Contaminants in Great Lakes Environs

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The five Great Lakes touch eight states in the US from Minnesota East to New York and the Province of Ontario, Canada (see map, Figure 13.2). All but Lake Michigan are shared with Canada. A full description of the history and characterisation of the Great Lakes, including sizes, water depths and flow patterns, can be viewed at http://www.epa.gov/glnpo. The lakes provide hydroelectric energy, cooling water for coal, oil, gas and nuclear fuelled steam generated electricity and water for numerous industries including lumber, agriculture, fishing and shipping. Over 30 million people live in the Great Lakes Basin, and use the lakes for recreation and drinking water. Some of the beneficial uses of the lakes are compromised by the numerous contaminants affecting the air, water and land of the Great Lakes Basin including pathogens, nutrients, chemicals and metals with varying toxicity, and non-native species. The contaminants are introduced to the basin from industrial activities, municipal sewage overflows, private septic systems, pesticide applications, contaminated run-off from urban areas and cropland, both wild and domestic animal waste, ship ballast water harbouring alien species and through the atmosphere (see http://www.epa.gov/glnpo).

There are thousands of chemicals and biological organisms, both naturally occurring and those resulting from human activity, that abound in the environment. Biota and ecosystems have evolved the means to alleviate the physiological stress of exposure to contaminants that have existed since pre-historic times. However, some of the more recent introductions of chemical and biological stressors have disrupted the natural accommodation and caused ecosystem damage (polluted air and water resulting in retarded bird reproduction, fish kills and other disruptions of wildlife), eutrophication and hypoxia from excess nutrients, human respiratory ailments, systemic poisoning, cancer and many other impacts to life on earth.

Many contaminants result from activities that provide useful products and processes for humans and society. The benefits of automobiles, electrical equipment, functional metals and polymers, fuels, fluids, pest control, coatings, adhesives, economical food production, etc. come with some hazards. We recognise some of the hazards (toxicity during manufacture and use, fertiliser run-off to waters, pesticide food residues, air and water emissions, mechanical hazards, potential explosions, accidental releases), which can be mitigated through design and various regulations for delivery and use. However, later we may find unanticipated contamination of air, water, avian and aquatic life, soil from wastes, long-range

*Deceased
transport from distant sources, the long-term presence of persistent contaminants, unknown health effects of continuous exposure to multiple chemical contaminants, and loss of beneficial uses due to ecosystem damage.

The following sections discuss some of the known effects of the various classes of pollutants on air, water and land, and provide references for more complete data and analysis. In the end, humans are concerned that the air they breathe is free of harmful pollutants, the water is safe to drink, the beaches are safe for swimming, the fish and wildlife contain no toxic residues, and the land they are exposed to is free of poisonous substances. The following contaminant groups were selected for consideration here, but there are others (e.g. nanoparticles) that may deserve research and regulatory consideration:

1. Currently used pesticides and other toxic chemicals
2. Persistent, bioaccumulative and toxic substances (PBTs)
3. Trace metals
4. Pharmaceuticals and personal care products (PPCPs)
5. Airborne contaminants

Currently Used Pesticides and other Toxic Chemicals in the Great Lakes

As with any toxic substance, we seek to answer the following:

1. What are the sources of the toxins of concern?
2. What quantities are being released?
3. What is the environmental fate? i.e. where do the toxins go?
4. Exposure and hazards to humans, wildlife and ecosystems.

Agriculture continues to rely on pesticides for the control of weeds, insects and fungal diseases. The 2007 State of the Great Lakes Report on Pesticide Management quoted an estimate of 21 million kg of pesticides used annually on agricultural crops in the Great Lakes watershed based upon a 1993 GAO report (GAO, 1993). A revised estimate was made using the US Department of Agriculture’s National Agricultural Statistics Service Database for pesticide use on major crops in the principal states bordering the Great Lakes (MI, NY, OH and WI). Comparing the pesticide usage in 1993/94 and 2005, several significant changes in pesticide use occurred over the 11-year period. Reductions occurred due to changes in cropping patterns, integrated pest management and the expanded use of genetically modified crops. Herbicides continued to dominate pesticide use, with atrazine remaining the leading herbicide, with little change in use. However, metolachlor and alachlor use declined in favour of acetochlor and glyphosate. Increased use of glyphosate-tolerant crops (principally soybean) over the 11-year period was a contributing factor. Overall, herbicide use in the basin was estimated to have declined by about 20% to a level of around 16-18 million kg per year. Agricultural insecticide use also declined by about 70%, with the use of plant incorporated protectants, such as Bt corn, playing an important role.

Pesticides applied to agricultural crops move through the environment in several ways. Some of the pesticides applied are absorbed by the plants with residues remaining in the food crop; some vaporise and are carried away in air currents; some are retained in the soil; some move through the soil to groundwater, and some are washed away and mixed into surface waters. Most of the currently used pesticides are not persistent to the extent exhibited by the former highly chlorinated pesticides such
as DDT and chlordane. Hence, currently used pesticides retained in the soil can eventually degrade by the action of soil chemicals and microorganisms. However, pesticides entering groundwater or surface waters are little degraded because of low concentrations of microorganisms and lower temperatures.

