Zooplankton Populations

Indicator #116

Overall Assessment

Status: **Mixed**
Trend: **Not Assessed**

Primary Factors Determining Status and Trend **Changes in community structure are occurring in lakes Michigan, Huron, and Ontario due to declines in cyclopoid copepods and cladocerans. Summer mean size has increased in these lakes concurrent with the increase in the percent of calanoid copepods**

Lake-by-Lake Assessment

Lake Superior

Status: Good
Trend: Unchanging
Primary Factors Determining Status and Trend Stable summer zooplankton community dominated by large calanoid copepods.

Lake Michigan

Status: Not Assessed
Trend: Undetermined (changing)
Primary Factors Determining Status and Trend Total summer biomass has been declining since 2004 due to fewer *Daphnia* and cyclopoid copepods. Summer mean size of zooplankton is increasing.

Lake Huron

Status: Not Assessed
Trend: Undetermined (changing)
Primary Factors Determining Status and Trend Total summer biomass has declined dramatically since 2003 due to fewer *Daphnia*, bosminids, and cyclopoid copepods. Summer mean size of zooplankton is increasing.

Lake Erie

Status: Not Assessed
Trend: Undetermined
Primary Factors Determining Status and Trend Variable biomass and composition of summer crustacean zooplankton community in each basin. Most diverse zooplankton community in Great Lakes. Very low biomass in Western Basin in August, 2001.

Lake Ontario

Status: Not Assessed
Trend: Undetermined (changing)
Primary Factors Determining Status and Trend Lowest percentage of calanoid copepods of all Great Lakes. Total summer biomass has declined since 2004 due to a decline in cyclopoid copepods. Summer mean size of zooplankton is increasing.

Purpose

- To directly measure changes in community composition, mean individual size and biomass of zooplankton populations in the Great Lakes basin;
- To indirectly measure zooplankton production; and
- To infer changes in food-web dynamics due to changes in vertebrate or invertebrate predation, system productivity, the type and intensity of predation, and the energy transfer within a system.

Ecosystem Objective

Ultimately, analysis of this indicator should provide information on the biological integrity of the Great Lakes, and lead to the support of a healthy and diverse fishery. Suggested metrics include zooplankton mean length, the ratio of calanoid copepod abundance to that of cyclopoid copepods plus cladocerans and zooplankton biomass. However, the relationship between these objectives and the suggested metrics have not been fully worked out, and no specific criteria have yet been identified for these metrics.

Planktivorous fish often feed size selectively, removing larger cladocerans and copepods. High densities of planktivores result in a reduction of the mean size of zooplankton in a community. A mean individual size of 0.8 mm has been suggested as "optimal" for zooplankton communities sampled with a 153 µm mesh net, indicating a balance between planktivorous and piscivorous fish. Declines in mean size of crustacean zooplankton between spring and late summer may indicate increased predation by young fish or the presence of a greater proportion of immature zooplankton. Interpretation of deviations from this average size objective, and the universality of this objective remain unclear at this time. In particular, questions regarding its applicability to systems impacted by predaceous cladocereans and dreissenids as well as planktivorous fish have been raised.

Gannon and Stemberger (1978) found that cladocerans and cyclopoid copepods are more abundant in nutrient enriched waters of the Great Lakes, while calanoid copepods dominate oligotrophic communities. They reported that areas of the Great Lakes where the density of calanoid copepods comprises over 50% of the summer crustacean zooplankton community (or the ratio of calanoids/cyclopoids + cladocerans >1) could be classified as oligotrophic. As with individual mean size, though, clear objectives have not presently been defined.

State of the Ecosystem

Summer biomass of crustacean zooplankton communities in the offshore waters of Lake Superior has remained at a relatively low but stable level for the past seven years (Figure 1). The plankton community is dominated by large calanoid copepods (*Leptodiaptomus sicilis* and *Limnocalanus macrurus*) that are characteristic of oligotrophic, cold water ecosystems. Biomass is generally higher in the nutrient enriched lower lakes with more annual variation produced by seasonal increases in cladocerans, primarily daphnids and bosminids. Since 2003 the biomass of cladocerans and cyclopoid copepods in Lake Huron has declined dramatically. Data from 2005 suggests that a similar decline may now be occurring in Lake Michigan. Cyclopoid abundance has also begun to decline in Lake Ontario. Mechanisms for these declines are not known at this time, but may be related to changes in nutrient levels, phytoplankton composition, exotic species interactions, or fish predation pressure.

The proportion of calanoid copepods in Lake Superior has remained fairly stable at 70% (Figure 2) indicating oligotrophic conditions. Summer zooplankton communities in Lakes Michigan and Huron have shown an increasing proportion of calanoid copepods in recent years, suggesting an improved trophic state. Lake Ontario has the lowest proportion of calanoids, followed closely by the nutrient enriched western basin of Lake Erie. Values for the central and eastern basins of Lake Erie are at intermediate levels and exhibit considerable annual variation.

Historical comparisons of this metric are difficult to make because most historical data on zooplankton populations in the Great Lakes seem to have been generated using shallow (20 m) tows. Calanoid copepods tend to be deep living organisms; therefore the use of data generated from shallow tows would tend to contribute a strong bias to this metric. This problem is largely avoided in Lake Erie, particularly in the western and central basins, where most sites are shallower than 20 m. Comparisons in those two basins have shown a statistically significant increase in the ratio of calanoids to cladocerans and cyclopoids between 1970 and 1983-1987, with this increase sustained throughout the 1990s. A similar increase was seen in the eastern basin, although some of the data used to calculate the ratio were generated from shallow tows and are therefore subject to doubt.

Mean length of crustacean zooplankton in the offshore waters of the Great Lakes is generally greater in the spring than during the summer (Figure 3). In the spring, mean zooplankton size in all of the Great Lakes is near the suggested level of 0.8 mm. Mean length in Lake Superior declines during the summer due to the production of immature copepodids, but is still above the criterion. Summer mean length in Lakes Huron and Michigan remain high and have begun to show an increase in recent years. In Lakes Erie and Ontario, the mean length of zooplankton declines considerably in the summer. Whether this decline is due to predation pressure or to the increased abundance of bosminids (0.4 mm mean length) and immature cyclopoids (0.65 mm mean length) is unknown.

Historical data from the eastern basin of Lake Erie, from 1985 to 1998, indicate a fair amount of interannual variability in zooplankton mean length, with values from offshore sites ranging from about 0.5 mm to 0.85 mm (Figure 4). As noted above, interpretation of these data are currently problematic.

Pressures

The zooplankton community might be expected to respond to changes in nutrient and phytoplankton concentrations in the lakes, although the potential magnitude of such “bottom up” effects is not well understood. The most immediate potential threat to the zooplankton communities of the Great Lakes is posed by invasive species. The continued proliferation of dreissenid populations can be expected to impact zooplankton communities through the alteration of the structure and abundance of the phytoplankton community, upon which many zooplankton depend for food. Predation from the exotic cladocerans *Bythotrephes longimanus* and *Cercopagis pengoi* may also have an impact on zooplankton abundance and community composition. *Bythotrephes* has been in the Great Lakes for approximately twenty years, and is suspected to have had a major impact on zooplankton community structure. *Cercopagis pengoi* was first noted in Lake Ontario in 1998, and has now spread to the other lakes, although in much lower densities. Continuing changes in predation pressure from planktivorous fish may also impact the system

Management Implications
Continued monitoring of the offshore zooplankton communities of the Great Lakes is critical, particularly considering the current expansion of the range of the non-native cladoceran *Cercopagis* and the probability of future invasive zooplankton and fish species.

Comments from the author(s)
Currently the most critical need is for the development of quantitative, objective criteria that can be applied to the zooplankton indicator. The applicability of current metrics to the Great Lakes is largely unknown, as are the limits that would correspond to acceptable ecosystem health.

The implementation of a long-term monitoring program on the Canadian side is also desirable to expand both the spatial and the temporal coverage currently provided by American efforts. Since the interpretation of various indices is dependent to a large extent upon the sampling methods employed, coordination between these two programs, both with regard to sampling dates and locations, and especially with regard to methods, would be highly recommended.

Acknowledgments

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Data Sources
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Figure 2. Average percentage of calanoid copepods (by abundance) in crustacean zooplankton communities from Great Lakes offshore stations sampled in August of each year. Samples were collected with 153µm mesh net tows to a depth of 100 m or the bottom of the water column, whichever was shallower. Line at 50% level is the suggested criterion for oligotrophic lakes. Source: U.S. Environmental Protection Agency, Great Lakes National Program Office.

Figure 3. Average individual mean lengths of crustacean zooplankton in the Great Lakes in May and August. Length estimates were generated from data collected with 153µm mesh net tows to a depth of 100 m or the bottom of the water column, whichever was shallower. Values are the indicate arithmetic averages of all sites sampled. Line at 0.8 mm is the suggested criterion for balanced fish community. Source: U.S. Environmental Protection Agency, Great Lakes National Program Office.

Figure 4. Trend in Jun27-Sep30 mean zooplankton length: NYDEC data (circles) collected with 153µm mesh net, DFP data (diamonds) converted from 64µm to 153µm mesh equivalent. Open symbols = offshore, solid symbols = nearshore (<12m). 1985-1988 are means +/- 1 S.E. Source: Johannsson *et al*. 1999.

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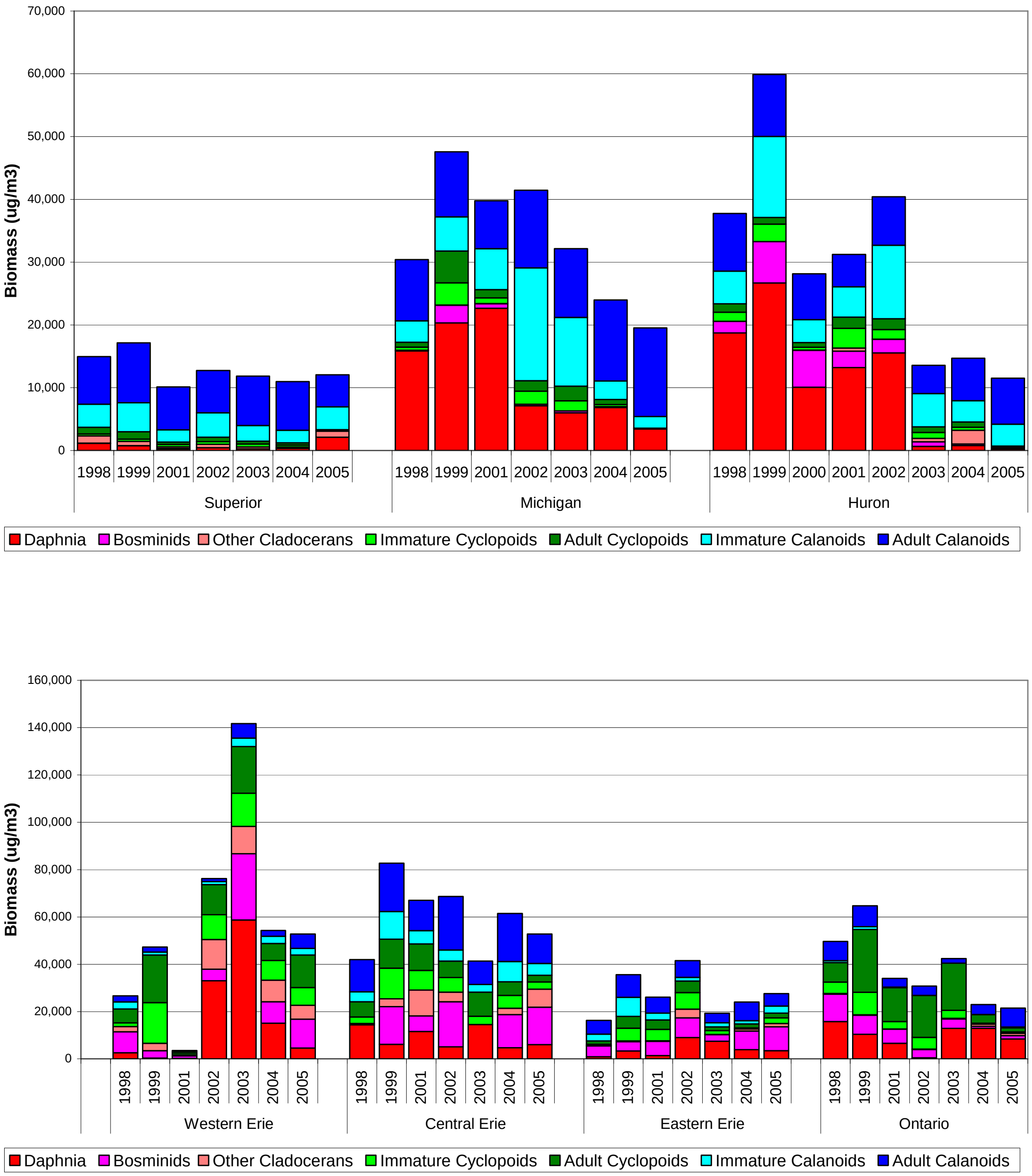

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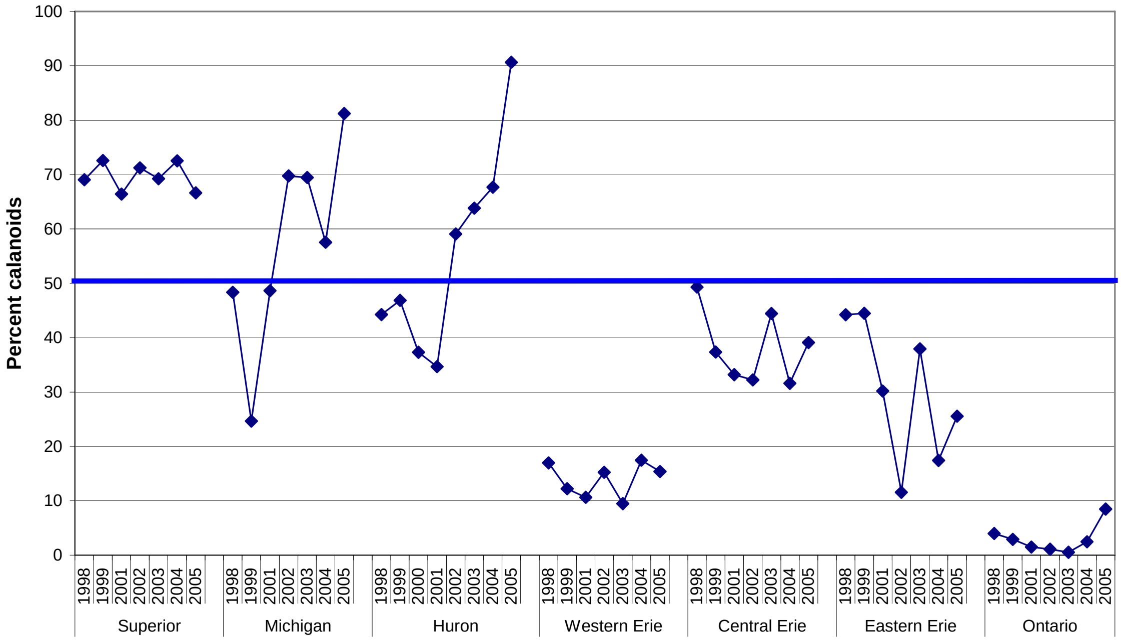

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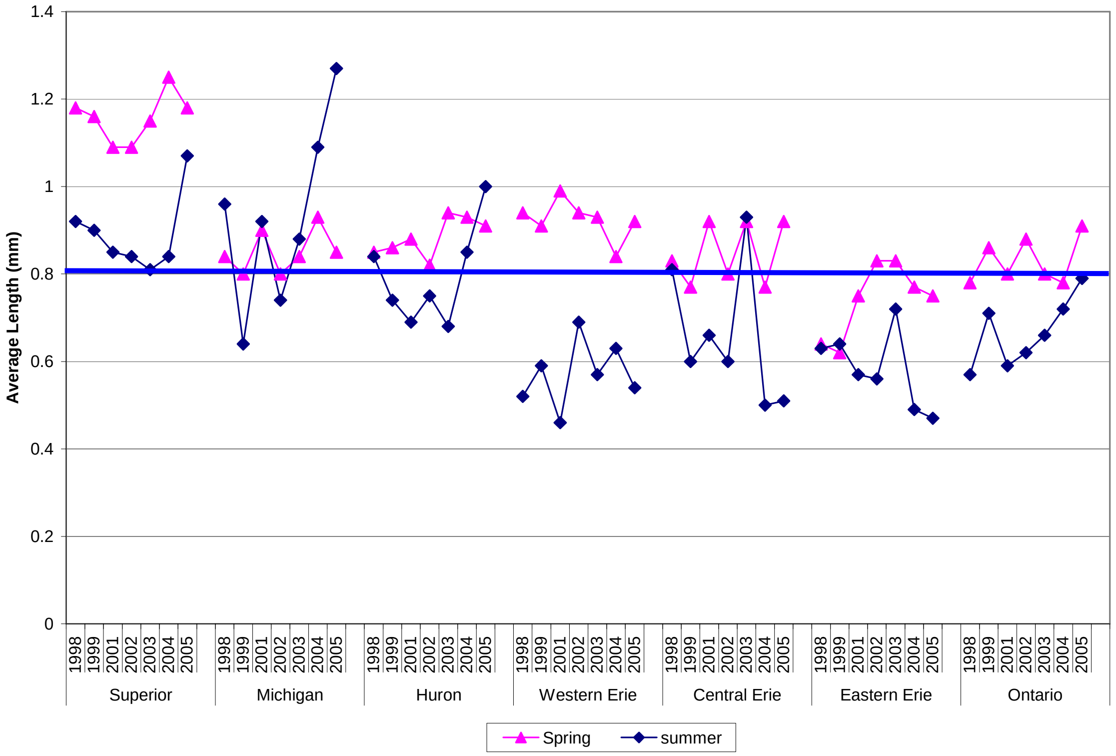

