



Results of the Lake Michigan Mass Balance Study: Polychlorinated Biphenyls and *trans*-Nonachlor Data Report

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Executive Summary

The U.S. Environmental Protection Agency's Great Lakes National Program Office (GLNPO) and its partners instituted the Lake Michigan Mass Balance (LMMB) Study to measure and model the concentrations of representative pollutants within important compartments of the Lake Michigan ecosystem. The goal of the LMMB Study was to develop a sound, scientific base of information to guide future toxic load reduction efforts at the Federal, State, Tribal, and local levels. Objectives of the study were to:

1. Estimate pollutant loading rates,
2. Establish a baseline to gauge future progress,
3. Predict the benefits associated with load reductions, and
4. Further understand ecosystem dynamics.

The LMMB Study measured the concentrations of mercury, polychlorinated biphenyls (PCBs), *trans*-nonachlor, and atrazine in the atmosphere, tributaries, lake water, sediments, and food webs of Lake Michigan. This document summarizes the PCB and *trans*-nonachlor data collected as part of the LMMB Study, and is one in a series of data reports that documents the project.

PCBs are synthetic organic chemicals that are chemically inert, nonflammable, and do not transmit electrical current. These properties, combined with high melting and boiling points, made PCBs useful in a wide variety of industrial applications, particularly as dielectric fluids in electrical transformers and capacitors. In the United States, the Monsanto Company produced commercial mixtures of PCBs by chlorinating biphenyl and sold the mixtures under the trade name Aroclor. The parent compound, biphenyl, consists of two six-membered aromatic carbon rings joined by a single carbon-carbon bond. Chlorination of biphenyl attaches one or more chlorine atoms to carbon atoms in the two ring structures. PCB production and export in the U.S. was halted in October 1977 under the auspices of the Toxic Substances Control Act (TSCA).

There are 209 possible arrangements of chlorine atoms, and each of the arrangements is referred to as a PCB "congener." The formal chemical name of each congener identifies the specific positions and the total number of chlorine atoms in the congener. However, individual PCB congeners are often referred to simply by "congener number," e.g., PCB 1 to PCB 209. This report focuses on the results for three congeners, PCB 33, PCB 118, and PCB 180 in all of the samples except sediments. For sediments (Chapter 6), the report focuses on the results for the sum of PCBs 28 and 31, PCB 118, and PCB 180.

trans-Nonachlor is the common name for 1,2,3,4,5,6,7,8,8-nonachloro-3a,4,7,7a-tetrahydro-4,7-methanoindan, a member of the class of cyclodiene pesticides. *trans*-Nonachlor was not produced as a pure compound, but was a major component of the pesticide "technical chlordane," which is a mixture of at least 140 related compounds. Chlordane mixtures were first produced in the U.S. in 1948 and various formulations of chlordane were widely used as pesticides on food crops and lawns, and for termite control from 1948 to 1988. In April 1988, EPA canceled all commercial uses of chlordane in the U.S.

Study Design

In the LMMB Study, PCBs and *trans*-nonachlor were measured in atmospheric, tributary, open-lake water column samples, sediments, lower pelagic food web organisms, and fish. From March 1994 through October 1995, over 1000 samples were collected from locations in and around Lake Michigan (see Figure 1-2 in Chapter 1) and analyzed by gas chromatography with either electron capture or mass spectrometry detectors. Atmospheric vapor, particulate, and precipitation samples were collected from eight stations surrounding Lake Michigan and three background stations outside the Lake Michigan basin. Tributary samples were collected from 11 rivers that flow into Lake Michigan. Open-lake water column

samples were collected from 38 sampling stations in Lake Michigan, 2 stations in Green Bay, and 1 station in Lake Huron. Sediment samples were collected from over 100 stations in Lake Michigan and Green Bay. Samples of particulate matter were collected in sediment traps deployed at eight stations in Lake Michigan. Samples of phytoplankton and zooplankton were collected from 12 stations in Lake Michigan. Samples of *Mysis* and *Diporeia* were collected at 10 stations in Lake Michigan. Specimens of lake trout, coho salmon, bloater chub, alewife, smelt, deepwater sculpin, and slimy sculpin were collected from three to 79 locations around the lake, depending on the species.

PCBs and *trans*-Nonachlor in Atmospheric Components

Vapor-phase PCB congeners were detected in the vast majority of the samples collected from all LMMB Study stations. Monthly composite concentrations of vapor-phase total PCBs ranged from 0 pg/m³ at Beaver Island and Brule River stations to 6300 pg/m³ at the IIT Chicago station. Vapor-phase PCB results exhibited a seasonal trend, with higher concentrations occurring in summer months and lower concentrations occurring in winter months and may be a result of the interaction of the vapor pressures of the PCBs and the increased temperatures during summer months. Vapor-phase PCB congener and total PCB concentrations varied by sampling station. Urban and urban-influenced sites had higher mean monthly composite concentrations for the duration of the study period than rural sites.

Vapor-phase *trans*-nonachlor was detected much less frequently than PCB congeners. Vapor-phase *trans*-nonachlor was not detected in the samples from two over-water stations. Of the 28 sampling stations, 13 stations had 13% to 50% of the individual samples below detection limits. Only one sample was collected at Stations 380 and 19M and each had a result of zero. Concentrations of vapor-phase *trans*-nonachlor ranged from 0 pg/m³ at over-water stations 380 and 19M to 118 pg/m³ at Bondville. Non-zero mean monthly composite concentrations of *trans*-nonachlor for each sampling station ranged from 2.1 pg/m³ measured at Brule River to 43 pg/m³ measured at Bondville. Vapor-phase *trans*-nonachlor results showed an even stronger seasonal variation than the vapor-phase PCB results. All of the sites exhibited similar trends in vapor phase *trans*-nonachlor concentrations, with higher concentrations generally occurring in the summer and lower concentrations in the winter, despite differences between sites of an order of magnitude or more. For the urban site IIT Chicago, concentrations of vapor-phase *trans*-nonachlor were 1.5 pg/m³ in February 1995 and were 50 times higher in July 1995, at 80 pg/m³. For the rural Bondville station, vapor-phase *trans*-nonachlor was 2 pg/m³ in February 1995 and was 60 times higher in July 1995 at 120 pg/m³.

Particulate-phase PCB congeners were detected in the majority of the samples collected from all LMMB Study stations. Concentrations of particulate-phase total PCBs ranged from 0 pg/m³ at the Beaver Island station to 250 pg/m³ at the IIT Chicago station. Particulate-phase PCB congener and total PCB concentrations varied by sampling station. Urban and urban-influenced sites had higher mean monthly composite concentrations for the duration of the study period than rural sites, consistent with the hypothesis that urban and urban-influenced areas contain significant sources of particulate-phase PCBs.

Particulate-phase *trans*-nonachlor was detected much less frequently than PCB congeners in the samples. Except for the samples collected at the Empire Michigan station, *trans*-nonachlor was reported as being below the sample-specific detection limit in 20 - 100% of the particulate-phase samples from the other 16 stations. Concentrations of particulate-phase *trans*-nonachlor ranged from 0 pg/m³ at 12 stations to 2.6 pg/m³ at Bondville. Mean monthly composite concentrations of *trans*-nonachlor for each sampling station ranged from 0.16 pg/m³ measured at GB24M to 1.2 pg/m³ measured at IIT Chicago, with a concentration of 1.8 pg/m³ for the only sample collected at over-water Station 1.

PCB congeners were detected in many of the precipitation samples collected from the LMMB Study stations. However, the overall frequency of occurrence of PCBs in the precipitation samples was lower

than for the vapor-phase and particulate-phase samples. For total PCBs, the mean concentrations in precipitation ranged from 290 pg/L at the Eagle Harbor station to 16,000 pg/L at the IIT Chicago station.

trans-Nonachlor was detected even less frequently than the PCB congeners in the precipitation samples. Except for the samples collected at the IIT Chicago station, *trans*-nonachlor was reported as being below the sample-specific detection limit in 75 to 100% of the precipitation samples from all stations. The concentrations of *trans*-nonachlor in the precipitation samples ranged from 0 pg/L at every site to a high of 630 pg/L at the Chiwaukee Prairie site.

PCBs and *trans*-Nonachlor in Tributaries

The dissolved total PCB concentrations ranged from not detected in four tributaries to 48 ng/L in the Grand Calumet, while particulate total PCB concentrations ranged from not detected in four tributaries to 120 ng/L in the Sheboygan River. Mean dissolved total PCB concentrations ranged from 0.43 ng/L in the Pere Marquette River to 35 ng/L in the Grand Calumet, while mean particulate concentration ranged from 0.25 ng/L in the Muskegon River to 55 ng/L in the Sheboygan River.

