



## Organochlorine Contaminants in The Great Lakes

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### Summary

Great Lakes sediments and biota are contaminated by persistent and toxic organochlorine compounds. Large areas of sediments are contaminated, however, much higher concentrations are observed in fish and birds due to bioaccumulation processes. The estimated total load of polychlorinated biphenyls in the sediments of the Lakes Ontario, Erie and Superior is approximately 50 metric tons. Spatial and temporal changes of sediment contamination can provide useful information on contaminant sources and pathways within the basin.

With increasing numbers and amounts of chemicals in use, the potential for further environmental damage is high. Environmental research, effluent limitations and public education are needed to restore and maintain high water quality in the Great Lakes.

### Introduction

Until recently, the pollution of the Great Lakes was largely viewed in terms of its visible ramifications. Algal blooms in the open waters leading to decaying algae masses on shorelines and anoxic bottom water conditions, oil and scum on the water surface, tainted fish and malodorous water were but a few of the "visible", partial results of man's activities. But recently, ecologically active compounds, such as the insecticides DDT and DDE, transformer

fluids, e.g., polychlorinated biphenyls (PCBs); and flame retardants, e.g., mirex, have been found to contaminate large parts of the ecosystem. In absolute quantities, the loading of these contaminants may appear minute when compared to the loading of phosphorus and other nutrients, however, the combination of their chemical and biological properties should make such contaminants a foremost concern. Recognition of the environmental danger of such compounds has led to the enactment of the Environmental Contaminants Act (1976) in Canada and the Toxic Substance Control Act (1976) in the U.S.A.

Many of these contaminants are summarily known as organochlorine compounds (OCs). Indeed a great number of OCs are highly chlorinated organic molecules which have certain common characteristics, such as their persistence, bioaccumulation potential and chronic toxicity. It is the combination of these three properties which makes such compounds hazardous to organisms remote from the direct vicinity of their application or loss to the environment. Compounds which combine only two of the three factors are likely to be more of a local problem rather than affecting the entire ecosystem. Of course, the above mentioned properties occur over a wide range of degrees and a classification of compounds in this way may be difficult. For practical purposes and based on studies by Eichelberger and Lichtenberg (1971), water quality objectives for the Great Lakes were developed with the following working-definition of persistence (GLWQ, 1975).

A persistent compound is defined as one which either (a) by itself or as its transformation product, has a half-life for degradation under natural environmental conditions of more than eight weeks, or (b) by itself or as its transformation product, on entering surface waters may bioconcentrate in the biota of the receiving system.

In many instances, the presence of environmental contaminants would be unrecognized without their concentration in biota through bioaccumulation. The terms bioconcentration and bioaccumulation describe the preferential transfer of a contaminant from

the water to the biota living in it. Although used synonymously in the past, the terms are now used to describe the adsorption of a contaminant, for example by a fish, directly from the water (bioconcentration) or its uptake through the food chain (bioaccumulation). At present, it is not clear which of these mechanisms is more prevalent in the Great Lakes system.

Perhaps the least obvious effect of a contaminant may be its toxicity. Except for the event of a massive spill, no immediate or local effect may be noticed with the contamination. In many cases, effects may be delayed for months; with mutagenic and carcinogenic compounds, latency periods can be in the order of decades. Because of such delayed effects, and given the persistence of some compounds it is often extremely difficult to determine the precise cause of an observed phenomenon. Examples of such phenomena are the low reproductive success rate of herring gulls in the Lake Ontario basin (Gilbertson and Fox, 1977), the decline of the walleye population in Nipigon Bay (Ryder, 1968), and the disappearance of the blue pike from Lake Erie (McAllister, 1970). In none of these cases could positive identification of the cause of the environmental problem be established, although there were good correlations between contaminant residues and some of the field observations. Compounding the problem of cause and effect relations is the simultaneous presence of a multitude of other organic as well as inorganic toxicants, which may lead to unknown synergistic and antagonistic effects of two or more single contaminants. Moreover, natural environmental stresses and increased exploitation can reduce the reproductive success of a species beyond recuperation.

### Compartments and Pathways

In a simple description, a lake basin comprises four major ecosystem compartments: the water itself, the shoreline bluff and sediment, the air, and the biota inhabiting the basin. To a considerable extent, the pathways of contaminants follow the relationships among the compartments and their subgroups.

Many persistent organochlorine contaminants, such as DDT and its major

metabolite DDE on entering the water are readily adsorbed from water to any particle's surface. In many laboratory experiments, the surfaces of aquarium walls and the experimental fish are large relative to the water mass involved, leading to high apparent bioconcentration factors (Picer *et al.*, 1977). In a lake, however, this surface to volume ratio is quite different, and the surface of algae and other particulates is much larger in relation to the fish and sediment surface. As a result, adsorption of contaminants onto limnetic particulates will play a major role with subsequent bioaccumulation through the food web, providing the major pathway for the accumulation of contaminants: this is not the case for laboratory experiments. Such particulate matter has been shown to be associated with the majority of OCs in the water column (Munson *et al.*, 1976). In sediments, the relatively lipophilic clay and organic detritus contain more OCs than the less lipophilic quartz fraction (Frank *et al.*, 1977; Thomas, 1972).

