

Toxic Chemical Concentrations in Offshore Waters

Indicator #118

Overall Assessment

Status: **Mixed**
 Trend: **Undetermined**
 Rationale: **Data for this indicator are 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.

Lake-by-Lake Assessment

Lake Superior

Status: Fair
 Trend: Undetermined
 Rationale: Thirteen of a possible 21 organochlorine pesticide compounds (OCs) were detected in Lake Superior and their concentrations were generally very low. Mercury concentrations were very low offshore with higher concentrations near Thunder Bay and Duluth. Polycyclic aromatic hydrocarbons (PAHs) are present throughout Lake Superior at extremely low concentrations.

Lake Michigan

Status: Fair
 Trend: Undetermined
 Rationale: Concentrations of PCBs and organochlorine pesticides have either decreased slightly or remained constant since the mid-1990s. Total mercury concentrations in 2005 were below water quality criterion for protection of wildlife. Atrazine concentrations in the open lake waters were well below drinking water criteria.

Lake Huron

Status: Fair
 Trend: Undetermined
 Rationale: In 2004, 16 of a possible 21 organochlorine compounds were detected in Lake Huron, but only 11 were commonly found, including hexachlorocyclohexane (HCH), lindane, dieldrin, and chlordane. The concentrations were generally low, reflecting historical or diffuse sources. Mercury and PAH concentrations in Lake Huron and Georgian Bay are low.

Lake Erie

Status: Mixed
 Trend: Undetermined
 Rationale: In 2004, 15 of a possible 21 organochlorine compounds were detected in Lake Erie, including HCH, hexachlorobenzene (HCB), lindane and dieldrin. Concentrations of most compounds were highest in the shallow western basin and much lower in the central and eastern basins. Mercury concentrations in 2005 were the highest of the Great Lakes and reflected a decreasing concentration from west to east. PAH concentrations and distributions reflected urban source areas and upstream sources within the St. Clair River – Detroit River corridor.

Lake Ontario

Status: Mixed
 Trend: Undetermined
 Rationale: Seventeen of a possible 21 organochlorine pesticides were detected in Lake Ontario waters in 2005. Dieldrin, lindane, and HCH were routinely found. Mercury concentrations in Lake Ontario were low in the offshore areas and higher in the nearshore, but only samples taken from Hamilton Harbour exceeded the criteria of 1.3 ng/L. PAH distribution and concentrations reflected urban source areas.

Purpose

- To assess the concentration of priority toxic chemicals in offshore waters
- To infer the potential for impacts on the health of the Great Lakes aquatic ecosystem by comparison to criteria for the protection of aquatic life and human health
- To infer progress toward virtual elimination of toxic substances from the Great Lakes basin

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 (Great Lakes Water Quality Agreement Article III(d), United States and Canada 1987).

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 2006 Progress report.

Surveys conducted between 1992 and 2000 (Marvin *et al.* 2004) and during 2004-2005 (Environment Canada Great Lakes Surveillance Program, unpublished data) on Lake Superior, Lake Huron, Lake Erie and Lake 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, γ -HCH, lindane (γ -HCH), and heptachlor epoxide were the only OC pesticide compounds routinely detected in Lake Superior, Lake Erie and Lake Ontario (Marvin *et al.* 2004). The in-use herbicides atrazine and metolachlor were ubiquitous (Marvin *et al.* 2004). Generally, organochlorine pesticide concentrations exhibit a north to south gradient from lowest to highest (Lake Superior less than Lake Huron, Lake Huron less than Lake Ontario, Lake Ontario less than Lake Erie). An example of the spatial distribution of dieldrin using 2004-2005 data is provided in Figure 1.

Many organic compounds (such as PCBs, HCB, octachlorostyrene (OCS), and DDT) show a spatial pattern that 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.

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).