An analysis of the pesticides found in the nation's waters has been carried out under the by the US Geological Survey’s NAWQA Program (National Water-Quality Assessment Program). The NAWQA studies included two areas of the Great Lakes basin: Lake Erie-Lake Saint Clair drainages, and western Lake Michigan drainage. The samples were taken from streams, but did not include finished drinking water. Over 30 pesticides were detected, with the most heavily applied herbicides, atrazine, metolachlor, acetochlor, and alachlor, being most frequently detected in agricultural areas, and the insecticides diazinon, chlorpyrifos and malathion more frequently found in urban areas. While the time weighted average of the concentrations of each pesticide are below the individual regulatory MCL (Maximum contaminant levels) for drinking water (http://water.epa.gov/drink/contaminants/index.cfm#List), peak values of atrazine following application and rainfall reach concentrations well above the MCL in May or June.

The US EPA has set the following standards for protection of human health and aquatic life at the following values for atrazine:

<table>
<thead>
<tr>
<th>Standard</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drinking MCL</td>
<td>3 µg/L</td>
</tr>
<tr>
<td>Aquatic life criteria for acute effects (proposed)</td>
<td>350 µg/L</td>
</tr>
<tr>
<td>Aquatic life criteria for chronic effects (proposed)</td>
<td>12 µg/L</td>
</tr>
</tbody>
</table>

Environment Canada studied the presence of pesticides in the waters of the four Great Lakes that are shared with the US (http://www.on.ec.gc.ca). Their findings were similar to those of the NAWQA study, with 33 pesticides being detected. As expected, the herbicides in greatest use were found to have the highest concentrations. Atrazine showed peak values of 1 µg/L, metolachlor 0.7 µg/L, and simazine 0.28 µg/L. Lake Erie had the highest concentrations, followed by Lakes Ontario, Huron and Superior. No pesticide was found to exceed the water quality criteria established for the pesticide. The US Environmental Protection Agency’s (EPA) Mass Balance Study (http://www.epa.gov/greatlakes/lakemich/study.pdf) for Lake Michigan measured PCBs, mercury, trans-nonachlor and atrazine in rivers, air, sediments, lake water and the food chain. A mathematical model was developed to predict the effects that increases or decreases of pollution will have on the lake and its large fish (lake trout and coho salmon). The study measured the concentration of atrazine as a marker for currently used pesticides in waters of the lake. Open water concentrations ranged from 33.0 to 48.0 ng/L, with average values increasing from 37.0 to 39.7 ng/L over the one-year period of the study.

The EPA Office of Pesticide Programs (http://www.epa.gov/pesticides) registers pesticides using a system of risk assessment that is designed to ensure that exposure is minimal when used according to pesticide labels. New information regarding toxicity, exposure, or environmental damage can result in more restrictive use, as has occurred recently with chlorpyrifos and diazinon, for which residential uses were removed. Pesticides are widely used on crops producing food. Because such applications have the potential to result in high residues of pesticides in the food products, the EPA sets tolerance limits for pesticide residues in food under the authority of the Federal Food, Drug and Cosmetic Act. The US Department of Agriculture (USDA) monitors crops and foods for residual pesticides annually. The latest report for 2006 includes five of the eight Great Lakes states, and continues to report a safe food supply, with residues rarely found above the allowed tolerance levels set by EPA (Pesticide Data Program, USDA Agricultural Marketing Service).

**Legacy Pesticides and Other Persistent Bioaccumulative and Toxic Chemicals (PBTs)**

PBTs are persistent, bioaccumulative and toxic compounds that continue to have an environmental presence, even though some are no longer in production. The past usage of ‘legacy pesticides’ (such as DDT, chlordane, toxaphene, etc.) and PCBs was large enough to cause widespread environmental contamination during the
years of their production, and, due to the resistance of these contaminants to degradation, they continue to be found in the environment. Despite bans on ‘open uses’ in 1973 and production in 1979, PCBs still remain in electrical transformers, capacitors and other equipment. The US production of DDT, the first pesticide to be used on a large scale, is reported to have reached a peak of 80-85 million kg in 1962. Polycyclic aromatic hydrocarbons (PAHs) are another important persistent and bioaccumulative group of concern. PAHs are formed by the incomplete combustion of organic matter, and occur both naturally (e.g. volcanoes, forest fires) and through anthropogenic activities such as combustion processes in industry, power plants, home heating, waste incineration (including rural backyard burning), etc.