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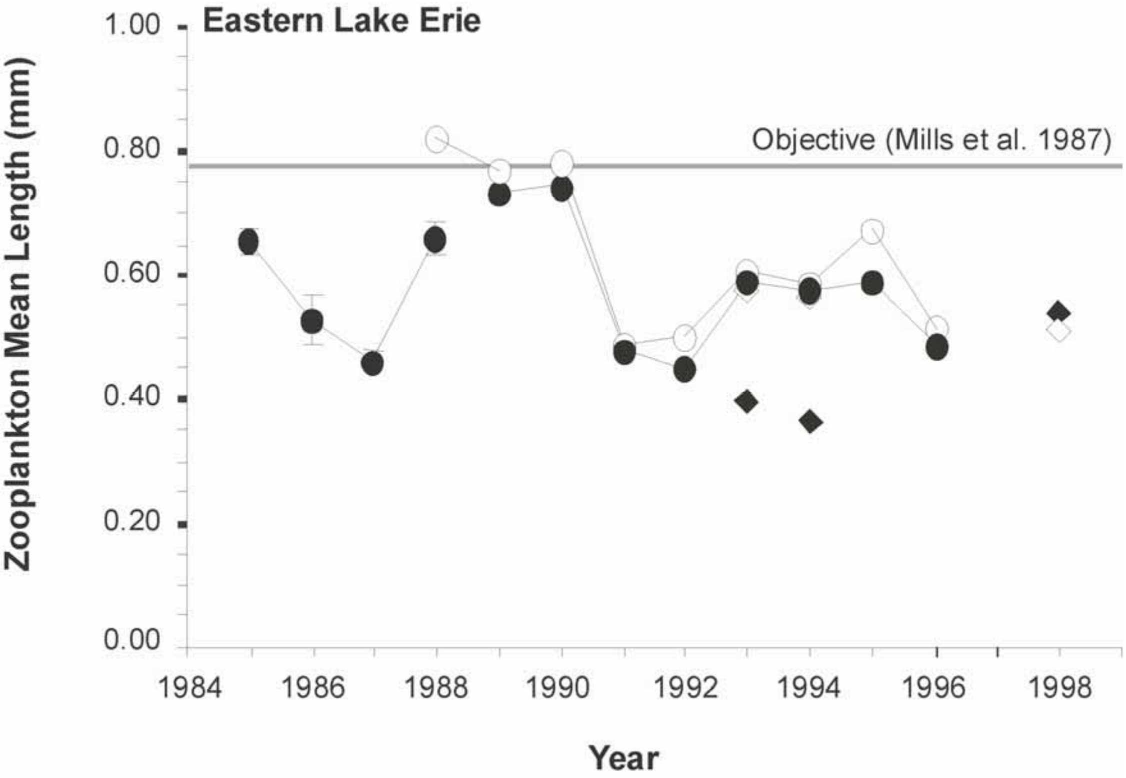

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Atmospheric Deposition of Toxic Chemicals

Indicator #117

Overall Assessment

Status:	**Mixed**
Trend:	**Improving for polychlorinated biphenyls (PCBs), banned organochlorine pesticides, and dioxins and furans** **Unchanging or slightly improving for polycyclic aromatic hydrocarbons (PAHs) and mercury**
Primary Factors Determining Status and Trend	**Mixed since different chemical groups have different trends over time; levels in cities can be much higher than in rural areas**

Lake-by-Lake Assessment

The indicator status is **mixed** for all Lakes. Levels of PBT chemicals in air tend to be lower over Lakes Superior and Huron than over the other three Lakes (which are more impacted by human activity), but their surface area is larger, resulting in a greater importance of atmospheric inputs.

While concentrations of some of these substances are very low at rural sites, they may be much higher in “hotspots” such as urban areas. Lakes Michigan, Erie, and Ontario have greater inputs from urban areas. The Lake Erie station tends to have higher levels than the other remote master stations, most likely since it is located closer to an urban area (Buffalo, NY) than the other master stations; it may also receive some influence from the East Coast of the U.S.

In general for PBT chemicals, atmospheric inputs dominate for Lakes Superior, Huron, and Michigan due to their large surface areas (Strachan and Eisenreich 1991, Kreis 2005). Connecting channel inputs dominate for Lakes Erie and Ontario, which have smaller surface areas.

Purpose

- To estimate the annual average loadings of persistent bioaccumulative toxic (PBT) chemicals from the atmosphere to the Great Lakes;
- To determine trends over time in contaminant concentrations;
- To infer potential impacts of toxic chemicals from atmospheric deposition on human health and the Great Lakes aquatic ecosystem; and
- To track the progress of various Great Lakes programs toward virtual elimination of toxic chemicals to the Great Lakes.

Tracking atmospheric inputs is important since the air is a primary pathway by which PBTs reach the Great Lakes. Once PBTs reach the Great Lakes, they can bioaccumulate in fish and other wildlife and cause fish consumption advisories.

Ecosystem Objective

The Great Lakes Water Quality Agreement (GLWQA) and the Binational Toxics Strategy both state the virtual elimination of toxic substances in the Great Lakes as an objective. Additionally, GLWQA General Objective (d) states that the Great Lakes should be free from materials entering the water as a result of human activity that will produce conditions that are toxic to human, animal, or aquatic life.

State of the Ecosystem

The Integrated Atmospheric Deposition Network (IADN) consists of five master sampling sites, one near each of the Great Lakes, and several satellite stations. This joint United States-Canada project has been in operation since 1990. Since that time, thousands of measurements of the concentrations of PCBs, pesticides, PAHs and trace metals have been made at these sites. Concentrations are measured in the atmospheric gas and particle phases and in precipitation. Spatial and temporal trends in these concentrations and atmospheric loadings to the Great Lakes can be examined. Data from other networks are used here to supplement the IADN data for mercury, dioxins and furans.

PCBs. Concentrations of gas-phase PCBs (ΣPCB) have generally decreased over time at the master stations (Figure 1). ΣPCB is a suite of congeners that make up most of the PCB mass and represent the full range of PCBs. Some increases are seen during the late 1990s for Lakes Michigan and Erie and during 2000-2001 for Lake Superior. These increases remain unexplained, although there is some evidence of connections with atmospheric circulation phenomena such as El Nino (Ma *et al*. 2004a). Levels decrease again by 2002. It is assumed that PCB concentrations will continue to decrease slowly. It should be noted that PCBs in precipitation samples at the rural master stations are nearing levels of detection.

The Lake Erie site consistently shows relatively elevated ΣPCB concentrations compared to the other master stations. Back-trajectory analyses have shown that this is due to possible influences from upstate New York and the East Coast (Hafner and Hites 2003). Figure 2 shows that ΣPCB concentrations at urban satellite stations in Chicago and Cleveland are about fifteen and ten times higher, respectively, than at the remote master stations at Eagle Harbor (Superior) and Sleeping Bear Dunes (Michigan).

Pesticides. In general, concentrations of banned or restricted pesticides measured by the IADN (such as hexachlorocyclohexane [a-HCH] and DDT) are decreasing over time in air and precipitation (Sun *et al*. 2006a, Sun *et al*. submitted). Concentrations of chlordane are about ten times higher at the urban stations than at the more remote master stations, most likely due to the use of chlordane as a termiticide in buildings. Dieldrin shows a similar urban elevation; this pesticide was also used as a termiticide until 1987, after all other uses were banned in 1974. Current-use pesticide endosulfan shows mixed trends, with significant decreases at some sites in some phases, but no trends at other sites. Concentrations of endosulfan were generally higher in the summer, following application of this current-use pesticide (Sun *et al*. submitted).

PAHs. In general, concentrations of polycyclic aromatic hydrocarbons can be roughly correlated with population, with highest levels in Chicago and Cleveland, followed by the semi-urban site at Sturgeon Point, and lower concentrations at the other remote master stations. In general, PAH concentrations in Chicago and Cleveland are about ten to one hundred times higher than at the master stations.

Concentrations of PAHs in the particle and gas phase are decreasing at Chicago, with half-lives ranging from 3-10 years in the vapor phase and 5-15 years in the particle phase. At the other sites, most gas phase PAH concentrations showed significant, but slow long-term decreasing trends (>15 years). For most PAHs, decreases on particles and in precipitation were only found at Chicago (Sun *et al*. 2006b, Sun *et al*. submitted).

An example of a PAH is benzo[a]pyrene (BaP), a PAH, is produced by the incomplete combustion of almost any fuel and is a probable human carcinogen. Figure 3 shows the annual average particle-phase concentrations of BaP.

Dioxins and Furans. Concentrations of dioxins and furans have decreased over time (Figure 4) with the largest declines in areas with the highest concentrations (unpublished data, T. Dann, Environment Canada 2006).

Mercury. Data from the Canadian Atmospheric Mercury Network (CAMNet) for the IADN stations at Egbert, Point Petre, and Burnt Island show decreases in total gaseous mercury (TGM) concentrations between 1995 and 2004, with more of the decrease occurring in the 2000-2004 time period (Figure 5). Median TGM concentrations decreased by 7-19% from 2000 to 2004 for those stations (Temme *et al*. 2006).

Data from the Mercury Deposition Network (MDN) show that concentrations of mercury in precipitation are decreasing for much of the U.S., but there is no trend for the stations in the upper Midwest (Gay *et al*. 2006).

PBDEs. Total PBDE concentrations during 2003-2004 were in the single pg/m^3 range for the rural master stations and in the 50-100 pg/m^3 range for the urban stations (Venier 2006). This is lower than total PCB levels, which are generally in the 10s to 100s of pg/m^3 range. A meta-analysis of PBDE concentrations in various environmental compartments and biota worldwide revealed exponentially increasing concentrations with doubling times of about 4-6 years and higher levels in North America than in Europe (Hites 2004). US manufacturers of penta- and octa-PBDEs phased out production in 2004, but deca-PBDEs are still being produced. Future data will confirm whether PBDEs increase or decrease in the air of the Great Lakes.

Loadings. An atmospheric loading is the amount of a pollutant entering a lake from the air, which equals wet deposition (rain) plus dry deposition (falling particles) plus gas absorption into the water minus volatilization out of the water. Absorption minus volatilization equals net gas exchange, which is the most significant part of the loadings for many semi-volatile PBT pollutants. For many banned or restricted substances that IADN monitors, net atmospheric inputs to the lake are headed toward equilibrium; that is, the amount going into the lake equals the amount volatilizing out. Current-use pesticides, such as g-HCH (lindane) and endosulfan, as well as PAHs and trace metals, still have net deposition from the atmosphere to the Lakes.

A report on the atmospheric loadings of these compounds to the Great Lakes for data through 2004 will be published in late 2006 or early 2007. It will be available online at:
http://www.epa.gov/glnpo/monitoring/air/iadn/iadn.html.
To receive a hardcopy, please contact one of the agencies listed at the end of this report.

Pressures

Atmospheric deposition of toxic compounds to the Great Lakes is likely to continue into the future. The amount of compounds no longer in use, such as most of the organochlorine pesticides, may decrease to undetectable levels, especially if they are phased out in developing countries, as is being called for in international agreements.

Residual sources of PCBs remain in the U.S. and throughout the world; therefore, atmospheric deposition will still be significant at least decades into the future. PAHs and metals continue to be emitted and therefore concentrations of these substances may not decrease or will decrease very slowly depending on further pollution reduction efforts or regulatory requirements. Even though emissions from many sources of mercury and dioxin have been reduced over the past decade, both pollutants are still seen at elevated levels in the environment. This problem will continue unless the emissions of mercury and dioxin are reduced further.

Atmospheric deposition of chemicals of emerging concern, such as brominated flame retardants and other compounds that may currently be under the radar, could also serve as a future stressor on the Great Lakes. Efforts are being made to screen for other chemicals of potential concern, with the intent of adding such chemicals to Great Lakes monitoring programs given available methods and sufficient resources.

Management Implications

In terms of in-use agricultural chemicals, such as lindane, further restrictions on the use of these compounds may be warranted. Transport of lindane to the Great Lakes following planting of lindane-treated canola seeds in the Canadian prairies has been demonstrated by modellers (Ma *et al*. 2004b). On January 1, 2005, Canada withdrew registration of lindane for agricultural pest control; lindane is still registered for use in the U.S.

Controls on the emissions of combustion systems, such as those in factories and motor vehicles, could decrease inputs of PAHs to the Great Lakes' atmosphere.

Although concentrations of PCBs continue to decline slowly, somewhat of a "leveling-off" trend seems to be occurring in air, fish, and other biota as shown by various long-term monitoring programs. Remaining sources of PCBs, such as contaminated sediments, sewage sludge, and in-use electrical equipment, may need to be addressed more systematically through efforts like the Canada-U.S. Binational Toxics Strategy and national regulatory programs in order to see more significant declines. Many such sources are located in urban areas, which is reflected by the higher levels of PCBs measured in Chicago and Cleveland by IADN, and by other researchers in other areas (Wethington and Hornbuckle 2005; Totten *et al*. 2001). Research to investigate the significance of these remaining sources is underway. This is important since fish consumption advisories for PCBs exist for all five Great Lakes.

Progress has been made in reducing emissions of dioxins and furans, particularly through regulatory controls on incinerators. Residential garbage burning (burn barrels) is now the largest current source of dioxins and furans (Environment Canada and U.S. Environmental Protection Agency 2003). Basin- and nationwide efforts are underway to eliminate emissions from burn barrels.

Regulations on coal-fired electric power plants, the largest remaining source of anthropogenic mercury air emissions, will help to decrease loadings of mercury to the Great Lakes.

Pollution prevention activities, technology-based pollution controls, screening of in-use and new chemicals, and chemical substitution (for pesticides, household, and industrial chemicals) can aid in reducing the amounts of toxic chemicals deposited to the Great Lakes. Efforts to achieve reductions in use and emissions of toxic substances worldwide through international assistance and negotiations should also be supported, since PBTs used in other countries can reach the Great Lakes through long-range transport.

Continued long-term monitoring of the atmosphere is necessary in order to measure progress brought about by toxic reduction efforts. Environment Canada and USEPA are currently adding dioxins and PBDEs to the IADN as funding allows. Mercury monitoring at Canadian stations is being conducted through the CAMNet. Additional urban monitoring is needed to better characterize atmospheric deposition to the Great Lakes.

Acknowledgments

This report was prepared on behalf of the IADN Steering Committee by Melissa Hulting, IADN Program Manager, U.S. Environmental Protection Agency, Great Lakes National Program Office. Thanks to Tom Dann of Environment Canada's National Air Pollution Surveillance Network (NAPS) for dioxin and furan information, David Gay of the Mercury Deposition Network for mercury in precipitation information, and Ron Hites and Marta Venier of Indiana University for PBDE data.

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Source: IADN Steering Committee, unpublished, 2006.

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Source: Environment Canada National Air Pollution Surveillance (NAPS) network, unpublished, 2006.

Figure 5. Trends from 2000 to 2004 for median concentrations of total gaseous mercury (ng/m^3) at CAMNet stations.
Source: Temme *et al*. 2006.

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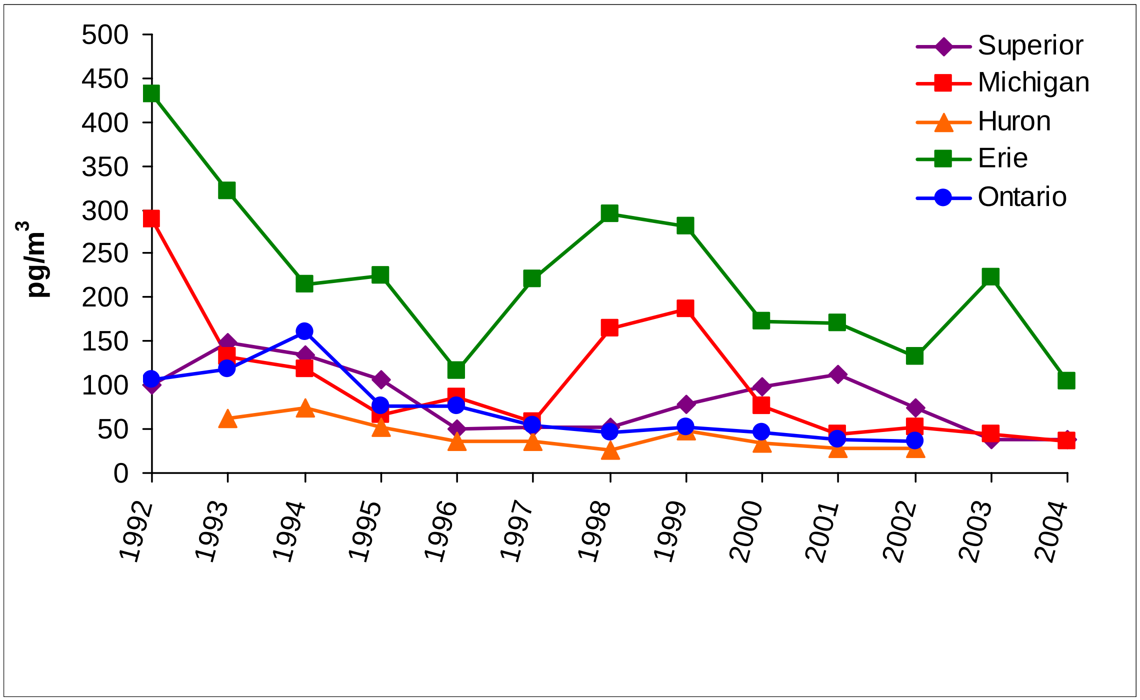

