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Polychlorinated Biphenyls in the Great Lakes

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Abstract This chapter reviews the scientific understanding of the concentrations, trends, and cycling of polychlorinated biphenyls (PCBs) in the Great Lakes. 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 the phase-out in the 1970s. Unfortunately, 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 $100–300\,\mathrm{pg\,L^{-1}}$, 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.

Keywords Bioaccumulation · Mass balance · PCBs · Toxicity

Abbreviations

PCBs	Polychlorinated biphenyls
$\mathrm{Sol}_{\mathrm{aq}}$	Water solubility
VP	Vapor pressure
K_{H}	Henry's Law constant
K_{OW}	Octanol–water partition coefficient
K_{OA}	Octanol–air partition coefficient
AhR	Aryl hydrocarbon receptor
AHH	Aryl hydrocarbon hydroxylase
PCDD/F	Polychlorinated dibenzo-*p*-dioxins and dibenzofurans
FDA	Food and Drug Administration
ELS	Early life stage
BNL	Benthic nepheloid layer
GLFMP	Great Lakes Fish Monitoring Program

TEQ	Toxicity equivalence
BAF	Bioaccumulation factor
BCF	Bioconcentration factor
BSAF	Biota-sediment accumulation factor
BMF	Biomagnification factor
LMMB	Lake Michigan Mass Balance

1
Introduction

1.1
History: Discovery in the Great Lakes

Polychlorinated biphenyls (PCBs) were first identified in environmental samples from the Great Lakes region by Gilman Veith, who found PCBs in lake trout and bloater chubs from Lake Michigan in 1968 [1]. Jensen [2] had just demonstrated the existence of PCBs in the Swedish environment, and the Michigan Department of Environmental Quality was interested in whether some unusual peaks in the gas chromatograms of fish extracts might also be PCBs. Veith confirmed the identity of PCBs in these extracts by mass spectrometry, and the newly established Federal Research Laboratory in Duluth, MN (of which Veith eventually served as director, now the US EPA Mid-Continent Division of the National Health Effects Research Laboratory) began investigating this contamination.

The intense research on PCBs in the Great Lakes over the intervening decades is important in three ways. First, the region is a major economic resource and population center for the USA and Canada, and as such the human and environmental health of the region is of great significance. Second, the ecosystem is unique and valuable in its own right. And third, as a heavily studied region with well-defined but diverse characteristics, studying the behavior of PCBs in the Great Lakes has served to greatly enhance our knowledge of the fate and transport of PCBs and other contaminants in the environment in general.

PCBs contaminated the environment of the Great Lakes as a result of historical use and discharge of PCBs from many different industries within the Great Lakes basin, including packing plants, paper mills, breweries, tanneries, machine shops, and foundries. These industries prospered in the Great Lakes throughout the 20th century, with major growth concurrent with the growth in production and sales of PCBs between 1929 and the mid-1970s. At this time, PCBs were common additives to oil to prevent breakdown of the oil and to maintain specific viscous properties when heated. PCBs were commonly used by the power industry in electrical transformers, capacitors, hydraulic equipment, and as lubricants. They were used as plasticizers in rubber and synthetic resins. These useful compounds were also added to many products used directly by the public or by light industry, including carbonless copy paper, adhesives, waxes, inks, pesticide extenders, sealants, and caulks [3]. New uses of PCBs were discontinued in the mid-1970s and all production ceased by 1979. Since then, PCBs have been removed from active use although they are still found in high concentrations in waste disposal sites and in reservoirs of old stockpiles throughout the Great Lakes basin.

1.2
Formulations

PCBs were sold by Monsanto in North America as technical mixtures of PCB congeners. A PCB congener is a chlorinated biphenyl (one to ten chlorines) with a unique chemical structure. There are 209 possible congeners, although less than ~ 150 were produced for industrial use. Twelve different technical mixtures were produced by reacting biphenyls with anhydrous chlorine in the presence of an iron catalyst. The various mixtures were produced by controlling the residence time of the chlorine in the reactor. The technical mixtures were generally named according to the percentage chlorine in the PCB mixture. For example, Aroclor 1242 was 42% chlorine by mass while Aroclor 1254 was 54% chlorine by mass. The most common mixtures used were Aroclors 1242, 1248, 1254, and 1260 [3]. The exact mass percentage for the production and sales of the individual mixtures is unknown, although more than half of PCBs produced in the USA were in the form of Aroclor 1242, used for capacitors and transformers [4]. Aroclor 1242 was also used in the emulsion applied to carbonless copy paper and has been identified as a dominant mixture released from paper mills on the Fox River, Wisconsin [5]. A mixture of 1242 and 1248 was used in the hydraulic fluid of a die-casting industry in Waukegan, Illinois [6]. In both systems, the original mixture of congeners is still evident in sediments. The total mass of Aroclors produced in North America is estimated to be 570×10^6 kg [7] but the mass used in the Great Lakes basin is unknown.

1.3
Widespread Contamination

There are at least 31 locations in the Great Lakes Basin identified by the US-Canada Water Quality Agreement as Areas of Concern due to impairment to beneficial uses [8]. Of the 14 identified impairments, PCBs are implicated in seven: restrictions on fish and wildlife consumption; degradation of fish and wildlife populations; fish tumors or other deformities; bird or animal deformities or reproduction problems; degradation of benthos (bottom dwelling organisms); restrictions on dredging activities; and added costs to agriculture or industry. Most of the sites that are contaminated with PCBs were originally exposed as a result of direct use and disposal. These sites continue to contribute to PCBs in the Great Lakes system though tributary flow, volatilization, erosion, and uptake by local fish and other biota. The majority of sites have not been fully characterized and the extent of contamination is unknown. Some of the sites, including the Fox River, Green Bay, and Waukegan Harbor (Lake Michigan), have associated PCB inventories (Table 1). The mass of PCBs in these areas is very large. In some cases, the total amount of PCBs in the Area of Concern is larger than that estimated for all the sediment in the

Table 1 Published sediment inventories of PCBs in the Great Lakes

System	Inventory (kg)	Refs.
Lake Michigan (open lake)	75 000	[10]
Waukegan Harbor (Lake Michigan)	900 [a]	[9]
Green Bay (Lake Michigan)	14 565	[11, 12]
Lower Fox River (Lake Michigan)	28 602	[13]
Lake Ontario (open lake)	130 000	[14]
Lake Superior (open lake)	4900	[10]

[a] More than 100×10^3 kg have been removed from navigational channels in Waukegan Harbor [9]

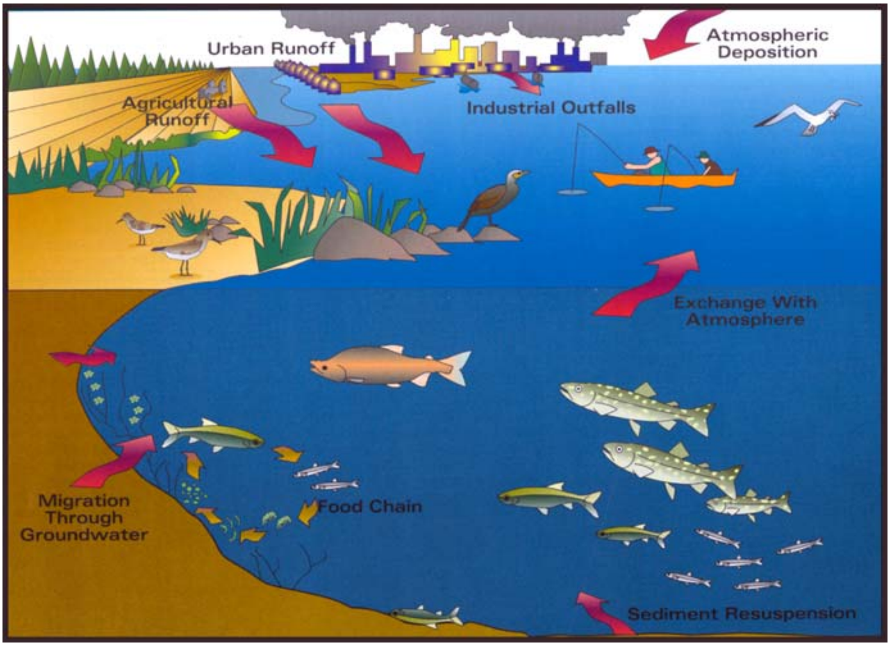

Fig. 1 Sources and cycling of PCBs in the Great Lakes [15]

open waters of the Great Lakes. For example, Waukegan Harbor was burdened with as much as 136×10^3 kg of PCBs before dredging began in 1990 [9]. That is more than the entire PCB inventory buried in the sediments of Lake Michigan's open waters [10].

PCBs can travel from their sources via the air or water. Volatilization and deposition (gas absorption) are known major routes for PCB input and loss to the Great Lakes. Direct input via tributaries is also still significant in some places. In the lakes, partitioning to water column particles leads to settling and eventual burial of PCBs, but sediment may be frequently resuspended, effectively serving as an additional source. Uptake by phytoplankton and subsequent bioaccumulation through the food chain results in continuing contamination of Great Lakes predators with substantial amounts of PCBs. Indeed, consumption of fish from the Great Lakes is the major exposure pathway for humans in the region. PCBs are now distributed throughout all compartments of the Great Lakes, and several programs routinely monitor concentrations in fish, birds, and air. Figure 1 describes the pathways (except degradation pathways) that contribute to PCB cycling in the lakes and uptake into the food chain. Degradation (photolysis, metabolism, and other forms of chemical decay) is not effective in decreasing total PCB concentrations in dilute systems.

2
Physical-Chemical Properties

The 209 different PCB congeners vary widely in their properties because of differing degrees and patterns of chlorination. Determining values of relevant physical-chemical constants ($\mathrm{Sol}_{\mathrm{aq}}$, VP, K_{H}, K_{OW}, and K_{OA}) is difficult both because of the large number of congeners and the difficulty of working with very hydrophobic compounds. Often, there is a large amount of disagreement between published literature values. Two studies, published in 2000 [16] and 2003 [17], reviewed all available data to determine suggested values for a suite of properties, but only for a limited number of congeners.

Nonetheless, there is widespread agreement in the literature on the overall trends and relative magnitudes of PCB properties. Figure 2 shows data for PCB vapor pressure, octanol–water (K_{OW}) and octanol–air (K_{OA}) partitioning coefficients, and Henry's Law constant [18–21]. The sources were chosen because they represented self-consistent values for large numbers of congeners, and they are widely considered the best values available. In each case, values were determined experimentally for some congeners, and these data were used to predict the values of the remaining congeners.

The values of solubility, vapor pressure, K_{OW}, and K_{OA} vary over nearly six orders of magnitude for PCB congeners. Such a large range means the behavior in the environment should also vary greatly among congeners. The exception is Henry's Law constant, which is relatively invariant for all congeners, although the spread in values increases with increasing chlorination. Note that other published values for the Henry's Law constant, while different, are still within two orders of magnitude of those shown in Fig. 2 [16, 17, 22] and thus the range is still small relative to other physical and chemical properties.

Ranges are given in Table 2 for the properties plotted in Fig. 2 and for solubility [16, 17]. In most cases, a variation of one to two orders of magnitude is observed among PCBs with the same number of chlorines. For vapor pres-

Table 2 Ranges of physical-chemical properties for PCBs. All values for 25 °C except log K_{OA} (20 °C)

Number of chlorines	log VP (Pa)	log K_H (Pa m^3 mol^{-1})	log K_{OA}	log K_{OW}	log Sol_{aq} (mol m^{-3})
1	0	1	7	4 to 5	- 2
2	- 1 to - 0	1	7 to 8	5	- 4 to - 2
3	- 2 to - 1	1 to 2	8 to 9	5 to 6	- 4 to - 3
4	- 3 to - 1	1 to 2	8 to 10	5 to 6	- 6 to - 4
5	- 3 to - 2	1 to 2	9 to 11	6 to 7	- 5
6	- 4 to - 2	1 to 2	9 to 11	6 to 7	- 6 to - 5
7	- 4 to - 3	1 to 2	10 to 12	7 to 8	- 6
8	- 5 to - 3	1 to 2	10 to 12	7 to 8	- 6
9	- 5 to - 4	1 to 2	11 to 12	8	- 7
10	- 5	2	12	8	- 7

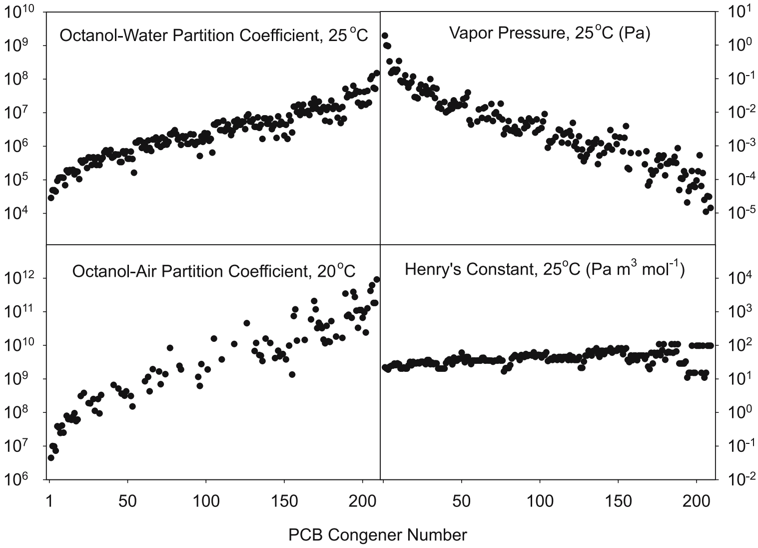

Fig. 2 Properties of PCB congeners [18–21]

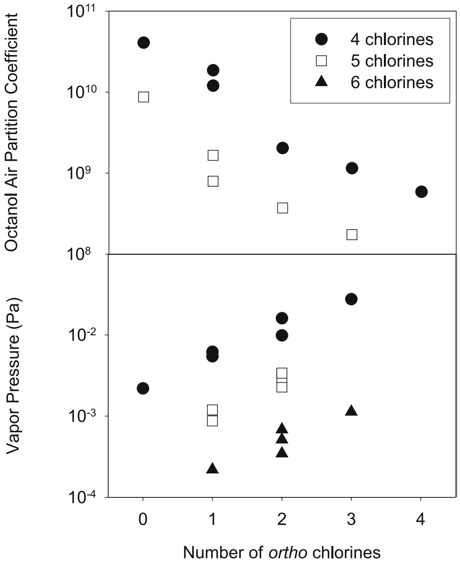

Fig. 3 Variation of the octanol–air partition coefficient and vapor pressure within homolog groups as a function of the number of *ortho* chlorine substituents [18, 23]

sure and K_{OA}, we can see that this variation is partly explained by chlorine position (Fig. 3). Measured values of the properties vary with the number of chlorines in the *ortho* position [18, 23]. The vapor pressure increases, and K_{OA} decreases, exponentially with more *ortho* chlorines. Indeed, for these two parameters, the variation *within* a homolog group is greater than the variation *between* homolog groups (for congeners with the same number of *ortho* chlorines).