To monitor the PBTs in air and precipitation, Canada and the US established the Integrated Atmospheric Deposition Network in 1990 to cover the Great Lakes region (http://www.ec.gc.ca/natchem/default.asp?lang=en&n=1590DD07-1). The network consists of seven major stations and several satellite stations. The latest IADN report covers the period up to 2003, and presents long-term temporal and spatial trends of atmospheric toxic substances in the Great Lakes Basin. Most contaminant groups (HCB, PCBs, organochlorine pesticides and PAHs) showed decreasing trends over time, with half-lives from 4 to over 15 years. Spatial analysis showed a high urban influence, with most contaminants increasing in the environment along with local human populations.

In another study, using an analysis of sediment cores from 38 lakes across the US to develop a historical record of persistent contaminant deposition, Van Metre and Mahler (2005) found that DDT (including metabolites) and PCBs have declined since production ceased in the 1970s, as expected, while PAHs have trended upward, with growing urban areas showing larger increases. These compounds are toxic to benthic biota, and PAH concentrations in sediments are increasingly rising above concentrations where adverse effects on benthic biota are likely.

Under the Clean Air Act (CAA), the EPA has listed 190 air toxics for consideration, and has selected 33 from a published list of 70 industrial sources for regulation of emissions (http://www.epa.gov/air/CAA/). Six pollutants, called criteria pollutants, are used as indicators of air quality. By 2006, these pollutants (carbon monoxide, ozone, lead, nitrogen dioxide, fine particulate matter and sulphur dioxide), had declined by 49% from the base year of 1980. The Great Waters Program, as part of the 1990 amendments to the CAA, was put in place to determine whether the current provisions of the CAA are sufficient to prevent atmospheric deposition of pollutants to the Great Lakes. The Great Waters Program found that the bioaccumulative pollutants that move up in the food chain, as noted in the PBT, Critical Contaminants and Fish Advisory sections (http://www.epa.gov/air/airtrends/sixpoll.html), play an important role in human and ecological health.

Radon is a naturally occurring product of uranium decay, and is estimated to cause 20,000 lung cancer deaths annually (http://www.epa.gov/radon/). Although not regulated, EPA and state partners have engaged in a nationwide campaign to inform citizens of the hazards of radon and instructions on testing their homes.

While the concentrations of the PBTs found in waters are generally below drinking water standards, they bioaccumulate in aquatic life to levels of concern such that fish consumption advisories are published by the Great Lakes states. Organised international efforts to reduce the presence of many of these PBTs include the Great Lakes Binational Toxic Strategy (BTS) between Canada, and the US, and the international agreement to control 12 Persistent Organic Pollutants (POPs) (http://www.pops.int/). The substances included in the BTS and POPs lists are shown in Table 13.1, along with the
"Critical Contaminants" identified by the Lakewide Area Management Programs (LaMPs) for the Great Lakes. The dates of discontinuance of the legacy pesticides can be found in the Pesticide Report of the BTS (http://www.epa.gov/gl npo).

Mercury is a critical contaminant and a major source of fish consumption advisories (http://www.epa.gov/gl npo; http://www.epa.gov/waterscience/models/maps). Mercury is transported through the atmosphere to the earth’s surface, where conversion to methyl mercury occurs in areas where certain anaerobic reducing conditions exist. It is the methylated form that is bioaccumulative in aquatic life and that leads to higher concentrations in fish. Coal combustion is an important source of mercury, but waste incineration, batteries, electrical switches, chloralkali production, thermometers, thermostats, medical equipment, dental amalgam and preservatives are additional uses that can have emissions to the environment.

Critical Contaminants for the Great Lakes

Of the thousands of potential contaminants, 12 have been identified by the programmes to protect the Great Lakes as critical on the basis of their toxicity, presence in the environment, and bioavailability. These critical contaminants are shown in Table 13.1 with sources and health concerns. Substances included in the BTS and the international agreement for POPs are listed for comparison. Table 13.1. Critical contaminants (condensed from http://www.great-lakes.net/humanhealth/fish/critical.html), Level I substances under the BTS are targeted for virtual elimination. Contaminants indicated as ‘L2’ are Level II substances listed for voluntary pollution prevention activities.

Over time, pollutants discharged to waters entering the Great Lakes are absorbed by particulate matter suspended in the waters. Such particles settle to the bottom of lakes, rivers and harbours and hold the contaminants in the bottom sediments until disturbed. Because of the need to dredge shipping channels and harbours, the toxicants bound to the sediments are re-introduced into the water column. As the result, there are 43 Areas of Concern (AOCs) in the Great Lakes basin, where approximately 200 contaminants have been detected in sediments. Concentrations of toxicants bound by the sediments are typically higher than concentrations found in the waters above. To address the problem of these highly contaminated areas, the US Congress has created ‘The Great Lakes Legacy Act’, which provides funds for the restoration of the AOCs (http://www.epa.gov/gl npo/sediment/legacy).

