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Persistent Organic Pollutants in the Great Lakes: An Overview

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Abstract This chapter presents background information on the Great Lakes and summarizes the content of each chapter of this book.

1 Introduction: The Great Lakes [1]

The Laurentian Great Lakes (not to be confused with the Great Lakes in Africa) are located near the middle of the North American continent. There are five Great Lakes, and they are called Lakes Superior, Michigan, Huron, Erie, and Ontario; see Fig. 1. Lake St. Clair is, strictly speaking, not one of the Great Lakes, but it is part of the connection between Lakes Huron and Erie. The United States-Canadian international border runs through four of the lakes, and collectively the Great Lakes are closely tied to the cultural heritage of both the United States and Canada. Early on, the lakes were the highway that led to the exploration, settlement, and eventual industrialization of this region of North America. The lakes have provided a thriving commercial fishery (now largely vanished) and water for drinking, transportation, power, industry, and recreation.

The Great Lakes are big; see Table 1. From the westernmost corner of Lake Superior to the easternmost shore of Lake Ontario, these lakes cover a distance of > 1200 km. The total water area of the lakes is 244 000 km^2—an area

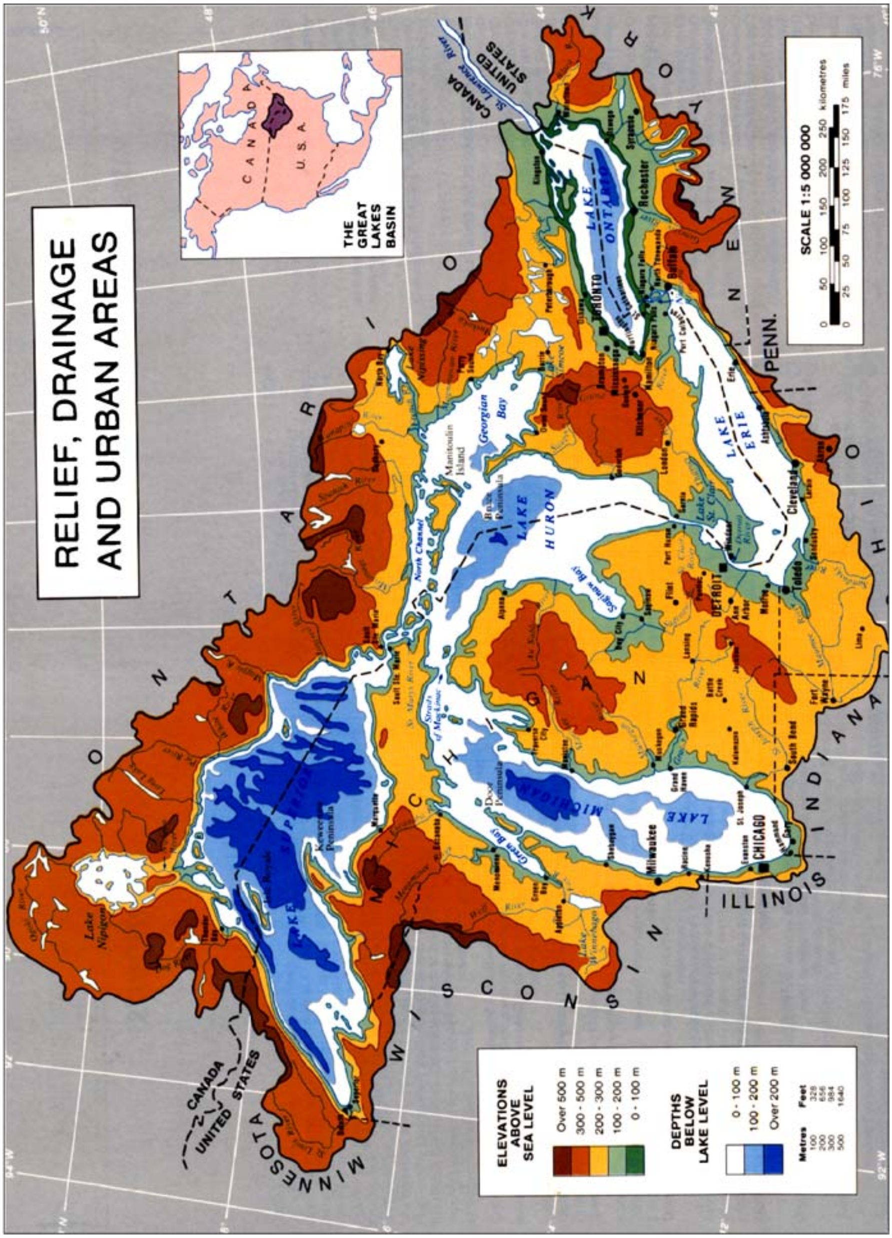

Fig. 1 Map of the Great Lakes showing the major geographic features (from [1])

about the size of Great Britain. The total area of the Great Lakes' drainage basin is 766 000 km^2—an area much larger than the combined areas of Germany and Italy and $\sim 40\%$ larger than France. In this drainage basin, the