Based on the observed properties of PCBs, we would expect to see a large range of behavior in environmental transport and partitioning. In particular, differences in bioconcentration, vapor–particle partitioning, and water–particle partitioning should be apparent both between and within homolog groups. We would not expect one congener to be representative of an entire homolog group.

2.1
Analytical Challenges

The analysis of samples on a congener basis was not possible in the early years of investigation of PCBs in the Great Lakes region. The commercial availability of high resolution capillary gas chromatographic columns and the concurrent synthesis, identification, and production of individual PCB congener standards [24] in the mid-1980s was a significant breakthrough. Through a transition period before the congener composition of individual chromatographic peaks was known, capillary GC analysis of Great Lakes water improved "Aroclor-level" quantification by reducing interferences and by improving matches to Aroclor standards through multiple linear regressions routines like COMSTAR [25] and PCBQ [26]. The pioneering work of Mullin and coworkers [24] and the determination of PCB congener physicochemical properties K_{OW} by Hawker and Connell [21], and of vapor pressures and Henry's Law constants by Burkhard et al. [27, 28]) catalyzed congener-specific geochemical studies in the Great Lakes in the 1980s and 1990s. More recently, analytical methods for PCBs have been further improved through the use of high resolution mass spectrometry, which provides substantially better signal-to-noise ratios and, therefore, instrumental sensitivity [29]. Due largely to high per-sample costs, high resolution mass spectrometry has not been widely used to date to measure PCB congeners in Great Lakes waters.

Congener-specific analysis of PCBs is now the norm for determination in natural matrices. Determination by Aroclor mixture is ineffective in the open waters and in biological samples. Congener distributions in natural matrices are often very different compared to any of the original Aroclor mixtures. This is primarily a result of weathering that removes or enriches some congeners over others. Weathering of PCB mixtures via volatilization, sedimentation, bioaccumulation, metabolism, and other natural processes has tremendous impact on the overall half-life of PCBs in the environment, their ultimate fate, and their toxicological impact on humans and organisms. The mechanisms that control these processes are of major concern to Great Lakes scientists.

3

Human and Wildlife Toxicological Concerns

Many of the properties described above, such as degree of chlorination, low water solubility, and hydrophobicity, lead to concerns about PCB toxicological effects. They are resistant to breakdown or metabolism and are bioaccumulative, and possess the ability to pass through cell membranes and bind to a variety of receptors that elicit their toxicity. There have been decades of research demonstrating that exposure to PCBs results in the risk of adverse impacts on wildlife populations as well as human populations. These impacts vary by species, and the degree and level to which they are exposed, thus resulting in a wide variety of toxicological endpoints (e.g., reproductive impairment, cancer, chloracne). Furthermore, the number and placement of the chlorine atoms on the biphenyl ring greatly affects toxicity as well as physical properties. PCBs with no *ortho*-substituted chlorines exhibit dioxin-like effects associated with the induction of numerous enzymes, most notably that of microsomal cytochrome P4501A1 and its associated monooxygenase activity, aryl hydrocarbon hydroxylase (AHH) [30]. PCBs with *ortho*-substituted chlorines exhibit a different mode of toxicity [31, 32] that is linked to adverse neurological effects. Several studies have implicated low molecular weight PCBs and their metabolites as potential tumor-initiating compounds that may induce oxidative DNA damage or formation of DNA adducts [33, 34].

Much of our current understanding of these impacts arose from research on wildlife and human populations within the Great Lakes basin. Despite being banned in North America more than 25 years ago, the toxicological risks from PCB exposure are still a present-day concern. For example, current PCB concentrations in fish in the Great Lakes are sufficiently large as to drive the need for fish consumption advisories for sport fish and to restrict commercial fisheries.

Humans, fish, and wildlife are exposed to PCBs from a number of different exposure routes, including respiration, water consumption, food consumption, and dermal contact with contaminated water, soil, etc. However, the dominant exposure route is food consumption, and especially the consumption of fish. This is because PCBs bioaccumulate effectively in fats and lipids [35]. As a result, most PCB congeners (including the most toxic ones) biomagnify in the food web, which means that the higher levels of the food web will have greater concentrations than lower ones (see full discussion in the section on food web dynamics). As a result, adverse effects have been observed in fish-eating animals and birds, and in humans that have consumed fish (occupationally exposed workers are not considered in this discussion).

The literature on PCB toxicological effects is vast, and only those studies that relate more directly to the Great Lakes will be discussed here. There have been numerous workshop publications as well as reviews on this topic over time [3, 4, 36–48].

3.1
Effects on Fish and Other Animals

While much attention is paid to the consumers of fish, there are also concerns that PCBs have impacts on fish themselves. The native species of lake trout (*Salvalinus namaycush*) was extirpated in the Great Lakes in the mid-1900s (with the exception of a few isolated self-reproducing populations in Lake Superior), likely due to a combination of stressors including overfishing, the invasion of the sea lamprey, and synthetic toxic organic compounds such as PCBs and PCDD/Fs. Efforts to restore the lake trout to the Great Lakes began in the 1950s under the direction of the Great Lakes Fisheries Commission, and while stocked fry resulted in adult stocks, no natural reproduction was achieved until recently [49]. Given that PCBs are the dominant organic contaminant across the lakes, much of the research has focused on the impacts of PCBs on fish reproduction.

The results of numerous laboratory studies on fish and a number of other aquatic species (daphnids, algae, minnows) were used to establish water quality criteria for regulatory purposes, using the LD_{50} of the most sensitive species to protect aquatic life in the Great Lakes. PCB-126 has also been shown to impact two species of frogs (green, *Rana clamitans*, and leopard, *Rana pipiens*) at high concentrations in laboratory studies [50]. Several laboratory studies have implicated PCBs, particularly the AHH PCBs, in early life stage mortality (ELS) of fish [51–56].

Congener 126 is the most potent of the PCBs in binding to the AHH receptor of fish [57]. A number of studies demonstrated the correlation between organic contaminant levels and fish reproductive effects, but specific mechanisms were not identified [58–60]; it was assumed that PCBs and PCDD/Fs were the causative contaminants. Wilson et al. [61] demonstrated that fish eggs injected with Lake Michigan lake trout extract exhibited embryonic toxicity.

A definitive study by Guiney at al. [55] demonstrated the link between AHH-active compound exposure to lake trout eggs and blue-sac syndrome, an edema condition that develops in exposed fry and results in mortality. This established a mechanism and dose-response that was hypothesized to explain some of the natural reproduction impairment of lake trout in the Great Lakes. Cook and colleagues [56] tested this hypothesis for Lake Ontario by estimating the dose of AHH compounds to lake trout over time from lake sediment cores, and concluded that the lack of natural reproduction in Lake Ontario was consistent with their contaminant exposure. PCBs typically comprise the majority of the AHH-active compounds in Great Lakes fish [62]. However, other factors alone and in combination with organic contaminants may play a role in the low natural reproduction of lake trout. For example, over-exploitation, lack of genetic diversity, sea lamprey predation, and thiamine deficiency in eggs have all been suggested as possible stressors on lake trout recruitment. ELS and swim-up syndrome can both be caused by thiamine deficiency, and are not associated with exposure to AHH-active contaminants [63].

More recently, PCB-126 has been implicated in disrupting thyroid function in fish (see references in [64]). Brown et al. [64] demonstrated in laboratory studies that lake trout exposed to PCB-126 at $40\,\mu g\,kg^{-1}$ in food had increased levels of the growth regulator T4, but unaffected T3 levels, and thus the thyroid system could compensate. However, PCB exposure could result in significant impacts when T4 needs are greatest, such as during temperature changes, periods of rapid growth, or metamorphosis.

One of the most sensitive mammals to dioxin-like PCB and dioxin exposure is the mink. Effects have been documented in both farmed mink [65, 66] and wild mink [67–72]. Extensive work was done in the 1970s and 1980s by Auerlich, Ringer, and colleagues [65, 66, 73–76] that documented the impact of feeding Great Lakes fish to mink. These impacts included reproductive failure and mortality. A recent study [77] showed the presence of squamous epithelial lesions on the mandibles and maxillae of wild mink from a heavily PCB-contaminated area along the Kalamazoo River in Michigan. While seen previously in laboratory studies [78], this is the first report of such an effect in wild mink, which can lead to significant tooth loss.

Fish-eating and colonial nesting birds have also been adversely impacted by contaminant exposures, with effects ranging from mortality and chick deformities to reproductive effects and thyroid toxicity to alterations in nesting behavior, female–female pairing, and laying of super-clutches [42, 79–90]. While most studies have examined effects in wild populations, the effects are correlated with the exposures to dioxin and dioxin-like PCBs, mostly through eating contaminated Great Lakes fish. Populations that have been affected include terns, herring gulls, eagles, kestrels, and cormorants from throughout the Great Lakes, concentrated in areas with greater concentrations of contaminants.

3.2
Effects on Humans

There is a growing body of literature on PCB toxicity to humans, with current research examining more subtle effects associated with chronic exposures, and the associations of those effects with specific congeners. One of the first epidemiological studies to demonstrate effects from exposure to the contaminants in Great Lakes fish was done by Joseph and Sandra Jacobson and colleagues [91–93]. This study examined development and behavior outcomes in children born to mothers who consumed varying amounts of Lake Michigan fish that were highly contaminated with PCBs. They found deficits in a number of measures, including head circumference, birth weight, and gestational age, which related to fish consumption by the mothers in a dose-dependent fashion, after controlling for a number of confounding variables. This cohort of children has been followed for several years, and additional deficits have been associated with their exposure to PCBs in utero as measured by cord blood concentrations, including effects on cognitive function, memory, motor activity, and intellectual development [94–99]. Caution must be exercised in the interpretation of the epidemiology studies, as results correlated with fish consumption or PCB measurements may covary with other contaminants. Thus PCBs may be a tracer of, or acting in concert with, other toxic contaminants that produce some of these effects [100]. Nevertheless, the weight of evidence is strong in various human studies that have isolated the impacts of PCBs [101]. Many other similar findings corroborating the Michigan study. The multigenerational effects of PCBs on infants have been corroborated by other human epidemiological studies conducted in New York [102], The Netherlands [103], Germany [104], and the Faroe Islands [105]. The agreement of many animal studies with primates [44, 106–108] and other animals (see references in [48]) has lent significant support to the conclusions of the human studies.

Neurological effects in humans have been a particular focus of recent research, and appear to be related to exposures of the *ortho*-substituted congeners as well as the co-planar configurations [43, 44, 107, 109–112]. Impacts on immune function [113], some aspects of thyroid function [114], gender ratios, and endocrine disruption [40, 115] have also been documented.

Consumption advisories in the Great Lakes are designed to protect people from the harmful effects of PCBs and other contaminants in fish. There are several benchmarks that are used to assess PCB levels in fish. The Food and Drug Administration (FDA) regulates allowable contaminants (including PCBs) in food as part of interstate commerce, which includes the commercial fisheries. The FDA Action Level is $2\,\mu g\,g^{-1}$ wet weight (ww) in the edible portion. The FDA Action Levels are based on evaluating economic impacts on the regulated industry in light of concerns for public health. The FDA Action Limit for PCBs for fish was lowered from $5\,\mu g\,g^{-1}$ (ww) to $2\,\mu g\,g^{-1}$ (ww) as the levels in most of the commercial species of interest dropped below the $2\,\mu g\,g^{-1}$ (ww) benchmark in the 1980s. This is not considered protective of public health, nor was it derived by any risk assessment approach.

The individual states issue Fish Consumption Advisories for fish in their inland waters, which are aimed at providing anglers health-based guidance on the consumption of sport fish. Each state approaches the development of their guidance differently. Because the Great Lakes are shared across eight US states and two Canadian provinces, a common protocol for an advisory for PCBs was developed so that conflicting advice was not given on fish common to several jurisdictions [116]. PCBs were chosen since they are the contaminant that drives the Fish Consumption Advisories in every state and province (with one exception by the Ministry of Environment of Ontario which issues an advisory for toxaphene in Lake Superior). Thus each state and province issues separate guidance on fish consumption relative to PCBs in Great Lakes fish compared to their fish from inland waters.

The continued elevated concentrations of PCBs in sport fish in the Great Lakes necessitates that fish consumption advisories be issued by all of the US Great Lakes states and the Canadian provinces of Ontario and Quebec. Unlimited consumption is not advised until fish tissue concentrations decline below $0.05\,\mu g\,g^{-1}$ (ww), a level not expected to be reached for many decades (see Sect. 8). Thus PCBs will be of significant concern well into the future.

4
Atmospheric Processes

Concentrations of PCBs in air vary as a function of temperature. The temperature effect has been observed in samples collected in urban and remote areas and has been recognized as a major factor in observed concentrations since the late 1980s and early 1990s [117, 118]. The first convincing report of the seasonal trend came in 1992 when Hoff and coworkers published the results of an annual study of PCB concentrations measured at Egbert, Ontario [119, 120]. This pair of papers first showed that gas-phase PCBs and many other persistent organic compounds exhibited strong seasonal signals, with summertime concentrations exceeding wintertime concentrations by almost an order of magnitude. Their papers also showed that there was a good fit between the logarithm of the concentrations and inverse temperature. This relationship is predicted by the Clausius–Clapeyron equation if volatilization and sorption to surfaces is governing the atmospheric concentrations. Since then, others have confirmed that the temperature effect can be observed in the Great Lakes region on both a diurnal and seasonal basis [121–125]. At Chicago, there is enough data to demonstrate that the temperature effect is generally more pronounced for more chlorinated congeners [126], with significant variation within homolog groups, as with other physical properties.