Fish Consumption Limits

Recommended limits on fish consumption may be necessary due to the bioaccumulation of contaminants through the food chain. Contaminants with water concentrations of just nanograms per litre can accumulate and magnify a million fold to concentrations of parts per million in fish. This is the case for toxaphene in Lake Superior where recommended fish consumption limits have been issued by the Province of Ontario, Canada. In the US, fish consumption limits for the ingestion of sport fish are produced by each state. The US EPA Office of Water (http://www.epa.gov/waterscience/) produces The National Listing of Fish Advisories (NLFA), based upon data from States and Tribes. Each state provides recommended limits for specific waters, and includes information on the species, size of fish, specific sub-populations (i.e. pregnant women), and recommended consumption rate. Five contaminants account for about 90% of the 2006 fish Advisories: mercury, PCBs, chlordane, dioxins, and DDT and its metabolites (DDE and DDD). While these substances are declining in the environment, they continue to be detected in fish, indicating that re-entry from contaminated sediments is likely still occurring (http://iisgcp.org).

Contaminants of Emerging Concern

Table 13.1 shows a list of the contaminants of current concern in the Great Lakes basin, the Great Lakes Binational Toxics Strategy and International list of 12 Persistent Organic Pollutants (POPs). However, in addition to these well recognised pollutants, there are other chemicals increasingly present in the environment.
Table 13.1. Critical contaminants (condensed from http://www.great-lakes.net/humanhealth/fish/critical.html). Level I substances under the BTS are targeted for virtual elimination. Contaminants indicated as ‘L2’ are Level II substances listed for voluntary pollution prevention activities.

<table>
<thead>
<tr>
<th>Critical Contaminant (CC)</th>
<th>BTS List</th>
<th>POPs List</th>
<th>Uses and Sources</th>
<th>Health Concerns</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDT and (CC) Metabolites</td>
<td>Yes</td>
<td>Yes</td>
<td>Large use as crop insecticide and mosquito abatement. Most uses cancelled in 1973.</td>
<td>Cause of diminished reproduction of eagles and other wild life.</td>
</tr>
<tr>
<td>Aldrin &amp; (CC) Dieldrin</td>
<td>Yes</td>
<td>Yes</td>
<td>Uses of both insecticides now cancelled. Aldrin converts to dieldrin in environment.</td>
<td>Dieldrin concentrations in fish exceed GLI criteria in many areas of the basin.</td>
</tr>
<tr>
<td>Dioxins &amp; (CC) Furans</td>
<td>Yes</td>
<td>Yes</td>
<td>Inadvertent by-product of incineration, pulp &amp; paper bleaching and chemical manufacturing</td>
<td>Poorly understood, but wildlife sensitive at low levels in laboratory studies.</td>
</tr>
<tr>
<td>Mercury and (CC) Methyl mercury</td>
<td>Yes</td>
<td>No</td>
<td>Released in combustion of coal. Use in batteries, electrical components and dental amalgam declining.</td>
<td>Toxic to human and animal foetuses. Fish consumption limits due to bioaccumulation of methyl mercury in fish.</td>
</tr>
<tr>
<td>Lead, nickel, copper, zinc and cadmium (CC)</td>
<td>alkyl Lead</td>
<td>No</td>
<td>Common in hazardous waste. Degradation of benthos and plankton in Lake Huron due to sediment concentrations.</td>
<td>Organ damage at low concentrations. Accumulate in food chain.</td>
</tr>
<tr>
<td>Mirex (CC)</td>
<td>Yes</td>
<td>Yes</td>
<td>Pesticide and flame retardant now cancelled in North America. Found in Niagara River and Lake Ontario.</td>
<td>Fish consumption limits for Lake Ontario due to exceedance of GLI criteria.</td>
</tr>
<tr>
<td>Polychlorinated biphenyls (PCBs) (CC)</td>
<td>Yes</td>
<td>Yes</td>
<td>Use began in 1929 and dis-continued in 1978. Used in electrical transformers, capacitors and switches.</td>
<td>Fish advisories due to bio-accumulation in the food chain. Health and reproduction problems in eagles, mink, etc.</td>
</tr>
<tr>
<td>Polybrominated biphenyls (PBDEs) (CC)</td>
<td>No</td>
<td>No</td>
<td>Manufactured in Michigan as flame retardant. Plant closed and site being remediated.</td>
<td>Food chain contamination in 1973 from accidental mixing of PBDEs with animal feed.</td>
</tr>
<tr>
<td>Nutrients: nitrogen &amp; phosphorous (CC)</td>
<td>No</td>
<td>No</td>
<td>Discharged by wastewater treatment and run-off from urban and agriculture areas.</td>
<td>Not completely understood, but cause eutrophication in waters and hypoxia in Gulf of Mexico.</td>
</tr>
<tr>
<td>Sediments and suspended solids (CC)</td>
<td>No</td>
<td>No</td>
<td>Deposited in water channels from urban and agricultural run-off and stream bank erosion.</td>
<td>Carries pollutants downstream and covers fish spawning and aquatic life habitat.</td>
</tr>
<tr>
<td>Tritium (CC)</td>
<td>No</td>
<td>No</td>
<td>A radioactive by-product from water cooled nuclear reactors.</td>
<td>Exposure and health effects not well known.</td>
</tr>
<tr>
<td>Poly Aromatic Hydrocarbons (PAHs)</td>
<td>Yes</td>
<td>No</td>
<td>Unintended by-product of combustion and other high temperature processes</td>
<td>Benthic organisms</td>
</tr>
<tr>
<td>Toxaphene</td>
<td>Yes</td>
<td>Yes</td>
<td>Cancelled pesticide. Moves to GL via air-borne transport from legacy sites.</td>
<td>Bioaccumulative in aquatic life. Fish consumption limits for Lake Superior</td>
</tr>
<tr>
<td>Endrin</td>
<td>L2</td>
<td>Yes</td>
<td>Cancelled pesticide – isomer of dieldrin</td>
<td>See dieldrin</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>Yes</td>
<td>Yes</td>
<td>Formerly used as fungicide. By-product of incineration.</td>
<td>Probable carcinogen. Produces many systemic symptoms.</td>
</tr>
</tbody>
</table>