Table 1 Physical features and population of the Great Lakes (from [1])

	Superior	Michigan	Huron	Erie	Ontario	Total
Elevation [a] (in meters)	183	176	176	173	74	
Length (in km)	563	494	332	388	311	
Breadth (in km)	257	190	245	92	85	
Average depth [a] (in meters)	147	85	59	19	86	
Maximum depth [a] (in meters)	406	282	229	64	244	
Volume [a] (in km^3)	12 100	4920	3540	484	1640	22 700
Water area (in km^2)	82 100	57 800	59 600	25 700	19 000	244 000
Land drainage area [b] (in km^2)	128 000	118 000	134 000	78 000	64 000	522 000
Total area (in km^2)	210 000	176 000	194 000	104 000	83 000	766 000
% Water relative to total area	39	33	31	25	23	32
Shoreline length [c] (in km)	4380	2630	6160	1400	1150	17 000 [d]
Retention time (years)	191	99	22	2.6	6	
Population: U.S. (1990)	425 500	10 057 000	1 503 000	10 018 000	2 704 000	24 707 000
Canada (1991)	181 600		1 191 000	1 665 000	5 447 000	8 484 000
Totals	607 100	10 057 000	2 694 000	11 683 000	8 151 000	33 191 000

[a] Measured at low water height. [b] Land drainage area for Lake Huron includes the St. Marys River; Lake Erie includes the St. Clair-Detroit system; and Lake Ontario includes the Niagara River. [c] Including islands. [d] These totals are greater than the sum of the shoreline lengths for the lakes because they include the connecting channels (excluding the St. Lawrence River).

lakes themselves cover about 32% of this area. The lakes contain 22 700 km^3 (or 2.27×10^{16} L) of freshwater, much of which is still pure enough to be consumed with minimal treatment. The Great Lakes contain the largest reservoir of fresh, surface water on earth—about 18% of the world's supply; only the polar ice caps contain more fresh water.

The Great Lakes basin is highly populated in the south and includes such major cities as Chicago, Illinois; Detroit, Michigan; Cleveland, Ohio; and Toronto, Ontario. More than 10% of the United States' population and more than 25% of the Canadian population live in the Great Lakes basin. Large concentrations of industry are located in the Great Lakes region; for example, the U.S. and Canadian automobile industry is located there. Agriculture is also an important part of the Great Lakes basin's economy; $\sim$ 25% of Canadian and $\sim$ 7% of United States agricultural production is in the Great Lakes basin. Of course, all of this activity is not without its environmental costs. Agricultural runoff, urban waste, industrial discharge, and landfill leachate all contribute to the pollution of the lakes. In addition, the large surface area and slow flushing rates of the lakes makes them vulnerable to the deposition of contaminants from the atmosphere.

Because of the sheer magnitude of the Great Lakes' watershed size, physical characteristics, such as climate and soils, vary across the basin. In the north, the climate is relatively cold, and the terrain is dominated by granite bedrock called the Canadian (or Laurentian) Shield, which consists of Precambrian rocks under a generally thin layer of acidic soils. Conifers dominate the northern forests. In the southern areas of the Great Lakes basin, the climate is warmer, and the soils are deeper with layers of clay, silt, sand, and gravel, which were deposited by glaciers. In the southern basin, the lands can be readily used for agriculture. In several places in the basin, the original landscape has been replaced by sprawling urban development.

The lakes have very different depths, and thus they have very different properties and responses to environmental insult. The depth profile of the lakes is shown in Fig. 2.

Lake Superior is by far the largest, deepest, and coldest of the five lakes. This lake has a water retention time of almost 200 years. There is little agriculture in Lake Superior's basin (largely because of the poor soils and cold climate); instead most of the basin is forested. The sparse human population around Lake Superior results in relatively little pollution entering the lake as a result of local human activity, but because of its large surface area and its small drainage area, large amounts of pollutants are delivered by deposition from the atmosphere.