As part of a mass balance study of PCBs entering Lake Michigan, a stochastic model was developed to describe the measured variation in air concentrations at more than a dozen sites on and around Lake Michigan [127–130]. Figure 4 illustrates the results of this effort for three of the sites. Airborne PCBs in Chicago were predicted to vary on a daily and seasonal basis by more than an order of magnitude with concentrations reaching as high as 15 ng m^{-3} once or twice a year. South Haven had much lower concentrations, and the remote Sleeping Bear Dunes site had concentrations nearly two orders of magnitude less than Chicago. Concentrations have since declined somewhat (Hites RA, personal communication), but otherwise the model remains consistent with observations.

Total airborne PCBs are dominated by the gas phase. Less than 10% of PCBs in ambient air are associated with aerosol particles, even in urban areas. For example, the average PCB gas-phase concentration (sum of ∼ 120 congeners) in Milwaukee was 1.9 ± 0.78 ng m^{-3} (standard deviation), while the average and standard deviation for the particulate-associated PCBs was 0.05 ± 0.02 ng m^{-3}. Particulate phase PCBs therefore accounted for less than 5% of the total atmospheric concentration [131]. This has been observed by many researchers and has been successfully predicted as a function of PCB physical-chemical properties [132–137]. For example, Pankow [138] and Harner and colleagues [23, 139, 140] have shown that the octanol–air partition coefficient (K_{OA}) can be used to accurately predict gas–particle partitioning of PCBs and other semivolatile organic compounds. This correlation has important implications about the nature of gas–particle partitioning of PCBs. The reason why PCBs are found in the gas phase is because of the low organic carbon content and total surface area (and volume) provided by atmospheric particles.

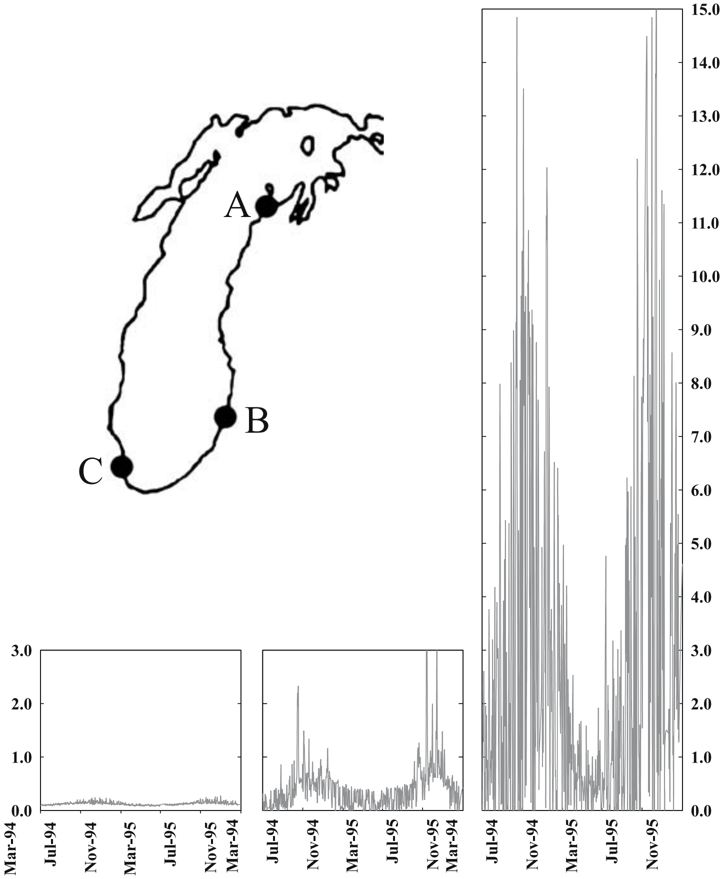

Fig. 4 Concentrations of airborne PCBs as a function of season at Sleeping Bear Dunes (*left plot and point A*), South Haven (*center plot and point B*), and Chicago (*right plot and point C*) around Lake Michigan. Concentrations shown are daily predictions based on fits to data

PCBs in air are enriched in the less chlorinated congeners although the higher molecular weight compounds are regularly observed (albeit at very low concentrations). Figure 5 shows the mean congener distributions found in air from Milwaukee [131] and Chicago (Hites RA, personal communication). The congener profile is fairly similar (qualitatively) in both cities. The atmospheric PCB profiles share their most prominent congeners with one of the two technical mixtures that were commonly used in the Great Lakes region, although significant differences are observed as a result of environmental processing and degradation. The preponderance of less chlorinated PCBs in the atmospheric samples may simply be a result of the greater volatility of these congeners, and does not necessarily indicate the relative emissions of Aroclor 1242 versus Aroclor 1254 in the region.

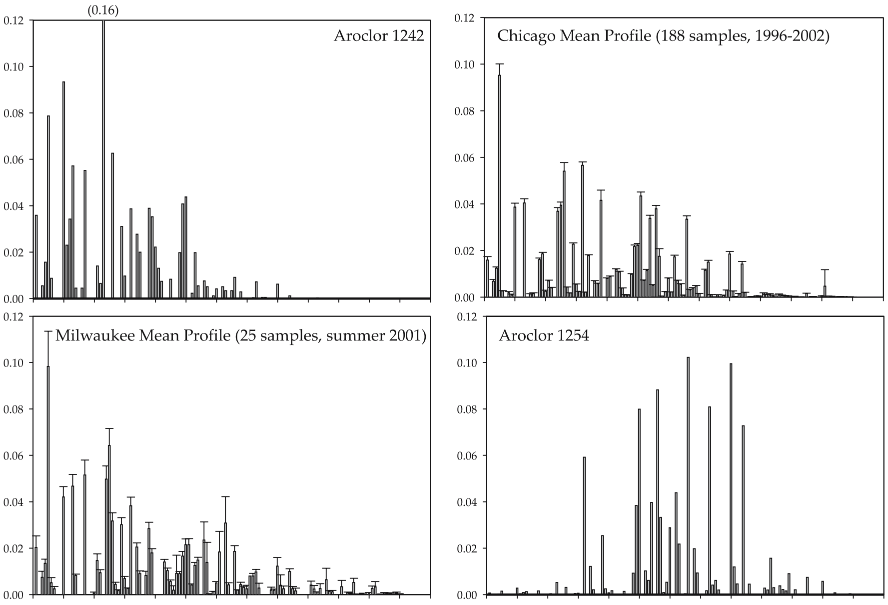

Fig. 5 Mean PCB congener profiles for two technical mixtures (Aroclor 1242 and Aroclor 1254) and at two urban locations (Milwaukee and Chicago). Data from Milwaukee is from [131] and data from Chicago is from the IADN network (Hites RA, 2005, Personal communication). Congener distributions for Aroclor 1242 and 1254 are from [141]

4.1
Atmospheric Sources

Present day PCB sources for the atmosphere are not well defined [142–144]. Without much exaggeration, the extent of understanding about atmospheric PCB sources is that they are larger in heavily populated cities and industrial areas and they are dominated by volatilization sources. Much more is known about non-atmospheric sources of PCBs. Direct discharges from industry have decreased since the phase-out. Disposal and handling of PCB contaminated soils and sediments are also controlled, at great expense and effort. But, current atmospheric sources are unregulated and uncontrolled because their locations are unknown and their relative contribution to human and ecosystem exposure is not well understood.

The major sources of PCBs, globally, are found in northern latitudes. Breivik et al. [144, 145] published a complete assessment of global historical usage of PCBs and, using a mass balance approach, predicted emissions of PCBs to the air as a function of their use and climate factors (primarily temperature). They identified major sources of PCBs as directly contaminated soils, fires, open use, use in capacitors, use in closed systems, disposal to landfills, waste incineration, and PCB destruction. They found that use of PCBs was focused in the USA, Europe, the former Soviet Union, and Japan. The consumption of PCBs was strongly linked to population, and Breivik et al. used population densities to illustrate the distribution of PCB sources.

PCB concentrations are high in cities because of historical use. Cities in the Great Lakes basin have a long history of PCB use in many industries such as steel mills, aluminum processing, paper mills, electrical generation and distribution, packing plants, breweries, tanneries, machine shops, and foundries [146]. These industries developed through the middle part of the 20th century and served as the economic foundation for many lakeside cities. During this time, PCBs were common additives to cutting fluids, electrical transformers, light ballasts, and lubricants [147]. After 1977, all new uses of PCBs were eliminated and industries began to remove PCBs from active use.

Atmospheric sources are presumed to be on the decline, although there are few measurements from before the 1990s. In the 1990s, several major measurement initiatives began that have given scientists a much better picture of the trends in airborne PCBs. For example, in 1990 the Integrated Atmospheric Deposition Network (IADN) installed five master stations to measure PCBs and other compounds in background air [148]. In 1995, the first urban monitoring site was installed by IADN in Chicago. Data from all the sites indicate declines in concentrations of airborne PCBs, despite strong interannual variability (Fig. 6). Most, but not all, of the variability is due to temperature. Hites

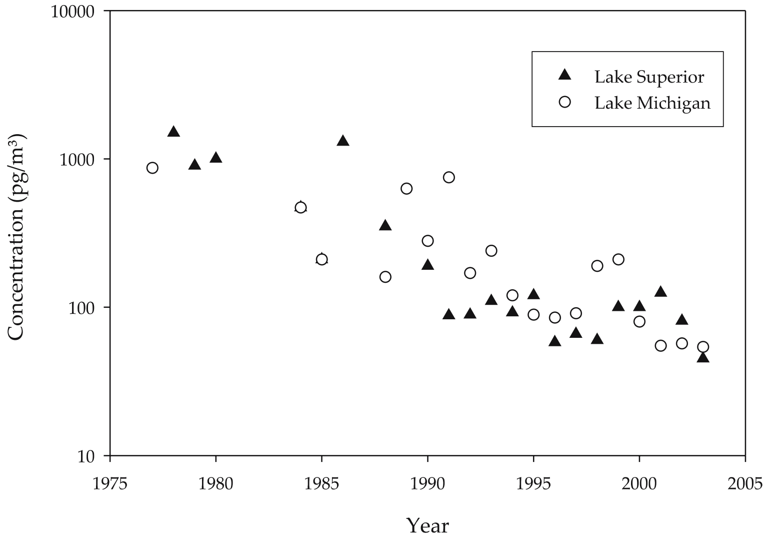

Fig. 6 Annual average gas-phase PCB concentrations in non-urban air near Lake Michigan and Lake Superior, as compiled in [124] including additional data from IADN (Hites RA, 2005, Personal communication)

and coworkers have provided a full statistical review of the relatively slow decline ($\sim$ 3% per year since 1990) in airborne PCBs [124, 149–151].

Data from long-term monitoring stations confirm major atmospheric emissions in the cities of Chicago, Cleveland, and the New York City area; these sites are either part of IADN or the New Jersey Atmospheric Deposition Network [152–160]. Extensive analysis based on air trajectories for sites in IADN indicate that Chicago is an important source area for the western Great Lakes region, while the heavily populated East Coast from Boston to Washington, DC is a source for the eastern portion of the Great Lakes [161].

Despite the clear evidence of PCB sources in urban air, the magnitude of these sources is unknown. Emission inventories that have proved useful for other pollutants (mercury, dioxins, and furans) are inadequate for PCBs. Emission inventories for PCBs maintained by the US EPA show a total release of about 15 kg year^{-1} released to the atmosphere in the entire Great Lakes region [162]. This value grossly underestimates what is actually released. For demonstration purposes, we can compare this emission value to observed concentrations. For example, consider the air over a city as a well-mixed box. Let us assume that the bulk of the PCB emissions from the urban landscapes of Chicago, Milwaukee, Detroit, Cleveland, Toronto, or Buffalo into the local atmosphere are each focused in a 5×5 km area with an atmospheric mixing height of 1 km. Then the surface-normalized burden for atmospheric ΣPCBs at 1 ng m^{-3} average annual concentration is 1 µg m^{-2} or 25 g in the 25 km^3 of atmosphere. Occasionally, PCB concentrations are as high as 10 ng m^{-3}, in which case the surface-normalized burden is 10 µg m^{-2} or 250 g. Emission rates of around 1 kg per *day* in *each* city are necessary to achieve the observed atmospheric concentrations, assuming a slow wind speed and residence time of the atmosphere of 30 min. Thus the vast majority of PCB atmospheric sources are unaccounted for.

People living near potential sources of atmospheric PCBs are very concerned about the magnitude of emissions and their exposure. In East Chicago, IN, for example, citizens are concerned about the effects of dredging on airborne concentrations of PCBs. As a result, environmental and community advocacy groups have released public documents citing their concerns and some have actively evaluated the planned activities by the Army Corp of Engineers [163, 164]. This concern appears to have motivated the US EPA and the US ACE to issue several documents evaluating the major dredging methods, including hydraulic dredging and clamshell dredging [165–167]. The activity of the community also seems to have encouraged a more open dialog about the relationship between dredging activities and atmospheric concentrations of PCBs. The public concern is reasonable. PCB exchange between air and water is dynamic. Human activities in heavily contaminated water are likely to have some impact on atmospheric emissions of PCBs.