Polybrominated biphenyl ethers (PBDEs) are increasingly found in humans and the environment. About 75 million pounds of PBDEs are used in the US annually as flame retardants in foams, plastics, fabrics, computer cases and circuit boards (http://www.epa.gov/fishadvisories/forum/2004/proceedings.pdf). PBDEs were first detected in the US in 1979 and in Sweden in 1981 (Alaee and Wenning, 2002). In further studies, PBDEs were found in fish-eating birds and marine mammals in the Baltic Sea, North Sea and Arctic Ocean, and in marine fish, shellfish and sediments in the Pacific region. PBDEs have now been detected in all parts of the US and Canada, including the Great Lakes. Being structurally similar to PCBs, the PBDEs have 209 possible congeners, of which the tetra-, penta- and hexa- brominated congeners are most often found in waters, wildlife and humans. In the atmosphere, PBDEs are found above the waters from 5 pg/m³ at Lake Superior to about 52 pg/m³ over Chicago (Strandberg et
al., 2001). Partitioning of the congeners between gas and particles was noted, with about 80% of the tetrabrominated homologues being found in the gas phase, and about 70% of the hexabrominated homologues in the particle phase. Partitioning of the congeners was also noted in Great Lakes fish and Lake Michigan water (Streets et al., 2006). This higher absorption of the more highly brominated congeners to particles was noted in sediment cores as well, with decabromo (BDE-209) making up 95-99% of the PBDE load (Zhu et al., 2005). Bioaccumulation of PBDEs in fish was reported by the Wisconsin Sea Grant Program. An average level of 80 ppb in Lake Michigan salmon was measured in 1996, which is about six times higher than the levels reported for Baltic Sea salmon in 1999. Fish archived during 1980 to 2000, analysed for 15 PBDE congeners, were found to have PBDE concentrations increasing rapidly, with 3-4-fold annual increases (Zhu and Hites, 2004). By the year 2000, total PBDE concentrations in Lake Michigan lake trout were the highest at about 1,400 ng/g of lipid, followed by Lakes Superior (990 ng/g), Erie (600 ng/g), Ontario (550 ng/g) and Huron (370 ng/g).

As an indicator of potential human health effects, Dye et al. (2007) reported that serum PBDE concentrations of 23 cats ranged from 4.3 to 12.7 ng/ml; cats exhibiting hyperthyroidism had higher concentrations than young control cats. Analysis of cat food showed PBDEs were present in both dry and canned foods, with dry food having higher concentrations, on average. The presence in humans has been rising, with Johnson-Restrepo et al. (2005) reporting a median level of 77.3 ng/g of lipid fat in a group of 52 people. The highest values were 9630 and 4060 ng/g, which are higher than any previously reported and some initial data show that 10% of California residents have higher PBDE concentrations in tissue than PCBs. Rodent studies have shown adverse neurological effects of PBDE exposure, prompting current studies in humans (http://cf-pub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/8044/report/2008).

Perfluorinated compounds such as perfluoroctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and many other perfluorinated compounds of various carbon chain lengths and functional end groups are ubiquitous in the environment. These contaminants are released from the manufacturing and breakdown of products used for non-stick surfaces, stain repellents, fire fighting foams, surfactants and numerous other beneficial uses. The compounds resist degradation, are persistent in the environment and are found in water, humans and wildlife (Herbert et al., 2002). Perfluorinated compounds have been detected in wastewater treatment effluent in New York, Kentucky, Georgia, in drainage basins of North Carolina, Ariake Sea, Japan, in fishes, birds, benthic organisms and in the general human populations in many countries. (e.g., Nakayama et al., 2007; Lau et al., 2007; Sinclair et al., 2006; Moody et al., 2001; Taniyasu et al., 2003).