Lake Michigan is the second largest of the lakes, and it is the only lake entirely within the United States. The northern part of Lake Michigan is in the colder and less developed upper Great Lakes region, and this region is sparsely populated, except for the Fox River Valley, which drains into Green Bay. In fact, this bay has been contaminated by wastes from a large concen-

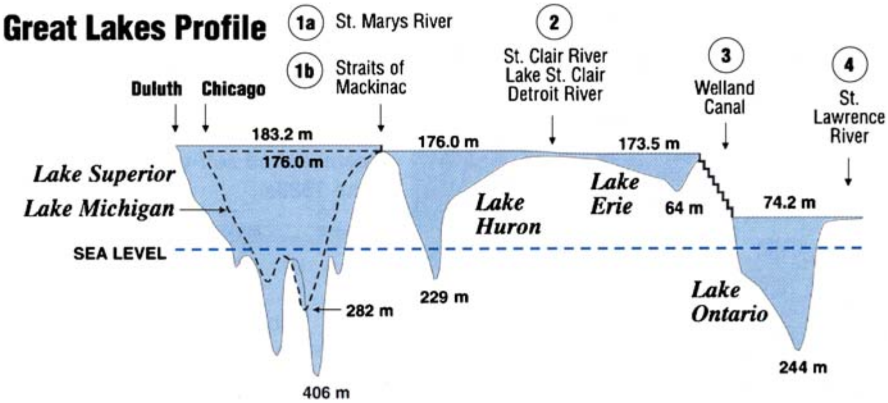

Fig. 2 Diagram indicating the relative depths (in meters below the lake surface) and surface elevations (in meters above sea level) of the five Great Lakes measured along the long axis of each lake. The vertical exaggeration is 2000 : 1. The inter-lake lock and river systems are numbered. From [1]

tration of pulp and paper mills in this part of Wisconsin. The Southern Lake Michigan basin is among the most urbanized areas in the Great Lakes system, being the home of the greater Milwaukee, Chicago, and Gary metropolitan areas. About 12 million people live in this region.

Lake Huron (including Georgian Bay) is the third largest of the lakes. The human impacts in the Lake Huron basin are relatively minor, consisting mostly of recreational uses. For example, many Canadians have cottages on the shallow, sandy beaches of Lake Huron or along the rocky shores of Georgian Bay. On the United States side of the lake, the Saginaw River basin is farmed and contains the Flint, Saginaw, and Bay City metropolitan areas. Saginaw Bay has also received industrial waste from the chemical industry centered in Midland, Michigan.

Lake Erie is the smallest and shallowest of the lakes, and it has been heavily impacted by urbanization and agriculture. Lake Erie receives runoff from agricultural areas in southwestern Ontario, northern Ohio, and southern Michigan. In addition, there are numerous metropolitan areas located in the Lake Erie basin; these include Cleveland, Ohio, and Buffalo, New York. The average depth of Lake Erie is only 19 meters, and as a result, it warms rapidly in the spring and summer, and it frequently freezes over in winter. Lake Erie also has the shortest water residence time of the lakes (2.6 years), and thus, the condition of this lake can change rapidly.

Lake Ontario is much deeper than its upstream neighbor, having an average depth of 86 meters and a water residence time of ~ 6 years. Major Canadian urban industrial centers, such as Hamilton and Toronto, Ontario, are located on its shore. The southern (U.S.) shore of Lake Ontario is less urbanized and is not intensively farmed, except for a narrow band along the lake itself. Lake Ontario has also received contaminants from the chemical industry operating along the Niagara River in New York.

In the late 1960s, growing public concern about the deterioration of environmental quality of the Great Lakes stimulated research on the inputs and behavior of pollutants in the lakes. Governments in both the United States and Canada responded to the concern by regulating pollutant discharges and initiating research on the sources, fates, and effects of pollutants in the lakes. These efforts were formalized in the first Great Lakes Water Quality Agreement between Canada and the U.S. in 1972.

Because of this increased attention, major reductions were made in pollutant inputs, and by the 1970s, some results were clear. Floating debris and oil slicks disappeared; dissolved oxygen levels improved; odor problems were eliminated; beaches reopened; and algal mats disappeared. Attention shifted to persistent toxic contaminants in the 1980s, as reflected in the 1987 Amended Great Lakes Water Quality Agreement. Given that some of these toxic substances accumulate as they move through the food chain, top predators such as lake trout, fish-eating birds (such as cormorants, ospreys, and herring gulls), and people can receive relatively high doses of these contaminants.