4.2
Calculating Air–Water Exchange

Air–water exchange of PCBs is often determined using coordinated measurements of PCBs in air and water and the modified two-film theory. The two film theory of mass transfer was first described in 1923 by Whitman [168] and its modifications have been used many times for predicting air–water exchange of PCBs in the Great Lakes, smaller lakes, rivers, harbors, and bays [131, 169–177]. Its basic assumption is that molecular diffusion across the air–water interface is the rate-limiting step. Turbulence in air and water is very fast and so the total flux can be calculated as a function of molecular diffusion and film width only. This is a straightforward application of Fick's law, which states that the flux of mass across a boundary is a function of the concentration gradient and a diffusion or mass transfer coefficient. Examples of Fick's law in the environment include uptake of oxygen into surface waters, absorption of carbon dioxide by the earth's oceans, release of hydrogen sulfide from aerated ground water, and emission of methane gas from swamps. Examples in the human body include transfer of oxygen, carbon dioxide, nicotine and other gases between inhaled air and blood circulating in the lung. Equation 1 is the general form for predicting the direction and rate of exchange:

$$F_{\mathrm{gas,net}} = k_{\mathrm{ol}} \left(C_{\mathrm{w}} - \frac{C_{\mathrm{g}} RT}{H} \right) \tag{1}$$

where $F_{\mathrm{gas,net}}$ is the net mass flux (mass area^{-2} time^{-1}), C_{w} is the concentration dissolved in water, C_{g} is the concentration in the gas phase, R is the universal gas constant, T is temperature, and H is Henry's Law constant. The terms of Eq. 1 that are in parentheses define the chemical concentration gradient. The concentration gradient is measured from samples collected near the air–water surface. The mass transfer coefficient (length time^{-1}) is a rate constant. The value of the mass transfer coefficient is determined by the nature of the interface and the molecular diffusivity of the chemical. In the case of transport across a physical membrane, the mass transfer coefficient could be approximated by the molecular diffusivity of the compound divided by the width of the membrane. Liss and Slater defined the model for air–water exchange in the environment [178]. This analogy makes the mathematical derivation of the mass transfer coefficient easier. The overall mass transfer coefficient, k_{ol}, is described as two resistances in series:

$$\frac{1}{k_{\mathrm{ol}}} = \left(\frac{1}{k_{\mathrm{w}}} + \frac{RT}{H k_{\mathrm{g}}} \right) \tag{2}$$

where k_{w} is the mass transfer coefficient through a stagnant water layer and k_{g} is the mass transfer coefficient through a stagnant air layer. The other terms are the same as before. If the stagnant layers were real (i.e., constant and measurable) then the mass transfer coefficients could be calculated as a function of the thickness of the layers. If an oil film is present, the mass transfer equation will include a third term for the mass transfer coefficient for each congener in oil. However, one cannot measure these widths, so the mass transfer coefficients are found through experiment. Many laboratory and field studies have been conducted to determine the values of k_w and k_g as a function of measurable factors such as molecular diffusivity, wind speed, surface roughness, and wave height. Classic experiments include studies of oxygen and carbon dioxide uptake in wind tunnels and flumes. Recently studies in open oceans, rivers, and sheltered lakes have been performed using volatile tracers like sulfurhexafluoride and helium isotopes [179–183]. The design of the tracer experiments is to predict the mass transfer coefficients as a function of measured wind speed and molecular diffusivities (expressed as Schmidt numbers). These findings permit determination of mass transfer coefficients for compounds with other diffusivities and under other meteorological conditions.

Input via wet and dry particle deposition is not as important for the Great Lakes as for other bodies of water because of their large surface area relative to the size of their drainage basins. This results in air–water gas exchange dominating the atmosphere–lake interaction. However, direct deposition is not negligible. Deposition occurs through two processes: deposition of atmospheric particles, and precipitation. The magnitude of these fluxes depends on concentrations in the atmosphere, which vary themselves, as discussed above. Particulate deposition can be measured directly [152, 158, 184], but it is difficult to produce an artifact-free collection surface that accurately reflects the conditions of the Great Lakes water surface. Therefore, PCB particle deposition is often modeled as a function of the size of the aerosol particles and the concentration of PCBs on those particles. Particle size distributions have been measured over and around the Great Lakes but there are no reports of PCB congener concentrations as a function of particle size. Current analytical methods are not sensitive enough to collect such data and so most studies of PCB deposition have assumed that PCB concentrations are not a function of particle size [129, 131, 185]. Deposition fluxes are then modeled as a function of deposition velocity to water surfaces [186–188].

Wet deposition may be an important source of PCBs to the Great Lakes. Unfortunately, like dry particle deposition, it is difficult to measure directly because of the low PCB concentrations, the problem of sampling artifacts, and the distribution of rain and PCB concentrations over space and time. Some trends are evident, however [189]. Snow has been shown to be much more effective than rain in scavenging PCBs from both vapor and particulate phases at a site in Minnesota [190, 191]. This leads to a seasonal effect, in that precipitation concentrations of PCBs are highest in the winter in Chicago (Hites, personal communication), as with the concentrations of many other persistent organic pollutants [192]. Possible reasons include sorption to an aqueous or organic film on the snowflake, a filtering effect of the snowflake in scavenging particles from the atmosphere, and lower temperatures associated with snow events [190, 193]. The environmental conditions and hydrometer properties can also have a large effect on scavenging efficiency. Research in the southern Lake Michigan area has shown that scavenging ratios for PCBs vary significantly (over more than two orders of magnitude for total PCBs) from storm to storm, and even over the course of the same storm, in the case of rain [194].

Air–water exchange fluxes for the Great Lakes have been calculated in many cases [195], and they have been found to be highly variable even within a lake [129], as might be expected with the large variability of the region. Proximity to population centers is one important variable that affects the net direction of flux [131, 159, 196]. A discussion of the magnitude of atmospheric exchange processes can be found in Sect. 9.

5
Tributaries

Industrial emissions of PCBs to the lakes via rivers, tributaries, and connecting channels have been a significant source in many places. Local areas with very high PCB concentrations have been identified throughout the basin (see Table 3 and Fig. 7 for examples of sediment and stream concentrations). In some cases, local contamination with PCBs alone or in combination with other contaminants has been linked to adverse effects in wildlife [77, 197–199]. For example, mink living near a contaminated reach of the Kalamazoo River in Michigan displayed lesions of the jaw known to be caused by PCB-126 and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin [77], as mentioned earlier.

Long after industrial emissions have been reduced, contaminated sediments in affected reaches can still serve as a significant PCB source for the Great Lakes. The most-studied Great Lakes tributary is the Lower Fox River in Wisconsin, which drains to Lake Michigan via Green Bay. Paper mills in the area first starting using PCBs to make carbonless copy paper in 1954, and it

Table 3 Sediment PCB concentrations in Great Lakes tributaries (ng g^{-1} dry weight)

Location	Min	Max	Average	Date	Refs.
Ashtabula, OH	500	7000	2000	1998	[201]
Fox, WI	132	223 000	24 300	1987–1994	[202]
Detroit, MI/ON	8	25 000	4800	1998	[203]
Rouge, MI	470	10 900	2500	1998	[203]
Manitowoc/Pine Creek, WI	< 50	1 900 000	44 000	1993–1995	[204]
Milwaukee, WI	< 50	870 000		1993–1995	[204]

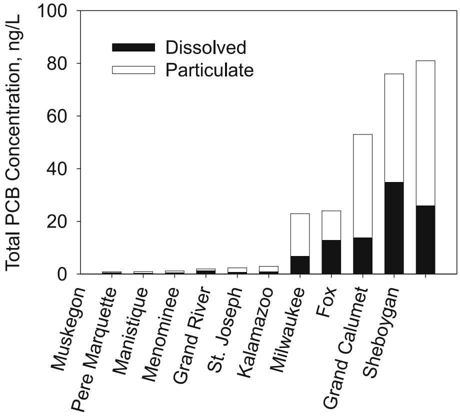

Fig. 7 PCB concentrations in Lake Michigan streams [200]

is estimated that between 120×10^3 and 400×10^3 kg of PCBs were released to the Fox River since that time from the manufacture and recycling of carbonless copy paper [13]. An estimated 95% of PCBs in Green Bay originated in the Fox River; as much as 70×10^3 kg of PCBs may have been transported to Green Bay sediments in this way [13]. Prevailing counterclockwise currents led to the accumulation of PCBs in the eastern part of the bay, where concentrations were measured as high as 1302 ng g^{-1} [13]. In comparison, the maximum observed concentration of PCBs in the sediment of northern Lake Michigan was 91.2 ng g^{-1}, and the maximum for the entire lake was 220 ng g^{-1}, with averages of 40–70 ng g^{-1} for regions of the lake [200].

6
Sediments

6.1
Accumulation

PCBs accumulate in bottom sediments and are recalcitrant to decay. As a result, sediments harbor some of the most concentrated levels of PCBs near regions of intense PCB usage. For example, measurements as high as 3.6 g kg^{-1} dry weight (0.36%) have been found in the sediments of the Waukegan harbor [205]. These local areas had severe problems, driving regulatory initiatives. Researchers then expanded their studies to explore contamination lakewide. One large study collected more than 1700 surficial sediment samples in a grid across the Great Lakes Basin between 1969 and 1975 [206], at the time of peak PCB concentrations. Average concentrations were lowest in Lake Superior (3.3 ng g^{-1}) and highest in Lakes Ontario (57.5 ng g^{-1}) and Erie

(94.6 ng g^{-1}). Concentrations were highly variable spatially in all lakes with much higher concentrations typically found in depositional areas [206]. The most recent lakewide surveys show significant decreases in concentrations since the 1970s and 1980s [207, 208].

The history of environmental exposure to PCBs is well recorded in Great Lakes sediments. Sediment cores show increases in concentrations and accumulation rates that begin in the early part of the 20th century and peak in the late 1960s to mid-1970s [209, 210]. Since the 1970s, most sediment cores show significant declines in PCB accumulations [211]. The most recently dated samples (Fig. 8) show that PCB accumulation rates in the sediment of Grand Traverse Bay have decreased to a level similar to that recorded for 1960, a time of widespread PCB use in the region [210]. Accumulation of PCBs in sediments exhibit slow declines and reflect the continuing exposure to these compounds in today's environment.

Accumulation in sediments from isolated lakes has sometimes been used to determine atmospheric inputs [212]. For example, rates of accumulation in Lake Superior [213] were found to be similar to rates in lakes with atmospheric sources only [205, 212], confirming that the atmosphere is the largest source of PCBs.

PCB accumulation in the sediment is not a straightforward function of downward settling of falling particles. Several field and laboratory studies have shown that PCBs can be recycled back to the water column via biological

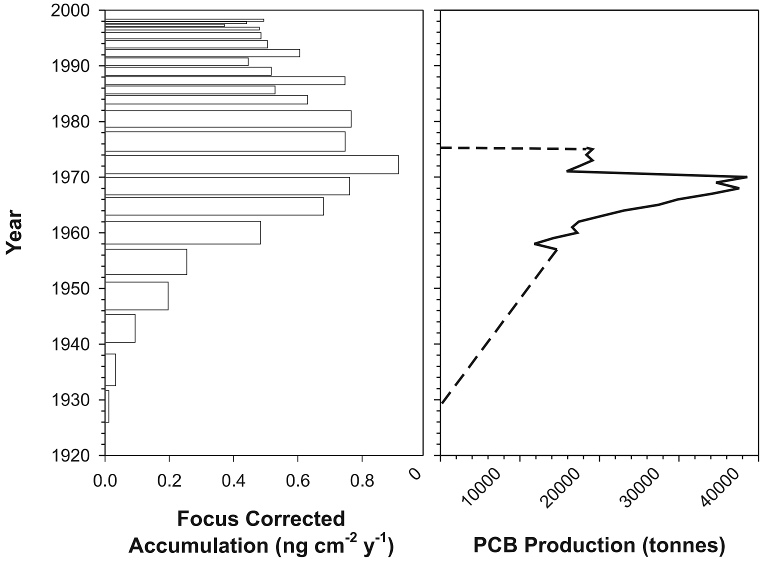

Fig. 8 PCBs in a sediment core collected in Grand Traverse Bay, Lake Michigan (modified from [210] and PCB production data [3])

and physical processes occurring at the sediment–water interface. Baker and Eisenreich used a submersible to sample the benthic nepheloid layer (a region of particle-rich lake water extending a few meters above the lake floor), the sediment boundary layer, and sediment cores [214]. They found a dynamic system: the nature of particles changes with the season, and cycling within the lake occurs [214]. There is rapid settling of organic-rich particles to the benthic environment, where organic material is utilized by biota [214]. Further research revealed that the accumulation rate of PCBs was much less than the flux of PCBs associated with settling particles [213, 215]. Calculations show that 50% of PCBs in the Lake Superior water column are transported to the benthic environment each year via settling particles. This represents a total flux approximately 17 times that of the estimated atmospheric deposition. However, of the PCBs associated with settling particles, only 1–10% end up in the sediments [213, 216].

The sorptive properties of PCBs are largely controlled by their hydrophobicity and by the particle organic carbon content, which is generally associated with the clay or fine-sized particles. As a result, PCBs are carried by fine particles, deposited to sediments, and focused into the more quiescent depositional basins. Once delivered to the bottom sediments, PCB burial can be slowed by sediment resuspension and bioturbation. PCBs may also partition into porewater or bind to colloidal organic matter and migrate within and from the sediments via diffusion or bioirrigation. The potential effect of these processes is to alter the depositional history of the contaminant as recorded in the sediments and to increase the residence time of the contaminant in the ecosystem. PCBs may also be subject to biotic or abiotic transformation in sediments, which can further alter the sediment input history. Studies on the accumulation of PCBs have found that their depositional history is often preserved in the sediment bed, as local and non-local redistribution processes are not sufficiently intense over the time scale of HOC inputs to alter the profiles significantly. However, much of the work was done in the 1980s, and there have been only a few more cores collected since then [210]. Sediment profiles of PCBs are needed to determine the recovery of aquatic ecosystems impacted by PCB deposition, the effectiveness of chemical bans, and the data needed to model chemical behavior. The diagenesis of PCBs within sediments over time is important to evaluate the extent that redistribution and transformation processes have altered the recent historical record. In addition, previous estimates of the total sediment burden of PCBs, which are necessary to construct a mass balance, have not reported on sufficient cores to form a reliable estimate. The work of Eisenreich et al. [209] and Wong et al. [14] represents a unique field study of PCB accumulation and diagenesis in sediments. The investigators collected sediment cores from the same location in Lake Ontario in 1981 and in 1990. The results are illustrated in Fig. 9. Between the two cores, there is a shift in the depth of peak PCB concentration with the peak moving downcore at the rate of sedimentation. In both cores, it is clear

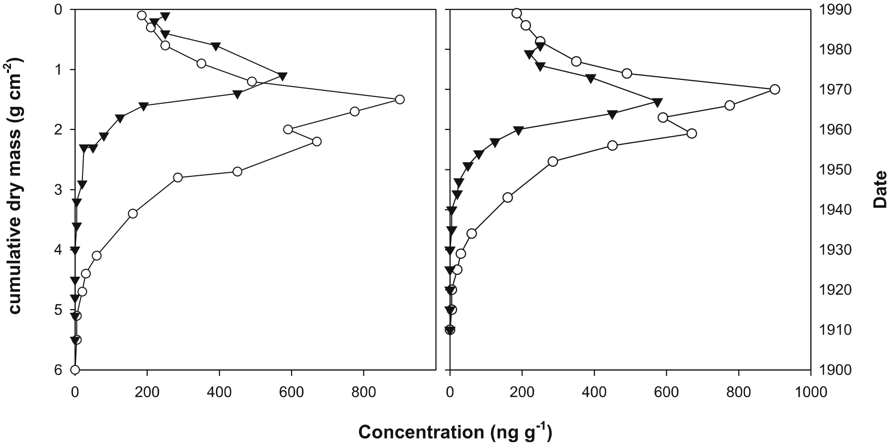

Fig. 9 PCB accumulation in Lake Ontario sediment, modified from [14]. The *left plot* shows the downward shift in the PCB peak as cleaner sediment accumulates at the sediment water interface and older sediment is buried. The *right plot* shows that the peak of the PCB accumulation rate occurred in ~ 1970 and that peak is retained over time. The core collected in 1981 (*filled triangles*) was analyzed for 25 congeners while the core collected in 1990 (*open circles*) was analyzed for 85 congeners. When corrected for the same congeners, there is no evidence of PCB decay or loss from the sediments over the 9-year period

that the depositional history shows a peak at about 1970, similar to most other Great Lakes cores and the record of PCB production. Moreover, focusing-corrected inventories of the two cores are similar at about 320–340 ng cm^{-2}, with inventories statistically the same.

