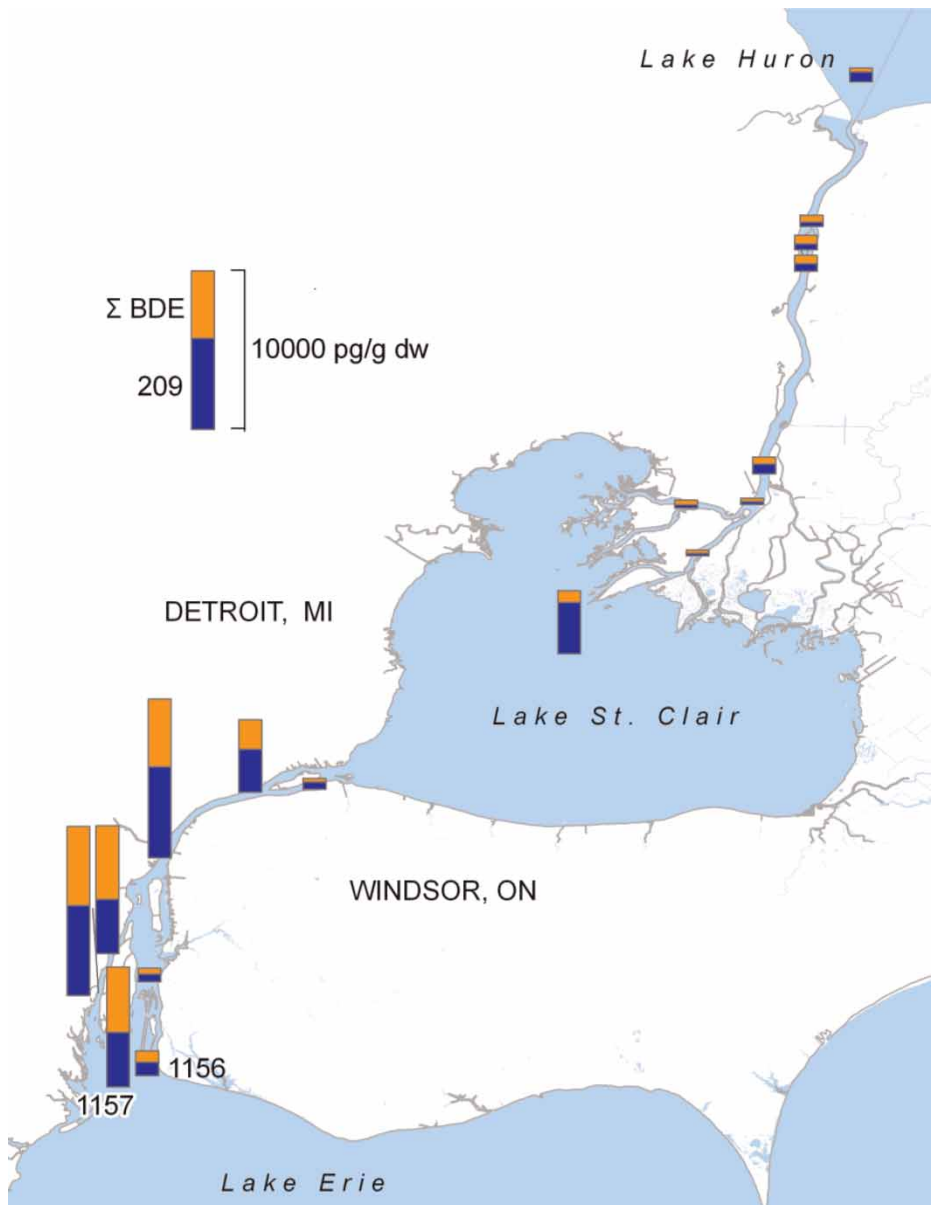


Figure 5 | PBDE concentrations in suspended sediment in the St. Clair/Detroit River corridor in 2001.

those of other modern chemicals, including the BFR hexabromocyclododecane (HBCD, *Marvin et al. 2006*). The distribution of PBDEs in suspended sediments in the Detroit River appeared to be heavily influenced by shoreline-based contemporary urban and industrial activities, which stands in contrast to PCBs that are associated with areas of historic industrial activity. The widespread occurrence, but relatively low concentrations, of PBDEs in suspended sediments suggests that large urban areas can act as diffuse sources of these chemicals that are used in modern industrial applications *Marvin et al. (2006)*.