This book brings together what is known about the major classes of these persistent organic pollutants (the so-called POPs). Each chapter reviews our knowledge of the extent of contamination of the various parts of the Great Lakes ecosystem (air, water, sediment, fishes, birds, etc.), what is known about the trends over time of this contamination, and information about the mechanisms by which these compounds are mobilized in the lakes. The following section presents abstracts of the contents of each chapter.

2 Overview of Chapters

2.1 Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) were widely used in the Great Lakes region primarily as additives to oils and industrial fluids, such as dielectric fluids in transformers. PCBs are persistent, bioaccumulative, and toxic to animals and humans. The compounds were first reported in the Great Lakes natural environment in the late 1960s. At that time, PCB production and use was near the maximum level in North America. Since then, inputs of PCBs to the Great Lakes have peaked and declined: Sediment profiles and analyses of archived fish indicate that PCB concentrations have decreased markedly in the decades following their phase-out in the 1970s. Unfortunately, PCB concentrations in some fish species remain too high for unrestricted safe consumption. PCB concentrations remain high in fish because of their persistence, tendency to bioaccumulate, and the continuing input of the compounds from uncontrolled sources. PCBs are highly bioaccumulative, and many studies have shown that the complex food webs of the Great Lakes contribute to the focusing of PCBs in fish and fish-eating animals. PCB concentrations in the open waters are in the range of 100–300 pg/L and are near equilibrium with the regional atmosphere. PCBs are hydrophobic yet are found in the dissolved phase of the water column and in the gas phase in the atmosphere, and they continue to enter the Great Lakes environment. The atmosphere, especially near urban-industrial areas, is the major source to the open waters of the lakes. Other sources include contaminated tributaries and in-lake recycling of contaminated sediments. Until these remaining sources are controlled or contained, unsafe levels of PCBs will be found in the Great Lakes environment for decades to come.

2.2 Dioxins

Good information exists on the occurrence, geographical distribution, and temporal trends of dioxins in Great Lakes' air, water, sediments, fish, seabirds, and people. Dioxin congener patterns and concentrations in sediment indicate that atmospheric input dominated in Lake Superior, southern Lake Michigan, and Lake Erie. Inputs from the Saginaw River to Lake Huron and from the Fox River to upper Lake Michigan added some dioxin loading to these lakes above atmospheric deposition. Lake Ontario was heavily impacted by the input of dioxins, particularly 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, from the Niagara River. Sediment core and bio-monitoring data revealed that dioxin contamination peaked in most lakes in the late 1960s to early 1970s, followed by rapid, order of magnitude declines in the mid to late 1970s. The downward trend stalled in some lakes in the 1980s, but seems to have continued after the late 1990s, probably in response to various remediation efforts and reductions in dioxin emissions to the atmosphere. During the height of contamination, effects attributed in whole or in part to dioxin contamination included reproductive failure in lake trout and herring gulls in Lake Ontario. Aryl hydrocarbon receptor-mediated sub-lethal effects may still be occurring in seabirds and fish, but much of this is thought to be due to dioxin-like PCBs rather than dioxins.

2.3 Pesticides

Spatial distributions and temporal trends of pesticides in sediment, water, and fish indicate good progress in the reduction of persistent organochlorine pesticides in the Great Lakes Basin. Concentrations of many of the organochlorine pesticides have decreased significantly in Great Lakes wildlife, subsequent to restriction of these compounds' usage in the Great Lakes basin in the 1970s and the 1980s. Nevertheless, concentrations of several organochlorine pesticides in the Great Lakes are currently either not declining or are declining only slowly. The current concentrations of several organochlorine pesticides seem to be at a steady state, such that the amount lost to the sediments and exported either to the atmosphere or flowing out through the St. Lawrence River is balanced by input from rivers and the atmosphere. Thus, further reductions in the input of organochlorine pesticides and the continued recovery of wildlife populations are dependent, in part, on the control of new inputs.

The frequency of detection of current-use pesticides in the Great Lakes generally increased in the order Superior < Huron and Georgian Bay < Ontario < Erie. The highest concentrations among current-use pesticides were measured for atrazine, metolachlor, 2,4-D, and diazinon in the western basin of Lake Erie, because of the close proximity to areas where these pesticides are applied in both agricultural and urban settings. Future monitoring activities should focus on the major pesticides that are in current use. At present, programs are in place to analyze for about half of the pesticides used. Additive and synergistic effects of pesticide mixtures must be examined more closely, since existing guidelines have been developed for individual pesticides only.