The concentrations of dissolved and particulate total PCBs exhibited a seasonal trend for many of the tributaries, with higher mean concentrations occurring in summer months and lower mean concentrations occurring in winter months. There were significant differences between seasons for the dissolved total PCB concentrations in nine of the eleven tributaries, and significant differences between season for the particulate total PCB concentration in six of the eleven tributaries. However, the trend was not consistent across all of the tributaries. The mean seasonal concentrations of dissolved and particulate total PCBs across all 11 tributaries span at least two orders of magnitude.

Concentrations of dissolved *trans*-nonachlor ranged from not detected in seven tributaries to 0.19 ng/L in the Manistique River, while particulate *trans*-nonachlor ranged from not detected in five tributaries to 0.38 ng/L in the Manistique River. Mean dissolved *trans*-nonachlor concentrations ranged 0.0033 ng/L in the Menominee River to 0.026 ng/L in the St. Joseph River, while mean particulate *trans*-nonachlor concentrations ranged from 0.0028 ng/L in the Menominee River to 0.074 ng/L in the St. Joseph River.

The mean concentrations of dissolved and particulate *trans*-nonachlor show fewer significant differences than the total PCB results. Eight of the eleven tributaries exhibit no statistically significant differences in mean dissolved *trans*-nonachlor concentrations among the seasons. Of the other three tributaries, the mean dissolved *trans*-nonachlor in the Kalamazoo River is never the lowest in spring or summer, and never the highest in autumn, while in the Sheboygan River, mean dissolved *trans*-nonachlor is never the lowest in the summer, or the highest in the winter. The dissolved *trans*-nonachlor results for the Manistique River are characterized by a very high mean concentration in the winter which is significantly different from the other three seasons, which in turn, are not significantly different from one another. The very high winter mean concentration is repeated in the particulate *trans*-nonachlor results in this tributary.

PCBs and *trans*-Nonachlor in Open-lake Water

The concentrations of dissolved PCB congeners are generally lowest in the far northern areas of the lake that are removed from urban influences. The highest dissolved concentrations generally are found in the southwest area of the lake, near the urban areas of Chicago and Milwaukee.

The particulate PCB concentrations are highest in Green Bay, at Station GB 17, with much lower particulate PCB concentrations in the remainder of the lake. The particulate concentrations of PCBs 118 and 180 show a slight increase in the southeast portion of the lake, in the area between the mouths of the

St. Joseph and Kalamazoo Rivers. However, the concentrations of particulate PCBs 118 and 180 in that area are still 2 to 5 times lower than in the upper reaches of Green Bay.

The dissolved concentrations of *trans*-nonachlor are similar to those of the dissolved PCB congeners, with an apparent increase in concentration in the southwest portion of the lake, near Chicago. The particulate concentrations of *trans*-nonachlor are similar to those of the particulate PCB congeners, with the highest concentrations in Green Bay, near Station GB 17. However, particulate *trans*-nonachlor concentrations appear to increase in areas of the lake adjacent to most of the major urban areas around the lake. Similar increases occur near the discharges of the Manistique and Pere Marquette Rivers, which are not associated with urban areas, suggesting that the increases near the urban area may be a function of river-borne sources of particulate *trans*-nonachlor, including resuspension of contaminated sediments.

PCBs and *trans*-Nonachlor in Sediments

The mean concentrations of the PCB congeners and total PCBs exhibit a general trend of decreasing concentrations from south to north, with the lowest concentrations in the Straits region. In contrast, the mean concentrations of *trans*-nonachlor, while lowest in the Straits region, exhibit no south to north trend. The organic carbon content data exhibit a pattern similar to that for *trans*-nonachlor.

Total PCBs exhibit a wide range in concentration. Although not a true bimodal distribution, two distinct groups are evident within the total PCB distribution. The first group of samples, from nondepositional and transitional stations, has very low concentrations that exponentially decline in number with increasing concentration (0 - 30 ng/g). The second group of samples taken mainly from depositional sites (35 - 225 ng/g) is more normally distributed, though tailing toward higher levels is evident.

Concentrations of PCBs and *trans*-nonachlor in surficial sediments increase with increasing organic carbon (OC) content. The spread in the data suggest that the southern basin stations were significantly higher in contamination. This finding was expected as hydrophobic compounds are known to partition strongly to organic matter. The southern basin the relationships of the PCB congeners and organic carbon content exhibited an additional feature not seen in other basins. A peak in PCB concentration was observed at ~25 mg/g OC for PCB 28+31 and at ~35 mg/g for PCB 118 and PCB 180. The relationship of *trans*-nonachlor with OC did not follow the same pattern as any particular PCB congener.

PCBs and *trans*-Nonachlor in Lower Pelagic Food Web Organisms

PCB and *trans*-nonachlor concentrations measured in the lower pelagic food web differed significantly among phytoplankton, zooplankton, *Mysis* spp., and *Diporeia* spp. Concentrations of total PCBs and *trans*-nonachlor were highest in samples of *Diporeia* spp., followed by *Mysis* spp., zooplankton, and phytoplankton, respectively. Total PCB concentrations were 9 times higher in *Diporeia* spp. than in phytoplankton, averaging 420, 250, 170, and 49 ng/g dry weight in *Diporeia* spp., *Mysis* spp., zooplankton, and phytoplankton samples, respectively. *Trans*-Nonachlor concentrations were 19 times higher in *Diporeia* spp. than in phytoplankton, averaging 32, 25, 16, and 1.7 ng/g dry weight in *Diporeia* spp., *Mysis* spp., zooplankton, and phytoplankton samples, respectively.

A portion of the difference in PCB and *trans*-nonachlor concentrations among lower pelagic food web sample types is likely due to variations in the lipid content of the samples. Hydrophobic organic contaminants such as PCBs and *trans*-nonachlor preferentially concentrate in the fatty tissues of organisms, so those organisms with higher lipid content will likely concentrate more of these contaminants. The differences in lipid content among the sample types, however, explained only a quarter to less than half of the variability in total PCB and *trans*-nonachlor concentrations. Even when total PCB and *trans*-nonachlor concentrations were normalized by lipid content, the trends in PCB and

trans-nonachlor concentrations among the sample types were almost always the same. Normalized total PCB and *trans*-nonachlor concentrations in *Diporeia* spp. and *Mysis* spp. were significantly higher than in zooplankton and phytoplankton, and normalized *trans*-nonachlor concentrations in zooplankton were significantly higher than in phytoplankton. Normalized total PCB concentrations in zooplankton, however, were not significantly different than in phytoplankton.

PCBs and *trans*-Nonachlor in Fish

PCB and *trans*-nonachlor concentrations differed significantly among species. Significantly higher levels of total PCBs and *trans*-nonachlor were observed in Lake trout, a top predator in the Lake Michigan pelagic food web, than in any other fish species. Mean wet-weight concentrations of total PCBs and *trans*-nonachlor in lake trout were 3.6 and 2.9 times higher than for any other species. This trend was similar for dry-weight basis PCB and *trans*-nonachlor concentrations. Mean dry-weight basis total PCB concentrations in lake trout were from 1.2 to 16 times higher than in other species, and mean dry-weight basis *trans*-nonachlor concentrations were 2.4 to 34 times higher in lake trout than in other species.

When PCB and *trans*-nonachlor concentrations were compared among fish species on a lipid-normalized basis, lake trout still contained higher levels of contamination than all other species with the exception of adult coho salmon. Mean lipid-normalized total PCB and *trans*-nonachlor concentrations were highest in adult coho salmon and second highest in lake trout. Lipid-normalized total PCB and *trans*-nonachlor concentrations in these two top predator fish species were significantly higher than in any of the forage fish species. The higher mean concentrations of lipid-normalized contaminants in adult coho salmon were due to the relatively low lipid content in this species. Lipid content in adult coho salmon averaged only 4%, compared to 16% in lake trout. Of the species analyzed in this study, only smelt contained lower lipid content (3.6%) than adult coho salmon.

The lowest total PCB and *trans*-nonachlor concentrations on a wet-weight, dry-weight, or lipid-weight basis were consistently found in hatchery and yearling coho salmon. This species is raised in hatcheries and annually stocked in Lake Michigan. Hatchery samples consisted of immature coho collected directly from the Platte River hatchery, and yearling samples consisted of immature coho collected in Lake Michigan. The reduced contamination in these sample types most likely reflects both the young age of the fish and reduced contaminant exposure from hatchery food and water sources.