At the local scale, studies of the water column and suspended sediments in the Detroit River/Lake St. Clair/St. Clair River corridor further provides more detailed information on local mercury sources. The upper reaches of the St. Clair have been the focus of intensive monitoring by the major agencies due to the historical presence of numerous industrial and municipal point sources and non-point sources (*Richman & Milani 2010*). Mercury contamination in the aquatic environment of the corridor is a primary concern. *Figure 6* illustrates mercury concentrations in water, lake and tributary bottom sediments and suspended

sediments within the corridor. The integration of the open-lake, tributary screening and suspended sediment contaminant information enables a weight-of-evidence approach to the assessment of contaminants. Although declines in mercury contamination in both fish and sediments since the late 1970s are apparent, more recent improvements are less evident, suggesting that historically contaminated sediment may continue to be an important source of mercury contamination to the entire corridor (*Richman & Milani 2010*).

Fish

Fish contaminant monitoring has provided information on spatial distributions, temporal trends and biomagnification of priority pollutants in fish from Canadian waters of the Great Lakes. The programme is designed to monitor general environmental contamination and assess risk to non-human consumers of fish in the Great Lakes basin. As such, contaminants are measured in whole-body homogenates of individual fish to eliminate variability caused by tissue-specific differences in contaminant burden and within-fish variability in contaminant concentration. The programme

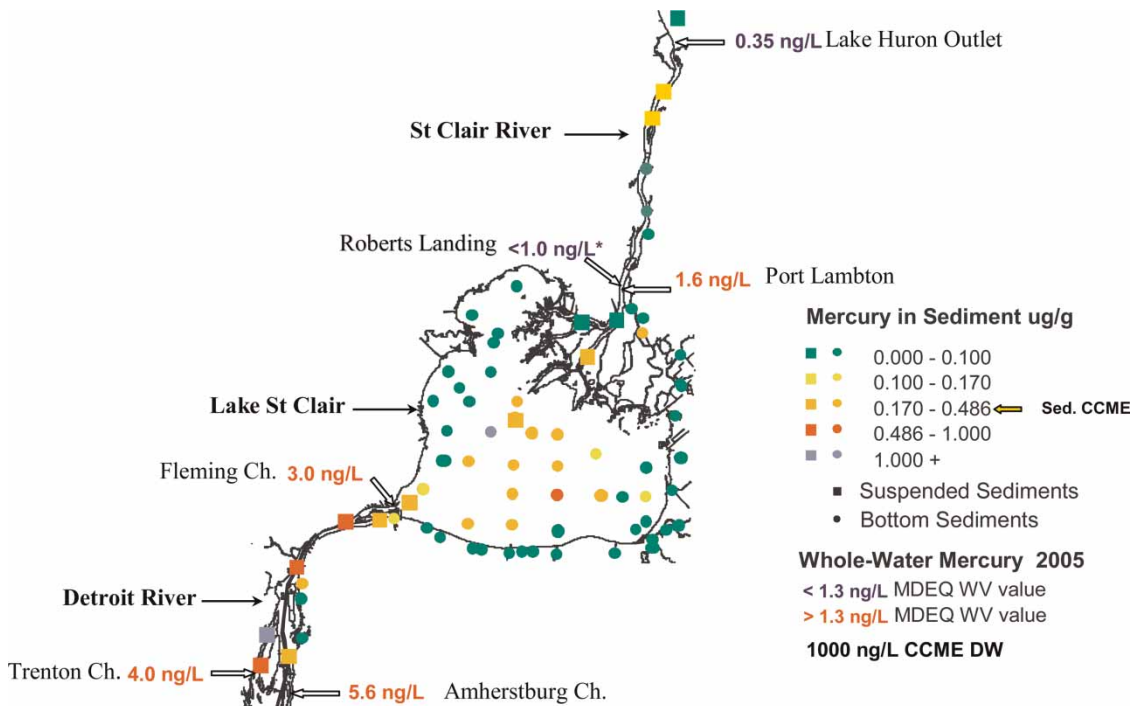


Figure 6 | Mercury concentrations in sediments (mean values for 2002–2004) and whole water (2005) in the St. Clair/Detroit River corridor. * High detection limit due to low-level contamination.