Perfluorinated alkylated compounds were detected in 89% of the water samples collected in waters of Lakes Michigan, Huron and Superior, with concentrations as high as 36 ng/L (Kannan et al., 2005). Concentrations of PFOS in the livers and muscle of chinook salmon, lake whitefish, brown trout and carp were 1,000 times or more higher than in water. Values in Lake Michigan chinook salmon ranged from 32 to 173 ng/g wet weight in livers, and up to 189 ng/g in muscle. Similar values were observed in Lake Huron, with the exception of Saginaw Bay carp, which had concentrations up to 297 ng/g. Lake Superior brown trout had lower values of up to 26 ng/g in liver, 46 ng/g in muscle and 75 ng/g in eggs. In other areas of the Great Lakes basin, perfluorinated compounds were found in livers of 10 species of waterfowl in the Niagara River, and elevated concentrations of PFOS were reported in the surface waters of Lake Onondaga (Sinclair et al., 2006).

Studies in rodents have shown dose-dependent responses in maternal and developmental toxicity of PFOA, such as early pregnancy loss, reduced postnatal survival, delays in growth and development, and sex-specific alterations in pubertal maturation (Lau et al., 2006). However, the long-term effects of exposure to perfluorinated organic compounds are largely unknown, prompting the US EPA, under the Toxic Substances Control Act (TSCA), to add 50 perfluorinated chemicals that have the potential to persist and bioconcentrate to the TSCA reporting requirement; this action solicits information on uses, exposures, ecological effects, environmental fate and human health effects.

In addition to the brominated flame retardants discussed earlier, there are other flame retardants that have an environmental presence, even though they have not...
reached the critical contaminant lists. Notable are the short- and medium-chain chlorinated paraffins and dechlorane plus. Although the chlorinated paraffins can only be metabolised slowly in rainbow trout, bioaccumulation still occurs, with concentrations reported to be over 100 ng/g wet wt in lake trout from Lake Ontario (Muir, 2006). Dechlorane plus, formed from hexachlorocyclopentadiene, is persistent, with a half-life of over 182 days in soil. However, it does not bioaccumulate and no toxicity data are available to rank the compound’s hazards.

Bisphenol-A (BPA) is a key monomer in the formation of polycarbonate resins. Polycarbonate resins are widely used for shatter-proof bottles, including baby bottles, and as coatings to line containers such as liquid infant formula cans. It has been found that BPA leaches from the bottles and coatings, and is now found in the tissues of 90% of Americans. The National Institute of Environmental Health Sciences’ National Toxicology Program Expert Panel concluded that ‘The scientific evidence that supports a conclusion of some concern for exposures in fetuses, infants, and children comes from a number of laboratory animal studies reporting that ‘low’ level exposure to bisphenol A during development can cause changes in behavior and the brain, prostate gland, mammary gland, and the age at which females attain puberty’ (http://ntp.niehs.nih.gov/ntp/ohat/bisphenol/bisphenol.pdf). Much research is ongoing and at the time of publication local, state or federal bans or restrictions on biphenol A use have been proposed or enacted. Millions of pounds of phthalate esters are used as vinyl plasticisers and solvents. They are a concern because some of the phthalate esters are emitted to the environment as by-products of manufacturing and use or breakdown of end-products. These esters are not currently found in all waters, and studies of four phthalate esters (dimethyl, diethyl, di-n-butyl, and butylbenzyl phthalate) have shown that concentrations are generally well below the predicted no-effect concentrations for aquatic life.

Samples collected during 1992 and 1993 showed that low concentrations of trace metals were widespread throughout the Great Lakes ecosystem (Nriagu et al., 1995; http://www.cprm.gov.br/pgagem/Manuscripts/pirronenatmospheric.htm). Concentrations of trace metals in Great Lakes water were generally below the drinking water MCL but much higher concentrations were found in diving duck livers, fish and zebra mussels (Table 13.2). Many of the metals are rapidly taken up by the suspended particulate matter; while concentrations vary by location, no systematic increase in concentration of the metals from Lake Superior to Lake Ontario was found. However, higher concentrations were observed in nearshore areas close to urban centres and river mouths. As to the fate of the metals entering the lakes, large amounts of dissolved copper, nickel and chromium exit the system through the St. Lawrence River, while the loadings of cadmium, lead and zinc appear to be retained in the basin.

Based on data collected via the Integrated Atmospheric Deposition Network (IADN) (http://www.ec.gc.ca/rs%2Ddmn/default.asp?lang=En&n=BFE9D3A3-1), atmospheric deposition of trace metals was found to be an important source to the Great Lakes. Total deposition of most trace metals to the Great Lakes declined over the period 1976 to 1993-94. A very large decline for lead was likely due to the phase-out of alkyl lead in automotive gasoline. There was a considerable industrial-urban effect, with concentrations at NW Indiana during 1975-1980 being many times higher than the 1976 open-water values from Lake Michigan. Furthermore, deposition rates were higher for Lake Erie than for Lakes Michigan and Superior.