The Great Lakes Fish Consumption Advisory Task Force has set a fish advisory category of “no consumption” at PCB levels above 2000 ng/g, and established four lesser consumption categories ranging from unrestricted consumption to no more than 6 meals per year. Of the Lake Michigan fish analyzed in the LMMB Study, only lake trout contained PCBs above the 2000 ng/g level. In fact, 56% of lake trout samples exceeded this tolerance level, and the mean total PCB concentration for Lake Michigan lake trout was 3000 ng/g (or 3 ppm), which is 50% above the 2000 ng/g tolerance level. No coho salmon or lake trout samples fell into the unrestricted consumption category. Coho salmon primarily fell into the 1 meal/mo and 6 meals/yr categories. These categories contained 46% and 44% of coho salmon samples, respectively, with only 9% of coho salmon samples falling into the 1 meal/wk category. Lake trout primarily fell into the no consumption category (56%), with only 0.4%, 17%, and 26% in the 1 meal/wk, 1 meal/mo, and 6 meals/yr categories, respectively.

Mass Balance and Modeling Efforts

The data collection and quality assurance efforts described in this report were designed to support the LMMB Study and related efforts to model the concentrations of pollutants in the Lake Michigan ecosystem. However, the mass balance itself and the associated modeling efforts are beyond the scope of this data report but will be described in later documents from GLNPO.

Chapter 1

Project Overview

The U.S. Environmental Protection Agency's Great Lakes National Program Office (GLNPO) and its partners instituted the Lake Michigan Mass Balance (LMMB) Study to measure and model the concentrations of representative pollutants within important compartments of the Lake Michigan ecosystem. Concentrations of polychlorinated biphenyls (PCBs), *trans*-nonachlor, atrazine, and mercury in the atmosphere, tributaries, lake water, sediments, and food webs of Lake Michigan. This document summarizes the PCB and *trans*-nonachlor data collected as part of the LMMB Study.

1.1 Background

The Great Lakes, which contain 20% of the world's freshwater, are a globally important natural resource that are currently threatened by multiple stressors. While significant progress has been made to improve the quality of the lakes, pollutant loads from point, non-point, atmospheric, and legacy sources continue to impair ecosystem functions and limit the attainability of designated uses of these resources. Fish consumption advisories and beach closings continue to be issued, emphasizing the human health concerns from lake contamination. Physical and biological stressors such as invasion of non-native species and habitat loss also continue to threaten the biological diversity and integrity of the Great Lakes.

The United States and Canada have recognized the significance and importance of the Great Lakes as a natural resource and have taken steps to restore and protect the lakes. In 1978, both countries signed the Great Lakes Water Quality Agreement (GLWQA). This agreement calls for the restoration and maintenance of the chemical, physical, and biological integrity of the Great Lakes by developing plans to monitor and limit pollutant flows into the lakes.

The GLWQA, as well as Section 118(c) of the Clean Water Act, required the development of Lake-wide Management Plans (LaMPs) for each Great Lake. The purpose of these LaMPs is to document an approach to reducing inputs of critical pollutants to the Great Lakes and restoring and maintaining Great Lakes integrity. To assist in developing these LaMPs and to monitor progress in pollutant reduction, Federal, State, Tribal, and local entities have instituted Enhanced Monitoring Plans. Monitoring is essential to the development of baseline conditions for the Great Lakes and provides a sound scientific base of information to guide future toxic load reduction efforts.

The LMMB Study is a part of the Enhanced Monitoring Plan for Lake Michigan. The LMMB Study was a coordinated effort among Federal, State, and academic scientists to monitor tributary and atmospheric pollutant loads, develop source inventories of toxic substances, and evaluate the fates and effects of these pollutants in Lake Michigan. A mass balance modeling approach provides the predictive ability to determine the environmental benefits of specific load reduction scenarios for toxic substances and the time required to realize those benefits. This predictive ability will allow Federal, State, Tribal, and local agencies to make more informed load reduction decisions.

1.2 Description

The LMMB Study used a mass balance approach to evaluate the sources, transport, and fate of contaminants in the Lake Michigan ecosystem. A mass balance approach is based on the law of conservation of mass, which states that the amount of a pollutant accumulating in a system is equal to the amount entering the system, less the amount of that pollutant leaving or chemically changed in the system (Figure 1-1).

If the system is defined as the Lake Michigan/Green Bay water column, then pollutants may enter the system via tributaries, direct runoff, the atmosphere (wet deposition, dry deposition, and sorption from the vapor phase), the sediment, and the Straits of Mackinac. Pollutants may leave the system through volatilization to the atmosphere, loss to the sediment, or discharge through the Straits of Mackinac and the Chicago water diversion. The law of conservation of mass also can be applied to other systems such as biota, sediment, or air.

The LMMB Study measured contaminant concentrations in various inputs and ecosystem compartments over spatial and temporal scales. Mathematical models that track the transport and fate of contaminants within Lake Michigan are being developed and calibrated using these field data. The LMMB Study is the first lake-wide application of a mass balance determination for toxics in the Great Lakes and will serve as the basis of future mass budget/mass balance efforts.

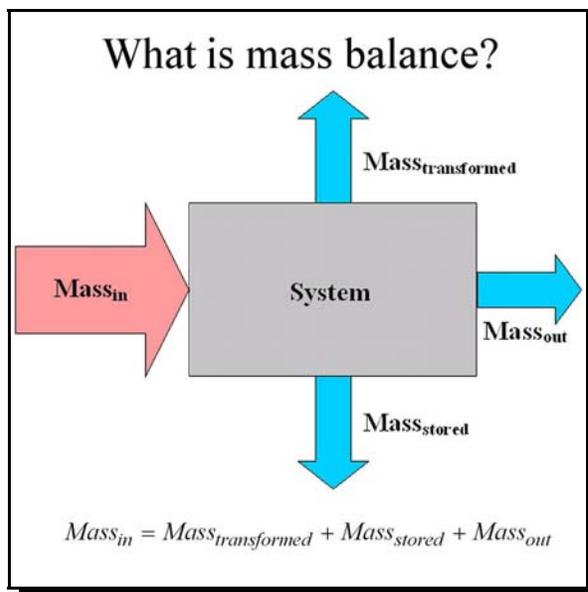


Figure 1-1. Simplified Mass Balance Approach

1.3 Scope

1.3.1 Modeled Pollutants

When EPA published the *Water Quality Guidance for the Great Lakes System* (58 FR 20802), the Agency established water quality criteria for 29 pollutants. Those criteria are designed to protect aquatic life, terrestrial wildlife, and human health. PCBs, *trans*-nonachlor, and mercury are included in the list of 29 pollutants. The water quality criteria and values proposed in the guidance apply to all of the ambient waters of the Great Lakes system, regardless of the sources of pollutants in those waters. The proposed criteria provide a uniform basis for integrating Federal, State, and Tribal efforts to protect and restore the Great Lakes ecosystem.

The number of pollutants that can be intensively monitored and modeled in the Great Lakes system is limited by the resources available to collect and analyze thousands of samples, assure the quality of the results, manage the data, and develop and calibrate the necessary models. Therefore, the LMMB Study focused on constructing mass balance models for a limited group of pollutants. PCBs, *trans*-nonachlor, atrazine, and mercury were selected for inclusion in the LMMB Study because these pollutants currently or potentially pose a risk to aquatic and terrestrial organisms (including humans) in the Lake Michigan ecosystem. These pollutants also were selected to cover a wide range of chemical and physical properties and represent other classes of compounds which pose current or potential problems. Once a mass budget for selected pollutants is established and a mass balance model calibrated, additional contaminants can be modeled with limited data and future resources can be devoted to activities such as emission inventories and dispersion modeling.

1.3.1.1 Polychlorinated Biphenyls

PCBs are a class of man-made, chlorinated, organic chemicals that include 209 congeners, or specific PCB compounds. The highly stable, nonflammable, non-conductive properties of these compounds have made them useful in a variety of products including electrical transformers and capacitors, plastics, rubber, paints, adhesives, and sealants. PCBs were produced for such industrial uses in the form of complex mixtures under the trade name “Aroclor” and were commercially available from 1930 through 1977, when EPA banned their production due to environmental and public health concerns. PCBs also may be produced by combustion processes, including incineration, and can be found in stack emissions and ash from incinerators.

Seven Aroclor formulations were included in the Priority Pollutant List developed by the EPA Office of Water under the auspices of the Clean Water Act because they were found by EPA in the effluents from one or more wastewater treatment facilities. Aroclors may have entered the Great Lakes through other means, including spills or improper disposal of transformer fluids, contaminated soils washing into the watershed, or discharges from ships. The PCBs produced by combustion processes may be released to the atmosphere, where they are transported in both vapor and particulate phases and enter the lakes through either dry deposition or precipitation events (e.g., rain).

The stability and persistence of PCBs, which made them useful in industrial applications, have also made these compounds ubiquitous in the environment. PCBs do not readily degrade and thus accumulate in water bodies and aquatic sediments. PCBs also bioaccumulate, or buildup, in living tissues. Levels of PCBs in some fish from Lake Michigan exceed U.S. Food and Drug Administration tolerances, prompting closure of some commercial fisheries and issuance of fish consumption advisories. PCBs are a probable human carcinogen, and human health effects of PCB exposure include stomach, kidney, and liver damage, liver and biliary tract cancer, and reproductive effects, including effects on the fetus after exposure of the mother.