also adopts an ecosystem approach to monitoring by collecting specimens representing different trophic levels of the pelagic food web. Zooplankton, benthic macroinvertebrates, forage fishes and top predators are collected from all monitoring stations allowing investigations into fate and bioaccumulation of contaminants across the Great Lakes (Muir *et al.* 2004; Tomy *et al.* 2004; Helm *et al.* 2005). Lake trout and walleye are key top predators targeted for collection at each monitoring station. These species are considered to be good spatial and temporal indicators of environmental contamination in the Great Lakes as they are wide-ranging, long-lived and bioaccumulate contaminants. Collection methods, specimen processing and a list of parameters measured are provided in McGoldrick *et al.* (2010).

For much of the history of the programme, the focus has been on organochlorine compounds such as PCBs, DDT, mirex, chlordane, dieldrin, hexachlorobenzene, heptachlor epoxide and lindane as well as toxic metals such as mercury.

The concentrations of many of the legacy contaminants measured in lake trout and walleye are currently below the targets established in the GLWQA or are detected at very low concentrations (SOLEC 2009). Conversely, levels of PCBs remain above the target of 0.1 µg/g (ww) in all the Great Lakes despite annual declines of on average 7.2% in Lake Ontario, 2.9% in Lake Erie, 7.4% in Lake Huron and 5.4% in Lake Superior (Figure 7). The rate of decline appears to be slowing in recent years, an observation that has been demonstrated in other fish contaminant data sets in the Great Lakes (Bhavsar *et al.* 2007; 2010; Carlson *et al.* 2010). Mercury is a global pollutant present in all fish in the Great Lakes; total mercury has been measured in fish tissues since the inception of the programme. In general, since the early 1980s mean total mercury concentrations in lake trout have declined in Lakes Huron and Ontario, but have remained consistent in trout from Lake Superior and walleye from Lake Erie (Figure 8).