2.4 Toxaphene

Toxaphene is a major persistent organic contaminant in air, water, and fish in the Great Lakes. The story of toxaphene in the Great Lakes, like that of most other persistent organochlorine compounds, has only become clear after the ban on the use of this pesticide in the mid-1980s. The spatial and temporal trends of toxaphene in the Great Lakes are now reasonably well documented. Highest concentrations in fish and lake water are found in Lake Superior. Concentrations of toxaphene declined in lake trout from Lakes Michigan, Huron, and Ontario during the 1990s (half-lives of 5–8 years) but not in Lake Superior. Recent measurements suggest no declines from the mid-1990s to 2000 in all four lakes. Modeling has demonstrated that the colder temperatures and low sedimentation rates in Lake Superior, and to some extent in Lake Michigan, conspire to maintain high toxaphene concentrations in the water column. Sediment core profiles from Lakes Michigan, Ontario, and Superior all show declining inputs in the past 10–20 years, mirroring reduced emissions following toxaphene deregistration in the United States in 1986. Atmospheric transport of toxaphene from agricultural soils in the southern United States continues and modeling results suggest that 70% of the atmospheric inputs to the Great Lakes are due to long range atmospheric transport and deposition from outside of the basin itself. Some degradation is apparent in the Lake Superior food web based on non-racemic enantiomer fractions for selected chlorobornanes, but for most congeners this process is slow and does not result in negative food web biomagnification in Lake Superior. High proportions of hexa- and heptachlorobornanes have been found in some lake sediments and tributary waters, indicating that slow degradation, mainly via dechlorination, is proceeding within the Great Lakes basin.

Toxaphene concentrations probably did not reach levels that would, by themselves, cause effects on salmonid reproduction, survival, or growth in the Great Lakes. The levels and effects of toxaphene in fish-eating birds and mammals (such as mink) in the Great Lakes have never been thoroughly investigated; however, it seems likely that exposure levels for birds and mammals would have been lower than for PCBs. In some Great Lakes jurisdictions, concerns remain about human exposure to toxaphene via consumption of Lake Superior lake trout. Given the long half-lives in fish and water, elevated toxaphene is likely to remain a contaminant issue in the Great Lakes until the middle of the 21st century.

2.5 Polychlorinated Naphthalenes

Polychlorinated naphthalenes (PCNs) have entered the Great Lakes through the production and use of Halowax technical mixtures, as trace contaminants in Aroclor PCB mixtures, and through industrial processes such as chlor-alkali production and waste incineration. Air concentrations of PCNs were highest in urban areas, and congener profiles indicate that evaporative emissions relating to past uses are the dominant sources, but combustion processes also contribute. Sediment measurements indicate that the highest PCN concentrations are in the Detroit River, and congener profiles indicate Halowax contamination from past inputs. Fish from this area had the highest reported concentrations in the Great Lakes region, followed by lake trout from Lake Ontario. Estimates of dioxin toxic equivalents of PCNs indicate their contributions are as important as the dioxin-like PCBs in some aquatic species, and more important in air and sediments. No time trend information for PCNs in the Great Lakes exists, and further spatial assessment, and toxic equivalent comparisons of PCNs, dioxins, and PCBs in additional fish species should be undertaken.

2.6 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are produced during the incomplete combustion of organic material. PAHs can also be produced through natural, non-combustion processes, and they may be present in uncombusted petroleum. Uncombusted petroleum can be a direct source to the waters of the Great Lakes, but combustion sources discharge PAHs into the coastal atmosphere. Atmospheric deposition of combustion-related PAHs seems to be the dominant source to the Great Lakes, except in nearshore areas where point sources can be significant. Once airborne, PAHs partition in the atmosphere between the gas and particle phases and can undergo long-range transport. During transport, PAHs can be degraded or modified by photochemical reactions. Both the original PAH species and their degradation products can be washed out of the atmosphere by wet and dry deposition, air-water exchange, and air-terrestrial exchange. Once in an aquatic system, PAHs partition between the dissolved and particle phases. In general, PAHs are particle reactive and settle out in sediments. PAH contamination of Great Lakes sediments is higher in the near-shore regions where ports, harbors, and urban/industrial areas are the densest. In the open lake areas, sediment concentrations are uniform, with Lake Superior having slightly less PAHs in its surficial sediments. That portion of the PAHs that does not partition to particles can bioaccumulate in the lipid reserves of organisms.