PCB congeners exhibit a wide range of physical and chemical properties (e.g., vapor pressures, solubilities, boiling points), are relatively resistant to degradation, and are ubiquitous. These properties make them ideal surrogates for a wide range of organic compounds from anthropogenic sources.

In the LMMB Study, PCBs were selected as a model for conservative organic compounds (USEPA, 1997a).

1.3.1.2 *trans*-Nonachlor

trans-Nonachlor is a component of the pesticide chlordane. Chlordane is a mixture of chlorinated hydrocarbons that was manufactured and used as a pesticide from 1948 to 1988. Prior to 1983, approximately 3.6 million pounds of chlordane were used annually in the U.S. In 1988, EPA banned all production and use of chlordane in the U.S.

Like PCBs, chlordane is relatively persistent and bioaccumulative. *trans*-Nonachlor is the most bioaccumulative of the chlordanes. *trans*-Nonachlor is a probable human carcinogen. Other human health effects include neurological effects, blood dyscrasia, hepatotoxicity, immunotoxicity, and endocrine system disruption.

Historically, *trans*-nonachlor may have entered the Great Lakes through a variety of means related to the application of chlordane, including improper or indiscriminate application, improper cleaning and disposal of pesticide application equipment, or contaminated soils washing into the watershed.

In the LMMB Study, *trans*-nonachlor was selected as a model for the cyclodiene pesticides (USEPA, 1997a).

1.3.1.3 Atrazine

Atrazine is a herbicide based on a triazine ring structure with three carbon atoms alternating with three nitrogen atoms. Atrazine is the most widely used herbicide in the U.S. for corn and sorghum production. Atrazine has been used as an agricultural herbicide since 1959 and 64 to 75 million pounds of atrazine are used annually in the U.S. Atrazine is extensively used in the upper Midwest, including the Lake Michigan watershed, where it is primarily associated with corn crops.

Unlike PCBs and *trans*-nonachlor, atrazine is not extremely persistent or bioaccumulative. Atrazine is moderately susceptible to biodegradation, with a half-life in soils of about 60 - 150 days. Atrazine may persist considerably longer in water and is relatively non-reactive in the atmosphere. Atrazine rarely exceeds the maximum contaminant level (MCL) set by USEPA as a drinking water standard, but localized peak values can exceed the MCL following rainfall events after atrazine application. Atrazine can cause human health effects such as weight loss, cardiovascular damage, muscle and adrenal degeneration, and congestion of heart, lungs, and kidneys. Atrazine is also toxic to aquatic plants.

In the LMMB Study, atrazine was selected as a model for reactive, biodegradable compounds in current use (USEPA, 1997A).

1.3.1.4 Mercury

Mercury is a naturally-occurring toxic metal. Mercury is used in battery cells, barometers, thermometers, switches, fluorescent lamps, and as a catalyst in the oxidation of organic compounds. Global releases of mercury in the environment are both natural and anthropogenic (caused by human activity). It is estimated that about 5,500 metric tons of mercury are released annually to the air, soil, and water from anthropogenic and natural sources (USEPA 1997b). These sources include combustion of various fuels such as coal; mining, smelting and manufacturing activities; wastewater; agricultural, animal and food wastes; chlor-alkali plants; and pulp and paper mills.

As an elemental metal, mercury is extremely persistent in all media. Mercury also bioaccumulates with reported bioconcentration factors in fish tissues in the range of 63,000 to 100,000. Mercury is a neurotoxin and possible human carcinogen and causes the following human health effects: stomach, large intestine, brain, lung, and kidney damage; blood pressure and heart rate increase, and fetus damage.

In the LMMB Study, mercury was selected as a model for bioaccumulative metals (USEPA, 1997a).

Table 1-1. Characteristics of Lake Michigan Mass Balance Modeled Pollutants

Pollutant	Sources	Uses	Toxic Effects	Bioconcentration Factor ¹	EPA Regulatory Standards ²
PCBs	<ul style="list-style-type: none"> Waste incinerators (unintentional byproducts of combustion) Industrial dischargers Electrical power 	<ul style="list-style-type: none"> Electrical transformers and capacitors Carbonless copy paper Plasticizers Hydraulic fluids 	<ul style="list-style-type: none"> Probable human carcinogen Hearing and vision impairment Liver function alterations Reproductive impairment and deformities in fish and wildlife 	1,800 to 180,000	MCL = 0.5 µg/L CCC = 14 ng/L HH = 0.17 ng/L
<i>trans</i> -Nonachlor ³	<ul style="list-style-type: none"> Application to crops and gardens 	<ul style="list-style-type: none"> Pesticide on corn and citrus crops Pesticide on lawns and gardens 	<ul style="list-style-type: none"> Probable human carcinogen Nervous system effects Blood system effects Liver, kidney, heart, lung, spleen, and adrenal gland damage 	4,000 to 40,000	MCL = 2 µg/L CMC = 2.4 µg/L CCC = 4.3 ng/L HH = 2.1 ng/L
Atrazine	<ul style="list-style-type: none"> Application to crops 	<ul style="list-style-type: none"> Herbicide for corn and sorghum production 	<ul style="list-style-type: none"> Weight loss Cardiovascular damage Muscle and adrenal degeneration Congestion of heart, lungs, and kidneys Toxic to aquatic plants 	2 to 100	MCL = 3 µg/L CMC ⁴ = 350 µg/L CCC ⁴ = 12 µg/L
Mercury	<ul style="list-style-type: none"> Waste disposal Manufacturing processes Energy production Ore processing Municipal and medical waste incinerators Chlor-alkali factories Fuel combustion 	<ul style="list-style-type: none"> Battery cells Barometers Dental fillings Thermometers Switches Fluorescent lamps 	<ul style="list-style-type: none"> Possible human carcinogen Damage to brain and kidneys Adverse affects on the developing fetus, sperm, and male reproductive organs 	63,000 to 100,000	MCL = 2 µg/L CMC = 1.4 µg/L CCC = 0.77 µg/L HH = 50 ng/L FWA ⁵ = 2.4 µg/L FWC ⁵ = 12 ng/L Wildlife ⁶ = 1.3 ng/L

¹ From: USEPA. 1995a. *National Primary Drinking Water Regulations, Contaminant Specific Fact Sheets, Inorganic Chemicals, Technical Version*. EPA 811/F-95/002-T. U.S. Environmental Protection Agency, Office of Water, Washington, D.C.; and USEPA. 1995b. *National Primary Drinking Water Regulations, Contaminant Specific Fact Sheets, Synthetic Organic Chemicals, Technical Version*. EPA 811/F-95/003-T. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

² MCL = Maximum Contaminant Level for drinking water. CMC = Criterion Maximum Concentration for protection of aquatic life from acute toxicity. CCC = Criterion Continuous Concentration for protection of aquatic life from chronic toxicity. HH = Water quality criteria for protection of human health from water and fish consumption. Data from: USEPA. 1999. *National Recommended Water Quality Criteria-Correction*. EPA 822/Z-99/001. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

³ Characteristics presented are for chlordane. *trans*-Nonachlor is a principle component of the pesticide chlordane.

⁴ Draft water quality criteria for protection of aquatic life. From: USEPA. 2001a. *Ambient Aquatic Life Water Quality Criteria for Atrazine*. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

⁵ FWA = Freshwater acute water quality criterion. FWC = Freshwater chronic water quality criterion. From National Toxics Rule (58 FR 60848).

⁶ Wildlife criterion. From the Stay of Federal Water Quality Criteria for Metals (60 FR 22208), 40 CFR 131.36 and the Water Quality Guidance for the Great Lakes System (40 CFR 132).

1.3.2 Other Measured Parameters

In addition to the four chemicals modeled in the LMMB Study, many other chemicals and parameters were measured in the LMMB Study as part of the Enhanced Monitoring Program. A survey of these chemicals and parameters will aid in understanding the overall ecological integrity of Lake Michigan. These additional parameters include various biological indicators, meteorological parameters, and organic, metal, and conventional chemicals in Lake Michigan. A complete listing of all parameters included in this study is provided in Table 1-2.