Another important route for contaminants between compartments is the exchange between air and water. Theoretical calculations show an unexpectedly rapid evaporation of such high boiling-point compounds as PCBs from water surfaces (Mackay and Wolkoff, 1973). At the same time, contaminants are precipitated as wetfall or dryfall together with rain, snow, and dust directly onto the lake surface as well as onto the tributaries' catchments. Based on PCB in precipitation, the atmospheric load of PCB to Lake Superior has been estimated to be as much as 1000 kg/year (Strachan, pers. commun.). Hence there is considerable evidence for a dynamic contaminant exchange between the air and water compartments.

The most complex compartment of the aquatic ecosystem is probably the aquatic biota. It is the link between the water and its chemical constituents derived from its tributaries, sediments and the air, and also forms an important part of the terrestrial food web. Aquatic life is in dynamic exchange with the chemical constituents of water. As with the nutrients, contaminants are taken up, metabolized, stored or excreted by aquatic organisms although at vastly different rates. Some of the

biota, in particular fishes, are an important source of food for man. It has been shown that more than 90 per cent of known human exposure to OC contaminants are derived from our food, including fish, and therefore, it is not only an ecological problem but also a public health concern to eliminate such contaminants from the aquatic ecosystem.

**Polychlorinated Biphenyls (PCB)**

The hydrophobic nature of many organochlorine contaminants is the reason for their ready adsorption on solid surfaces. It has been shown that PCBs in the water column are associated with particulate matter to greater than 95 per cent (Munson *et al.*, 1976). In the Great Lakes, large amounts of PCBs were found in the sediments. Highest concentrations were observed near the outfalls of industrial and urban centres (ULRG, 1977). In the sediments of Hamilton Harbour, for example, PCB concentrations were in the order of several mg/kg (GLWQ, 1976).

The concentrations of organochlorine contaminants in the open lake waters are frequently below present

routine analytical quantification limits; for PCB this limit is presently around 0.010 µg/l (GLWQ, 1975). However, bioaccumulation processes result in high contaminant concentrations in fish and in fish-consuming birds and mammals, and in man. Surveys of eggs of herring gulls and other fish-consuming birds showed PCB residues of more than 100 mg/kg in eggs, approximately 100 times the concentration in commercial fish, from many localities within the Great Lakes (Table I). Concurrent with such residues, greatly reduced hatching success and symptoms of chick edema disease were noted in surviving chicks (Gilbertson and Fox, 1977), as well as behavioral abnormalities of adult herring gulls (Fox *et al.*, 1978).

In order to elucidate the adsorption and bioaccumulation processes taking place, it may be of interest to compare the relative contaminant concentrations and estimated total lake load in some of the compartments. As evident from the data in Table I, both the concentrations and total amounts of PCB in fish and herring gull eggs are similar for each species in Lakes On-

**Table I.** Concentrations and total quantities of PCBs in selected Great Lakes' sediments and biota.

Sample	Unit	L. Ontario	L. Erie	L. Superior
<b>Sediments</b>				
Average concentration				
range a, b	µg/kg	77-89	74-252	30
Estimated load of PCBs b	kg	9000	35600	4000
<b>Fish, common species</b>				
	µg/kg			
Walleye c	µg/kg	2020	1160	370
White sucker c	µg/kg	1200	1650	
Longnose sucker d	µg/kg			900
Coho salmon e	µg/kg	8050	2360	
Lake trout	µg/kg	9380 e		2020 f
<b>Fish, biomass</b>				
Commercial fish catch (1977)	kg/year	1200 x 10 <sup>3</sup>	20500 x 10 <sup>3</sup>	3750 x 10 <sup>3</sup>
Estimated mean concentration of PCB b	µg/kg	2370	880	610
Estimated load of PCB h	kg	14	90	14
<b>Birds</b>				
Herring gull eggs c	µg/kg	125000	55000	55000

a) In depositional areas; b) PLUARG, 1978. c) TFPCB, 1976. d) Veith *et al.*, 1977 e) Spagnoli and Skinner, 1977; f) ULRG, 1977. g) GLFC, 1978; h) Calculated from estimated mean concentration of PCB times commercial fish catch times five

tario, Erie, and Superior. However, the estimated total amounts bound with the sediment are quite different in each lake. The total amount of PCB in Lake Erie sediments is approximately nine times greater than that of Lake Superior and also four times greater than that of Lake Ontario (PLUARG, 1978). Although these estimates are based on a limited number of data, and assume uniform concentration profiles of PCBs in the sediments, the relative amounts estimated are probably realistic. Moreover, it can be deduced from such data that water quality conditions, in particular turbidity and algal density, inversely affect the amount of contaminant available for food chain transfer. It is assumed, therefore, that most of the PCB entering Lake Erie is or becomes quickly adsorbed on particulates, such as the abundant algae, most of which are sedimented before they enter the food chain. In contrast, the phytoplankton concentration in the less productive Lake Superior is approximately four times less than that of Lake Erie (Dobson *et al.*, 1974), hence in Lake Superior, a higher percentage of PCB containing phytoplankton is scavenged by the zooplankton and, as a result, enters the food chain. It has been speculated that a massive reduction of Lake Erie phytoplankton through phosphate control without concurrent reduction in the contaminant loads, would lead to an increase in contaminant levels in Lake Erie fish.