6.2
Resuspension

PCBs that have historically accumulated in the sediments may return to the water through resuspension–desorption and through continuous diffusion from sediment porewaters.

Resuspension moves a large mass of PCBs into the water column. As part of the Episodic Events: Great Lakes Experiment (EEGLE) study in southern Lake Michigan, Hornbuckle and colleagues showed that hundreds of kilograms of PCBs are resuspended during major wintertime storms [217–219]. The origin of the resuspended sediments includes coastal sediments and sediments from deep regions of the lake, where PCB concentrations are highest. This episodic input of PCBs into the lake would not be considered in the annual loadings determined by mass balance studies.

It is possible that resuspension of PCBs during major storms may be as large a source as the tributaries. However, the fate of the resuspended contaminants is unclear. The EEGLE study found that most of the resuspended

PCBs appear to remain sorbed to the sediment particles [220]. Concentrations of dissolved PCBs did not increase after a large storm, despite evidence of resuspended PCBs in the particle phase [219]. In fact, Bogdan et al. reported *decreased* concentrations of dissolved PCBs after a major storm in southern Lake Michigan [218]. The authors suggested that the resuspended sediments actually cleansed dissolved PCBs from the water. In either case, it appears that resuspended PCBs may simply return to the lake bottom after the storm subsides. This hypothesis is well supported in the experimental literature. For example, in a well-constructed laboratory study, Gong and Depinto measured and modeled the rate of desorption from suspended particles pre-equilibrated with PCB congeners 52 and 153 [221, 222]. They show that desorption exhibits two-stage behavior: a fast rate followed by a much slower rate. The fraction of PCBs lost during the first stage depends on how long the particles have been equilibrated with the PCBs. When PCBs have been in contact with the sediment for a very long time (~3 years), only about 10% of the PCB is desorbed from the particles in 24 h. Even after a year of suspension, these particles only desorb about 50% of the total exchangeable PCB. A review article by Pignetello and Xing shows that these findings are consistent with many other hydrophobic organic compounds [223]. Short-term resuspension of PCB contaminated sediments appears to be a small or even negligible source of PCBs in the Great Lakes.

A study of resuspension and downward settling of sediments in Grand Traverse Bay supports the contention that resuspension events do not change the net flux of PCBs in the system. Schneider et al. deployed sequencing sediment traps at two locations in the western arm of Grand Traverse Bay, Lake Michigan [224]. The traps collected integrated samples of settling particles every two weeks from May 1997 to September 1999. Storm-driven episodic events, which occurred only 20% of the time, accounted for 65% of both the mass flux and total PAH flux. The annual PCB flux was not influenced by these episodic events: only 18% of the total PCB flux occurred during these events. PAHs and PCBs appear to be tracing different types of particles in the water column. Several large mass flux events characteristic of seiches were observed simultaneously in the benthic nepheloid layer (BNL) at both the northern and southern sites. The particles settling as a result of these resuspension events had lower PCB and PAH concentrations than particles settling at other times, suggesting that material settling into the traps on the high mass flux days is a mixture of the less contaminated resuspended sediment and the “regular” contaminant-rich particles settling into the BNL.

Diffusion of PCBs from highly contaminated surficial sediments in areas of concern may be an important net source to the Great Lakes. In fact, PCB diffusion from the porewaters of heavily contaminated coastal and riverine sediments may justify the removal of those sediments. Porewater diffusion in open lake sediments is not a major source. Diffusion of PCBs from porewater is governed by an effective diffusion or mass transfer coefficient and the sediment–water concentration gradient. The concentration gradient is controlled by the fraction of organic carbon in the sediment and the sediment–water equilibrium distribution coefficient [225]. Ortiz et al. reported the equilibrium distribution constant, K_{OC}, and the mass transfer coefficients for PCBs in sediment–water systems similar to those found in the Great Lakes [225]. While the rate of diffusion from sediment porewaters is slow, the constant release may result in a significant source of PCBs to waters exposed to contaminated sediments.

7

Water Column Processes

From a geochemical perspective, the inventories of chemicals in the water column play a central role in the aquatic cycling of pollutants. The large quantity of water in the Great Lakes is a significant reservoir for anthropogenic chemicals, moderating the long-term movement of chemicals from their sources to their ultimate environmental fates. Although a large mass of PCBs have been historically stored in the Great Lakes water column, PCB concentrations dissolved in the water are generally quite low (femtogram to nanogram per liter range for individual congeners), which presents significant analytical challenges. Nonetheless, the Great Lakes region enjoys a nearly 30-year record of high-quality measurements of water column PCBs, especially in Lakes Superior and Michigan.

The Great Lakes water columns are cold, deep, and generally contain only modest amounts of suspended solids and dissolved organic carbon. PCB congeners distribute between truly dissolved, colloidal, and particulate phases according to their individual hydrophobicities and the amount of suspended solids and dissolved organic matter in the water column. The dissolved–particulate partitioning of PCBs controls the relative magnitude of fate processes, the exposure to and accumulation within the food web, and the ecosystem-level response to altered loadings. While the two-phase partitioning model is the standard description of PCB behavior in surface waters, field measurements from the Great Lakes consistently show deviations from this model [216, 226]. Specifically, the PCB congener partitioning is substantially more variable than can be attributed to sampling or analytical variance, and the relationship between observed PCB partition coefficients and their octanol–water partitioning coefficients is "flatter" that predicted by empirical models. Field-measured partition coefficients for higher molecular weight PCB congeners are often less than K_{OW}, perhaps due to either slow sorption kinetics or the presence of "third phase" colloidal material, which biases the operationally-defined dissolved PCB measurements. Interestingly, the lower chlorinated PCB congeners in the Great Lakes often have partition coefficients greater than predicted from models. The mechanism(s) for this enrichment of these less hydrophobic congeners on Great Lakes particles is unclear, but may involve differential partitioning into plankton [227], and/or magnification through microbial loops [228].

7.1
Concentrations

PCB congeners and other synthetic organic chemicals are present in the waters of the Great Lakes at concentrations generally ranging from femtograms per liter to nanograms per liter, with the majority of PCB congeners in the "dissolved" or "non-filterable" phase (Table 4). Measuring these low concentrations requires quantitative concentration of the analytes from large volumes of water. Historically, sampling techniques for PCBs in the Great Lakes involve a particle separation step (usually filtration through flat glass fiber filters with about 1 μm nominal size cutoffs, and, less commonly, continuous-flow centrifugation) followed by isolation of PCBs from the filtrate by adsorption to a pre-cleaned resin (usually XAD-2) or extraction via liquid–liquid partitioning. Resin isolation can efficiently extract PCBs from large volumes of Great Lakes water, but requires careful cleaning and conditioning prior to use and attention to not exceed optimal flowrates and resin capacity. Liquid–liquid partitioning has been employed either in batch mode (extracting a few liters with dichloromethane in sealed glass bottles aboard ship or in standard glassware in the laboratory) or using the Goulden counter-current liquid–liquid extraction system [229]. Due to the large volume of solvent required to extract sufficient amounts of Great Lakes water, liquid–liquid extraction techniques are susceptible to elevated blanks. These techniques have routinely been used to process tens to hundreds of liters of Great Lakes water, resulting in methods sufficiently sensitive to reliably measure total PCBs greater than about 1 $\mathrm{ng\,L^{-1}}$.

It is recognized that filtration is operational, that colloidal-bound PCB congeners are not retained by the filter, and that operational "dissolved" measurements may be biased positively by colloidal material. Techniques to measure truly dissolved PCBs include gas sparging, differential diffusion into membrane-bound lipids (e.g., semipermeable membrane devices, [230]), and selective adsorption (e.g. non-equilibrium solid phase microextraction [231, 232]). Unfortunately, none of these techniques has sufficient sensitivity to reliably and unambiguously measure truly dissolved PCB congeners at the levels present in the Great Lakes.

The first published measurements of PCBs in the Great Lakes surface waters are those of Veith et al. [233], who reported total PCB concentrations in western Lake Superior (at the Duluth EPA laboratory intake) of 0.8 $\mathrm{ng\,L^{-1}}$ in 1972. An initial attempt to survey PCB levels in the Great Lakes was that of Glooschenko et al. [234], who sampled Lakes Superior and Huron in late July and early August, 1974. Two liters of surface water (1 m depth) was

Table 4 Concentrations of PCBs in the water column of the Great Lakes. All values are the sum of PCB congeners measured in both the dissolved and particle phases

Lake	Location	Sampling year	Sampling month	mean t-PCB ng/L	*t*-PCB SD	min *t*-PCB ng/L	max *t*-PCB ng/L	N	Method	Refs.
Erie		1986	April/May	1.378	–	0.341	3.513	21	Capilliary	[239]
Erie		1993	April/May	0.70	0.67	0.2	1.6	6	Capilliary	[240]
Huron	Open Lake	1986	May	0.631	–	0.186	2.342	17	Capilliary	[239]
Huron	Georgian Bay	1986	May	0.688	–	0.279	1.434	7	Capilliary	[239]
Huron		1993	April/May	0.13	0.03	0.088	0.16	5	Capilliary	[240]
Huron		1994–1995		0.17	–	–	–	13	Capilliary	[241]
Michigan	Chicago	1976	–	41	–	–	–	2	Packed	[242]
Michigan	Beaver Island	1976	–	30	–	–	–	1	Packed	[242]
Michigan		1979	August	2.88	3.37	–	–	8	Packed	[237]
Michigan	Green Bay	1980	September	3.5	2.7	1.1	20	9	Capilliary	[243]
Michigan		1980	September	1.8	1.8	0.4	7.9	19	Capilliary	[243]
Michigan		1980	April	5.66	1.12	4.9	7.1	4	Packed	[237]
Michigan		1980	July	6.36	1.3	4.8	7.9	7	Packed	[237]
Michigan		1991	September	0.47	0.06	–	–	9	Capilliary	[244]
Michigan		1992	Spring	0.424	0.058	–	–		Capilliary	[245]
Michigan		1993	April/May	0.21	0.03	0.17	0.27	5	Capilliary	[240]
Michigan		1994	July	0.12	0.05	0.07	0.20	14	Capilliary	[156]

Table 4 (continued)

Lake	Location	Sampling year	Sampling month	mean t-PCB ng/L	*t*-PCB SD	min *t*-PCB ng/L	max *t*-PCB ng/L	N	Method	Refs.
Michigan	Green Bay	1994–1995		0.75	0.65	0.25	1.67	27	Capilliary	[241]
Michigan	Open Lake	1994–1995		0.26	0.10	0.13	0.67	307	Capilliary	[246]
Michigan		1994	May	0.21	0.02	0.19	0.24	4	Capilliary	[156]
Michigan		1995	January	0.31	0.03	0.27	0.36	5	Capilliary	[156]
Michigan	Grand Traverse Bay	1997		0.31	0.56	0.09	2.34		Capilliary	[247, 248]
Michigan	Grand Traverse Bay	1998		0.35	0.46	0.08	1.45		Capilliary	[247, 248]
Michigan	Grand Traverse Bay	1999		0.17	0.04	0.12	0.22		Capilliary	[247, 248]
Michigan		1998		0.35	0.10	0.16	0.60	11	Capilliary	[218]
Michigan		1999		0.27	0.052	0.12	0.56	23	Capilliary	[219]
Michigan		2000		0.16	0.029	0.071	0.28	19	Capilliary	[219]
Michigan		2003		0.149	0.042	0.092	0.199	5	Capilliary	[249]
Ontario		1986	April	1.41	–	0.484	2.614	31	Capilliary	[239]
Ontario		1993	April/May	0.22	0.02	0.19	0.25	5	Capilliary	[240]
Superior		1971–1975		400	–	–	2000	84	Packed	[250]
Superior	Western Arm ERL Lab Intake	1972		0.8	–	–	–		Packed	[233]

Table 4 (continued)

Lake	Location	Sampling year	Sampling month	mean t-PCB ng/L	t-PCB SD	min t-PCB ng/L	max t-PCB ng/L	N	Method	Refs.
Superior		1972–1975		110	–	–	1200	160	Packed	[250]
Superior		1974–1975		50	–	–	300	16	Packed	[250]
Superior		1974	November	6	–	5	7	2	Packed	[235]
Superior		1976	December	5	–	–	–	1	Packed	[235]
Superior	Western arm/ Duluth Harbor	1976	January	–	–	10	20	2	Packed	[235]
Superior	Isle Royale	1976	January	–	–	50	157	3	Packed	[235]
Superior		1978	July	1.3	1.3	0.4	7.4	28	Packed	[236, 251, 252]
Superior		1979	June	3.8	1.9	0.3	8.4	35	Capilliary	[236, 251, 252]
Superior		1980	August	0.9	0.4	0.3	2.1	56	Capilliary	[236, 251, 252]
Superior		1983	June–October	0.8	0.07	0.3	0.8	28	Capilliary	[252, 253]
Superior		1986	August	0.55	0.37	–	–	5	Capilliary	[169]
Superior		1986	May	0.337	–	0.193	0.578	19	Capilliary	[239]
Superior		1988	July	0.33	0.04	–	–	5	Capilliary	[254]
Superior		1990	August	0.32	0.03	–	–	6	Capilliary	[254]
Superior		1992	May	0.18	0.02	–	–	5	Capilliary	[254]
Superior		1993	April/May	0.08	0.01	0.07	0.1	3	Capilliary	[240]

Dashes indicated data that was not reported.

extracted from 18 stations in Lake Huron and 16 sites in Lake Superior. Extracts were purified with Florisil liquid-solid chromatography and analyzed with a packed column gas chromatograph with an electron-capture detector. PCBs were not detected in any of the water samples at a quantification limit of 0.1 ppb (0.1 $\mu g\,L^{-1}$ or 100 $ng\,L^{-1}$). Swain [235] reported total PCB concentrations in Lake Superior of 6 $ng\,L^{-1}$ in November, 1974 and 5 $ng\,L^{-1}$ in December, 1976. Corresponding concentrations in the western arm of Lake Superior and on Isle Royale ranged from 10–20 and 50–157 $ng\,L^{-1}$, respectively, in January 1976 [235]. Eisenreich et al. [236] measured total PCB concentrations in Lake Superior in July 1978 that averaged 1.3 ± 1.3 $ng\,L^{-1}$ (range 0.4–7.4 $ng\,L^{-1}$, N = 28) and Rice et al. [237] report levels of 2.9 ± 3.4 $ng\,L^{-1}$ (N = 8) in Lake Michigan in August 1979. Each of these studies in the 1970s used packed column chromatography with electron capture detection. The results may be biased high due to coelution of PCB and toxaphene components. Toxaphene is enriched in Lake Superior relative to the other Great Lakes [238].