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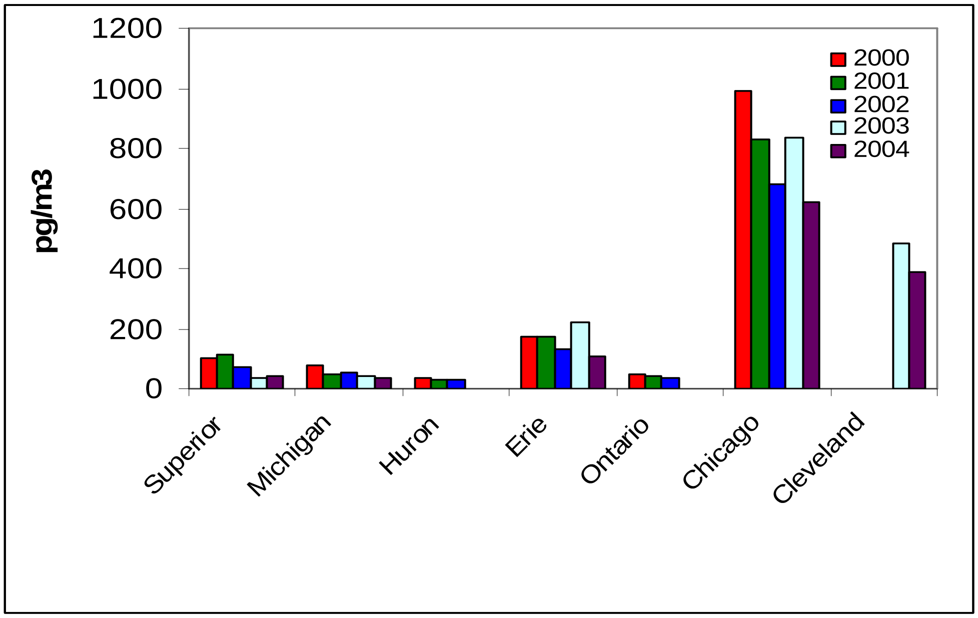

Figure 2. Gas Phase PCB concentrations for rural sites versus urban areas. Source: IADN Steering Committee, unpublished, 2006

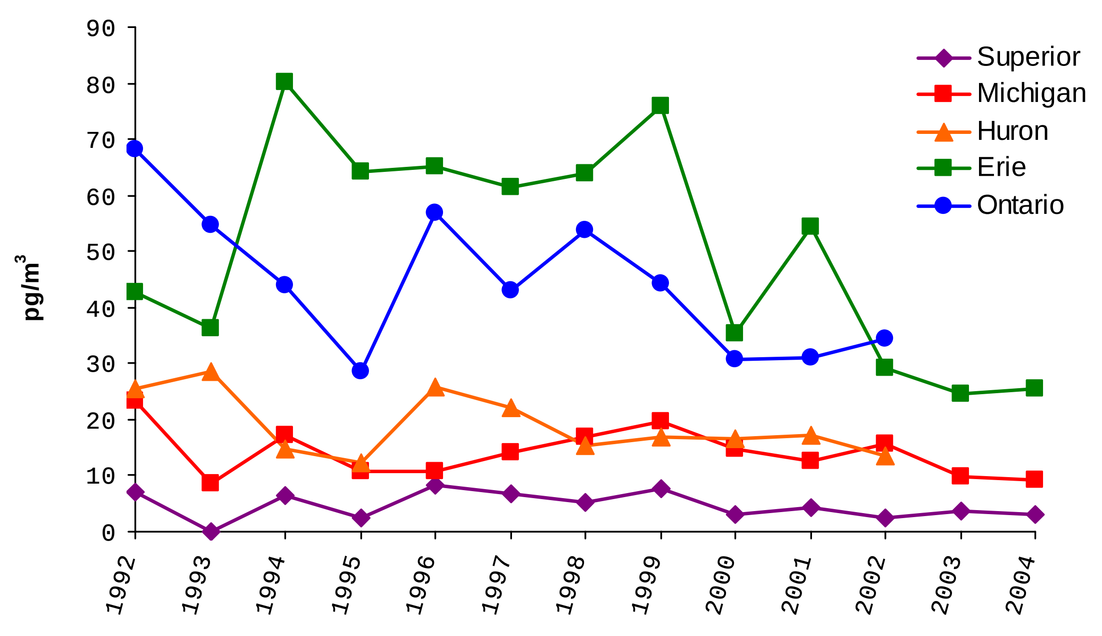

Figure 3. Annual Average Particulate Concentrations of Benzo(a)pyrene.
Source: IADN Steering Committee, unpublished, 2006

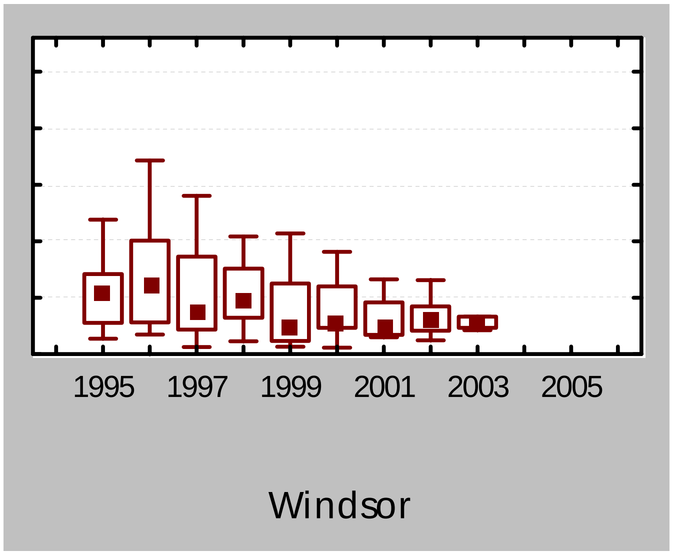

Figure 4. Concentrations of dioxins and furans expressed as TEQ (Toxic Equivalent) in fg/m3 in Windsor, Ontario.
Source: Environment Canada National Air Pollution Surveillance (NAPS) network, unpublished, 2006

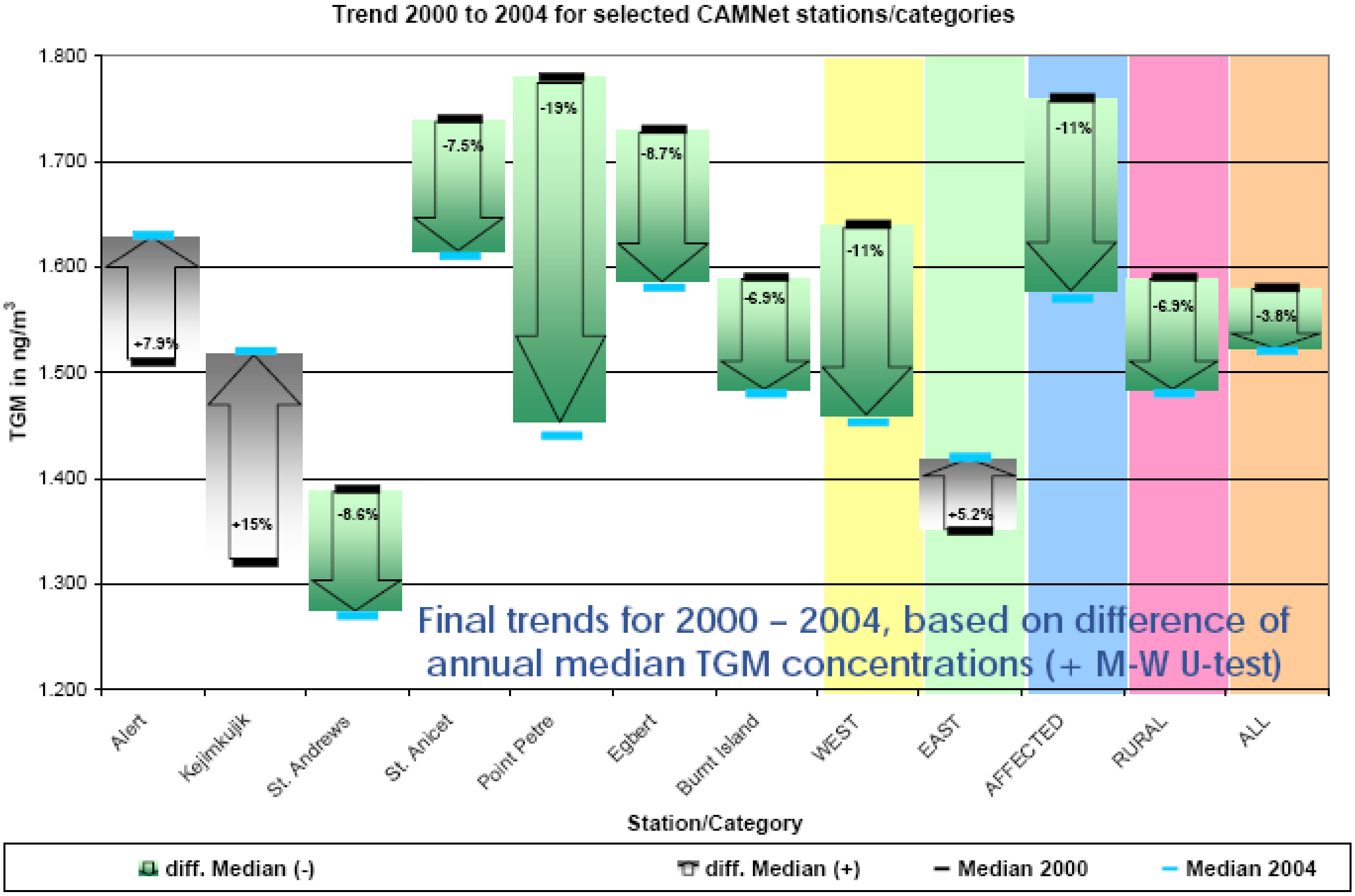

Figure 5. Trends from 2000 to 2004 for median concentrations of total gaseous mercury (ng/m^3) at CAMNet stations.
Source: Temme *et al*. 2006

Toxic Chemical Concentrations in Offshore Waters

Indicator #118

Overall Assessment

Status: **Mixed**
Trend: **Undetermined**
Primary Factors Determining Status and Trend: **Data for this indicator is not available system-wide for all chemicals.**

Concentrations of most organic compounds are low and are declining in the open waters of the Great Lakes, indicating progress in the reduction of persistent toxic substances. Insufficient data are available at this time to make a robust determination of the recent trend in concentrations of all compounds.

Generally, organochlorine pesticide concentrations exhibit a north to south gradient from lowest to highest (Superior<Huron<Ontario<Erie) based on work completed by Environment Canada. Exceptions to this pattern do exist; for example, compounds that are primarily distributed by atmospheric deposition rather than point sources, such as Lindane and Chlordane, are found at higher concentrations in the north. However, distributions and concentrations of most substances reflect sources from agricultural land use practices (i.e., higher concentrations in the lower Great Lakes where agriculture dominates). Direct discharges of currently used pesticides have greatly diminished so that indirect discharge is the more likely current source. Indirect discharges include atmospheric deposition, agricultural land runoff, leaching of discarded stocks, and resuspension of contaminated sediments (Kannan *et al* 2006).

Mercury concentrations overall are very low, and concentrations in the open lake areas are currently below the U.S. EPA's Great Lakes Initiative (GLI) water quality criterion of 1.3 ng/L. However, higher concentrations are observed in the western basin of Lake Erie in particular, and in some harbours and major urban areas as well (e.g., Detroit, Hamilton, Duluth/Superior Harbor, Rochester, Chicago) (Figure 1). Some samples from these urban areas exceed the GLI water quality criterion for protection of wildlife.

The distribution of PCBs in the Great Lakes indicates higher concentrations near historical, localized sources. Concentrations in offshore waters are lower than nearshore, and concentrations in the upper Great Lakes are lower than the lower Great Lakes. Reductions are largely due to the ban of PCBs and the subsequent control of point sources.

The spatial distribution of PAHs reflects the major source from the burning of fossil fuels. Concentrations of PAHs are therefore higher in the lower lakes, where usage is greater. The lighter PAHs are also ubiquitous in the upper Great Lakes, but their concentrations are much lower.

Little or no information is currently available for some compounds, such as dioxins, in offshore waters. Concentrations of these compounds are extremely low and difficult to detect in lake water samples. It may be more appropriate to measure them in fish and/or sediment samples. Information about compounds of new and emerging concern is being assessed and information should be available for a future SOLEC update.

Lake-by-Lake Assessment

Lake Superior

Status: Fair
Trend: Undetermined

Primary Factors Determining Status and Trend

Thirteen of a possible 21 organochlorines were detected in Lake Superior and their concentrations were generally very low. Their presence is most likely due to atmospheric deposition because the traditional sources (row-crop agriculture and urban land uses) are low in this basin. For example, concentrations of the insecticide Dieldrin (Figure 2) reflect its usage in the agricultural communities of the southern Great Lakes basin and are low in Lake Superior (2005: open lake average = 0.11 ng/L). In contrast, concentrations of Lindane (Figure 3), which was previously used in North American agriculture, reflect greater atmospheric deposition in the north (2005: open lake average = 0.31 ng/L).

Mercury concentrations in Lake Superior were very low offshore (2005 open lake average 0.41 ng/L), with higher concentrations near Thunder Bay and Duluth. With the exception of one station near Duluth, all samples met the US EPA Great Lakes Initiative (GLI) water quality criterion for protection of wildlife of 1.3 ng/L.

PAHs are present throughout the Lake at extremely low concentrations. Concentrations were many orders of magnitude below Ontario Water Quality Guidelines. For example, the open lake average concentration of Phenanthrene (Figure 4) was 0.03 ng/L and the Ontario Guideline is 30 ng/L.

Lake Michigan

Status: Fair
Trend: Undetermined

Primary Factors Determining Status and Trend

Preliminary data from 2004 indicate that concentrations of PCBs and organochlorine pesticides have either decreased slightly or remained constant since the mid-1990s, following a decrease in the 1970s through the early 1990s. 2005 total mercury concentrations were all below the U.S. EPA's Great Lakes Initiative (GLI) water quality criterion for protection of wildlife of 1.3 ng/L. Atrazine concentrations in the open lake waters were consistent across Lake Michigan stations with an average concentration ranging from 33 to 48 ng/L between 1994 and 2000; this is more than 50 times below the maximum concentration allowed for drinking water

(Kannan *et al* 2006).

Lake Huron

Status:	Fair
Trend:	Undetermined
Primary Factors Determining Status and Trend	In 2004, 16 of a possible 21 organochlorines were detected in Lake Huron, but only 11 were commonly found. Commonly found OCs included a-HCH, lindane, dieldrin, and g-chlordane. The concentrations were generally low, reflecting historical or diffuse sources. For example, average concentrations of dieldrin in 2004 were 0.08 ng/L in Lake Huron and 0.07 ng/L in Georgian Bay. These concentrations were lower than those found in the other Great Lakes and are well below the Ontario Water Quality Objective of 1.0 ng/L.

Mercury concentrations in Lake Huron and Georgian Bay were low (2005 open lake average: Lake Huron 0.58 ng/L, Georgian Bay 0.33 ng/L). The concentrations at all open lake stations were below the USEPA's Great Lakes Initiative (GLI) water quality criterion for protection of wildlife of 1.3 ng/L (Figure 1), and only one nearshore station in Georgian Bay exceeded this level.

PAH concentrations in Lake Huron and Georgian Bay are very low. Of the 20 and 19 PAH compounds found in Lake Huron and Georgian Bay, respectively, five were detected only within the North Channel (Dibenzo(a,h)antracene, Perylene, Benzo(a)pyrene, Anthracene, and 2-Chloronaphthalene). The open lake average concentration of Phenanthrene (Figure 4) was 0.08 ng/L in Lake Huron and 0.13 ng/L in Georgian Bay, well below the Ontario guideline of 30 ng/L.

Lake Erie

Status:	Mixed
Trend:	Undetermined
Primary Factors Determining Status and Trend	In 2004, Environment Canada's Great Lakes Surveillance Program detected 15 of a possible 21 organochlorine compunds in Lake Erie; 10 of these were commonly found, including a-HCH, HCB, Lindane and Dieldrin. Concentrations of most compounds were highest in the shallow western basin and much lower in the central and eastern basins. An exception is Lindane, which showed similar concentrations in all three basins. Almost all Canadian sources of Lindane to the Great Lakes are from the Canadian prairies (Ma *et al* 2003). Similar results were found in 1998 by Marvin *et al*. (2004). Between 1998 and 2004 average lakewide Lindane concentrations fell (2004: 0.16 ng/l; 1998: 0.32 ng/l) indicating a possible downward trend. Key contributors of hexachlorobenzene and octachlorostyrene were identified in the St. Clair River (Marvin *et al* 2004).

The intensively-farmed agricultural and urban lands draining into Lake Erie and Lake St. Clair are a major contributor of pesticides and other contaminants to the Great Lakes. In these watersheds, approximately 75%

of the land use is agriculture and about 40% of the Great Lakes population resides here. Pesticides were detected in every tributary monitored between 1996 and 1998 (Kannan *et al* 2006). Some tributaries contained as many as 18 different pesticides; among the highest counts for any watershed monitored in North America.

Mercury concentrations in 2005 in Lake Erie were the highest of the Great Lakes and reflected a decreasing concentration from west to east (average concentrations 2.53 ng/L in the western basin, 0.52 ng/L in the central basin, and 0.49 ng/L in the eastern basin). Higher concentrations (above 3.0 ng/L) were found near the mouths of the Detroit and Maumee rivers. Concentrations at all stations in the western basin, as well as some stations in the central and eastern basins, exceeded the GLI mercury criterion of 1.3 ng/L.

PAH concentrations and distributions reflected urban source areas on the Lake and upstream sources within the St. Clair River – Detroit River corridor. The highest concentrations of most PAHs were found in the western basin, and near the mouth of the Detroit River in particular. For example the phenanthrene concentration (Figure 4) at the mouth of the Detroit River was 2.5 ng/L, whereas the overall Lake average was 0.59 ng/L, an almost 5-fold difference.