There is still the open question as to what degree contaminants bound to sediments can be recirculated into the water column and enter the food chain. In principle, there are two mechanisms possible for such a process: (1) direct uptake and digestion of sediments by bottom dwelling organisms with retention of the contaminants in the organisms, and subsequent accumulation by predators; and (2) resuspension and/or leaching of the sediments into the water column with incorporation in fish by respiration or ingestion. The latter process is likely to be of particular importance in areas of active sediment transport and dredging activities. However, the question whether sediments will act predominantly as a sink or as a source of contaminants will depend on a number of physical and chemical characteristics of both the sediment and the contaminant in ques-

tion. For example, it has been shown that the lampricide TFM binds very strongly to organic matter in sediments, even to the extent of not being desorbed by common organic solvents (Fox and Hale, 1978). In contrast, the persistent contaminant Kepone was found to be leached from sediments into the water of the James River (Bender, 1976). Obviously, among the many factors which determine the adsorption-desorption rates are the characteristics of the contaminant, the sediments, and the overlying waters. Presumably also, the same type of sediment can act as a sink for a contaminant at one location or time, and behave as a source at another.

The transport of PCB and other contaminants together with sediments has clearly been shown in Lake St. Clair (Frank *et al.*, 1977). In the few years from 1971 to 1974, a substantial shift occurred in the PCB distribution due to sediment transport out of the lake. At the same time, control measures helped to reduce the new input from previously identified sources, resulting in an overall decline of the total PCB load in the sediments. Shifts of sediment contaminations were also observed in Lake Erie, initially high concentrations in the western basin appear to have become relocated to the depositional zone of the eastern basin.

#### Mirex and Chlorinated Styrenes

An interesting example of the detection of a contaminant and the research leading to the discovery of its source and distribution can be found in mirex. The flame retardant and insecticide was traced from its occurrence in fish from the Bay of Quinte, Lake Ontario, to its source at the Niagara River (Kaiser, 1978). The distribution of mirex in Lake Ontario sediments (Holdrinet *et al.*, 1978) was instrumental in the delineation of the source and distribution of this contaminant. Two distinct zones of mirex were shown to extend from the mouth of the Niagara River and off Oswego. A subsequent examination, showed an eastward movement of the contaminated areas, paralleling known sediment movement patterns. The total load of mirex in the Lake Ontario sediments is estimated to be 700 kg, considerably greater than the estimated load of 0.5 kg in all of the lake's

fish. Such data show the importance of adsorption and partitioning processes of such organochlorine compounds onto sediments and plankton, from where they may contaminate the entire food web. At the same time, the continued occurrence of mirex in the lake sediments proves the persistent nature of this compound.

The relative quantities of PCB (Table I) and mirex in the Great Lakes' sediments far outweigh the respective total loads in the fish. However, contaminants are often detected in fish before they are found in the sediments. This is not surprising in view of the distribution of contaminants over large parts of a lake's sediments and the high concentrations observed in predatory fish and animals resulting from bioaccumulation processes. An interesting example of that is the observation of polychlorinated styrenes in fish from Lake Ontario (Kuehl *et al.*, 1976) and in heron tissues and eggs from Lake St. Clair (Reichel *et al.*, 1977). Chlorinated styrenes were also observed in effluents and emissions from magnesium manufacturing plants in Norway. Although not used anywhere in manufacturing processes, the compounds are thought to be formed as by-products from the interaction of graphite electrodes with hot salt melts containing chloride ions (Lunde and Ofstad, 1976). Surprisingly, however, no such manufacturing plant appears to be located within the Great Lakes' areas where such contaminants were reported. Consequently their source is still unknown.

#### Outlook

Recent investigations by the Research Advisory Board of the International Joint Commission resulted in the compilation of a list of approximately 2800 synthetic chemicals known to be produced or used within the Great Lakes basin (RAB, 1978). Many of these compounds are only poorly defined with respect to their environmental and human health implications. Presuming rapid degradation, low toxicity and low bioaccumulation potential for the majority of these chemicals, the task confronting us is to identify those compounds which do pose an environmental risk or which may have been the cause of environmental or public health problems which have yet to surface.

with effects such as increased cancer rates or mortality. Recent observations showed significantly increased rates of birth defects in children born near a former landfill site for chemicals in Buffalo, N.Y., many years after the site had been levelled and built upon. Such local problems appear from time to time, making headlines in the daily news. However, the general contamination of our entire ecosystem appears less obvious and it is therefore, only rarely perceived in its catastrophic potential. It is to be hoped that high temperature incineration of waste chemicals, new legislative controls on effluents and emissions, as well as public concern will help to restore and maintain the Great Lakes as a valuable and unique resource for future generations.

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MS received October 25, 1978

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