In another study, total atmospheric emissions of trace metals to the Great Lakes region increased until 1988-89, after which most showed little change except nickel, which
### Table 13.2. Comparison of trace elements in Great Lakes water, diving ducks and mussels.

<table>
<thead>
<tr>
<th>Element</th>
<th>Year taken</th>
<th>Where sampled</th>
<th>Water column conc. Mg/l</th>
<th>Drink-water MCL(4) mg/l</th>
<th>Animal conc. dry wt. μg/g</th>
<th>Animal tissue analysed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>*0.030</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1993</td>
<td>S. Grt Lks</td>
<td>*0.05-0.2</td>
<td>1.700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>0.010</td>
<td></td>
<td>ND(2)</td>
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* Non-enforceable guidelines that may cause cosmetic or aesthetic effects (taste, colour, odour, etc.)
# Action levels for copper and lead that trigger the need for additional treatment.
1 Diving duck liver analysed in four species of migrating diving ducks sampled at migratory corridors in Western Lake Erie, Lake St. Clair, and two locations of Lake Michigan.
2 ND = Non Detect, i.e, below analytical detection limit.
3 Males, females had lower concentrations at 564 μg/g.
4 Maximum Contaminant Level for Primary Drinking Water Standards. See reference 3
5 STZM = Soft tissue of Zebra mussel
6 Detected at less than quantifiable level
7 Data are from Custer and Custer, 2000, except where otherwise noted as from Nriagu et al., 1995
declined (http://www.cprmn.gov.br/pgagem/Manuscripts/pirronenatmospheric.htm). Again, emissions were higher near industrial and urban areas. Similarly, the analysis of juvenile fish in Lake Ontario showed the urban-industrial effect, with median concentrations of copper and zinc at Toronto area tributaries exceeding the concentrations found in other areas of the lake. A study of the blood and urine of 32 sport fish consumers in Lakes Michigan, Huron and Erie did not find most trace metals, with the exception of lead and mercury, to be elevated (Anderson et al., 1998) compared with a group outside the Great Lakes basin. Mean blood lead and mercury concentrations were consistently higher than the mean from the comparison group, suggesting contributions due to the bioaccumulation of these metals in fish. However, the levels were below the NCEH/CDC reference range (<30 μg/L).

Pharmaceuticals and personal care products (PPCPs) are a group of contaminants that include prescription and over the counter therapeutic drugs, veterinary drugs, fragrances, cosmetics, sunscreens, vitamins and antimicrobial agents. These substances mostly enter the waters through municipal wastewater treatment effluent, private septic systems, or animal waste run-off. Wastewater treatment does not remove all of the PPCPs, as degradation rates vary among the products. As the human population increases, so does the use of the thousands of chemicals providing beneficial uses, while the supply of water remains the same or declines. A US study in 1999-2000 detected 82 substances at low concentrations in the nation’s waters (Kolpin et al, 2002; Daughton et al., 2005). The study sampled a network of 139 streams across 30 states that emphasised waters downstream of urban areas and livestock production and waste disposal (including the application to cropland) facilities. Table 13.3 shows the groups of chemicals and the compounds within these groups that were most frequently detected. Detection of many of these compounds resulted from the improved analytical methods, which greatly reduced the detection limits. While each of the compounds was detected in low concentrations, and generally below the health or aquatic criteria, long-term toxicity and the unknown effects of mixtures of 20 or more of such compounds in a given water supply are a concern. There are several hormones entering the waters, and some have been shown to exhibit endocrine disruption at levels as low as 1 ng/L (Ternes et al., 2004), which again raises the question of the cumulative effect of the large number of substances found in the waters.

Safety of Drinking Water and Beaches in the Great Lakes

For most communities consuming Great Lakes water, the toxic chemicals present in the water are at levels below drinking water standards. Some of the tributaries to the Great Lakes that receive wastes from industrial areas such as Lake Onondaga, New York are polluted to an extent requiring restoration (http://www.epa.gov/Region2/water/lakes/onondaga.htm). Community water supplies work with a network of government agencies to ensure the safety of public drinking water supplies (http://www.epa.gov/safewater/contaminants/index.html). Under the Safe Drinking Water Act (1974 and amended in 1986 and 1996) the USEPA sets drinking water Maximum Contaminant Levels (MCLs) and health advisory levels (HALs) for 14 inorganic chemicals including seven metals, over 50 organic chemicals, four radionuclides and six microorganisms. In addition, suggested standards for 15 secondary pollutants are listed, but not regulated. The levels are based upon toxicity information with risks estimated for human lifetime exposure. Monitoring is carried out by states, tribes, public water suppliers, and the federal government. Additional monitoring is performed by the United States Geological Survey (USGS). USGS monitors the quality of the nation’s waters under the National Water-Quality Assessment (NAWQA) Program, and reports the concentrations of contaminants found within several categories. (http://water.usgs.gov/nawqa).