Lake Ontario

Status:	Mixed
Trend:	Undetermined
Primary Factors Determining Status and Trend	Seventeen of a possible 21 OC pesticides were detected in Lake Ontario waters in 2005. Dieldrin, lindane, and a-HCH were routinely found. Probable sources of these compounds include a combination of historical watershed uses, upstream loadings (e.g. the Niagara River) and atmospheric deposition. Concentrations of many parameters were intermediate compared to the upper Great Lakes (which generally had lower concentrations) and Lake Erie (which generally had higher concentrations, especially in the western basin). Within Lake Ontario, spatial trends were reflective of localized (predominantly urban) sources.

Mercury concentrations in Lake Ontario were low in the offshore areas (average 0.48) and higher in the nearshore (average 0.80 ng/L). Spatial trends were reflective of localized sources (e.g. higher values in Toronto and Hamilton, Ontario and Rochester and Oswego, New York), but only samples taken from Hamilton Harbour exceeded the GLI objective of 1.3 ng/L for mercury.

PAH distribution and concentrations reflect urban source areas on the Lake (e.g., Rochester NY, Niagara River, and Hamilton, Ontario). All offshore concentrations were below Ontario Water Quality Guidelines.

Purpose
This indicator reports on concentrations of priority toxic chemicals in offshore waters, and, by comparison to criteria for the protection for aquatic life and human health, infers the potential for impacts to the health of the Great Lakes aquatic ecosystem. The indicator can be used to infer the progress of virtual elimination programs as well.

Ecosystem Objective
The Great Lakes should be free from materials entering the water as a result of human activity that will produce conditions that are toxic or harmful to human, animal, or aquatic life (GLWQA, Article III(d)).

State of the Ecosystem
Many toxic chemicals are present in the Great Lakes and it is impractical to summarize the spatial and temporal trends of them all within a few pages. For more information on spatial and temporal trends in toxic contaminants in offshore waters, the reader is referred to Marvin *et al*. (2004), Kannan *et al*. (2006), and *Trends in Great Lakes Sediments and Surface Waters* in Chapter 8 of the Great Lakes Binational Toxics Strategy 2004 Progress report.

Surveys conducted between 1992 and 2000 (Marvin *et al*), and between 2004-2005 (Environment Canada unpublished data) on Lakes Superior, Huron, Erie and Ontario showed that concentrations of most organic compounds are low (i.e., below the most stringent water quality guidelines) and declining in the open waters of the Great Lakes. The decline in the concentration of banned organochlorine pesticides has leveled off since the mid-1980s and current rates of decline are slow.

Dieldrin, a-HCH, lindane (g-HCH), and heptachlor epoxide were the only organochlorine pesticide compounds routinely detected in Lakes Superior, Erie and Ontario (Marvin *et al*. 2004). The in-use herbicides atrazine and metolachlor were ubiquitous (Marvin *et al*. 2004). An example of the spatial distribution of dieldrin using 2004/05 data is provided in Figure 2.

Many organic compounds (such as PCBs, hexachlorobenzene, octachlorostyrene, and DDT) show a spatial pattern that indicates higher concentrations near historical, localized sources. Currently emitted compounds, such as PAHs and mercury, which are released during fossil fuel combustion, also show spatial patterns that are indicative of sources. Concentrations of the heavier PAHs, which are not as subject to atmospheric transport due to their partitioning to particles, are highest in the lower Great Lakes, where human populations are greater.

Management Implications
Management efforts to control inputs of organochlorine pesticides have resulted in decreasing concentrations in the Great Lakes; however, historical sources for some compounds still appear to affect ambient concentrations in the environment. Further reductions in the input of OC pesticides are dependent, in part, on controlling indirect inputs such as atmospheric deposition and surface runoff. Monitoring programs should increase measurement of the major in-use pesticides, of which currently only half are monitored. The additive and synergetic effects of pesticide mixtures should be examined more closely, since existing water quality criteria have been development for individual pesticides only (Kannan *et al* 2006).

Beginning in 1986, Environment Canada has conducted toxic contaminant monitoring in the shared waters of the Great Lakes. Recently, Environment Canada has developed new measurement techniques and has invested in an ultra-clean laboratory in order to more accurately measure these trace concentrations of pollutants in the surface waters of the Great Lakes. The data presented here represent the results of this new methodology. Data is available for all of the shared waters, although only partial coverage of Lake Ontario has been analyzed to date. The analyte list includes PCBs (as congeners), organochlorines, polycyclic aromatic hydrocarbons (PAHs), trace metals including mercury, as well as a limited number of in-use pesticides and other compounds of emerging concern.

In 2003, USEPA initiated a monitoring program for toxics in offshore waters. EPA's spatial coverage is more limited than the Canadian program, focusing mainly on Lake Michigan, but the analyte list is more comprehensive and includes PCBs, organochlorine pesticides, toxaphene, dioxins/furans, PBDEs, selected PAHs, mercury, and perfluorinated compounds. Information from the USEPA is currently available for Lake Michigan for many organic compounds. Different measurement and analytical techniques are used, but good agreement with Canadian information is achieved for some parameters. Future efforts will need to focus on comparisons of the analytical methodologies used and the results obtained. In 2006, some work to this end is being initiated by the parties in Lake Michigan.

Efforts need to be maintained to identify and track the remaining sources and explore opportunities to accelerate their elimination (e.g. The Great Lakes Binational Toxics Strategy). Targeted monitoring to identify and track down local sources of LaMP critical pollutants is being conducted in many Great Lakes tributaries. However, an expansion of the track down program should be considered to include those chemicals whose distribution suggests localized influences.

Chemicals such as endocrine disrupting chemicals, in-use pesticides, and pharmaceuticals are emerging issues. The agencies' environmental researchers are working with the monitoring groups to include compounds of emerging concern in Great Lakes Surveillance cruises. For example, in-use pesticides and a suite of pharmaceuticals are being measured in each of the Great Lakes between 2005 and 2007.

Comments from the author(s)

Data for Lakes Superior, Huron, Erie and Ontario are from Environment Canada's Great Lakes Water Quality Monitoring and Surveillance Program. Data for Lake Michigan are from the US EPA's Great Lakes Aquatic Contaminant Surveillance (GLACS) program (Principal Investigators: Dr. Matt Simcik of the University of Minnesota and Dr. Jeff Jeremiason of Gustavus Adolphus College).

Lake Ontario 2005 data for PAHs and OC pesticides reflects sampling conducted in the western half of the lake only.

Acknowledgments

Authors: Jennifer Vincent and Alice Dove, Environment Canada, Burlington, ON, Melissa Hulting, Great Lakes National Program Office, USEPA, Chicago, IL.

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Figure 1. Great Lakes 2003-2005 Open Lake, Spring Cruise, Concentrations of Total Mercury (ng/L).
Source: Environment Canada's Great Lakes Water Quality Surveillance Program, Burlington, Ontario and U.S. Environmental Protection Agency's Great Lakes National Program Office, Chicago, Illinois.

Figure 2. Great Lakes 2004/05 Open Lake, Spring Cruise, Concentrations of Dieldrin (ng/L). Lake Ontario data for western half of the lake only.
Source: Environment Canada's Great Lakes Water Quality Surveillance Program, Burlington, Ontario.

Figure 3. Great Lakes 2004/05 Open Lake, Spring Cruise, Concentrations of Lindane (ng/L). Lake Ontario data for western half of the lake only.
Source: Environment Canada's Great Lakes Water Quality Surveillance Program, Burlington, Ontario.

Figure 4. Great Lakes 2004/05 Open Lake, Spring Cruise, Concentrations of Phenanthrene (ng/L).
Source: Environment Canada's Great Lakes Water Quality Surveillance Program, Burlington, Ontario.

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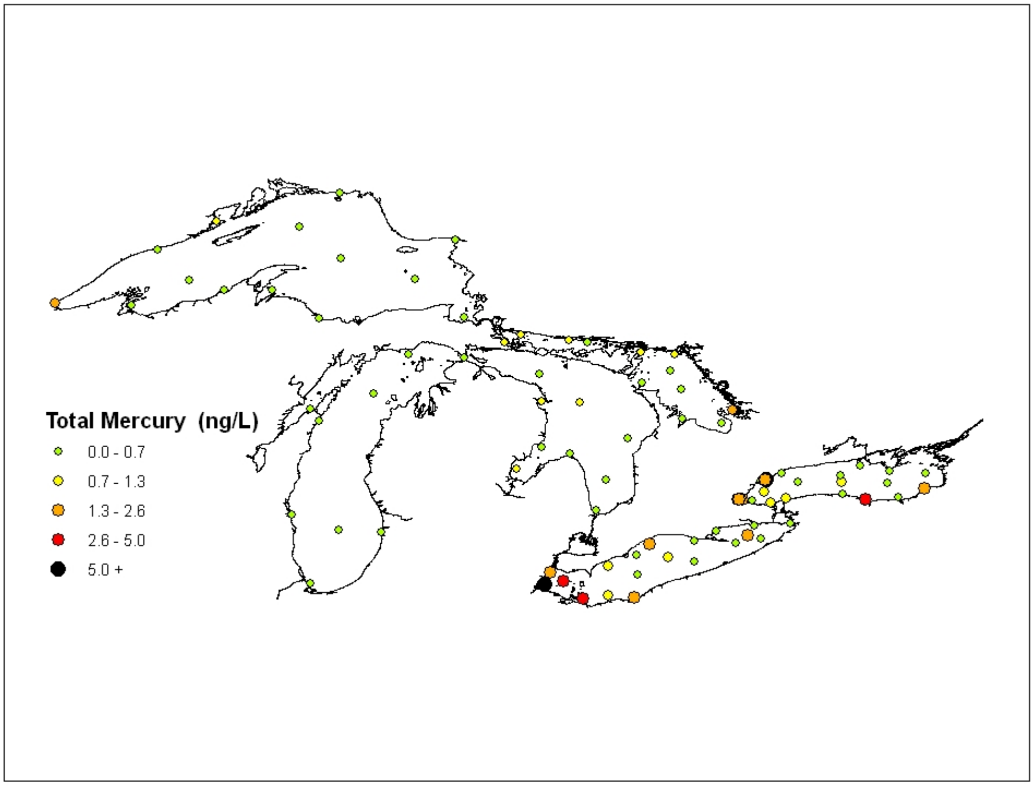

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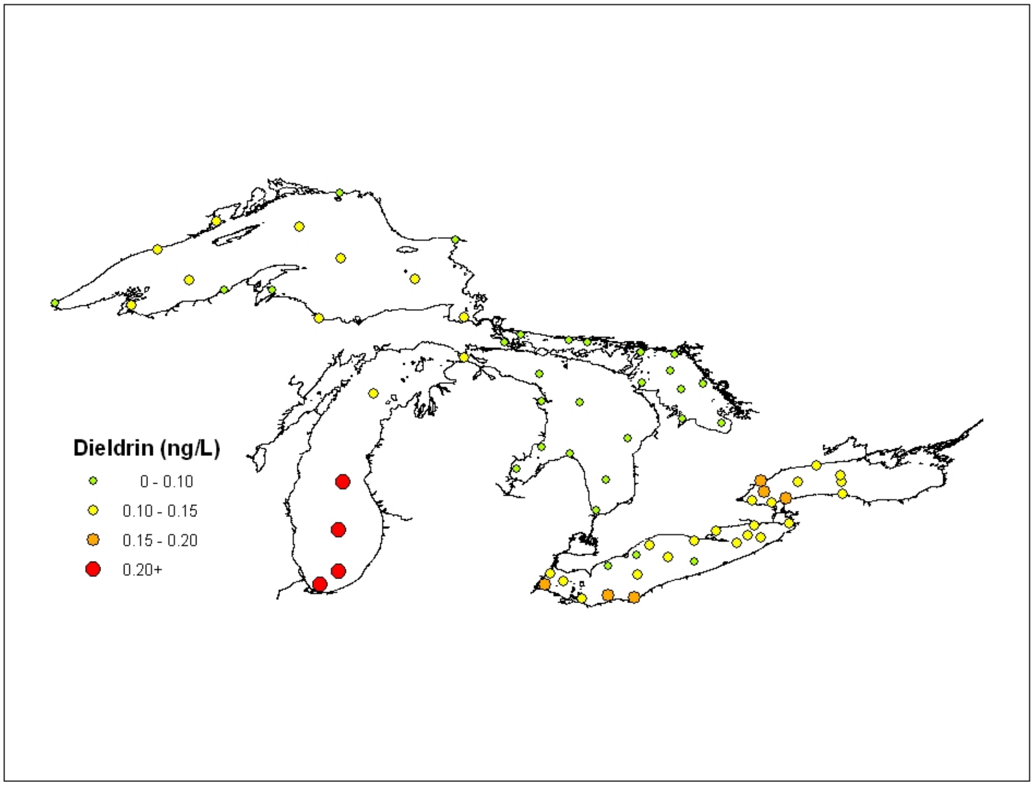

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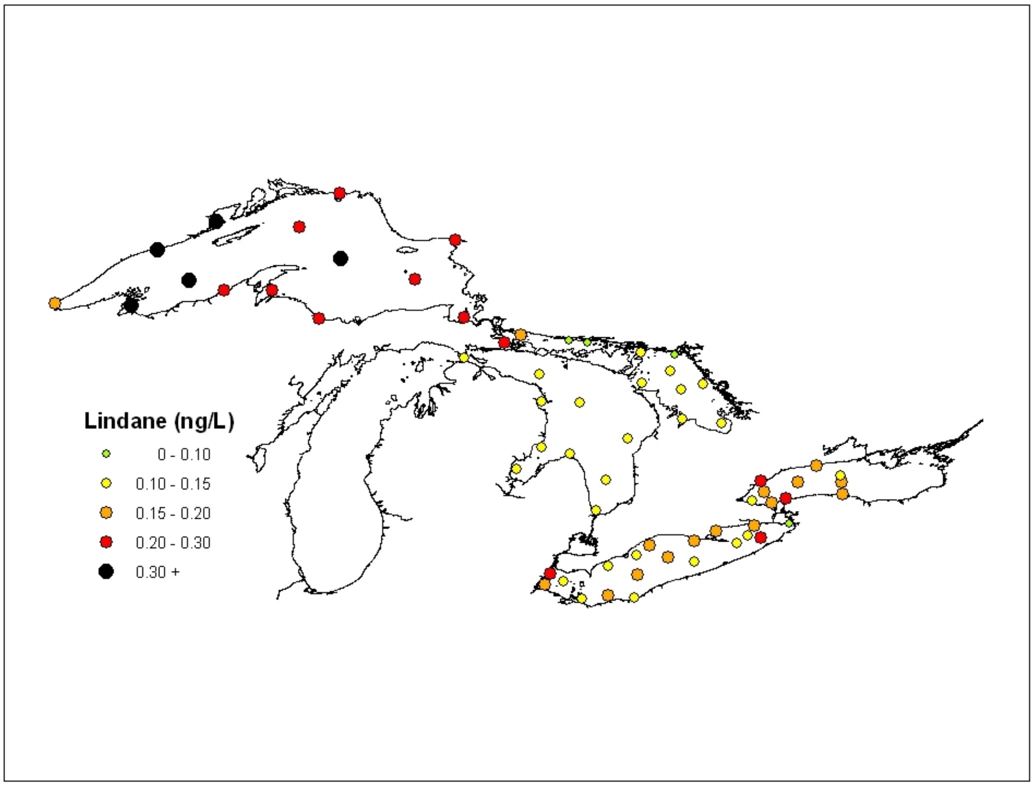

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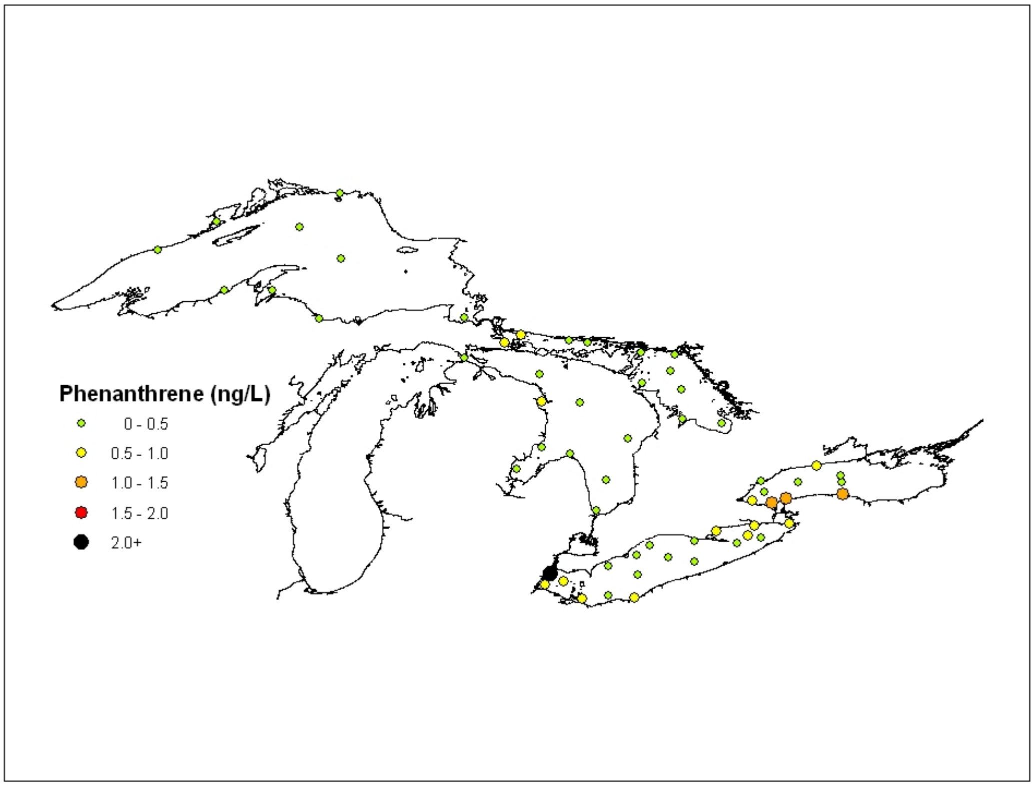

Figure 4. Great Lakes 2004/05 Open Lake, Spring Cruise, Concentrations of Phenanthrene (ng/L).
Source: Environment Canada's Great Lakes Water Quality Surveillance Program, Burlington, Ontario

Concentrations of Contaminants in Sediment Cores
Indicator #119

Overall Assessment
Status: **Mixed**
Trend: **Improving/Undetermined**
Primary Factors Determining Status and Trend: **There have been significant declines over the past three decades in concentrations of many contaminants including PCBs, DDT, lead, and mercury. Knowledge is lacking regarding the occurrence of many new contaminants including BFRs and fluorinated surfactants.**

Lake-by-Lake Assessment
Lake Superior
Status: Mixed
Trend: Improving/Undetermined

Lake Michigan
Status: Mixed
Trend: Improving/Undetermined

Lake Huron
Status: Mixed
Trend: Improving/Undetermined

Lake Erie
Status: Mixed
Trend: Improving/Undetermined

Lake Ontario
Status: Mixed
Trend: Improving/Undetermined

Purpose
•To infer potential harm to aquatic ecosystems from contaminated sediments by comparing contaminant concentrations to available sediment quality guidelines;
•To infer progress towards virtual elimination of toxic substances in the Great Lakes by assessing surficial sediment contamination and contaminant concentration profiles in sediment cores from open lake and, where appropriate, Areas of Concern index stations, and;
•To determine the occurrence, distribution, and fate of new chemicals in Great Lakes sediments.