PAHs accumulated in an organism may be metabolized to more toxic by-products or exert toxicity in their original form. When combined with ultraviolet radiation, this toxicity is greatly enhanced. In coastal areas where concentrations can be quite high, PAHs can be toxic to all forms of aquatic life during at least part of their life cycle. PAHs are expected to remain an ecological threat to the Great Lakes well into the future. This threat may even increase with the increasing combustion needed for increasing population centers and greater transportation needs. Of particular concern is the short-term increase in PAH concentrations that can result from dredging of ports and harbors, where highly contaminated sediments have been buried.

2.7
Brominated Flame Retardants

Brominated flame retardants in the Great Lakes have not been as well studied as many of the polychlorinated pollutants, especially the PCBs, but in the last 5–10 years, there has been some significant progress. The ubiquity of these compounds in the sediment and fishes of the lakes has now been well established, and perhaps more alarming, it is now clear that the concentrations of some of these compounds are actually increasing. This observation is particularly important given that the concentrations of most of the other persistent organic pollutants in the lakes are decreasing. Despite their production cessation in the mid-1970s, polybrominated biphenyls (PBBs) are still present in fishes and sediment from most of the lakes. In general, these PBB concentrations are decreasing slowly, if at all. Polybrominated diphenyl ethers (PBDEs) are present in air, fishes, birds, and sediment from the lakes. In lake trout and in herring gull eggs, the PBDE concentrations have doubled every 3–5 years; in sediment cores, the doubling time is $\sim$ 15 years. Hexabromocyclododecanes (HBCD) are also present in fishes and sediment from the lakes, but at much lower levels compared to the PBDEs. Two previously unreported flame retardants [1,2-bis(2,4,6-tribromophenoxy)ethane (TBE) and 1,2,3,4,5-pentabromoethylbenzene] have been found in the air and sediment of the lakes. Clearly, it would be good to monitor the concentrations of all of these compounds in (at least) the sediment and fishes of the lakes to determine long-term trends. One might want to focus especially on those BFRs that will continue to be in production; these include deca-BDE, HBCD, and TBE.

2.8 Perfluorinated Compounds

Perfluoroalkyl acids (PFAs) are released into the environment via their manufacturing processes, their use in commercial products, or indirectly via oxidation of precursor molecules containing perfluoroalkyl chains. PFA precursors are diverse and include perfluorinated alcohols and perfluoroalkyl sulfonamide derivatives. Products in which PFAs and their precursors have been used include wetting agents, lubricants, stain resistant treatments, and fire-fighting foams. The PFAs in the environment comprise two general classes: perfluoroalkyl carboxylates such as $CF_3(CF_2)_xCO_2^-$ and perfluoroalkyl sulfonates, such as $CF_3(CF_2)_xSO_3^-$. The predominant PFA in biota samples from the Great Lakes is perfluorooctane sulfonate (PFOS), but a homologous series of perfluoroalkyl carboxylates, where $x = 6–13$, is also detected in most samples at lesser concentrations.

The environmental behavior of most PFAs is not well studied, and our knowledge of the physicochemical properties of perfluorooctane sulfonate and carboxylate is limited. Both compound classes are persistent in the environment and are not expected to volatilize into the atmosphere to a significant extent, but they have much greater water solubilities than similar chlorinated compounds. Concentrations of PFOS in surface waters are usually less than those of perfluorooctanoic acid, but PFOS accumulates in aquatic organisms to a greater extent and appears to biomagnify in the food web of the Great Lakes region. PFAs or their precursors have been measured in air, surface waters, sediments, aquatic invertebrates, and in the tissues of fish, fish-eating water birds, mink, otter, and other wildlife from the Great Lakes. Although the sources of PFAs to the Great Lakes are not well understood, fluorotelomer alcohols and perfluorooctylsulfonamides degrade to perfluoroalkyl carboxylates and PFOS, respectively, in laboratory studies. On the basis of preliminary and incomplete information, current concentrations of PFOS in the Great Lakes environment do not seem to be sufficient to pose a significant risk to most aquatic organisms including fish. However, the margins of safety are less for mammals such as mink and birds, and when the concentrations of all PFAs are considered together, current concentrations may pose some risk to some sensitive species.

References

1. This section was generously paraphrased from: The Great Lakes, An Environmental Atlas and Resource Book. Third Edition, Government of Canada, Toronto, and the United States Environmental Protection Agency, Great Lakes National Program Office, Chicago, 1995