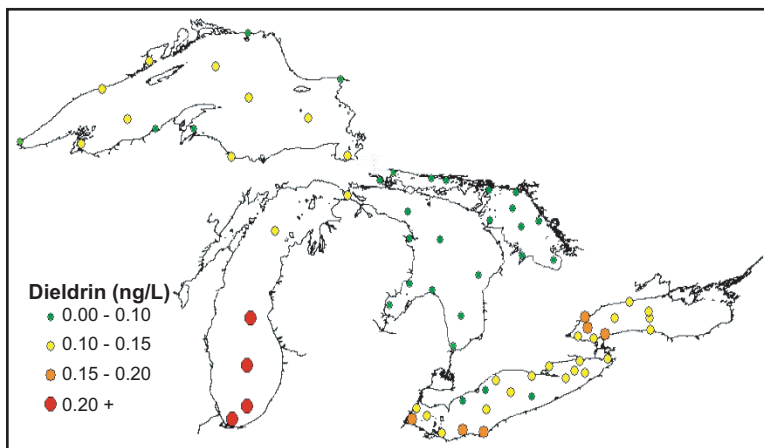


Figure 1. Great Lakes 2004/05 Open Lake, Spring Cruise, Concentrations of Dieldrin (ng/L).

Lake Ontario data for western half of the lake only.

Source: Environment Canada's Great Lakes Water Quality Surveillance Program, Burlington, Ontario

Currently-emitted compounds, such as PAHs, which are released during fossil fuel combustion, also show spatial patterns that are

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indicative of sources. 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. 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.

Mercury concentrations overall are very low, and concentrations in the open lake areas are currently below the U.S. EPA Great Lakes Initiative (GLI) water quality criterion of 1.3 ng/L (U.S. EPA 2006). However, higher concentrations are observed in the western basin of Lake Erie in particular, and in some harbors and major urban areas as well (e.g., Detroit, Hamilton, Duluth/Superior Harbor, Rochester, Chicago; Figure 2). Some samples from these urban areas exceed the GLI water quality criterion for protection of wildlife.

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 Superior

Thirteen of a possible 21 organochlorines (OCs) 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 1) reflect its usage in the agricultural communities of the southern Great Lakes basin and are low in Lake Superior (2005: open lake average of 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 of 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 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 (Rutherford *et al.* 1999). 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

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. Total mercury concentrations

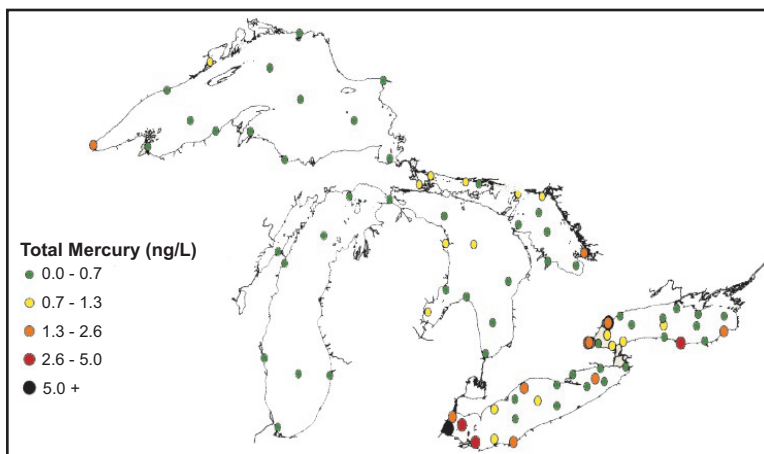


Figure 2. Great Lakes 2003-2005 Open Lake, Spring Cruise, Concentrations of Total Mercury (ng/L).