Ecosystem Objective
The Great Lakes should be free from materials entering the water as a result of human activity that will produce conditions that are toxic or harmful to human health, animal, or aquatic life (Great Lakes Water Quality Agreement (GLWQA), Article III(d)). The GLWQA and the Great Lakes Binational Toxics Strategy both state the virtual elimination of toxic substances to the Great Lakes as an objective.

State of the Ecosystem

Sediment Quality Index

A sediment quality index (SQI) has been developed that incorporates three elements: scope – the percent of variables that did not meet guidelines; frequency – the percent of failed tests relative to the total number of tests in a group of sites; and amplitude – the magnitude by which the failed variables exceeded guidelines. A full explanation of the SQI derivation process and a possible classification scheme based on the SQI score (0 – 100, poor to excellent) is provided in Grapentine *et al*. (2002). Generally, the Canadian federal probable effect level (PEL) guideline (CCME 2001) was used when available, otherwise the Ontario lowest effect level (LEL) guideline (Persaud *et al*. 1992) was used. Application of the SQI to Lakes Erie and Ontario was reported in Marvin *et al*. (2004). The SQI ranged from fair in Lake Ontario to excellent in eastern Lake Erie. Spatial trends in sediment quality in Lakes Erie and Ontario reflected overall trends for individual contaminant classes such as mercury and polychlorinated biphenyls (PCBs).

Environment Canada and USEPA integrated available data from the open waters of each of the Great Lakes. To date, data on lead, zinc, copper, cadmium, and mercury have been integrated. The site by site SQIs for Great Lakes sediments based on these metals are illustrated in Figure 1. The general trend in sediment quality across the Great lakes basin for the five metals is generally indicative of trends for a wide range of persistent toxics. Areas of Lakes Erie, Ontario and Michigan show the poorest sediment quality as a result of historical urban and industrial activities.

Application of the SQI has been expanded to include contaminants in streambed and riverine sediments for whole-watershed assessments. The SQI map for the Lake Erie – Lake St. Clair drainages is shown in Figure 2. Poorest sediment quality is primarily associated with Areas of Concern (AOC) where existing multi-stakeholder programs (e.g., Remedial Action Plans) are in place to address environmental impairments related to toxic chemicals.

Pressures

Management efforts to control inputs of historical contaminants have resulted in decreasing contaminant concentrations in the Great Lakes open-water sediments for the standard list of chemicals. However, additional chemicals such as brominated flame retardants (BFRs) and current-use pesticides (CUPs) may represent emerging issues and potential future stressors to the ecosystem.

The distribution of hexabromocyclododecane (HBCD) in Detroit River suspended sediments is shown in Figure 3. This compound is the primary flame retardant used in polystyrene foams, and is the third-most heavily produced BFR. Elevated levels of HBCD were associated with heavily urbanized/industrialized areas of the watershed. The HBCD distribution differs from PCBs, which are primarily associated with areas of contaminated sediment resulting from historical industrial activities including steel manufacturing and chlor-alkali production. These results corroborate observations made globally, which indicate that large urban centers act as diffuse sources of chemicals that are heavily used to support our modern societal lifestyle.

The temporal trend in the Niagara River of another class of BFRs, polybrominated diphenyl ethers (PBDEs), is shown in Figure 4. Prior to 1988, PBDEs were generally detected at low (parts per billion, ppb) concentrations, but showed a trend toward increasing concentrations over the period 1980 – 1988. After 1988, PBDE concentrations in the Niagara River showed a more rapidly increasing trend. PBDE concentrations in suspended sediments of the Niagara River are comparable to, or lower than, concentrations in sediments in other industrialized/urbanized areas of the world. The Niagara River watershed does not appear to be a significant source of PBDEs to Lake Ontario, and concentrations appear to be indicative of general contamination from a combination of local, regional, and continental sources.

Management Implications

•The Great Lakes Binational Toxics Strategy needs to be maintained to identify and track the remaining sources of contamination and to explore opportunities to accelerate their elimination.
•Targeted monitoring to identify and track down local sources of pollution should be considered for those chemicals whose distribution in the ambient environment suggests local or sub-regional sources.
•Ongoing monitoring programs in the Connecting Channels provide invaluable information on the success of binational management actions to reduce/eliminate discharges of toxics to the Great Lakes. These programs also provide important insights into pathways of new chemicals entering the Great Lakes.

Acknowledgments
Authors: Scott Painter, Environment Canada, Burlington, ON; and
Chris Marvin, Environment Canada, Burlington, ON.

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Figure 1. Site Sediment Quality Index (SQI) based on lead, zinc, copper, cadmium and mercury.
Source: Chris Marvin, Environment Canada (1997-2001 data for all lakes except Michigan); and Ronald Rossmann, U.S. Environmental Protection Agency (1994-1996 data for Lake Michigan)

Figure 2. Sediment Quality Index (SQI) for the Lake Erie-Lake St. Clair drainages. More detailed information on contaminants in sediments in the Lake Erie-Lake St. Clair drainages has been reported by the USGS (2000).
Source: Dan Button, U.S. Geological Survey

Figure 3. Distribution of hexabromocyclododecane (HBCD) and PCBs in suspended sediments in the Detroit River.
Source: Marvin *et al*. (2006).

Figure 4. Temporal trend in polybrominatd diphenyl ethers (PBDEs) in Niagara River suspended sediments.
Source: Marvin *et al*. (2006).

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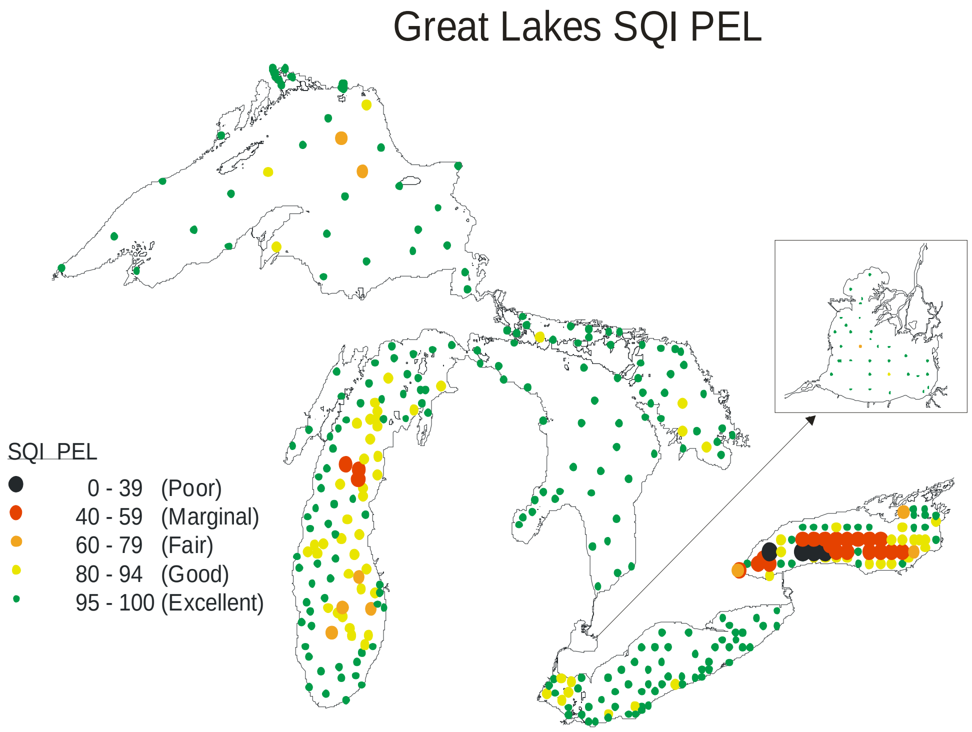

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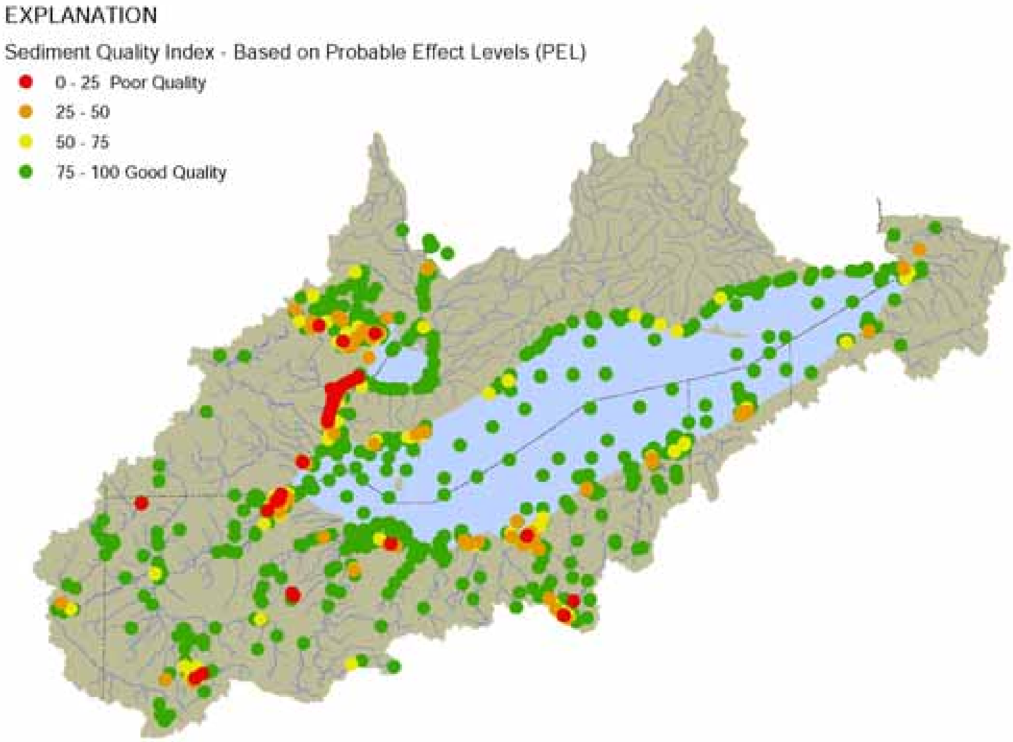

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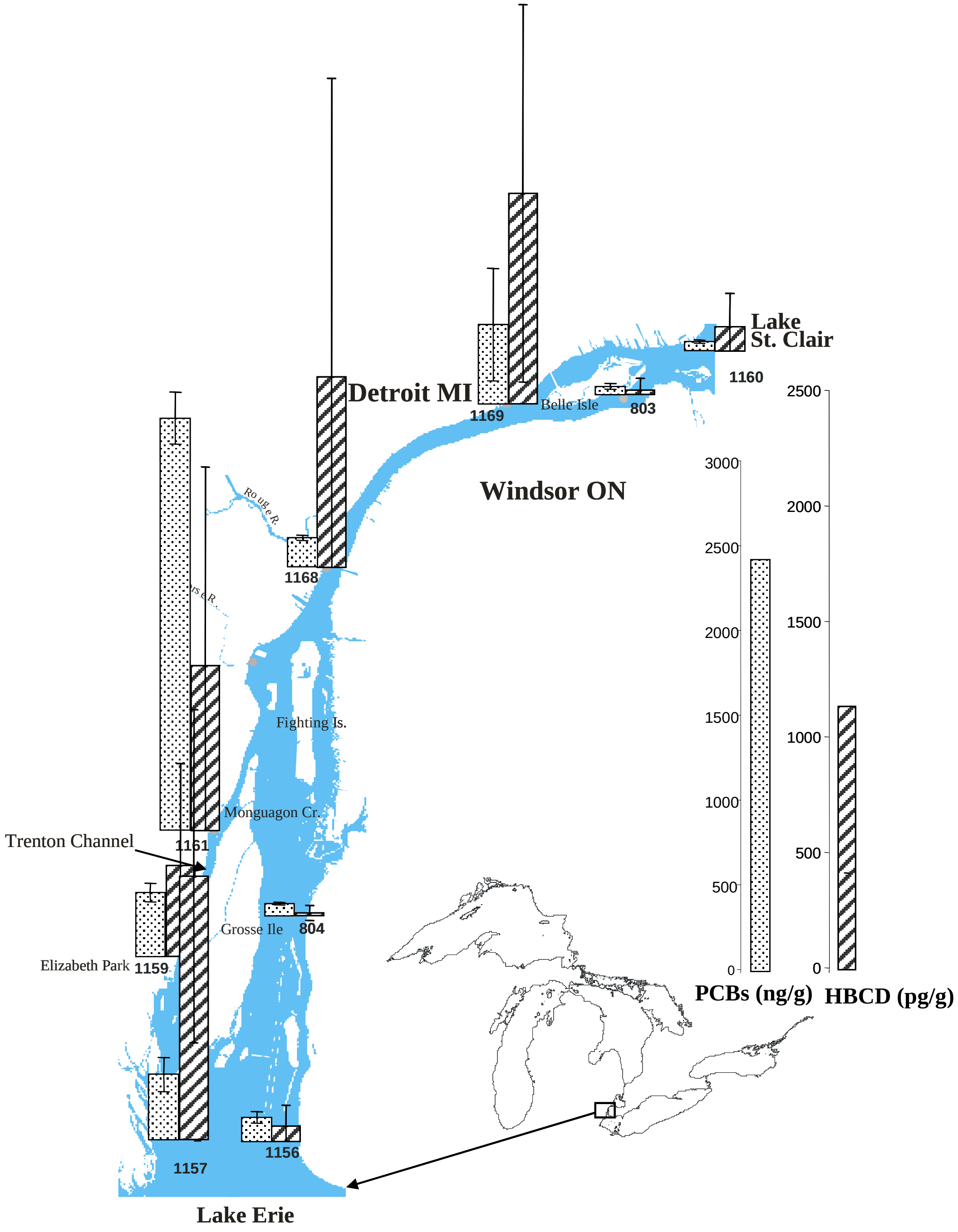

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Source: Marvin *et al*. (2006).

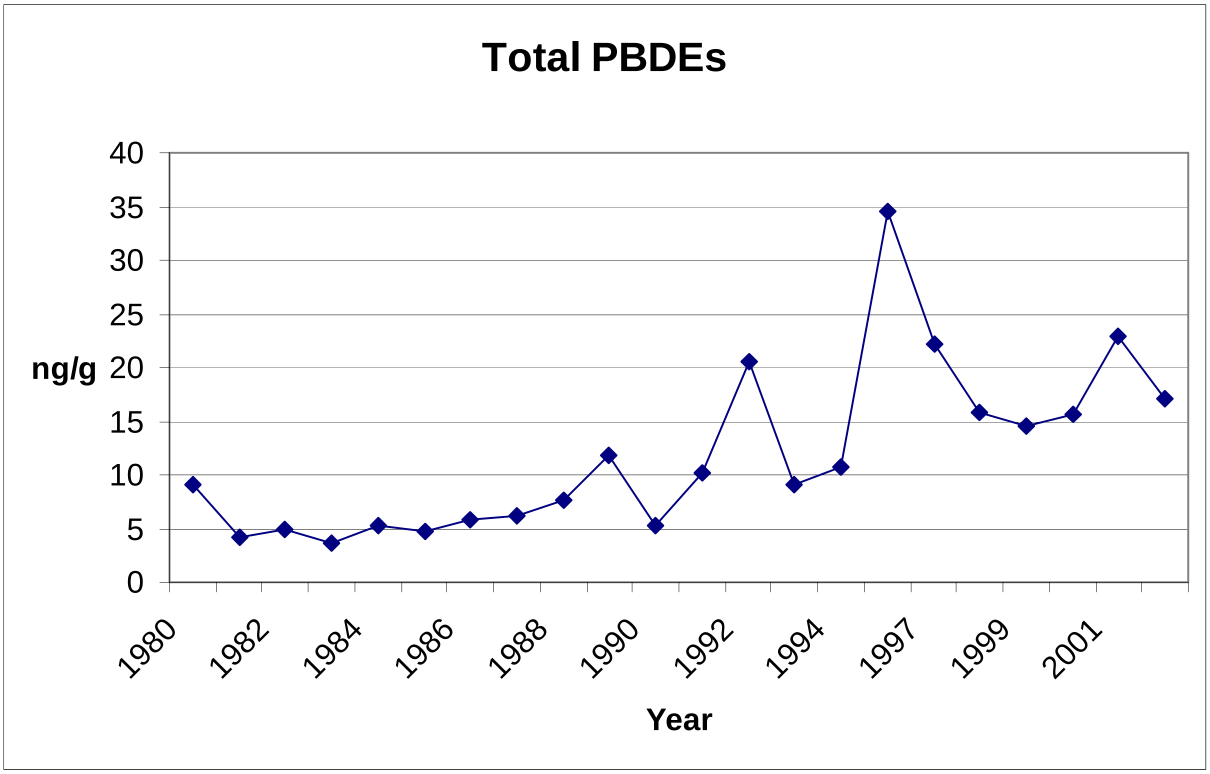

Figure 4. Temporal trend in polybrominatd diphenyl ethers (PBDEs) in Niagara River suspended sediments.
Source: Marvin *et al*. (2006).