Table 1-2. Lake Michigan Mass Balance Study Parameters

Organics	
acenaphthene	<i>p,p'</i> -DDT
acenaphthylene	endosulfan sulfate
aldrin	endosulfan I
anthracene	endosulfan II
atrazine	endrin
α -BHC	endrin aldehyde
β -BHC	endrin ketone
δ -BHC	fluoranthene
γ -BHC (Lindane)	fluorene
benzo [<i>a</i>] anthracene	heptachlor
benzo [<i>g,h,i</i>] perylene	heptachlor epoxide
benzo [<i>b</i>] fluoranthene	hexachlorobenzene (HCB)
benzo [<i>k</i>] fluoranthene	indeno [1,2,3- <i>cd</i>] pyrene
benzo [<i>e</i>] pyrene	mirex
benzo [<i>a</i>] pyrene	<i>trans</i> -nonachlor
α -chlordane	oxychlordane
γ -chlordane	PCB congeners
chrysene	phenanthrene
coronene	pyrene
<i>p,p'</i> -DDE	retene
<i>p,p'</i> -DDD	toxaphene
Metals	
aluminum	magnesium
arsenic	manganese
calcium	sodium
cadmium	nickel
chromium	lead
cesium	selenium
copper	thorium
iron	titanium
mercury	vanadium
potassium	zinc

Table 1-2. Lake Michigan Mass Balance Study Parameters

Conventionals	
alkalinity	particulate organic carbon
ammonia	percent moisture
bromine	pH
chloride	phosphorous
chlorine sulfate	silica
conductivity	silicon
dissolved organic carbon	temperature
dissolved oxygen	total Kjeldahl nitrogen
dissolved phosphorous	total organic carbon
dissolved reactive silica	total phosphorous
dry weight fraction	total suspended particulates
elemental carbon	total hardness
nitrate	turbidity
<i>ortho</i> -phosphorous	
Biologicals	
fish species	fish weight
fish age	fish length
fish maturity	fish taxonomy
chlorophyll <i>a</i>	fish diet analysis
fish lipid amount	primary productivity
Meteorological	
air temperature	wind direction
relative humidity	wind speed
barometric pressure	visibility
weather conditions	wave height and direction

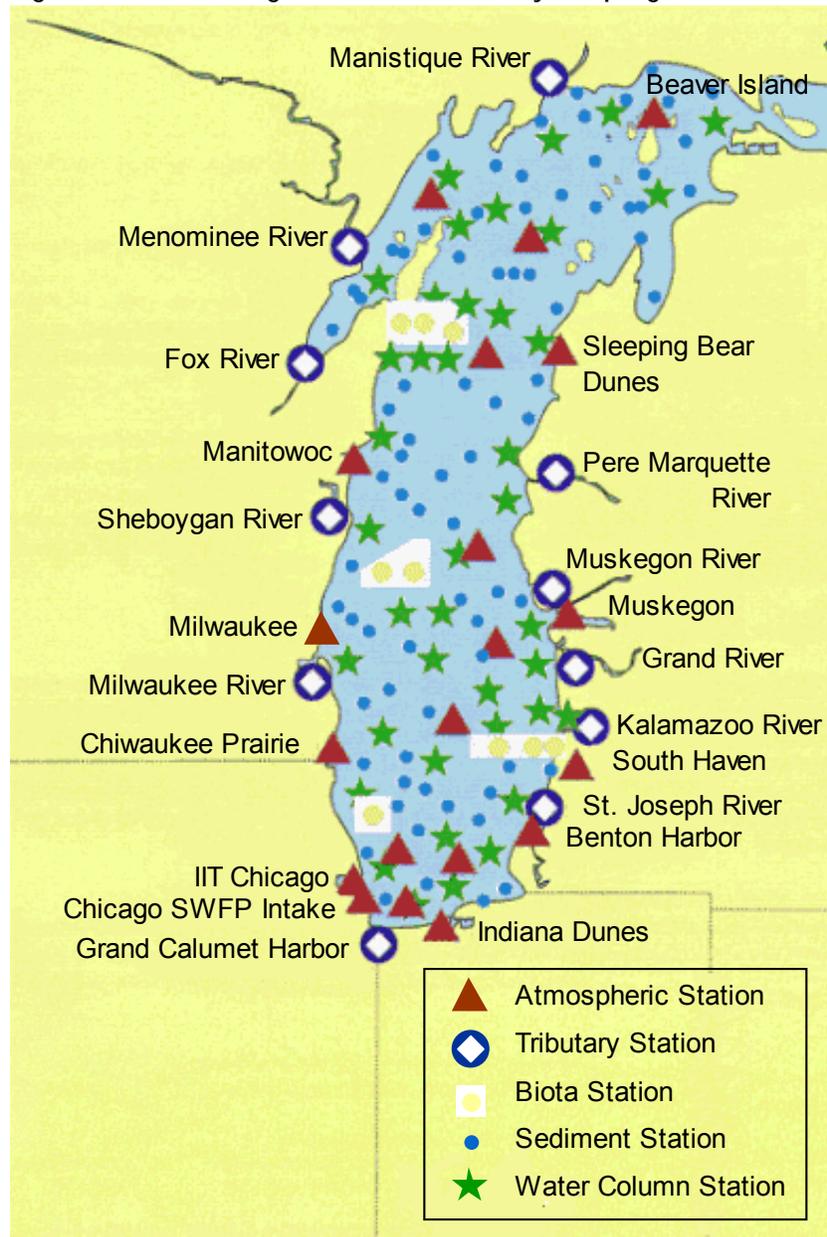
1.3.3 Measured Compartments

In the LMMB Study, contaminants were measured in the following compartments:

- **Open-Lake Water Column** – The water column in the open lake was sampled and analyzed for the modeled pollutants.
- **Tributaries** – Tributary water columns were sampled and analyzed for the modeled pollutants.
- **Fish** – Top predators and forage-base species were sampled and analyzed for diet analysis and contaminant burden. Fish were not analyzed for atrazine because atrazine is not bioaccumulative.
- **Lower Pelagic Food Web** – Lower pelagic food web organisms were sampled and analyzed for species diversity, taxonomy, and contaminant burden. Individual samples of the lower pelagic food web included mixed phytoplankton, mixed zooplankton, *Diporeia* spp., and *Mysis* spp. The lower pelagic food web was not analyzed for atrazine because atrazine is not bioaccumulative.
- **Sediments** – Cores were collected and trap devices were used to collect sediment for determination of contaminants and sedimentation rates. Sediments were not analyzed for atrazine because atrazine is relatively water soluble, degradable, and does not generally accumulate in sediments.
- **Atmosphere** – Vapor-, particulate-, and precipitation-phase samples were collected and analyzed for the modeled pollutants.

For the modeled pollutants, more than 20,000 samples were collected and analyzed, including more than 9000 quality control (QC) samples, at more than 300 sampling locations (Figure 1-2). Field data collection activities were initially envisioned as a one-year effort. However, it became evident early into the project that a longer collection period would be necessary to provide a full year of concurrent information on contaminant loads and ambient concentrations for modeling purposes. Therefore, field sampling occurred from April 1994 to October 1995.

Figure 1-2. Lake Michigan Mass Balance Study Sampling Locations



1.4 Objectives

The goal of the LMMB Study was to develop a sound, scientific base of information to guide future toxic load reduction efforts at the Federal, State, Tribal, and local levels. To meet this goal, the four following LMMB Study objectives were developed:

- **Estimate pollutant loading rates** – Environmental sampling of major media will allow estimation of relative loading rates of critical pollutants to the Lake Michigan Basin.
- **Establish baseline** – Environmental sampling and estimated loading rates will establish a baseline against which future progress and contaminant reductions can be gauged.
- **Predict benefits associated with load reductions** – The completed mass balance model will provide a predictive tool that environmental decision-makers and managers may use to evaluate the benefits of specific load reduction scenarios.
- **Understand ecosystem dynamics** – Information from the extensive LMMB monitoring and modeling efforts will improve our scientific understanding of the environmental processes governing contaminant cycling and availability within relatively closed ecosystems.

1.5 Design

1.5.1 Organization

The Great Lakes National Program Office proposed a mass balance approach to provide coherent, ecosystem-based evaluation of toxics in Lake Michigan. GLNPO served as the program sponsor for the LMMB Study. GLNPO formed two committees to coordinate study planning, the Program Steering Committee and the Technical Coordinating Committee. These committees were comprised of scientists from Federal, State, academic, and commercial institutions (see Section 1.5.2, Study Participants). The committees administered a wide variety of tasks including: planning the project, locating the funding, designing the sample collection, coordinating sample collection activities, locating qualified laboratories, coordinating analytical activities, assembling the data, assuring the quality of the data, assembling skilled modelers, developing the models, and communicating interim and final project results. The National Health and Environmental Effects Research Laboratory (NHEERL)/Mid-Continent Ecology Division (MED)/Large Lakes and Rivers Forecasting Research Branch (LLRFRB) at Gross Ile, Michigan, in cooperation with the National Oceanic and Atmospheric Administration (NOAA) Great Lakes Environmental Research Laboratory (GLERL) and the Atmospheric Sciences Modeling Division are supporting the modeling component of the mass balance study by developing a suite of integrated mass balance models to simulate the transport, fate, and bioaccumulation of the study target analytes.