7.2
Recycling in the Water Column

PCB congener dynamics in the Great Lakes water column is controlled by partitioning between dissolved chemical and the atmosphere, suspended particles (including plankton), and settling particles. Unlike shallower, more productive lakes with significant net sedimentation, burial of PCB congeners in Great Lakes sediments is inefficient, with considerable recycling within the water column [215, 217, 224]. Since the lakes have been net sources of PCBs to the atmosphere via volatilization since at least the late 1980s [169, 254–256], the waters of the Great Lakes served as a decadal-scale PCB capacitor – accumulating contaminants derived from the atmosphere, river loads, and local sources during periods of increasing PCB environmental burdens, then slowly releasing the chemicals into the regional atmosphere. Although sufficient PCBs accumulate in Great Lakes sediments to preserve historical loadings, long-term burial removes only a small fraction of the PCBs that cycle through the water column.

Water column recycling of PCBs is driven by efficient partitioning into rapidly-settling, organic-rich particles that move PCBs from surface waters to near the lake floor on time scales of days to months [213, 215, 217, 224]. This rapid communication between the atmosphere and near-bottom environments shortens lakewide contaminant residence times and exposes epibenthic organisms to atmospheric contaminants. Once delivered to the lake floor, more than 90% of the particle mass is degraded and the associated PCBs released into bottom waters, where they are remixed throughout the water column during turnover. Early evidence for this seasonal cycle were the observations of Eisenreich et al. [236] that total PCB concentrations in western Lake Superior surface waters were significantly higher in the spring prior to stratification (3.8 ng L^{-1} in June, 1979) than later in the summer (1.3 ng L^{-1} in July, 1978 and 0.9 ng L^{-1} in August, 1980).

7.3
Trends

PCBs were measured in the surface waters of Lakes Superior and Michigan using consistent congener-based quantification between about 1980 and the mid-1990s. Average total PCB concentrations reported for the two lakes are plotted versus the year of collection in Fig. 10. As noted earlier by Jeremiason et al. for Lake Superior [254], and by Offenberg and Baker [156] and Schneider et al. [210] for Lake Michigan, total PCB concentrations decreased exponentially in each lake during that period. In Lake Superior, the first-order rate of decline is 0.08 year^{-1} over that period. At this rate of decline, the current PCB concentration in Lake Superior surface waters should be less than 0.01 ng L^{-1} (10 pg L^{-1}). This extrapolation assumes that the rate of decline between 1980 and 1993 continued unabated in Lake Superior.

The temporal history of PCBs in Lake Michigan is apparently more complex (Fig. 10). There appears to be little if any change in total PCB concentrations between the spring 1993 measurements of Anderson et al. [240], those of Baker and colleagues in northern Lake Michigan in 1997–99 [247], and the EEGLE Program in southern Lake Michigan in 1998–2000 [217, 218], although the most recent measurement in 2003 was 149 pg L^{-1} [249]. Earlier, Pearson et al. [244] reported a first-order loss rate of 0.078 ± 0.018 year^{-1} for the period 1980–1991. Offenberg and Baker [156] extended this analysis, resulting in a loss rate between 1980 and 1994 of 0.17 ± 0.03 year^{-1}. These more recent measurements suggest that the rate of decrease in Lake Michigan has slowed (Fig. 10). This is consistent with the slow declines for PCBs in lake trout (discussed in Sect. 8). Whether this is "real", reflects the inherent difficulty of accurately characterizing an exponentially declining inventory, or is due to some unknown bias cannot be determined. Clearly, as PCB concentrations decline in the Great Lakes, the analytical challenge increases, and the potential for positive bias due to field and laboratory contamination increases. We note that there are no PCB data available for Lake Superior after 1993, so it is not possible to determine whether a similar apparent leveling off of the decline is occurring in Lake Superior.

Based on temporal extrapolations, it is likely that the PCB concentrations in the open waters of the lakes are less than 0.1 ng L^{-1}, requiring sampling and analytical methods than can reliably measure PCB congeners with method quantification limits in the pg L^{-1} range. This will require a reinvestment in method development, including in situ isolation samplers, ship-board clean rooms, and dedicated laboratory facilities. The application of high resolution mass spectrometry (EPA Method 1668A) greatly improves instrumental sen-

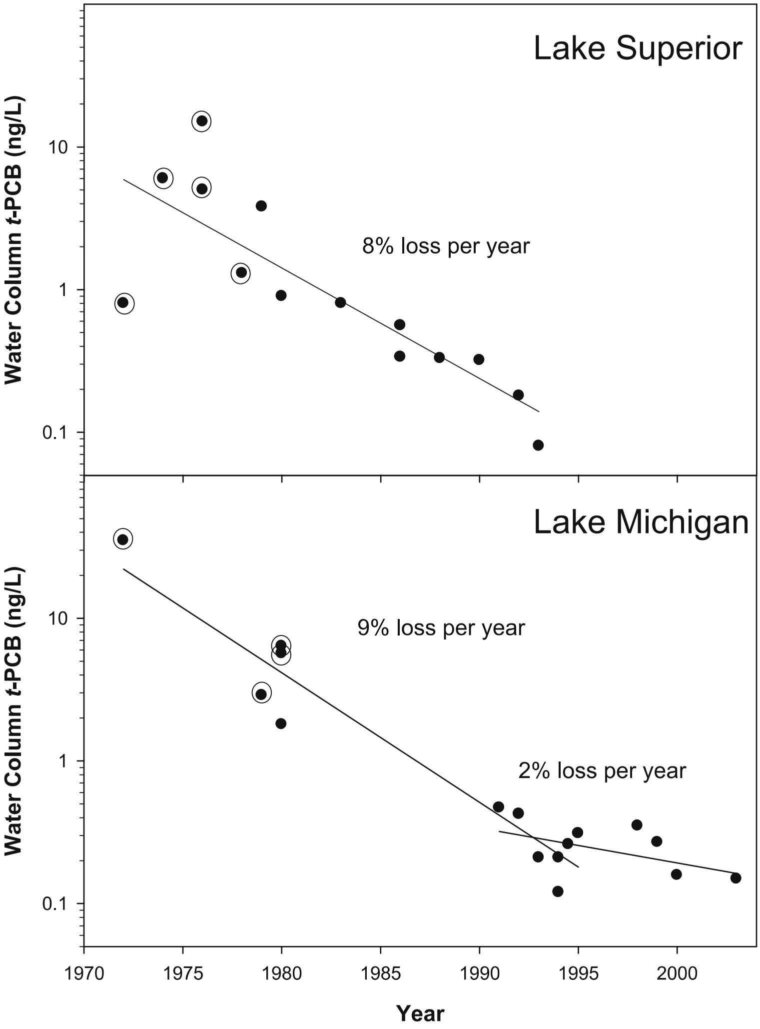

Fig. 10 Concentrations of PCBs in Lake Superior and Lake Michigan. References are listed in Table 4

sitivity but does not relieve the requirement of sufficiently clean field and laboratory blanks for the PCB congeners.

Prior to the late 1970s, PCBs were present in the Great Lakes water columns at relatively high concentrations but were not detectable with the available sampling and analytical tools. Currently, PCBs are present at much lower levels, and probably are not detectable using the "classic" methods used between 1980 and 1999. During the past two decades, concentrations of PCBs have declined in the Great Lakes water columns. Unfortunately, even very low concentrations of PCBs in water can cause unacceptably high concentrations in fish. For this reason, risk-based water quality guidelines for PCBs will require ever improving methods to continue the excellent long-term record of PCBs in the Great Lakes water column.

8
Food Web Dynamics

PCBs are often the prime example of a persistent, bioaccumulative, toxic (PBT) chemical. To fully understand the dynamics of PCB bioaccumulation, it is first necessary to define several terms. *Bioconcentration* refers to the accumulation of a chemical in an organism resulting from an equilibrium distribution of the chemical between the organism's tissue and its environment (usually referring to water). *Biomagnification* is the accumulation of a chemical by an organism from water and food exposure that results in a concentration that is *greater* than would have resulted from water exposure only and thus *greater* than expected from equilibrium. Compounds that biomagnify have greater concentrations in higher trophic levels of food webs. *Bioaccumulation* is a generic term that refers to either process, and describes what is observed in the field. These concepts are often described quantitatively, using ratios of what is found in the organism or trophic level compared to water, sediment, or another trophic level:

- Bioconcentration factor:
  BCF = C_{org}/C_{water} at equilibrium (expressed in equivalent units)
- Bioaccumulation factor:
  BAF = C_{org}/C_{water} observed in the environment (expressed in equivalent units)
- Biomagnification factor:
  BMF = BAF/BCF (unitless)
- Biota-sediment accumulation factor:
  BSAF = $C_{org,lipid}/C_{sed,oc}$ (expressed in equivalent units)

Note that the BSAF is an empirical ratio and does not necessarily indicate a mechanistic relationship or route of exposure.

There are many factors that affect the bioaccumulation of PCBs and other chemicals. The degree to which a chemical bioaccumulates is related primarily to its lipophilicity (or hydrophobicity), expressed as the octanol–water partition coefficient, K_{OW} [257, 258]. Because PCBs have K_{OW}s that span many orders of magnitude, PCB congeners have a wide range of bioaccumulation potential. The factors that influence bioaccumulation via K_{OW} include the degree of chlorination and the substitution pattern of the chlorination. These two factors also determine the extent to which the molecule is metabolized; the more readily the molecule is metabolized, the less it bioaccumulates. The molecular configuration, a direct function of degree and pattern of chlorination, is thought to control the ease of passage of the molecule across cell membranes, such that compounds having a cross-sectional diameter greater than 9.5 Å are limited in their ability to bioaccumulate [259].

8.1
Factors Affecting Fish Concentrations of PCBs

Properties of the organism that affect the degree of bioaccumulation include the amount and type of lipids (fatty organisms accumulate more PCBs), age (longer exposures lead to higher bioaccumulation of PCBs), metabolic systems (different species metabolize PCBs differently), and the diet of the organism (higher trophic levels have greater concentrations of PCBs). For example, the greater PCB concentrations in lake trout compared to rainbow trout are thought to be mostly due to age differences [260].

Thus, overall, the bioaccumulation of PCBs is a function of the uptake of PCBs from water and food, and the losses due to metabolism, excretion, and growth dilution; all are a function of time. A general model for estimating the concentration of PCBs (C_{fish}) in fish is:

$$dC_{\text{fish}}/dt = \text{water uptake} + \text{food uptake} - \text{losses} \qquad (3)$$

or

$$dC_{\text{fish}}/dt = (k_{\text{u}} \times C_{\text{water}}) + (\alpha \times F \times C_{\text{prey}}) - [(k_{\text{x}} + k_{\text{g}} + k_{\text{m}}) \times C_{\text{fish}}] \qquad (4)$$

where k_{u} is the uptake rate constant from water, α is the assimilation efficiency in the gut, F is the feeding rate for a given food preference, C_{prey} is the concentration of prey in the diet, k_{x} is the first-order excretion and egestion rate constant, k_{g} is the first-order rate constant of dilution due to growth, and k_{m} is the first order metabolism rate constant [261–265]. In top predators, as much as 98% of the PCB burden is due to uptake from food rather than water [262]. The biomagnification process is a result of the very slow clearance rates (excretion and egestion) relative to the uptake rates from water and food – the differences can be on the order of 10^6 [264, 266]. It should also be noted that fish and mammalian enzyme systems will hydroxylate certain PCB congeners, and these hydroxylated PCBs have also been shown to bioaccumulate [267].

The length of the food chain has the largest effect on the observed accumulation of PCBs in top predators [268]. However, one of the more sensitive aspects of trophic transfer in food webs is the initial uptake of PCBs into the primary trophic level, phytoplankton [263]. The BCF from water to phytoplankton is approximately 10^5–10^6, and subsequent BMFs to higher trophic levels are on the order of two to five. Due to the life cycle of most phytoplankton, their rate of growth is on the same order as their rate of uptake of PCBs, thus making their uptake very time-dependent [227, 269–271]. Bioaccumulation into top predators will be greater if phytoplankton have a chance to reach equilibrium (low growth conditions; oligotrophic conditions) or reduced if the phytoplankton grow quickly and sediment to the bottom before being consumed (high growth conditions; eutrophic conditions) [271].

Top predator concentrations can also be affected by changes in their food web. Madenjian et al. have showed that the variability seen in lake trout concentrations of PCBs and other organochlorine contaminants is driven by changes in prey concentration [260, 272–274]. The changes in food web structure [275] and lipid content [276] over time are likely responsible for some of the changes seen in the concentrations of PCBs in lake trout in the 1980s to 1990s [277]. The introduction of the invasive zebra mussel into the Great Lakes ecosystem in the 1980s and 1990s, for example, has been calculated to reduce PCB concentrations by nearly 50% in some forage fish [278].

Because of the concern over PCB exposure from eating contaminated fish, there has been widespread attention to documenting and studying the mechanism of PCB accumulation in the food webs of the Great Lakes. It is well-established in laboratory experiments that PCBs bioconcentrate in fish and other aquatic organisms [270, 279], and that they biomagnify in the environment [280], including the Great Lakes [281, 282].