Concentrations of Contaminants in Sediment Cores

Indicator #119

Overall Assessment

Status: **Mixed**
Trend: **Improving/Undetermined**
Primary Factors Determining Status and Trend: **There have been significant declines over the past three decades in concentrations of many contaminants including PCBs, DDT, lead, and mercury. Knowledge is lacking regarding the occurrence of many new contaminants including BFRs and fluorinated surfactants.**

Lake-by-Lake Assessment

Lake Superior
Status: Mixed
Trend: Improving/Undetermined

Lake Michigan
Status: Mixed
Trend: Improving/Undetermined

Lake Huron
Status: Mixed
Trend: Improving/Undetermined

Lake Erie
Status: Mixed
Trend: Improving/Undetermined

Lake Ontario
Status: Mixed
Trend: Improving/Undetermined

Purpose

- To infer potential harm to aquatic ecosystems from contaminated sediments by comparing contaminant concentrations to available sediment quality guidelines;
- To infer progress towards virtual elimination of toxic substances in the Great Lakes by assessing surficial sediment contamination and contaminant concentration profiles in sediment cores from open lake and, where appropriate, Areas of Concern index stations, and;
- To determine the occurrence, distribution, and fate of new chemicals in Great Lakes sediments.

Ecosystem Objective

The Great Lakes should be free from materials entering the water as a result of human activity that will produce conditions that are toxic or harmful to human health, animal, or aquatic life (Great Lakes Water Quality Agreement (GLWQA), Article III(d)). The GLWQA and the Great Lakes Binational Toxics Strategy both state the virtual elimination of toxic substances to the Great Lakes as an objective.

State of the Ecosystem

Sediment Quality Index

A sediment quality index (SQI) has been developed that incorporates three elements: scope – the percent of variables that did not meet guidelines; frequency – the percent of failed tests relative to the total number of tests in a group of sites; and amplitude – the magnitude by which the failed variables exceeded guidelines. A full explanation of the SQI derivation process and a possible classification scheme based on the SQI score (0 – 100, poor to excellent) is provided in Grapentine *et al*. (2002). Generally, the Canadian federal probable effect level (PEL) guideline (CCME 2001) was used when available, otherwise the Ontario lowest effect level (LEL) guideline (Persaud *et al*. 1992) was used. Application of the SQI to Lakes Erie and Ontario was reported in Marvin *et al*. (2004). The SQI ranged from fair in Lake Ontario to excellent in eastern Lake Erie. Spatial trends in sediment quality in Lakes Erie and Ontario reflected overall trends for individual contaminant classes such as mercury and polychlorinated biphenyls (PCBs).

Environment Canada and USEPA integrated available data from the open waters of each of the Great Lakes. To date, data on lead, zinc, copper, cadmium, and mercury have been integrated. The site by site SQIs for Great Lakes sediments based on these metals are illustrated in Figure 1. The general trend in sediment quality across the Great lakes basin for the five metals is generally indicative of trends for a wide range of persistent toxics. Areas of Lakes Erie, Ontario and Michigan show the poorest sediment quality as a result of historical urban and industrial activities.

Application of the SQI has been expanded to include contaminants in streambed and riverine sediments for whole-watershed assessments. The SQI map for the Lake Erie – Lake St. Clair drainages is shown in Figure 2. Poorest sediment quality is primarily associated with Areas of Concern (AOC) where existing multi-stakeholder programs (e.g., Remedial Action Plans) are in place to address environmental impairments related to toxic chemicals.

Pressures

Management efforts to control inputs of historical contaminants have resulted in decreasing contaminant concentrations in the Great Lakes open-water sediments for the standard list of chemicals. However, additional chemicals such as brominated flame retardants (BFRs) and current-use pesticides (CUPs) may represent emerging issues and potential future stressors to the ecosystem.

The distribution of hexabromocyclododecane (HBCD) in Detroit River suspended sediments is shown in Figure 3. This compound is the primary flame retardant used in polystyrene foams, and is the third-most heavily produced BFR. Elevated levels of HBCD were associated with heavily urbanized/industrialized areas of the watershed. The HBCD distribution differs from PCBs, which are primarily associated with areas of contaminated sediment resulting from historical industrial activities including steel manufacturing and chlor-alkali production. These results corroborate observations made globally, which indicate that large urban centers act as diffuse sources of chemicals that are heavily used to support our modern societal lifestyle.

The temporal trend in the Niagara River of another class of BFRs, polybrominated diphenyl ethers (PBDEs), is shown in Figure 4. Prior to 1988, PBDEs were generally detected at low (parts per billion, ppb) concentrations, but showed a trend toward increasing concentrations over the period 1980 – 1988. After 1988, PBDE concentrations in the Niagara River showed a more rapidly increasing trend. PBDE concentrations in suspended sediments of the Niagara River are comparable to, or lower than, concentrations in sediments in other industrialized/urbanized areas of the world. The Niagara River watershed does not appear to be a significant source of PBDEs to Lake Ontario, and concentrations appear to be indicative of general contamination from a combination of local, regional, and continental sources.

Management Implications

•The Great Lakes Binational Toxics Strategy needs to be maintained to identify and track the remaining sources of contamination and to explore opportunities to accelerate their elimination.
•Targeted monitoring to identify and track down local sources of pollution should be considered for those chemicals whose distribution in the ambient environment suggests local or sub-regional sources.
•Ongoing monitoring programs in the Connecting Channels provide invaluable information on the success of binational management actions to reduce/eliminate discharges of toxics to the Great Lakes. These programs also provide important insights into pathways of new chemicals entering the Great Lakes.

Acknowledgments

Authors: Scott Painter, Environment Canada, Burlington, ON; and
Chris Marvin, Environment Canada, Burlington, ON.

Data Sources

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Figure 1. Site Sediment Quality Index (SQI) based on lead, zinc, copper, cadmium and mercury.
Source: Chris Marvin, Environment Canada (1997-2001 data for all lakes except Michigan); and Ronald Rossmann, U.S. Environmental Protection Agency (1994-1996 data for Lake Michigan)

Figure 2. Sediment Quality Index (SQI) for the Lake Erie-Lake St. Clair drainages. More detailed information on contaminants in sediments in the Lake Erie-Lake St. Clair drainages has been reported by the USGS (2000).
Source: Dan Button, U.S. Geological Survey

Figure 3. Distribution of hexabromocyclododecane (HBCD) and PCBs in suspended sediments in the Detroit River.
Source: Marvin *et al*. (2006).

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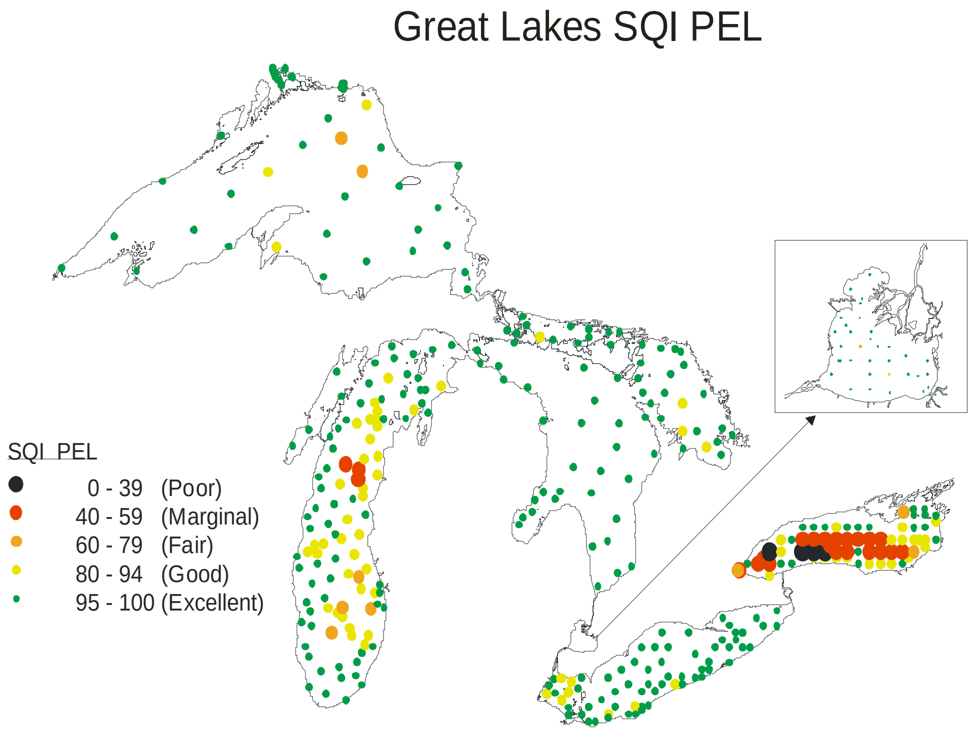

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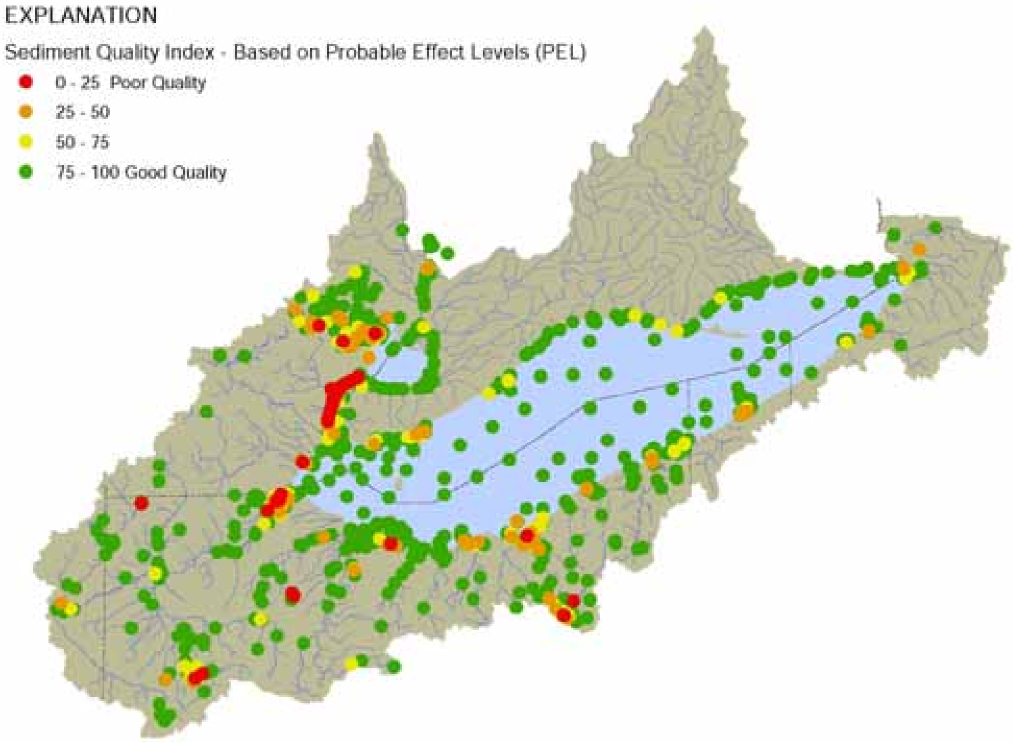

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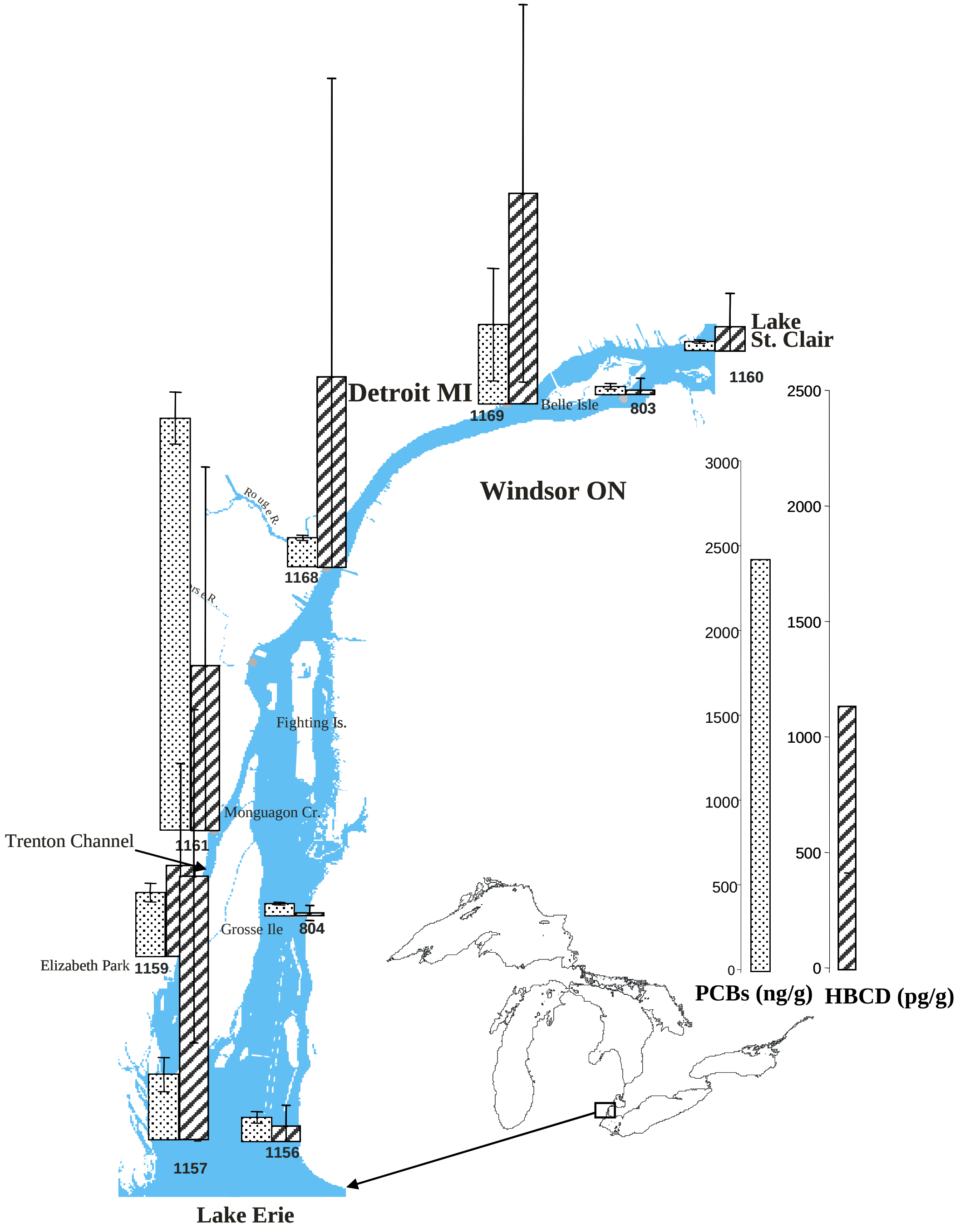

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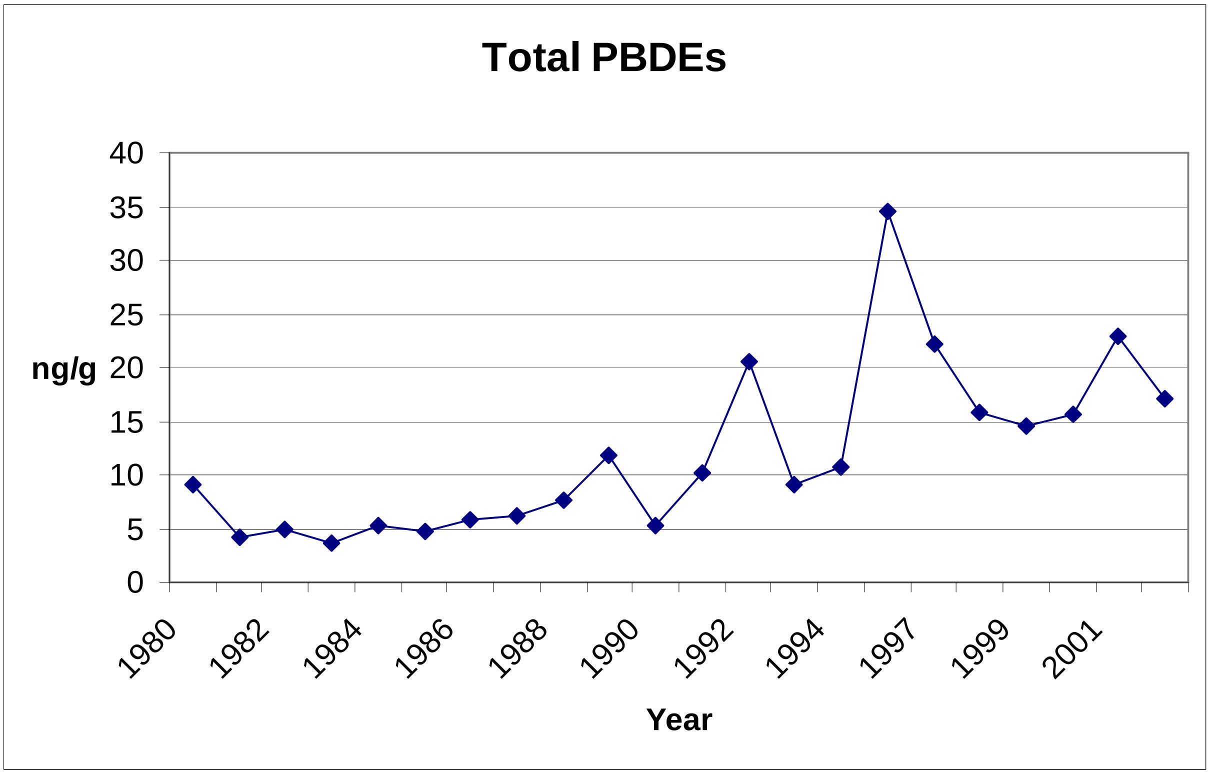

Figure 4. Temporal trend in polybrominatd diphenyl ethers (PBDEs) in Niagara River suspended sediments.
Source: Marvin *et al*. (2006).