1.5.2 Study Participants

The LMMB Study was a coordinated effort among Federal, State, academic, and commercial institutions. The following agencies and organizations have all played roles in ensuring the success of the LMMB Study. Except for the three organizations indicated with an asterisk (*), all of the participants were members of the LMMB steering committee.

Federal and International

- ▶ USEPA Great Lakes National Program Office (*Program Sponsor*)
- ▶ USEPA Region 5 Water Division
- ▶ USEPA Region 5 Air Division
- ▶ USEPA Office of Research and Development (ORD) NHEERL/MED/LLRFRB
- ▶ USEPA Office of Research and Development National Exposure Research Laboratory
- ▶ U.S. Department of Interior (USDOI) U.S. Geological Survey (USGS) Water Resources Division
- ▶ USDOI USGS Biological Resources Division Great Lakes Science Center (GLSC)
- ▶ U.S. Fish and Wildlife Service (USFWS)
- ▶ U.S. Department of Commerce NOAA/GLERL
- ▶ USEPA Office of Air and Radiation*
- ▶ USEPA Office of Water*
- ▶ U.S. Department of Energy, Battelle Northwest
- ▶ Environment Canada*

State

- ▶ Illinois Department of Natural Resources
- ▶ Illinois Water Survey
- ▶ Indiana Department of Environmental Management
- ▶ Michigan Department of Environmental Quality (MDEQ)
- ▶ Wisconsin Department of Natural Resources
- ▶ Wisconsin State Lab of Hygiene

Academic and Commercial

- ▶ Indiana University
- ▶ Rutgers University
- ▶ University of Maryland
- ▶ University of Michigan
- ▶ University of Minnesota
- ▶ University of Wisconsin
- ▶ Grace Analytical

1.5.3 Workgroups

Eleven workgroups were formed to provide oversight and management of specific project elements. The workgroups facilitated planning and implementation of the study in a coordinated and systematic fashion. The workgroups communicated regularly through participation in monthly conference calls and annual “all-hands” meetings. Workgroup chairs were selected and were responsible for managing tasks under the purview of the workgroup and communicating the status of activities to other workgroups. The workgroups and workgroup chairs are listed below.

- ▶ Program Steering Committee – Paul Horvatin (USEPA/GLNPO)
- ▶ Technical Coordinating Committee – Paul Horvatin (USEPA/GLNPO)
- ▶ Modeling Workgroup – William Richardson (USEPA/ORD/NHEERL/MED/LLRFRB)
- ▶ Air Monitoring Workgroup – Jackie Bode (USEPA/GLNPO)
- ▶ Biota Workgroup – Paul Bertram (USEPA/GLNPO) and John Gannon (USDOI/USGS/GLSC)
- ▶ Chemistry Workgroup – David Anderson (USEPA/GLNPO)
- ▶ Data Management Workgroup – Kenneth Klewin and Philip Strobel (USEPA/GLNPO)

- ▶ Lake Monitoring Workgroup – Glenn Warren (USEPA/GLNPO)
- ▶ Tributary Monitoring Workgroup – Gary Kohlhepp (USEPA Region 5 Water Division) and Robert Day (Michigan Department of Environmental Quality)
- ▶ Quality Assurance Workgroup – Louis Blume and Michael Papp (USEPA/GLNPO)
- ▶ Sediment Monitoring Workgroup – Brian Eadie (NOAA/GLERL)

1.5.4 Information Management

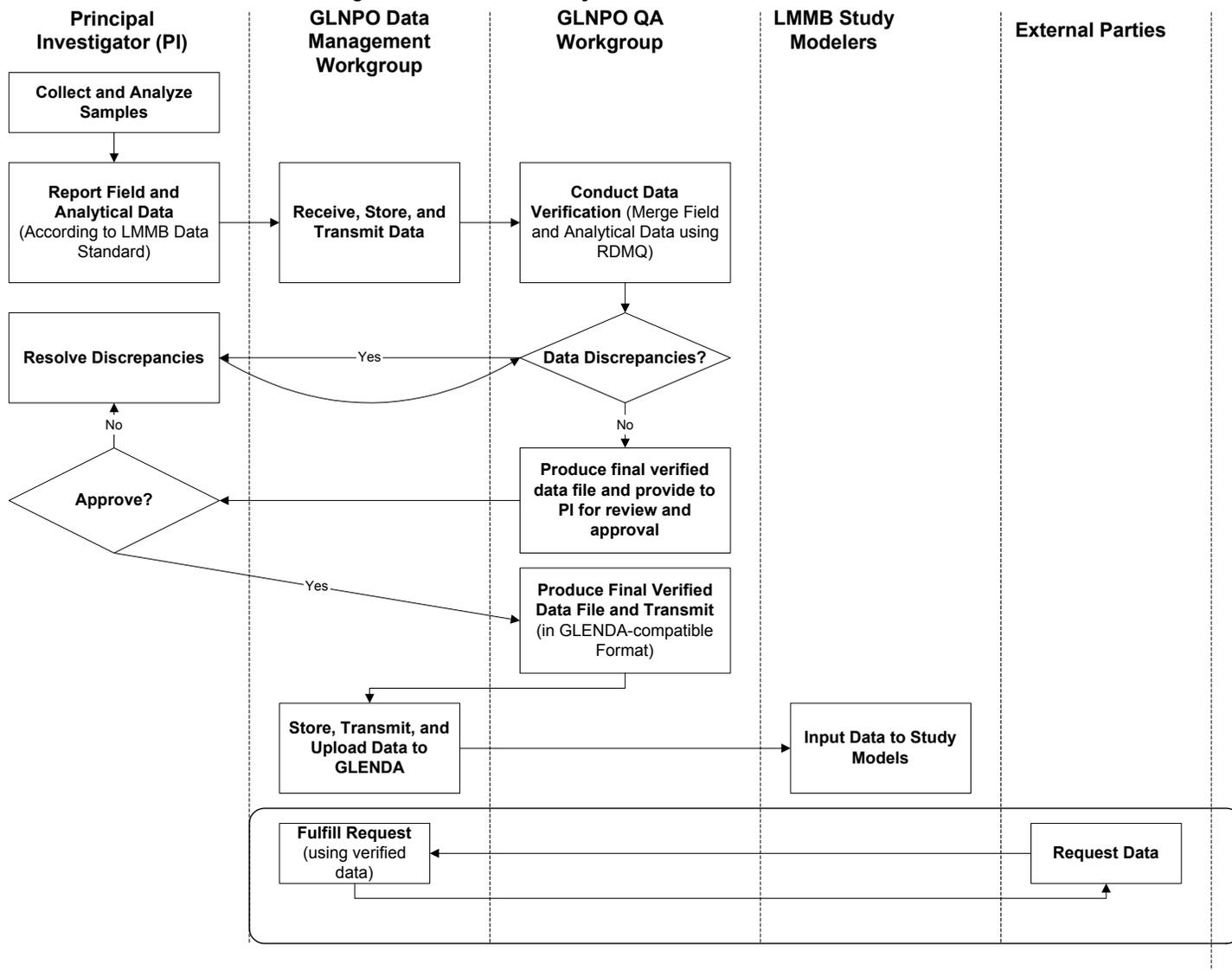
As program sponsor, GLNPO managed information collected during the LMMB Study. Principal investigators (PIs) participating in the study reported field and analytical data to GLNPO. GLNPO developed a data standard for reporting field and analytical data and a database for storing and retrieving study data. GLNPO also was responsible for conducting data verification activities and releasing verified data to the study modelers and the public. The flow of information is illustrated in Figure 1-3.

1.5.4.1 Data Reporting

More than twenty organizations produced LMMB data through the collection and analysis of more than 20,000 samples. In the interest of standardization, specific formats (i.e., file formats and codes to represent certain data values) were established for reporting LMMB data. Each format specified the “rules” by which data were submitted, and, in many cases, the allowable values by which they were to be reported. The data reporting formats were designed to capture all pertinent sampling and analytical information from the field crews and laboratory analysts. Data reporting formats and the resulting Great Lakes Environmental Monitoring Database (GLENDa, see Section 1.5.4.2,) were designed to be applicable to projects outside the LMMB as well. For the LMMB Study, special conditions were applied for reporting analytical results. Because the data were being used for input to study models, principal investigators were asked to report analytical results as measured, even when measurements were below estimated detection limits. The quality assurance program discussed in Section 1.5.5 included identifying (i.e., flagging) all analytical results that were below estimated detection limits.

Principal investigators (including sampling crews and the analytical laboratories) supplied sample collection and analysis data following the standardized reporting formats if possible. LMMB data were then processed through an automated SAS-based data verification system, the Research Data Management and Quality Control System (RDMQ), for quality assurance/quality control checking. After verification and validation by the PI, the data sets were output in a form specific for upload to GLENDa. Finally, these data sets were uploaded to GLENDa.