PCBs have been documented to occur in nearly all trophic levels throughout the Great Lakes ecosystem [282], including bacteria (Hudson, unpub-

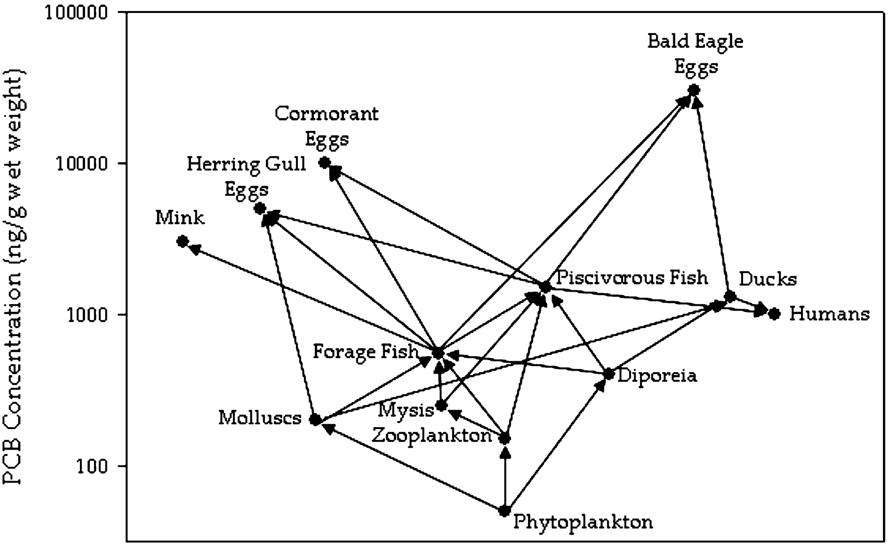

Fig. 11 Great Lakes food web, with approximate PCB concentrations. Note that PCB concentrations vary significantly among species in different locations, and among individuals of the same species. Concentrations in humans are estimated from the blood plasma concentrations in humans that eat Lake Michigan fish [314] and the distribution of PCBs in the body of rats [35]. See text for additional references

lished data, 2005); phytoplankton [271, 283]; zooplankton [281, 283, 284]; benthic invertebrates [283, 285–287]; zebra mussels [283, 288–291]; sea lamprey [292]; snapping turtles [293]; fish [277, 294–304]; ducks [305]; fish-eating birds such as cormorants [86, 306], herring gulls [85, 306–308], and eagles [307, 309–313]; and fish-eating wildlife such as mink [46, 67–69, 72, 77]. These data all support the conclusion that PCBs bioaccumulate and that the more hydrophobic congeners (those with five or more chlorines) biomagnify in food webs. A simplified diagram of the Great Lakes food web, with approximate concentrations of total PCBs, is shown in Fig. 11.

In the Great Lakes basin, many studies have also documented that PCBs accumulate in humans, and that concentrations are greater in those who consume greater amounts of Great Lakes fish [314–322]. PCB exposure is also high in at-risk populations [323], such as charter boat anglers [320] and subsistence populations such as Native Americans [324–327]. For example, PCB blood plasma concentrations in fish-eaters in Michigan were approximately 14 ppb on average, compared to 5 ppb for the general population [314].

8.2
Trends in Food Web Components

Both the USA and Canada have ongoing monitoring programs to assess the change in PCBs and other contaminants over time. In Canada, the Great Lakes Herring Gull Monitoring Program has been in operation since 1974 [328]. For fish, the US EPA, in cooperation with the US GS and Great Lakes States, has monitored PCBs in composites of lake trout (Lakes Superior, Michigan, Huron, and Ontario) and walleye (Lake Erie only) of constant size range (600–700 mm lake trout, 400–500 mm walleye) collected biennially from master sites within each lake since 1970, and the Department of Oceans and Fisheries Canada has a long-standing program of measuring PCBs in individual whole lake trout that are 4+ years in age. These programs were developed to provide exposure data for assessing human and wildlife effects, and provide some of the most extensive databases of PCBs in the world. The US program also analyzes coho and chinook salmon fillets from selected tributaries around the Great Lakes, and the Canadian program includes the analysis of smelt composites to assess trends in the dominant forage in Lake Ontario.

The current trend data for PCBs in lake trout collected for the US program are shown in Fig. 12 (Swackhamer, unpublished data, 2005). These data indicate that PCBs declined rapidly following their ban in both the USA and Canada in the early to mid-1970s. This decline was consistent with a first-order decay, and has been described in that manner previously [277, 304]. The rate of decline in PCBs in Lakes Superior, Huron, and Michigan clearly changed in the mid-1980s [277]. Since then, the PCB concentrations in the upper three lakes have declined at a much slower rate, if at all. The half-lives in the 1970s were on the order of 4–6 years, while the half-lives since the

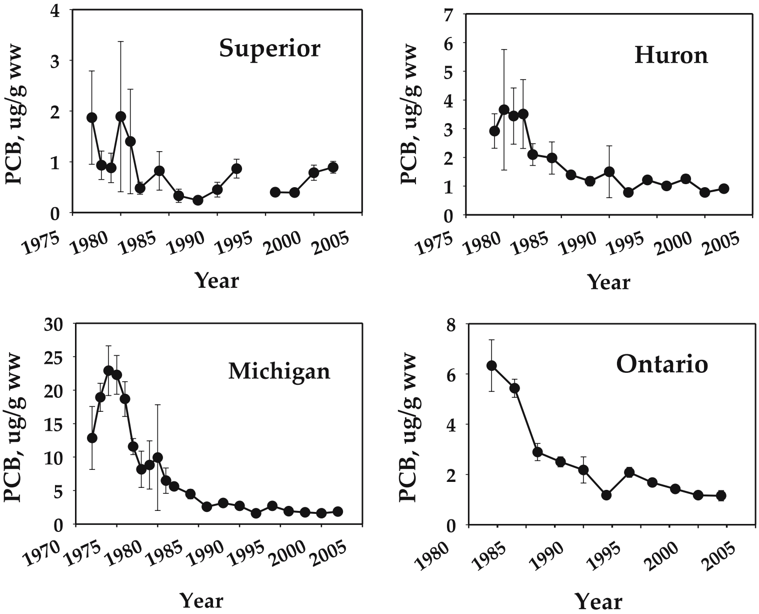

Fig. 12 Trends in PCBs in lake trout from Lakes Superior, Michigan, Huron, and Ontario. Data are means of approximately 10 composites of 5 whole fish, each 600–700 mm in length. All fish from a given lake are from the same site

mid-1980s are around 10–20 years (depending on the time range used for calculation) for Lakes Michigan and Huron, and concentrations have actually increased in Lake Superior. The rate of decline of PCBs in Lake Erie walleye and Lake Ontario lake trout has not changed significantly over time, with half-lives of 18 and 9 years, respectively.

8.3
Trophic Transfer and Biomagnification Studies

In the bioaccumulation process, not every congener biomagnifies to the same extent [329]. This is because K_{OW}, configuration, uptake and excretion rate constants, and metabolism vary by congener. This can be clearly seen in Fig. 13, which shows the PCB chlorine number for selected compartments of the Lake Michigan food web. Chlorine number is the average PCB chlorination level in the sample: low chlorine numbers are found in samples enriched in the less chlorinated, more volatile congeners while high chlorine numbers are found in samples enriched in the heavier congeners. The congener distribution in top predators is quite different than the congener distributions observed in the original technical mixtures and even in the current sources. In Lake Michigan, the congener distributions measured in

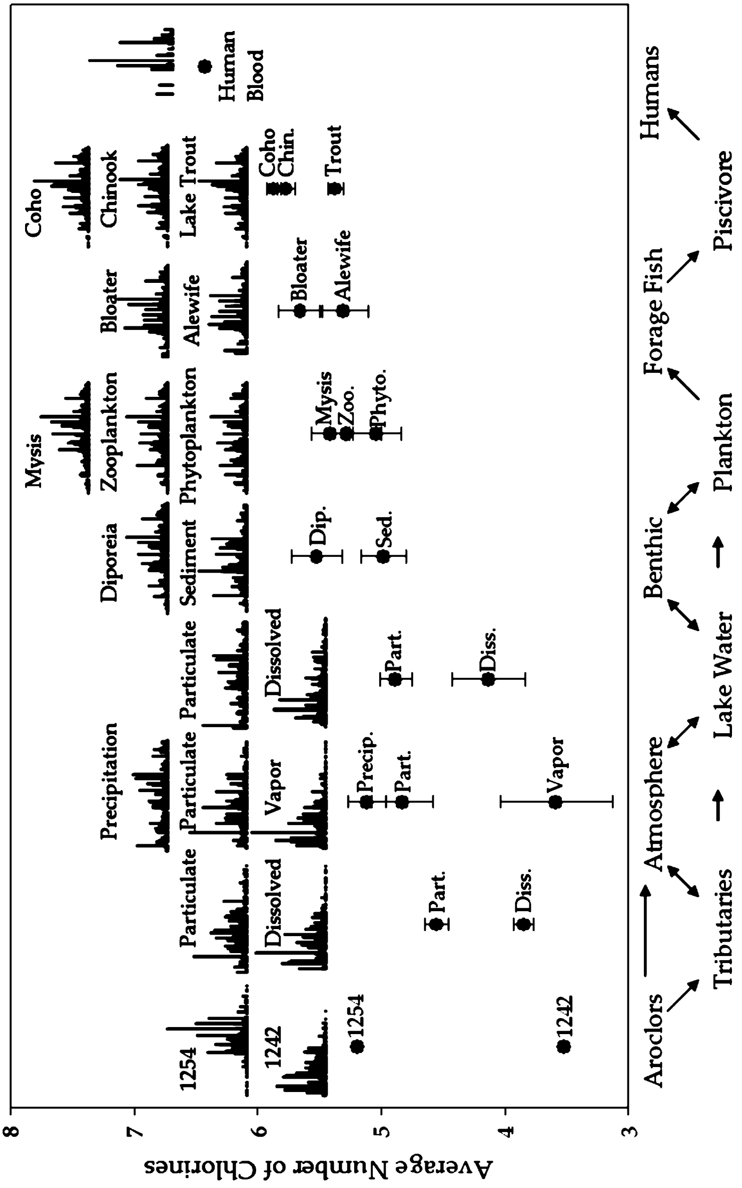

Fig. 13 Degree of chlorination and congener profiles of two Aroclor formulations [330] and PCBs in various media in Southern Lake Michigan. Dates of most samples vary from 1994 to 2000. Tributary data is from the Kalamazoo River and represents the mean and standard deviation in 27 dissolved and 26 particulate phase water samples [241]. Atmospheric samples are from Chicago (Hites RA, 2005, Personal communication) and represent 48 samples. Lake water [219, 241], sediment [331], and biota values [241] are from near the Saugatuck region in southeast Lake Michigan (GLFMP). Human blood samples were taken from frequent consumers of Lake Michigan fish in 1992 [314]

the most commonly used Aroclor mixtures (1242, 1248, and 1254) bear little resemblance to biotic samples, including those at the bottom of the food chain. Weathering due to volatilization, metabolism, and bioaccumulation has a major impact on the congener distributions. Figure 13 illustrates that there is a gradual shift of the congener composition from a dominance of the tri- and tetra-chlorinated congeners in the free forms (dissolved and gas phases), to penta-chlorinated congeners in sorbed phases (particles, sediments, phytoplankton), to a dominance of the hexa-chlorinated congeners in top predators. There is also a gradual increase in the percentages of the penta- through octa-chlorinated homologues with increasing trophic level.

Of particular interest is the bioaccumulation of the AHH PCB congeners. These congeners, as mentioned above, are thought to contribute to toxic effects in a number of species. The AHH congeners have been shown to preferentially biomagnify in the Lake Michigan lower food web relative to total PCBs [284]. In other words, the percentage contribution of AHH to total PCBs increases with increasing trophic level. This may be due to a greater degree of metabolism of the less-chlorinated congeners compared to the relatively nonreactive AHH congeners, which have four chlorines or more. Smith et al. [62] reported a similar finding in a study of fish and piscivorous birds in Lake Michigan. The potency, expressed as dioxin TEQs, increased with trophic transfer in the upper food web. Metcalfe and Metcalfe found that AHH congeners 77, 126, and 151 were not accumulated as well as other congeners with similar K_{OW}s between forage and predator fish in Lake Ontario, and attributed this to a greater propensity for metabolism [332]. Thus, preferential biomagnification is observed in the lower and upper food web, but not between fish tropic levels. The AHH PCBs make up more than 95% of the total dioxin-like toxicity in the Great Lakes food web [41].

There have been a few large-scale field studies of PCBs in the food webs of the lakes. These include two EPA mass balance studies, the Green Bay Mass Balance Study and the Lake Michigan Mass Balance Study. The field data collected for these studies was used to calibrate the complex contaminant models, which were developed as the primary goal of the studies. The ultimate objective of these mass balance studies was to predict concentrations of PBTs in top predator fish from only knowing the external loadings of the PBTs. Thus the models linked food web models to fate and transport, hydrologic, and nutrient models. To calibrate the food web models, an extensive collection of all major trophic levels over both space and time was done and analyzed for PCBs and other selected analytes.

The most extensive field collection effort to date on the Great Lakes, the Lake Michigan Mass Balance Study, collected net phytoplankton (< 100 μm), two sizes of zooplankton (> 100 μm and > 500 μm), *Mysis relicta* by handpicking from net tows, *Diporeia* sp. by handpicking from sled tows, five species of prey fish consumed by lake trout [alewife (*Alosa pseudoharengus*), rainbow smelt (*Osmerus mordax*), bloater (*Coregonus hoyi*), slimy sculpin

(*Cottus cognatus*), deepwater sculpin (*Myoxocephalus thompsoni*)], and lake trout. Lower food web components were collected from 11 locations in the lake on seven different cruises, including all seasons over a 2 year period. The fish were collected from three sites over the same 2 year period. The concentrations of PCBs in each of these food web components are shown in Fig. 14. The data are lipid-normalized to allow for better comparison across trophic levels. Note that concentrations increase with increasing trophic level, even when normalized to lipids. These data demonstrate that PCBs biomagnify in Great Lakes food webs, and are the most comprehensive and self-consistent data in the world for PCBs in a food web of a large aquatic system.