Contaminants in Whole Fish
Indicator #121

Overall Assessment

Status: **Mixed**

Trend: **Improving**

Primary Factors Determining Status and Trend

Whole fish are monitored by both EPA GLNPO and Environment Canada to determine the effects of contaminant concentrations on wildlife and monitor trends. Both governments collect and analyze whole fish independently from a variety of locations within each Great Lake using different methods. The differences between the two programs, collection sites in all 5 Great Lakes, and differences in species yield a mixed status for the basin as a whole.**

**** In the spring of 2006, Environment Canada assumed the responsibilities of the Department of Fisheries and Ocean (DFO) Fish Contaminant Surveillance Program. All data included in this indicator report were produced by DFO.**

Lake-by-Lake Assessment PCB and DDT levels are measured in lake trout and walleye while only smelt samples have recent Hg trend data available.

Lake Superior

Status: Fair

Trend: Improving

Primary Factors Determining Status and Trend

Concentrations of Total PCBs show little change and Total DDT show fluctuating concentrations while mercury concentrations continue to decline. Total PCB concentrations remain above GLWQA criteria while Total DDT and mercury remain below. Contaminants in Lake Superior are typically atmospherically derived. The dynamics of Lake Superior allow for the retention of contaminants much longer than any other lake.

Lake Michigan

Status: Fair

Trend: Improving

Primary Factors Determining Status and Trend

Concentrations of Total PCBs and Total DDT are both declining. Total PCBs remain above GLWQA criteria and Total DDT remains below. Food web changes are critical to Lake Michigan contaminant concentrations, as indicated by the failure of the alewife population in the 1980's and the presence of the round goby. Aquatic invasive species, such as asian carp, are also of major concern to the lake due to the connection of Chicago Sanitary and Ship canal and the danger they pose to the food web.

Lake Huron

Status: Fair

Trend: Improving

Primary Factors Determining Status and Trend

Both Total PCBs and DDT show general declines in concentrations while mercury displays flux in concentration. Total PCB concentrations remain above GLWQA criteria while Total DDT and mercury remain below.

	Contaminant loading to Saginaw Bay continues to be reflected in fish tissue.

Lake Erie

Status:	Fair
Trend:	Improving
Primary Factors Determining Status and Trend	Total PCBs and DDT show a pattern of annual concentration increases linked to changes in invasive species populations, such as zebra and guagga mussels. Aquatic invasive species are of major concern to Lake Erie because the pathways and fate of persistent toxic substances will be altered resulting in differing accumulation patterns, particularly near the top of the food chain. Mercury concentrations are the highest ever recorded in Lake Erie. Total PCB concentrations remain above GLWQA criteria while Total DDT and mercury remain below.

Lake Ontario

Status:	Fair
Trend:	Improving
Primary Factors Determining Status and Trend	Both Total PCBs and DDT show a pattern of decline while mercury concentrations show little change. Total PCB concentrations remain above GLWQA criteria while Total DDT and mercury remain below. Historic point sources of mirex and OCS in Lake Ontario have resulted in the highest concentration of these contaminants in any of the Great Lakes. The presence of contaminants of emerging concern, such as PBDEs and PFOS, continue to raise alarm in Lake Ontario, due to their continuing increases in concentration over time.

Purpose

- •To describe temporal and spatial trends of bioavailable contaminants in representative open water fish species from throughout the Great Lakes;
- •To infer the effectiveness of remedial actions related to the management of critical pollutants; and “To identify the nature and severity of emerging problems”.

Ecosystem Objective

Great Lakes waters should be free of toxic substances that are harmful to fish and wildlife populations and the consumers of this biota. Data on status and trends of contaminant conditions, using fish as biological indicators, support the requirements of the Great Lakes Water Quality Agreement (GLWQA, United States and Canada. 1987) Annexes 1 (Specific Objectives), 2 (Remedial Action Plans and Lakewide Management Plans), 11 (Surveillance and Monitoring), and Annex 12 (Persistent Toxic Substances).

State of the Ecosystem

Background

Long-term (>25 yrs), basin-wide monitoring programs that measure whole body concentrations of contaminants in top predator fish (lake trout and/or walleye) and in forage fish (smelt) are conducted by the U.S. Environmental Protection Agency (USEPA) Great Lakes National

Program Office (GLNPO) through the Great Lakes Fish Monitoring Program and Environment Canada (EC), formerly DFO, through the Fish Contaminants Surveillance Program. Canada reports annually on contaminant burdens in similarly aged lake trout (4+ - 6+ year range), walleye (Lake Erie), and in smelt. GLNPO annually monitors contaminant burdens in similarly sized lake trout (600-700 mm total length) and walleye (Lake Erie, 400-500 mm total length) from alternating locations by year in each lake.

Chemical Concentrations in Whole Fish Great Lakes Fish:
Since the late 1970s, concentrations of historically regulated contaminants such as polychlorinated biphenyls (PCBs), dichlorodiphenyl-trichloroethane (DDT) and mercury have generally declined in most monitored fish species. The concentrations of other contaminants, both currently regulated and unregulated, have demonstrated either slowing declines or, in some cases, increases in selected fish communities. The changes are often lake-specific and relate both to the characteristics of the substances involved and the biological composition of the fish community.

The GLWQA, first signed in 1972 and renewed in 1978, expresses the commitment of Canada and the United States to restore and maintain the chemical, physical and biological integrity of the Great Lakes basin ecosystem. When applicable, contaminant concentrations are compared to GLWQA criteria.

Σ PCBs –Total PCB concentrations in Great Lakes top predator fish have continuously declined since their phase out in the 1970s. However, rapid declines are no longer observed and concentrations in fish remain above the EPA wildlife protection value of 0.16 ppm and the GLWQA criteria of 0.1 ppm. Concentrations remain high in top predator fish due to the continued release of uncontrolled sources and their persistent and bioaccumulative nature.

Σ DDT – Total DDT concentrations in Great Lakes top predator fish have continuously declined since the chemical was banned in 1972. However, large declines are no longer observed. But rather, very small annual percent declines indicating near steady state conditions. It is important to note that the concentrations of this contaminant remain below the GLWQA criteria of 1.0 ppm. There is no EPA wildlife protection value for total DDT because the PCB value is more protective.

Mercury – Concentrations of mercury are similar across all fish in all lakes. It is assumed that concentrations of mercury in top predator fish are atmospherically driven. It is important to note that current concentrations in GLNPO top predator fish in all lakes remain above the GLWQA criteria of .5 ppm and that Canadian smelt have never been observed to be above the GLWQA criteria.

Σ Chlordane – Concentrations of total chlordane have consistently declined in whole top predator fish since the EPA banned it in 1988. Total Chlordane is composed of cis and trans-chlordane, cis and trans-nonachlor, and oxychlordane, with trans-nonachlor being the most prevalent of the compounds. While trans-nonachlor was the minor component of the total chlordane mixture, it is the least metabolized and predominates within the food web (Swackhamer, 2006).

Mirex – Concentrations of mirex are highest in Lake Ontario top predator fish due to its continued release from uncontrolled historic sources near the Niagara River.

Dieldrin – Concentrations of dieldrin in lake trout appear to be declining in all Lakes and are lowest in Lake Superior and highest in Lake Michigan. Concentrations in Lake Erie walleye were the lowest of all lakes. Aldrin is readily converted to dieldrin in the environment. For this reason, these two closely related compounds (aldrin and dieldrin) are considered together by regulatory bodies.

Toxaphene – Decreases in toxaphene concentrations have been observed throughout the Great Lakes in all media following its ban in the mid- 1980's. However, concentrations have remained the highest in Lake Superior due to its longer retention time, cold temperatures, and slow sedimentation rate. It is assumed that concentrations of toxaphene in top predator fish are atmospherically driven (Hites, 2006).

PBDEs – Both the US and Canada analyze for PBDEs in whole top predator fish. Retrospective analyses of archived samples have demonstrated the continuing increase in concentrations of polybrominated diphenyl ethers (PBDE) and are confirmed by present day concentrations in top predator fish. It is important to note that the concentration of most other persistent organic pollutants in top predator fish have declined, while PBDEs continue to increase.

Other Contaminants of Emerging Interest:
One of the most widely used BFRs is hexabromocyclododecane (HBCD). Based on its use pattern as an additive BFR, it has the potential to migrate into the environment from its application site. Recent studies have confirmed that HBCD isomers do bioaccumulate in aquatic ecosystem and do biomagnify as they move up the food chain. Recent studies by Tomy *et al.* (2004) confirmed the food web biomagnification of HBCD isomers in Lake Ontario (Table 4).

Perfluoroctanesulfonate (PFOS) has also been detected in fish throughout the Great Lakes and has also demonstrated the capacity for biomagnification in food webs. PFOS is used in surfactants such as water repellent coatings (i.e. Scotchguard ™) and fire suppressing foams. It has been identified in whole lake trout samples from all the Great Lakes at concentrations from 3 to 139 ng/g wet weight (Stock *et al.* 2003). In addition, retrospective analyses of archived lake trout samples from Lake Ontario have identified a 4.25-fold increase (43-180 ng/g wet weight, whole fish) from 1980 to 2001 (Martin *et al.*, 2004).

Pressures
Current – The impact of invasive nuisance species on toxic chemical cycling in the Great Lakes is still being investigated. The number of non-native invertebrates and fish species proliferating in the Great Lakes basin continues to increase, and they continue to spread more widely. Changes imposed on the native fish communities by non-native species will subsequently alter ecosystem energy flows. As a consequence, the pathways and fate of persistent toxic substances will be altered, resulting in different accumulation patterns, particularly at the top of the food web. Each of the Great Lakes is currently experiencing changes in the structure of the aquatic community, and hence there may be periods of increases in contaminant burdens of some fish species.

A recently published, 15 year retrospective Great Lakes study showed that lake trout embryos and sac fry are very sensitive to toxicity associated with maternal exposures to 2,3,7,8-

tetrachlorodibenzo-p-dioxin (TCDD) and structurally related chemicals (Cook *et al*. 2003). The increase in contaminant load of TCDD may be responsible for declining lake trout populations in Lake Ontario. The models used in this study can be used in the other Great Lakes.

Future - Additional stressors in the future will include climate change, with the potential for regional warming to change the availability of Great Lakes critical habitats, change the productivity of some biological communities, accelerate the movement of contaminants from abiotic sources into the biological communities, and effect the composition of biological communities. Associated changes in the concentration of contaminants in the water, critical habitat availability and reproductive success of native and non-native species are also factors that will influence trends in the quantity of toxic contaminants in the Great Lakes basin ecosystem.

Management Implications

Much of the current, basin-wide, persistent toxic substance data that is reported focuses on legacy chemicals whose use has been previously restricted through various forms of legislation. There are also a variety of other potentially harmful contaminants at various locations throughout the Great Lakes that are reported in literature. A comprehensive, basin-wide assessment program is needed to monitor the presence and concentrations of these recently identified compounds in the Great Lakes basin. The existence of long-term specimen archives (>25 yrs) in both Canada and the United States could allow retrospective analyses of the samples to determine if concentrations of recently detected contaminants are changing. Further control legislation might be needed for the management of specific chemicals.

Acknowledgments

Authors: Elizabeth Murphy, U.S. Environmental Protection Agency, Great Lakes National Program Office;
Cameron MacEachen, Environment Canada; D. Michael Whittle, Emeritus, Great Lakes Laboratory for Fisheries and Aquatic Sciences, Michael J. Keir, Environment Canada, and J. Fraser Gorrie, Bio-Software Environmental Data.

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Figure 1. Total PCBs levels in Even Year whole Lake Trout (Walleye in Lake Erie), 1972 - 2002 μg/g wet weight +/- 95% C.I., composite samples. Lake Trout = 600 - 700 mm size range. *Fish collected between 1972 and 1982 were collected at even year sites only. Walleye = 450 - 550 mm size range. Source: U.S. Environmental Protection Agency

Figure 2. Total PCBs levels in Odd Year whole Lake Trout (Walleye in Lake Erie), 1991 – 2003 μg/g wet weight +/- 95% C.I., composite samples. Lake Trout = 600 - 700 mm size range. Walleye = 450 - 550 mm size range. Source: U.S. Environmental Protection Agency

Figure 3. Total PCBs in 4 to 6 year old individual whole Lake Trout collected 1977 through 2005, μg/g wet weight. Source: Fisheries and Oceans Canada.

Figure 4. Total PCBs in composite rainbow smelt collected 1977 through 2005, μg/g wet weight. Source: Fisheries and Oceans Canada.

Figure 5. DDT levels in Even Year whole Lake Trout (Walleye in Lake Erie), 1972 - 2000. μg/g wet weight +/- 95% C.I., composite samples. Lake Trout = 600 - 700 mm size range. *Fish collected between 1972 and 1982 were collected at even year sites only. Walleye = 450 - 550 mm size range. Source: U.S. Environmental Protection Agency

Figure 6. DDT levels in Odd Year whole Lake Trout (Walleye in Lake Erie), 1991 - 2001. μg/g wet weight +/- 95% C.I., composite samples. Lake Trout = 600 - 700 mm size range. Walleye = 450 - 550 mm size range. Source: U.S. Environmental Protection Agency

Figure 7. Total DDT in 4 to 6 year old individual whole Lake Trout collected 1977 through 2005, μg/g wet weight. Source: Fisheries and Oceans Canada.

Figure 8. Total DDT in composite rainbow smelt collected 1977 through 2005, μg/g wet weight. Source: Fisheries and Oceans Canada.

Figure 9. Interactive GIS map of basin and web link

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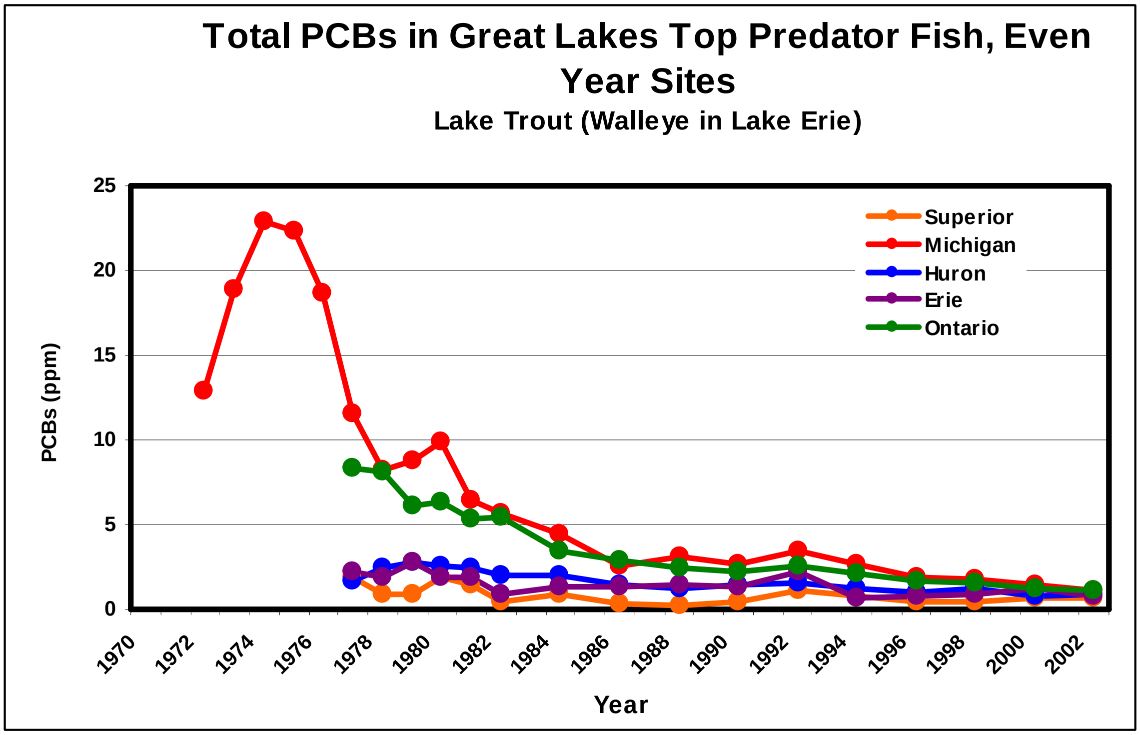