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

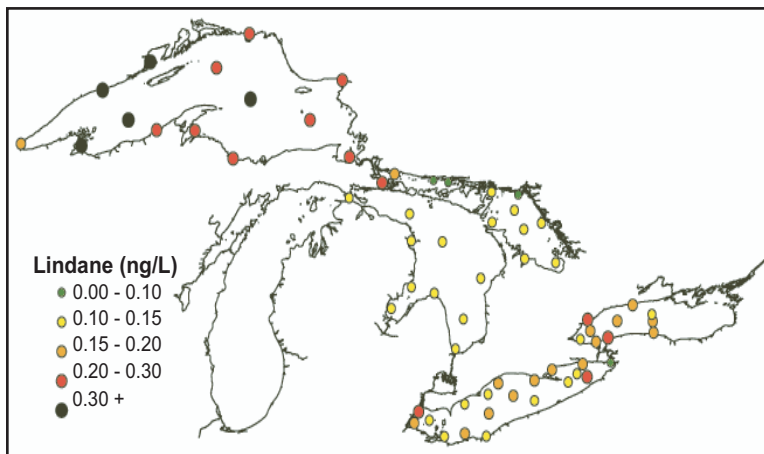


Figure 3. Great Lakes 2004/05 Open Lake, Spring Cruise, Concentrations of Lindane (ng/L).

Lake Ontario data for western half of the lake only.

Source: Environment Canada's Great Lakes Water Quality Surveillance Program, Burlington, Ontario

in 2005 were all below the 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

In 2004, 16 of a possible 21 organochlorine pesticides were detected in Lake Huron, but only 11 were commonly found. Commonly found OCs included α -HCH, lindane, dieldrin, and γ -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 GLI water quality criterion for protection of wildlife of 1.3 ng/L (Figure 2), 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)anthracene, 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

Environment Canada's Great Lakes Surveillance Program detected 15 of a possible 21 organochlorine compounds in Lake Erie. Ten of these were commonly found, including α -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 HCB and OCS 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 Lake Erie 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,

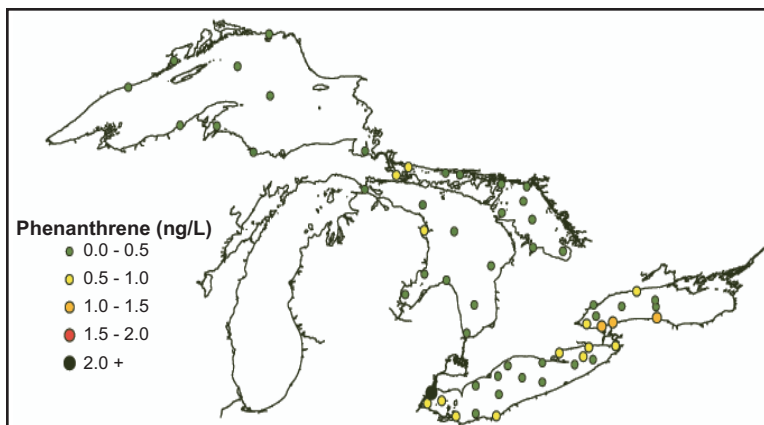


Figure 4. Great Lakes 2004/05 Open Lake, Spring Cruise, Concentrations of Phenanthrene (ng/L).

Source: Environment Canada's Great Lakes Water Quality Surveillance Program, Burlington, Ontario

whereas the overall Lake average was 0.59 ng/L, an almost 5-fold difference.

Lake Ontario

Seventeen of a possible 21 OC pesticides were detected in Lake Ontario waters in 2005. Dieldrin, lindane, and γ -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 ng/L) 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 Lake Ontario (e.g., Rochester, NY, Niagara River, and Hamilton, Ontario). All offshore concentrations were below Ontario Water Quality Guidelines.

Management Implications

Management efforts to control inputs of organochlorine pesticides have resulted in decreasing concentrations in the Great Lakes. Historical sources for some compounds, however, 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 developed 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 are 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, PAHs, trace metals including mercury, as well as a limited number of in-use pesticides and other compounds of emerging concern.

In 2003, U.S. EPA initiated a monitoring program for toxic contaminants 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 U.S. EPA 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.

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)

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

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Sources

Data

Data for Lake Superior, Lake Huron, Lake Erie and Lake Ontario are from Environment Canada, Great Lakes Water Quality Monitoring and Surveillance Program.

Data for Lake Michigan are from U.S. EPA, Great Lakes Aquatic Contaminant Surveillance (GLACS) program (Principal Investigators: Dr. Matt Simcik, University of Minnesota and Dr. Jeff Jeremiason, Gustavus Adolphus College).

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Last Updated

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