In the lower levels of the food web, there was significant seasonal and spatial variability in the concentrations and corresponding BAFs [333]. The phytoplankton and zooplankton concentrations were greater in southern and nearshore sites compared to northern and open lake sites. The spatial variability in BAFs, and the lack of a strong correlation of BAF with K_{OW} for a given sample collection, indicated that the PCBs were not in equilibrium with phytoplankton, net zooplankton, or Mysis. The collections where PCBs were closest to equilibrium were in winter and late summer, two periods when phytoplankton growth is lowest and when there is be more time for PCBs to reach equilibrium with the cells [227, 271]. The variability in BAF in zooplankton and *Mysis* tracked the variability in phytoplankton, and also reflected the rapid seasonal changes in lipid content in zooplankton. Thus the growth of phytoplankton, and the change in lipid content in zooplank-

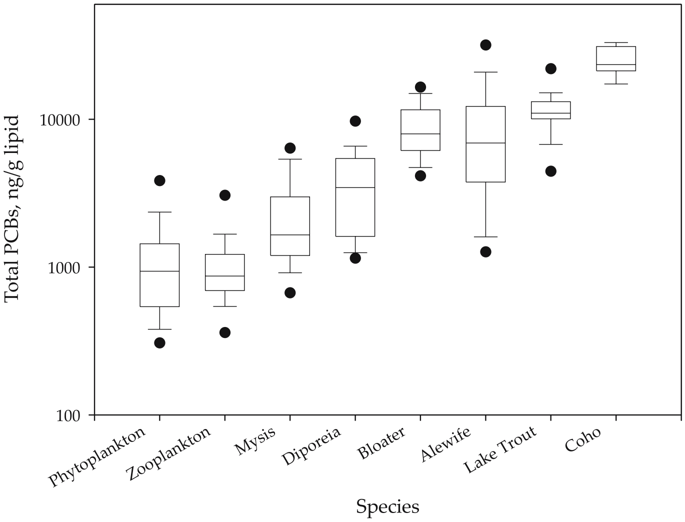

Fig. 14 Lipid-normalized PCB concentrations in the Lake Michigan food web, showing 95th, 90th, 75th, 50th, 25th, 10th, and 5th percentiles (data from the Lake Michigan Mass Balance study)

ton, occur over relatively short time frames such that PCBs do not easily reach equilibrium in these lower trophic levels. Conversely, the *Diporeia* BAFs showed little change in space or time, reflecting their stable environment and less dynamic life cycle. These observations of PCB seasonal dynamics in lower trophic levels were also observed in a study of Grand Traverse Bay, in northern Lake Michigan [247, 334, 335]. Stapleton and colleagues [247] also found that growth, lipid, and diet changes explained much of the observed seasonal variability in the Grand Traverse Bay food web. Furthermore, stable isotope analyses combined with the PCB data indicated that the majority of PCBs reaching the food web were atmospheric in origin, as opposed to coming from the sediment [334].

The LMMB also provided further insight into the food web dynamics of top predators. For example, Madenjian et al. [336] compared the forage fish and lake trout PCB concentrations at the three different collection sites, and found the forage fish concentrations did not vary with space, but lake trout concentrations were greater in the Sturgeon Bay site compared to the Saugatuck site. Using dietary information obtained from detailed gut analyses, they were able to conclude that dietary differences led to a more PCB-enriched diet in the fish from the Sturgeon Bay site. Additional data were collected by these researchers, and they were able to demonstrate that coho salmon retain approximately 50% of the PCBs in their prey [337], while lake trout retain approximately 80% of the PCBs in their prey [338].

9

Mass Balance for PCBs in the Great Lakes: Lake Michigan

With the accumulation of research into the various transport processes and partitioning behaviors of PCBs discussed above, a clearer picture of the overall fate of PCBs in the Great Lakes environment began to emerge. Models could be constructed based on this knowledge and physical/chemical properties. The earliest such models were published for Lake Ontario [339, 340]. However, more data were needed. Surprisingly little was known about the relative magnitudes of PCB sources to natural waters. Over the last decade, there have been several major research studies to quantify all the PCB sources to Lake Michigan [128–130, 217, 218, 244] and Green Bay [170, 341]. Although there have been studies in Lake Huron's Saginaw Bay [342], Lake Erie [343], and Lake Ontario [344–348], only Lake Michigan has benefited from a coordinated field study to assess all of the possible sources. The purpose of the Lake Michigan Mass Balance (LMMB) study was to develop a lakewide model that required inputs of atmospheric and tributary loadings of PCBs into a complex suite of linked models including a hydraulics model, nutrient dynamics and carbon model, toxics model, and a food web model. The model included all inputs, losses, and internal cycling of PCBs. The overall objective was to be able to predict concentrations of PCBs in top predator fish with an uncertainty factor of two. This is the most complex model for a toxic compound ever developed, and it required an enormous set of environmental and PCB measurements to support it.

The LMMB study included the collection of over 25 000 air, water, sediment, and biota samples at more than 200 locations in and around the lake. All samples were analyzed for 110 individual PCB congeners [241]. The Lake Michigan Mass Balance program reported a preliminary mass budget of PCBs (Fig. 15).

The inputs include the atmosphere, resuspension, and tributary flows. All samples were analyzed by congener-specific methods. Only the sum of the congeners is shown here. The losses include volatilization, export to Lake Huron, downward settling of sediments, and permanent burial. The inputs include gas absorption, wet and dry deposition, flow from tributaries, and resuspension. Non-tributary discharges were assumed to contribute a negligible PCB mass and were not surveyed. The budget is based on data collected in 1994 and 1995. However, more current measurements indicate that the budget remains a good measure of the state of PCBs through the early 2000s. Although other mass budgets have been developed for Lake Michigan [159, 243, 244], the analysis reported by the EPA is the first that used a consistent PCB data set.

Construction and calibration of the model has informed us a great deal about the overall dynamics of PCBs in the Great Lakes. The atmosphere is the largest source of PCBs to Lake Michigan. More than 2000 kg of atmospheric

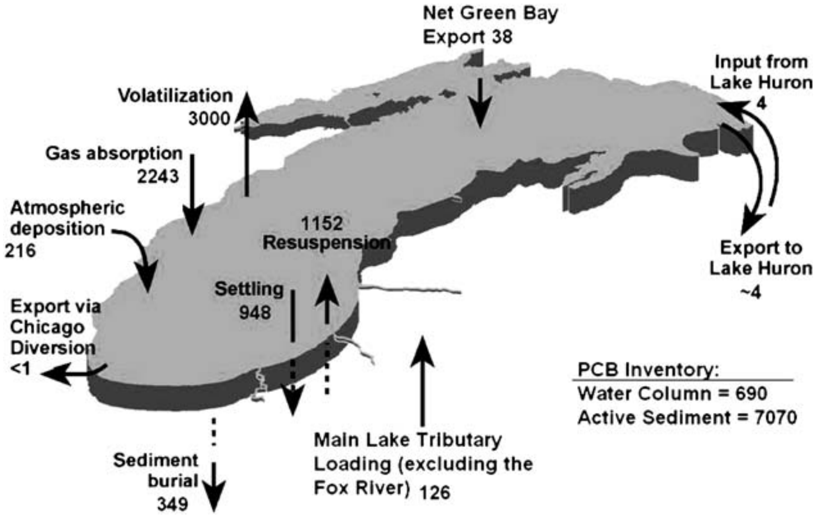

Fig. 15 The magnitude and direction of various processes (kg year^{-1}) that move PCBs into and out of Lake Michigan each year, modified from [241]

PCBs enter Lake Michigan each year. The majority of that input is through gas exchange. Deposition of PCBs associated with aerosol particles accounts for 100 kg each year [129]. Deposition of PCBs in rain contributes 90 kg each year. Atmospheric deposition (gas, dry particle, and wet deposition) is larger than inputs from resuspension of contaminated sediments and larger than inputs from direct discharge and contaminated tributaries. Resuspension of contaminated sediments is an important source of PCBs to the water, but still not as large as gross atmospheric deposition. Although not considered in the LMMB effort, a field study of resuspension after major storms concluded that annual wintertime storms contribute as much as 400 kg of PCBs per event [217]. There may be more than one major event each year, but the total amount of PCBs resuspended is still only about 1200 kg, and a large fraction of that mass may immediately return to the lake floor. The tributary load is only about 380 kg and that includes the Fox River discharge to Green Bay. A significant portion of the PCBs discharged by the Fox River are retained or volatilized from Green Bay and never reach Lake Michigan [241]. Most direct discharges from industrial waste, urban runoff, and wastewater treatment plants are included in the estimate of tributary loads.

The importance of the atmospheric pathway is easily misjudged. For example, sediment export from contaminated tributaries as a source of PCBs to Lake Michigan is often cited as a justification for dredging [163]. However, atmospheric releases from highly contaminated tributaries and harbors may be a larger net source of PCBs to the open lake than the corresponding direct discharge. In Milwaukee, atmospheric sources contribute about 150 kg each year to the open waters of Lake Michigan. The Milwaukee River, on the other hand, contributes only about 12 kg annually [131, 241]. The mass balance effort and other quantitative studies of PCB sources shows that the atmosphere is the primary source of PCBs to the lake. This implies that the atmosphere is also a major source of PCBs ultimately accumulated in fish.

The importance of atmospheric exchange processes is one of the most striking findings of the mass budget analysis. Atmospheric PCB losses from Lake Michigan are also large. In the dilute water of Lake Michigan, hydrolysis, photolysis, and microbial decay are considered negligible loss mechanisms for PCBs. Volatilization is larger than net burial of PCBs into the sediments and much larger than export to Lake Huron.

Predicting long-term trends in whole lake mean PCB concentrations using the mass balance model approach is problematic. PCBs are clearly declining in Lake Michigan as shown from the long-term monitoring results discussed above. Therefore, the PCB inputs must be less than the losses. This is difficult to observe in the full mass balance model because of the uncertainties in each of the input and loss calculations. For example, atmospheric inputs and losses are both large but the difference between them is small. Propagation of error shows that the net whole-lake annual exchange of PCBs across the air–water interface is not significantly different from zero. While this may seem disappointing, the analyses of uncertainty simply shows how dynamic the system is with respect to PCB exchange. On a smaller temporal scale, such as a day or a month, the difference between inputs and outputs can be much larger, especially near major sources like Chicago. For example, net gas exchange of total PCBs in southern Lake Michigan is illustrated for four consecutive days in Fig. 16. The figure shows that small changes in wind direction, temperature, and atmospheric PCB concentrations can change the direction of air–water exchange from net volatilization to net deposition. PCB gas exchange in Lake Michigan is highly dynamic over time and space.

The results of the Lake Michigan Mass Balance project are consistent with an analysis of PCB trends in Lake Superior, which, like Lake Michigan, has a long retention time among other similar characteristics. Jeremiason et al. examined the PCB congener profiles in buried sediment and long-term PCB trends in Lake Superior water and sediments [254]. The authors concluded, via a mass balance modeling exercise, that volatilization explains most of the post-1978 decline in PCB water concentrations. The importance of atmospheric exchange in Lake Michigan and Lake Superior can be explained by their physical characteristics, which are similar to many large lakes, including most of the Laurentian Great Lakes. They have a long retention time (inflows and outflows are small relative to lake volume), shallow depth relative to lateral dimensions (allowing for efficient settling of particles), and a small drainage basin relative to lake area [15]. Smaller lakes with large rela-

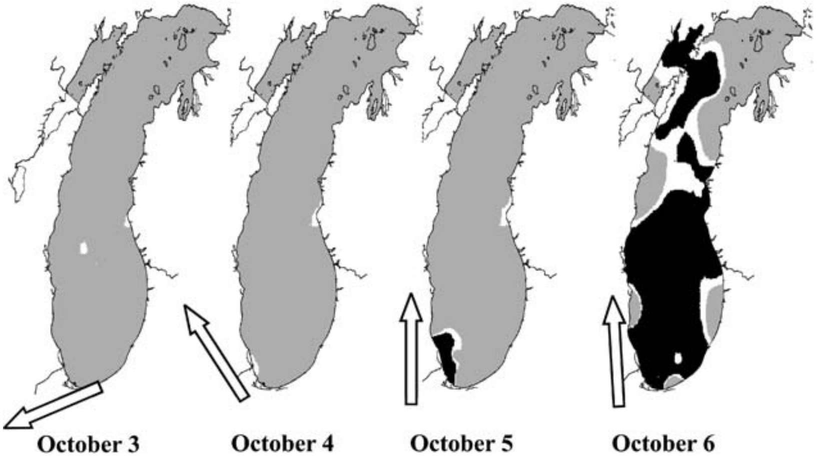

Fig. 16 Net gas exchange of total PCBs to Lake Michigan on four consecutive days, starting with 3 Oct 1994 on the *left*. The *darkest shade* represents net deposition (most evident on 6 Oct). *White* represents zero net exchange and the *light shade* represents net volatilization fluxes. *Arrows* indicate the average wind direction on that date. The average daily temperatures for 3–6 Oct were: 14.1 °C, 13.6 °C, 13.2 °C, and 17.9 °C, respectively. Reproduced from [130]

tive catchment areas, greater relative depth, and short residence times would be expected to have a greater influence from riverine inputs in the mass balance equations. As an example, in a small Arctic lake almost 80% of PCB loss was attributed to PCBs in the outflowing water [349]. Lake Erie has intermediate characteristics: it has a short retention time, but an average depth that is much less than Lake Superior or Lake Michigan [15]. In this case, the atmosphere would be expected to have an even greater influence on the mass balance than in Lake Michigan, but there could also be substantial input and export terms from connecting channels. Clearly, mass balance studies cannot be easily generalized, and characteristics of individual lakes must be considered carefully in formulating hypotheses regarding PCB fate.

10

Conclusions

PCBs are clearly declining in the Great Lakes environment. The long-term data from sediments, archived fish, and long term monitoring studies illustrate the results of reducing PCB sources to the lakes. Without legislation to stop production of these compounds and without regulation to remove residual industrial sources, such a reduction would not have been achieved. The enormous decrease in PCB concentrations is truly a success story.

The research behind this success story has also provided an exhaustive and detailed understanding of the environmental processes affecting the fate and transport of PCBs. The story of PCBs provides guidance for predicting the behavior of similar chemicals for which there is much less information available. This, too, is a success story.

PCBs are still a great concern in the Great Lakes ecosystem. Research continues to show that these chemicals are hazardous to animals and humans. The latest findings show particularly alarming effects on neurological function in humans and animals. Unfortunately, exposure to these compounds continues despite decades of effort and millions of dollars spent. The largest current sources are atmospherically driven. These are difficult to identify or control, and are nearly immune from the traditional tactics of point source regulation and enforcement. Atmospheric sources do not derive from a pipe that can be shut off or from an industrial process that can be retooled. Atmospheric sources are not, however, completely elusive. Scientists have shown that the most widely observed characteristics of atmospheric PCBs are also the clues to their origin. Atmospheric PCBs come from volatilization processes and they are at the highest concentration in the industrial regions where they were used. This means that surface contamination near sites where they were used, stored, or disposed should be monitored and remediated. Protection of future generations of humans and other animals depends on our creativity and determination to halt this continuing degradation of our environment.

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