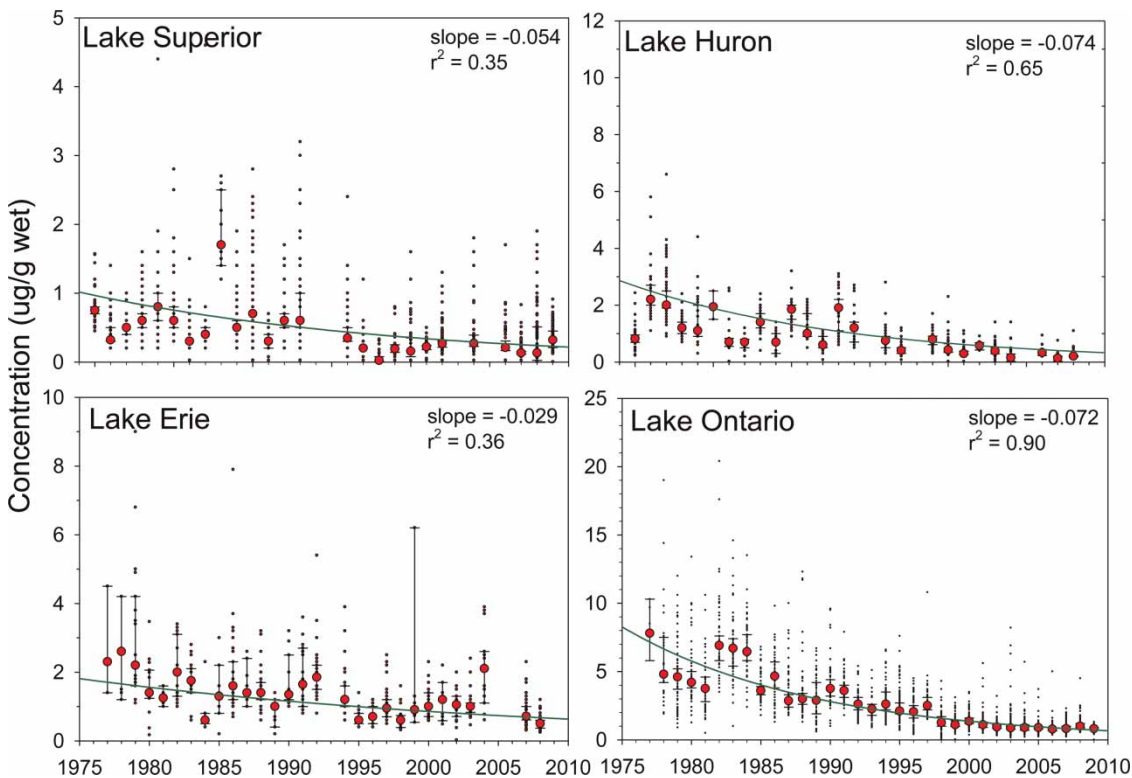


Figure 7 | Median (\pm IQR) total PCB (as arochlor) concentrations in whole body homogenates of 4- to 6-year-old lake trout and walleye (L. Erie) from the Canadian waters of the Great Lakes from 1977 to 2009. All data points are shown as dots and the solid line denotes log-linear regression models of annual median values. The slope and r -square of the regression are also shown for each lake.

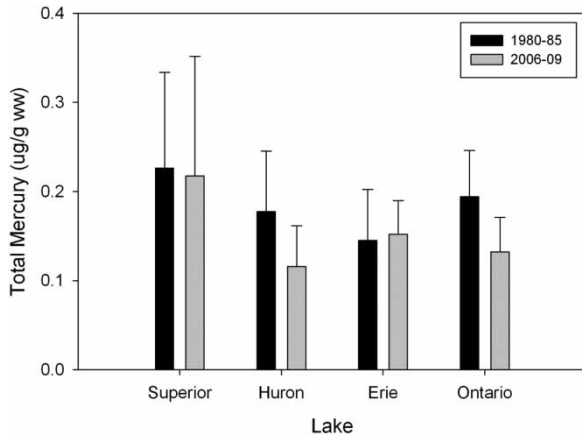


Figure 8 | Comparison of mean total mercury concentrations (\pm std dev.) between 1980–85 and 2006–09 in whole fish homogenates of lake trout from Lakes Superior, Huron and Ontario and walleye from Lake Erie.

General status of toxics in the Great Lakes

Open-lake and tributary bottom sediment contaminant information has been collected for all of the Canadian Great Lakes. For example, [Marvin *et al.* \(2004c\)](#) described mercury trends in bottom sediments from all of the Great

Lakes ([Figure 3](#)). Lakes Huron, Michigan and Superior exhibited relatively low mercury concentrations; meanwhile, the western basin of Lake Erie and Lake Ontario exhibited the highest levels. Concentrations of mercury in tributary bottom sediments suggest that their watersheds are not a significant source of mercury to the Great Lakes ([Figure 3](#)). Sources of mercury contamination in Lakes Erie and Ontario are primarily attributed to loadings from historical sources, including chlor-alkali production in the Detroit, St. Clair and Niagara Rivers. The spatial distributions of mercury in sediments of Lakes Huron and Superior suggest natural geochemical factors are an influence. Surficial sediment mercury concentrations have decreased markedly over time. [Figure 9](#) shows the trend in suspended sediment mercury concentrations from the Niagara River stations, and shows concentrations have decreased since 1984. Although there is considerable yearly variation, the polynomial trend lines suggest concentrations are levelling off, presumably because atmospheric deposition is now the predominant source of mercury loadings to Lake Ontario. Concentrations at the Niagara River U/D stations are now consistently below the [CCME \(2007\)](#)