Figure 1-3. Flow of Information in the Lake Michigan Mass Balance Study



1.5.4.2 Great Lakes Environmental Monitoring Database

Central to the data management effort is a computerized database system to house LMMB Study and other project results. That system, the Great Lakes Environmental Monitoring Database (GLENDAs), was developed to provide data entry, storage, access and analysis capabilities to meet the needs of mass balance modelers and other potential users of Great Lakes data.

Development of GLENDAs began in 1993 with a logical model based on the modernized STORET concept and requirements analysis. GLENDAs was developed with the following guiding principles:

- **True multi-media scope** – water, air, sediment, taxonomy, fish tissue, fish diet, and meteorology data can all be housed in the database
- **Data of documented quality** – data quality is documented by including results of quality control parameters
- **Extensive contextual indicators** – ensures data longevity by including enough information to allow future or secondary users to make use of the data
- **Flexible and expandable** – the database is able to accept data from any Great Lakes monitoring project
- **National compatibility** – GLENDAs is compatible with STORET and allows ease of transfer between these large databases

In an effort to reduce the data administration burden and ensure consistency of data in this database, GLNPO developed several key tools. Features including standard data definitions, reference tables, standard automated data entry applications, and analytical tools are (or will soon be) available.

1.5.4.3 Public Access to LMMB Data

All LMMB data that have been verified (through the QC process) and validated (accepted by the PI) are available to the public. Currently, GLNPO requires that written requests be made to obtain LMMB data. The data sets are available in several formats including WK1, DBF, and SD2. More information about the data sets is available on the LMMB web site at: <http://www.epa.gov/glnpo>.

The primary reason for requiring an official request form for LMMB data is to keep track of requests. This allows GLNPO to know how many requests have been made, who has requested data, and what use they intend for the data. This information assists GLNPO in managing and providing public access to Great Lakes data and conducting public outreach activities. As of November 2000, 38 requests for LMMB data have been made: 8 from EPA, 5 from other federal agencies, 5 from state agencies, 5 from universities, 10 from consultants, 3 from international agencies, and 2 from non-profit or other groups. In the future, after all data are verified and validated, GLNPO intends to make condensed versions of the data sets available on the LMMB web site for downloading. This will allow easy public access to LMMB data.

Additional details of the information management for the LMMB Study can be found in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b).

1.5.5 Quality Assurance Program

At the outset of the LMMB Study, managers recognized that the data gathered and the models developed from the study would be used extensively by decision makers responsible for making environmental, economic, and policy decisions. Environmental measurements are never true values and always contain some level of uncertainty. Decision makers, therefore, must recognize and be sufficiently comfortable

with the uncertainty associated with data on which their decisions are based. In recognition of this requirement, LMMB Study managers established a QA program goal of ensuring that data produced under the LMMB Study would meet defined standards of quality with a specified level of confidence.

The QA program prescribed minimum standards to which all organizations collecting data were required to adhere. Data quality was defined, controlled, and assessed through activities implemented within various parameter groups (e.g., organic, inorganic, and biological parameters). QA activities included the following:

- **QA Program** – Prior to initiating data collection activities, plans were developed, discussed, and refined to ensure that study objectives were adequately defined and to ensure that all QA activities necessary to meet study objectives were considered and implemented.
- **QA Workgroup** – EPA established a QA Workgroup whose primary function was to ensure that the overall QA goals of the study were met.
- **QA Project Plans (QAPPs)** – EPA worked with PIs to define program objectives, data quality objectives (DQOs), and measurement quality objectives (MQOs) for use in preparing QAPPs. Principal investigators submitted QAPPs to EPA for review and approval. EPA reviewed each QAPP for required QA elements and soundness of planned QA activities.
- **Training** – Before data collection activities, PIs conducted training sessions to ensure that individuals were capable of properly performing data collection activities for the LMMB Study.
- **Monthly Conference Calls and Annual Meetings** – EPA, PIs, and support contractors participated in monthly conference calls and annual meetings to discuss project status and objectives, QA issues, data reporting issues, and project schedules.
- **Standardized Data Reporting Format** – Principal investigators were required to submit all data in a standardized data reporting format that was designed to ensure consistency in reporting and facilitate data verification, data validation, and database development.
- **Intercomparison Studies** – EPA conducted studies to compare performance among different PIs analyzing similar samples. The studies were used to evaluate the comparability and accuracy of program data.
- **Technical Systems Audits** – During the study, EPA formally audited each PI's laboratory for compliance with their QAPPs, the overall study objectives, and pre-determined standards of good laboratory practice.
- **Data Verification** – PIs and EPA evaluated project data against pre-determined MQOs and DQOs to ensure that only data of acceptable quality would be included in the program database.
- **Statistical Assessments** – EPA made statistical assessments of the LMMB Study data to estimate elements of precision, bias, and uncertainty.
- **Data Validation** – EPA and modelers are evaluating the data against the model objectives.

Comparability of data among PIs participating in the LMMB Study was deemed to be important for successful completion of the study. Therefore, measurement quality objectives (MQOs) for several data attributes were developed by the PIs and defined in the QAPPs. MQOs were designed to control various phases of the measurement process and to ensure that the total measurement uncertainty was within the ranges prescribed by the DQOs. MQOs were defined in terms of six attributes:

- **Sensitivity/Detectability** – The determination of the low-range critical value that a method-specific procedure can reliably discern for a given pollutant. Sensitivity measures included, among others, method detection limits (MDLs) as defined at 40 CFR Part 136, system detection limits (SDLs), or instrument detection limits (IDLs).
- **Precision** – A measure of the degree to which data generated from replicate or repetitive measurements differ from one another. Analysis of duplicate samples was used to assess precision.

- **Bias** – The degree of agreement between a measured and actual value. Bias was expressed in terms of the recovery of an appropriate standard reference material or spiked sample.
- **Completeness** – The measure of the number of samples successfully analyzed and reported compared to the number that were scheduled to be collected.
- **Comparability** – The confidence with which one data set can be compared to other data sets.
- **Representativeness** – The degree to which data accurately and precisely represent characteristics of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

The PI-defined MQOs also were used as the basis for the data verification process. GLNPO conducted data verification through the LMMB QA Workgroup. The workgroup was chaired by GLNPO's Quality Assurance Manager and consisted of quality control coordinators that were responsible for conducting review of specific data sets. Data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. If a result failed to meet predefined criteria, the QC Coordinator contacted the PI to discuss the result, verify that it was correctly reported, and determine if corrective actions were feasible. If the result was correctly reported and corrective actions were not feasible, the results were flagged to inform data users of the failure. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Data that met all predefined requirements were flagged to indicate that the results had been verified and were determined to meet applicable MQOs. In this way, every data point was assigned one or more validity flags based on the results of the QC checks. GLNPO also derived data quality assessments for each LMMB Study data set for a subset of the attributes listed above, specifically sensitivity, precision, and bias. The LMMB Study modelers and the Large Lakes Research Station Database Manager also perform data quality assessments prior to inputting data into study models. Such activities include verifying the readability of electronic files, identifying missing data, checking units, and identifying outliers. A detailed description of the quality assurance program is included in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of quality implementation and assessment is provided in each of the following chapters.

1.6 Project Documents and Products

During project planning, LMMB participants developed study tools including work plans, a methods compendium, quality assurance project plans, and data reporting standards. Through these tools, LMMB participants documented many aspects of the study including information management and quality assurance procedures. Many of these documents are available on GLNPO's web site at: <http://www.epa.gov/glnpo/lmb>.

LMMB Work Plan

Designers of the LMMB Study have documented their approach in a report entitled *Lake Michigan Mass Budget/Mass Balance Work Plan* (USEPA, 1997a). The work plan describes the essential elements of a mass balance study and the approach used to measure and model these elements in the Lake Michigan system. This document was developed based upon the efforts of many Federal and State scientists and staff who participated in the initial planning workshop, as well as PIs.

Quality Assurance Program/Project Plans

The Lake Michigan Mass Balance Project Quality Assurance Plan for Mathematical Modeling, Version 3.0 (USEPA, 1998) documents the quality assurance process for the development and application of LMMB models, including hydrodynamic, sediment transport, eutrophication, transport chemical fate, and food web bioaccumulation models.

The Enhanced Monitoring Program Quality Assurance Program Plan

The Enhanced Monitoring Program Quality Assurance Program Plan (USEPA, 1997c) was developed in 1993 to ensure that data generated from the LMMB Study supports its intended use.

LMMB Methods Compendium

The *Lake Michigan Mass Balance Project (LMMB) Methods Compendium* (USEPA, 1997d, 1997e) describes the sampling and analytical methods used in the LMMB Study. The entire three volumes are available on GLNPO's web site mentioned above.