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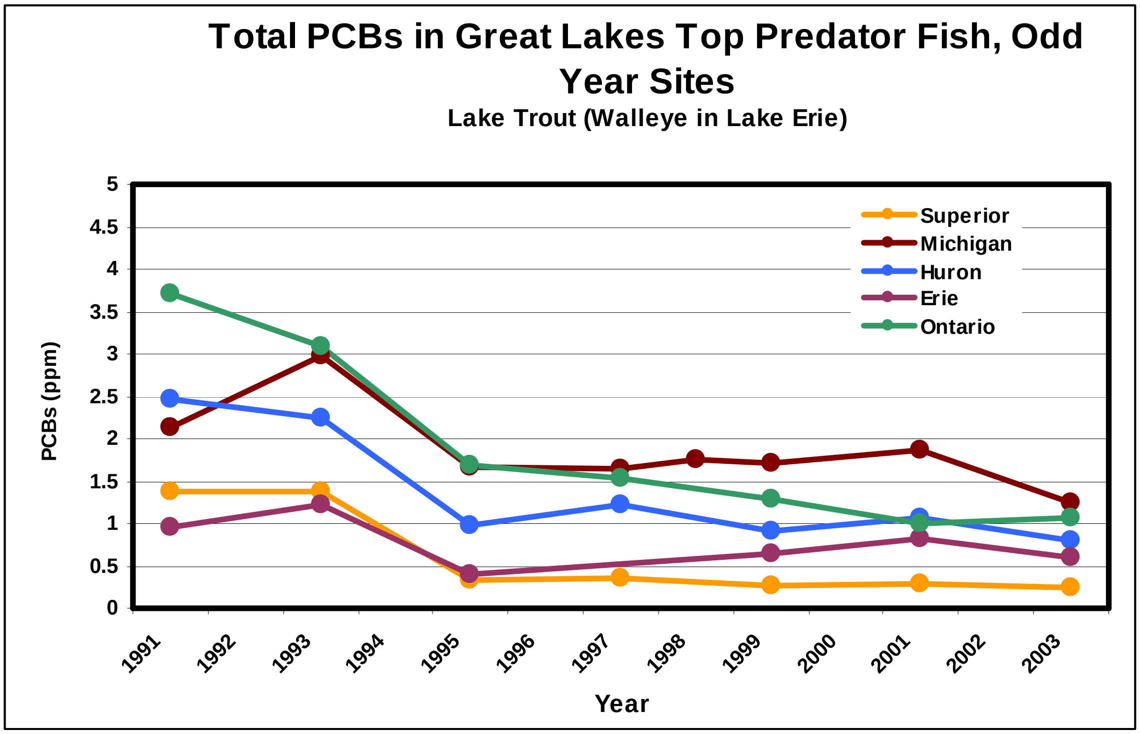

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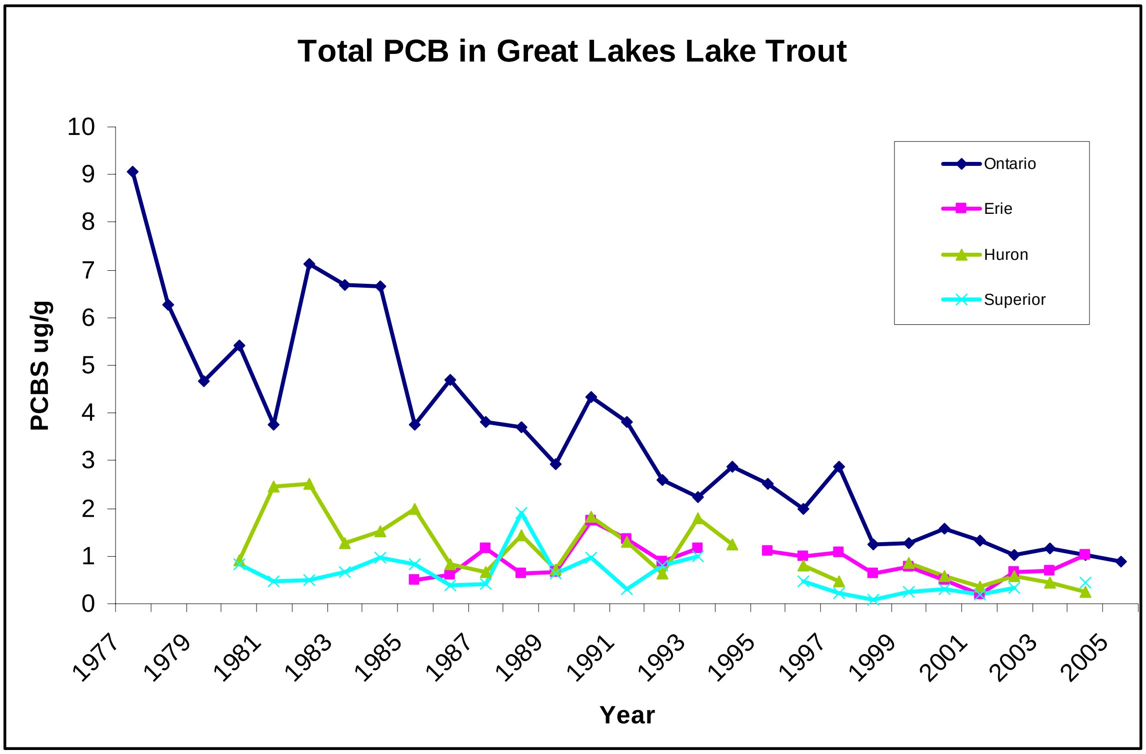

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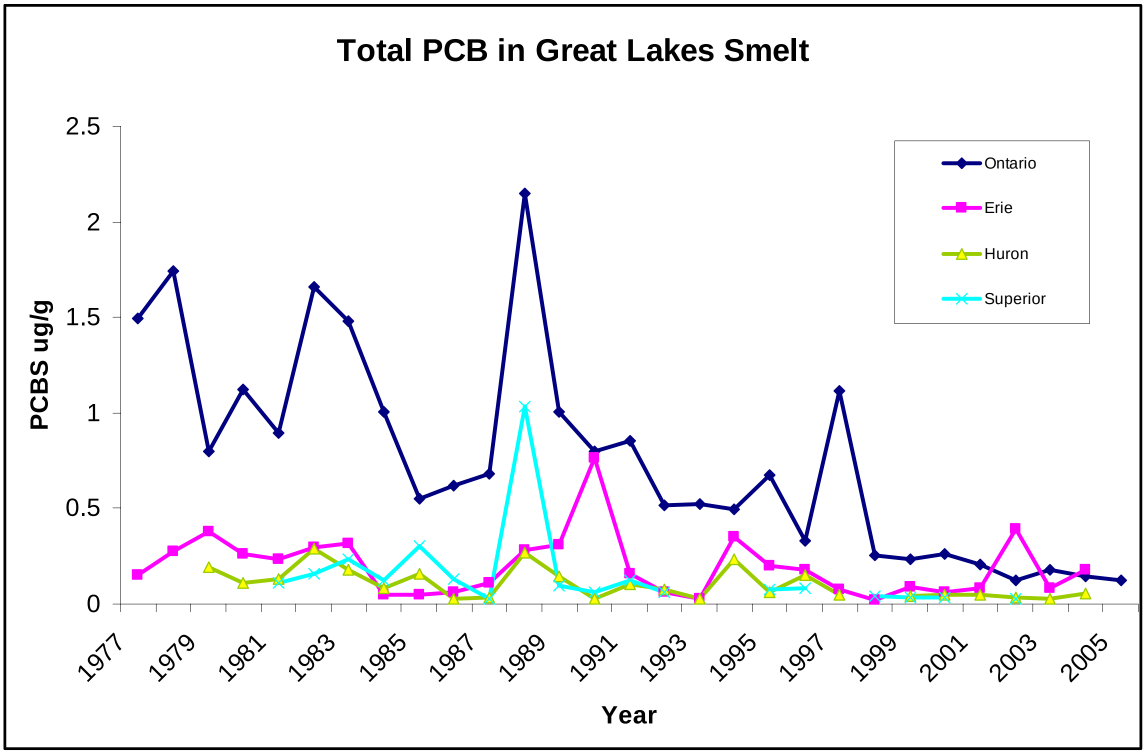
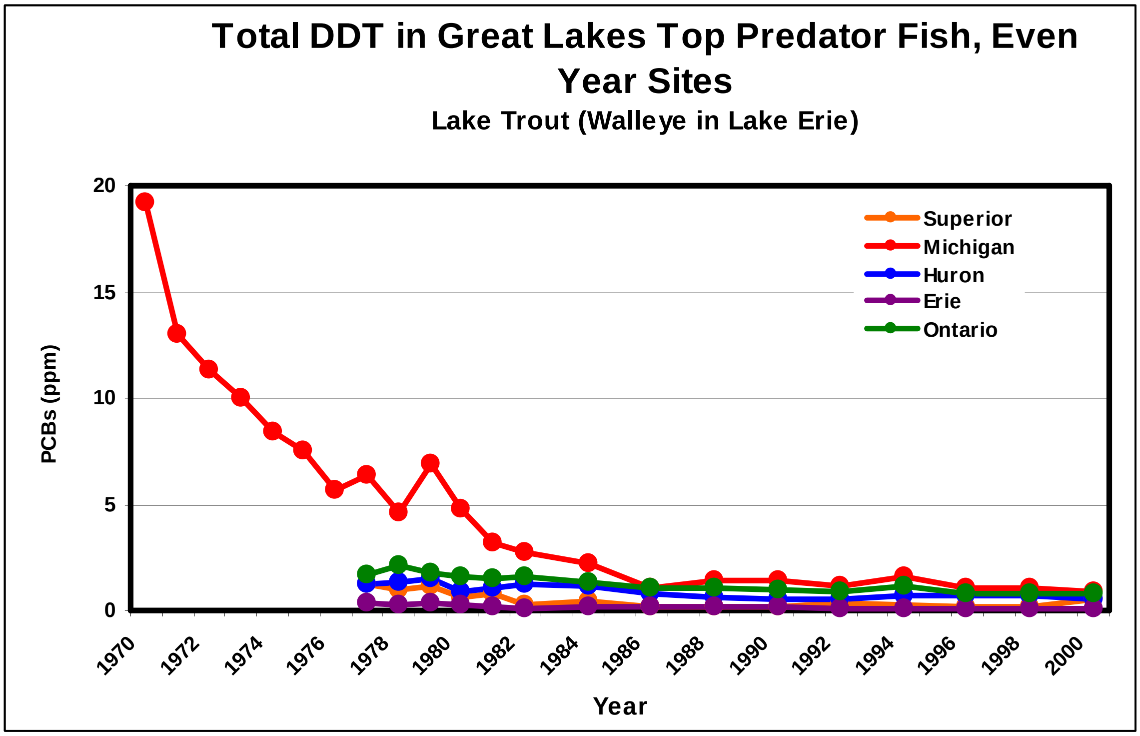


Figure 4. Total PCBs in composite rainbow smelt collected 1977 through 2005, µg/g wet weight.
Source: Fisheries and Oceans Canada



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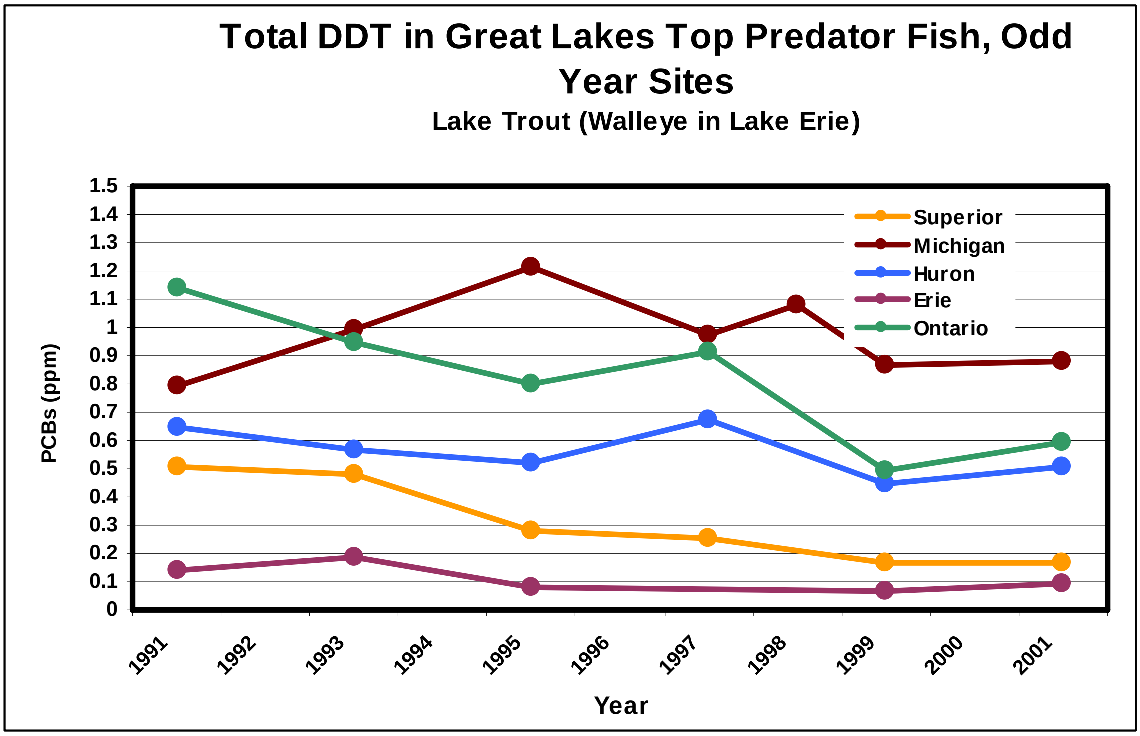

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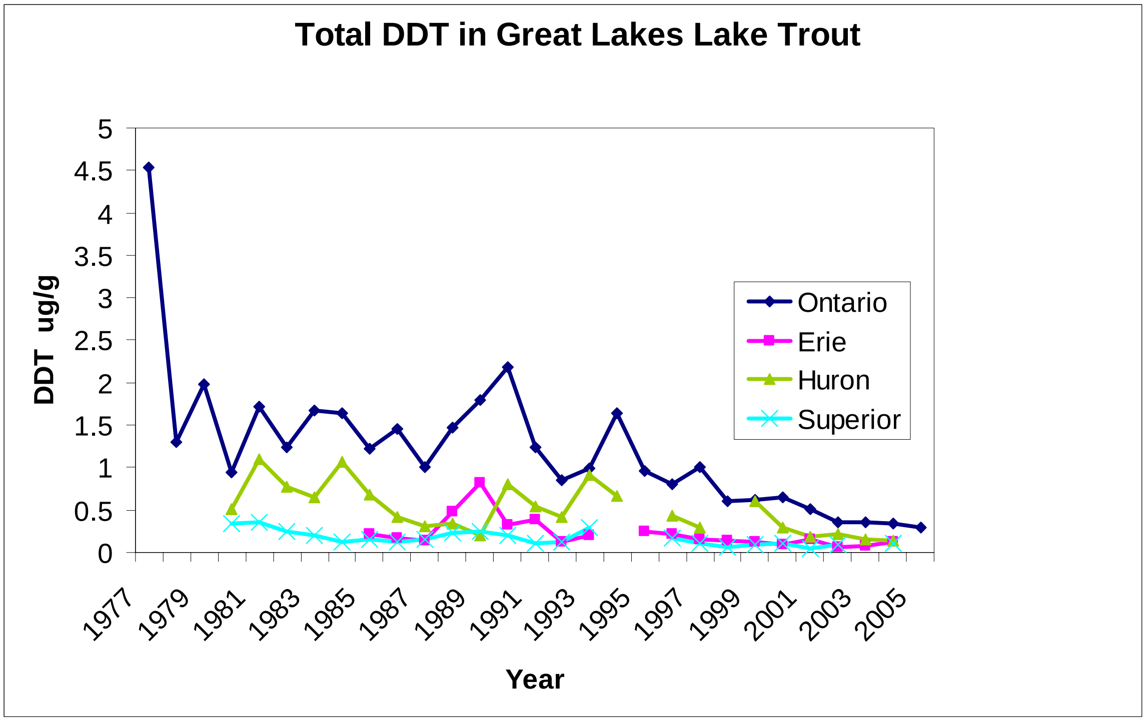

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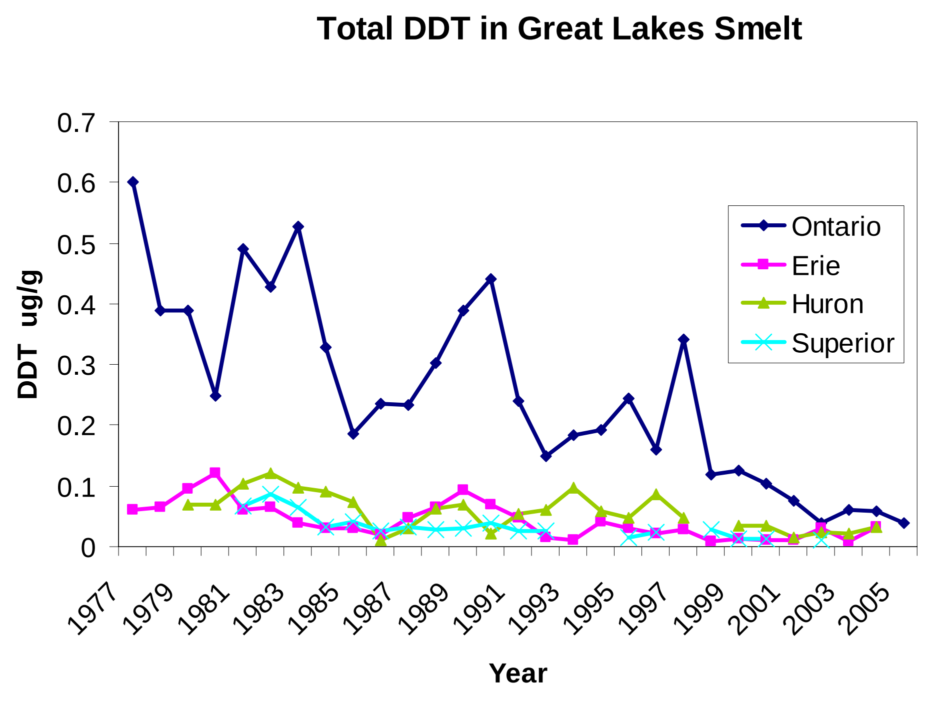

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