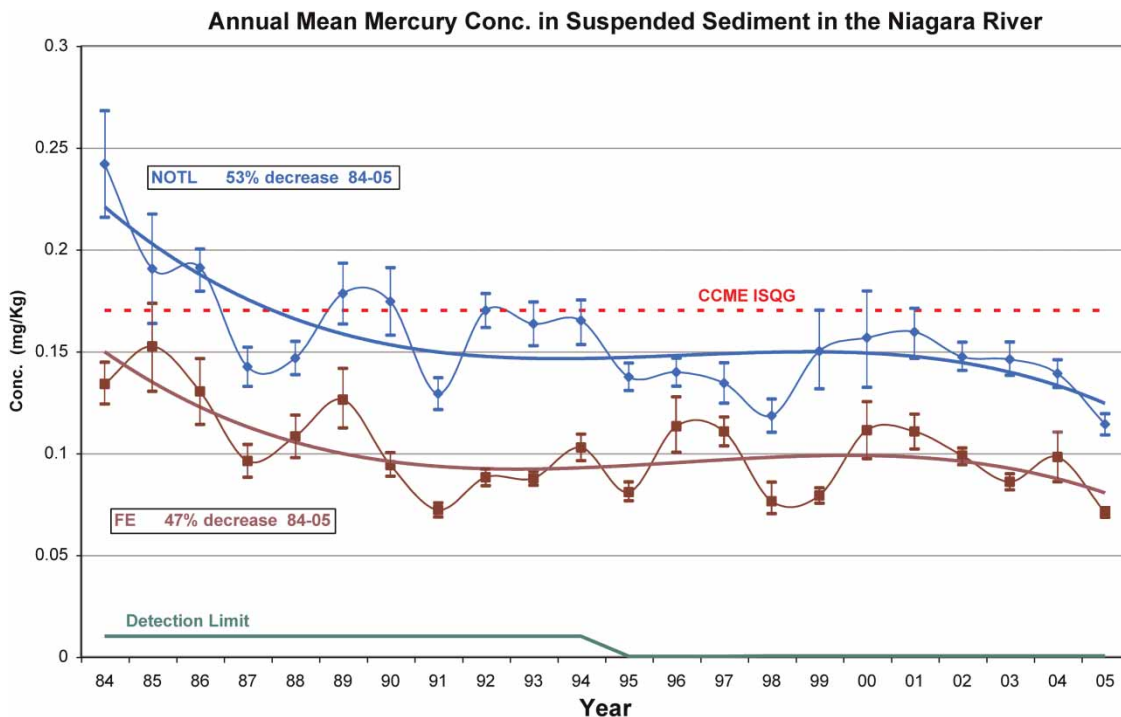


Figure 9 | Annual mean (\pm SE) mercury concentrations in suspended sediments in the Niagara River, 1984–2003.

sediment quality guidelines. These results are evidence of the effectiveness of binational initiatives to reduce discharges of toxic contaminants, e.g. Great Lakes Water Quality Agreement, Niagara River Toxics Management Plan and Great Lakes Binational Toxics Strategy. Concentrations of mercury in Niagara River suspended sediments are also well below typical open-lake sediment concentrations, indicating that further declines in sediment concentrations can be expected.

The presence of new persistent toxics represents an emerging threat to the health of the Great Lakes ecosystem. These compounds include the PFCs and the BFRs, the latter of which are heavily used globally in the manufacturing of a wide range of consumer products and building materials. Some BFRs have been found to be bioaccumulating in Great Lakes fish and breast milk of North American women (Alaee *et al.* 2003). Assessment of the occurrence and fate of these new compounds has recently been incorporated into the surface water, suspended sediment and bottom sediment monitoring programmes. While government initiatives in reducing indiscriminate urban and industrial discharges of legacy compounds like PCBs have resulted in decreasing trends, some new and emerging compounds have not shown corresponding trends. While end-of-the-pipe discharges may not be responsible for ongoing contamination, modern urban/industrial centres can act as diffuse sources of toxics (Marvin *et al.* 2007). The spatial distribution of PFOS entering the Great Lakes via tributary watersheds highlights this point as shown in Figure 4, where higher concentrations are found in more urbanized/industrialized areas. Archived suspended sediment samples from the Niagara River U/D programme have been used to establish the temporal trend in the occurrence of PBDEs (Marvin *et al.* 2007). There was a general trend toward increasing levels of PBDEs in Niagara River suspended sediments since the late 1980s (Marvin *et al.* 2007), which is similar to the trend for PBDEs in lake trout in the Great Lakes (Luross *et al.* 2002); however, the most recent data appear to indicate a levelling off of PBDE concentrations, presumably as a result of cessation of production of the penta- and octa-formulations in North America.

Long-term monitoring programmes are valuable tools for demonstrating effectiveness of remedial actions and management initiatives as well as acting as indicators of emerging

issues. Legacy compounds banned in North America, such as DDT, PCBs and dieldrin, have shown a consistent decline over the last two decades. For example, water exiting Lake Erie at Fort Erie has seen declines in concentrations of at least 70% since 1986. While water concentrations may react more quickly to remedial activities, sediment concentrations tend to decrease more slowly as a result of the extended time required for particulate material to traverse through open-lake environs and undergo physical processes such as sedimentation. Reductions are also evident in the sediment record. For example, DDT and PCBs in Lake Erie sediments have declined by 40% or more since their historical maximum values.

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