Surveillance monitoring of the open waters of the Great Lakes conducted by the United States and Canada report high water quality (http://www.great-lakes.net/humanhealth; Dreelin, 2005). However, nearshore waters that are affected by discharges from wastewater treatment plants, septic systems, combined sewer overflows, and run-off from agricultural and urban sources are subject to microbial contamination. The treatment rules (http://www.epa.gov/safewater/contaminants/index.html) for drinking water supplied from surface waters and groundwater require filtration and disinfection to remove several micro-
organisms including cryptosporidium, giardia, lamblia, legionella and viruses. Disinfection is most commonly performed by chlorination. While drinking water supplies are in general safe, an incident of cryptosporidium contaminated drinking water in 1993, believed to be caused by animal waste runoff to drinking water supply areas of Lake Michigan, resulted in severe distress and illness in over 400,000 people in Milwaukee, Wisconsin, USA.

Disinfection by-products (DBPs), such as chloroform, trichloroethylene, and other halogenated compounds are present in drinking water as the result of the addition of chlorine or bromine to control bacteria and viruses, reacting with trace organic substances present from human processes and the breakdown of plant and soil substances. The use of chlorine has virtually eliminated water-borne diseases such as typhoid fever, cholera and dysentery, but the unanticipated creation of DBPs is a concern still under investigation. USEPA has not been able to link the exposure to low concentrations of DBPs in drinking water with health risks that are known for high concentrations of the substances. Still, under the Safe Drinking Water Act, USEPA regulates four DBPs: bromates, chlorites, halocarboxylic acids and trihalomethanes (http://www.drinktap.org/consumerdnn/Home/WaterInformation/WaterQuality/DisinfectionByproducts/DBPsFactSheet/tabid/189/Default.aspx ).

There are thousands of acres of fine beaches on the Great Lakes. As noted above, microbial contamination of nearshore waters from waste treatment, septic systems, sewer overflows, and run-off from urban and agricultural areas does affect beach safety. Microorganisms cause beach closures to protect swimmers, using *E. coli* as a health marker for beach safety in communities that monitor beaches. Action levels are not uniform, but range from 100 organisms/100 mL for the Province of Ontario, Canada to 200 organisms/100 mL for the State of New York. In 2004, 13% of the Great Lakes beaches were closed at least 10% of the time due to contamination by pathogens. The closing orders lag behind the sample collection, as current testing methods require a day or more to provide results. More rapid tests for pathogen contamination are being developed in order to protect swimmers closer to real time. See http://www.glin.net/beachcast for health advisories and monitoring data for beaches.

### Conclusions

In conclusion, many contaminants are found in the Great Lakes Basin, although not all are governed by drinking water standards or aquatic life criteria. For the contami-
nants that have drinking water standards, concentrations rarely exceed such standards, except for pathogens in nearshore areas, which require the filtration and disinfection of drinking water supplies. However, numerous wildlife species, particularly invertebrates and fish, are affected by even the low concentrations of the bio-accumulative substances present in the Great Lakes (critical contaminants). The bioaccumulation of such contaminants in fish requires Canada and the Great Lakes states to issue recommendations on fish consumption limits. Many contaminants are preferentially absorbed by particulate matter in the water, only to be deposited as contaminated sediments in stream and river beds, harbours and other connections to the Great Lakes. Because of urban, industrial and agricultural practices, chemical contaminants, eroded soils and nutrients continue to add materials to contaminated sediments. Storm run-off and sewer overflows from urban areas and agricultural run-off carry pathogens to nearshore areas that result in periodic beach closures. Still, many open questions remain, such as the cumulative effect of the sum of the pollutants present at any time. Nutrients, discussed in another Chapter, also contribute negative impacts to the Great Lakes such as algal blooms producing microcystin toxins and causing hypoxia in embayments and other slow moving waterways.

Undoubtedly there are other toxic substances that are at concentrations below detection limits. As analytical methods continue to improve, more contaminants are expected to be found. Under the Safe Drinking Water Act, EPA considers other candidates for regulation. At present, there are 42 chemicals and 9 microbial contaminants under consideration as ‘candidates’ for regulation (http://www.epa.gov/safewater/contaminants/index.html). The vigilant surveillance of waters, sediments, terrestrial and aquatic wildlife by the many Great Lakes Agencies and Organisations in both Canada and the United States must continue to provide data to judge the health of the Great Lakes system.
Chapter 13


Custer, C.M. and Custer, T.W. 2000. Organochlorine and trace element contamination in wintering and migrating diving ducks in the southern great lakes, USA, since the zebra mussel invasion. In: Environmental Toxicology and Chemistry;19, pp. 2821-2829


Chapter 14


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