LMMB Data Reporting Formats and Data Administration Plan

Data management for the LMMB Study was a focus from the planning stage through data collection, verification, validation, reporting, and archiving. The goal of consistent and compatible data was a key to the success of the project. The goal was met primarily through the development of standard formats for reporting environmental data. The data management philosophy is outlined on the LMMB web site mentioned above.

Lake Michigan LaMP

"Annex 2" of the 1972 Canadian-American Great Lakes Water Quality Agreement (amended in 1978, 1983, and 1987) prompted development of Lakewide Area Management Plans (LaMPs) for each Great Lake. The purpose of these LaMPs is to document an approach to reducing input of critical pollutants to the Great Lakes and restoring and maintaining Great Lakes integrity. The Lake Michigan LaMP calls for basin-wide management of toxic chemicals.

GLEND A Database

Central to the data management effort is a computerized data system to house Lake Michigan Mass Balance and other project results. That system, the Great Lakes Environmental Monitoring Database (GLEND A), was developed to provide data entry, storage, access and analysis capabilities to meet the needs of mass balance modelers and other potential users of Great Lakes data.

LMMB Data Reports

This report is one in a series of data reports that summarize the data from monitoring associated with EPA's Lake Michigan Mass Balance Study. In addition to this data report on PCBs and *trans*-nonachlor, data reports are being published for atrazine (USEPA, 2001c) and mercury (USEPA, 2004).

Future Documents and Products

Following the completion of modeling efforts associated with the LMMB Study, GLNPO anticipates publishing reports summarizing the modeling results. In 2005, GLNPO also anticipates conducting a reassessment of Lake Michigan to calibrate and confirm modeling results with data collected 10 years after the initial LMMB sampling.

Chapter 2

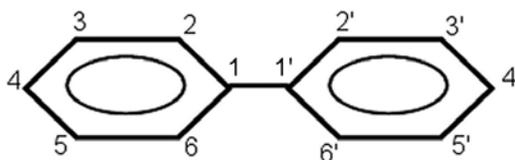
PCB/trans-Nonachlor Study Overview

2.1 PCB Introduction

2.1.1 Physical/Chemical Properties

Polychlorinated biphenyls (PCBs) are a class of synthetic organic chemicals characterized by two six-membered aromatic carbon rings joined by a single carbon-carbon bond that constitute the parent biphenyl. One or more chlorine atoms are attached to carbon atoms in the two ring structures. There are 209 possible arrangements of chlorine atoms, and each of the arrangements is referred to as a PCB “congener.” The carbon atoms on both of the aromatic rings are numbered 1 through 6, to indicate their position around each ring. The superscript prime (') is used to distinguish similar positions on the two rings. The two carbon atoms linking the rings are numbered 1 and 1'. Each of the remaining 10 carbon atoms (numbered 2 to 6 and 2' to 6') can bond with one hydrogen or chlorine atom. The formal chemical name of each of the 209 congeners identifies the specific positions and the total number of chlorine atoms in the congener, e.g., 2,2',4,5'-tetrachlorobiphenyl.

Figure 2-1. Generalized 2-D Structure of Biphenyl



There are 3 possible PCB congeners that contain a single chlorine atom. The two ring structures are symmetrical, such that the structures 2-monochlorobiphenyl and 2'-monochlorobiphenyl are identical. In addition, the two rings can rotate along the carbon bond that joins them, such that the 2 and 6 positions on each ring are equivalent, as are the 3 and 5 positions. By convention, the equivalent position with the lower number is used to describe the compound. Thus, a monochlorobiphenyl with the chlorine attached in the 2 or 2', or 6 or 6' position is named 2-monochlorobiphenyl. The monochlorobiphenyl with the chlorine attached in the 3 or 3', 5 or 5' position is named 3-monochlorobiphenyl. The monochlorobiphenyl with the chlorine attached in the 4 or 4' position is named 4-monochlorobiphenyl.

Table 2-1. Numbers of Congeners in Each Level of Chlorination

No. of Chlorine Atoms	Level of Chlorination	No. of Congeners
1	monochlorobiphenyl	3
2	dichlorobiphenyl	12
3	trichlorobiphenyl	24
4	tetrachlorobiphenyl	42
5	pentachlorobiphenyl	46
6	hexachlorobiphenyl	42
7	heptachlorobiphenyl	24
8	octachlorobiphenyl	12
9	nonachlorobiphenyl	3
10	decachlorobiphenyl	1

PCBs are often described in terms of the “level of chlorination,” which refers to the number of chlorine atoms attached to the biphenyl ring (e.g., monochlorobiphenyls, dichlorobiphenyls, and trichlorobiphenyls). The numbers of PCB congeners in each level of chlorination are shown in Table 2-1. The physical and chemical properties of PCBs are dependent on the number of chlorine atoms and their respective positions in the two ring structures, thus, they vary with the congener. In general, PCBs with the same number of chlorine atoms have similar physical and chemical properties.

GLNPO adopted the numbering system developed by Ballschmiter and Zell (1980) that simplifies the identification of each congener by assigning each possible congener a number 1 through 209. That notation is used throughout the remainder of this discussion.

There is a subset of PCB congeners in which the pattern of chlorine substitution causes "steric hindrance" that limits the rotation of the two aromatic rings around their common carbon-carbon bond such that the two rings lie in the same plane. These congeners are called "coplanar" PCBs and as a result of their flat configuration, they have a greater ability to penetrate the walls of living cells and generally exhibit greater toxicological effects (see Section 2.3).

In general, PCBs are chemically inert, nonflammable, and do not transmit electrical current. These properties, combined with high melting and boiling points made PCBs useful in a wide variety of industrial applications, particularly as dielectric fluids in electrical transformers and capacitors. Flash points for PCBs are in the range of 170 to 380°C (H. Fiedler, 2001)

PCBs are readily soluble in organic solvents, but have low solubility in water. Water solubility decreases dramatically as the number of chlorine atoms attached to the parent biphenyl structure increases. For example, the water solubility of unsubstituted biphenyl has been reported to be within the range of 5.9 to 7.5 mg/L, while the water solubility of PCB 209, containing 10 chlorine atoms, is estimated at 4×10^{-6} mg/L, or 4 ng/L (Shiu and Mackay, 1986). The vapor pressures of PCB congeners decrease in a similarly dramatic fashion with increased chlorination. Dunnivant and Elzerman (1988) report vapor pressures for several dichlorobiphenyl congeners on the order of 2×10^{-6} atmospheres, while the vapor pressures for some hexachlorobiphenyls are on the order of 3×10^{-10} or 3×10^{-11} atmospheres. In the LMMB Study, PCBs served as a model for conservative organic pollutants.

2.1.2 History of PCB Production

In the United States, the Monsanto Company produced commercial mixtures of PCBs by chlorinating biphenyl and sold the mixtures under the trade name Aroclor. There were nine Aroclor mixtures produced in the U.S. and they were differentiated by a series of four-digit numbers (e.g., Aroclor 1242). The names of eight of the nine mixtures begin with the number "12," representing the 12 carbon atoms in the parent biphenyl, and end in a two-digit number that represents the percentage of chlorine (by weight) in the mixture. Aroclor 1016 was the only mixture that violated this naming scheme, because its number began with "10" instead of "12," and it contained more than 16% chlorine. The nine Aroclor mixtures are shown in Table 2-2, along with their percent chlorine (by weight), and the approximate percentage of domestic production that they comprised for the period from 1957 to 1977.

Table 2-2. U.S. Domestic Production of Commercial Aroclor Mixtures from 1957 to 1977*

Mixture	Percent Chlorine by Weight	Percent of U.S. Production
Aroclor 1016	41	13
Aroclor 1221	21	1
Aroclor 1232	32	<1
Aroclor 1242	42	52
Aroclor 1248	48	7
Aroclor 1254	54	16
Aroclor 1260	60	11
Aroclor 1262	62	1
Aroclor 1268	68	<1

*Adapted from Brown, 1994. Total production percent is greater than 100%, due to rounding.

Table 2-3 contains the typical compositions of the five Aroclors with the greatest U.S. production, in terms of the percentages of various levels of chlorination.

PCB production facilities were built in Austria, Germany, France, Great Britain, Italy, Japan, Spain, the USSR, and the U.S. PCB mixtures were produced in Germany under the trade name Clophens, in Japan under the names Kanechlors and Sanotherm, and in France as Phenoclor and Pyralene. World-wide production of Aroclors is estimated to have been 1.5 million metric tonnes (3.3 billion pounds) (Rantanen, 1992; Ivanov and Sandell, 1992).

Table 2-3. Typical Composition (%) of the Five Aroclor Mixtures with Greatest U.S. Production*

Biphenyls by Level of Chlorination	Aroclor				
	1016	1242	1248	1254	1260
Monochlorobiphenyls	2	1	<1%	<1%	<1%
Dichlorobiphenyls	19	13	1	<1%	<1%
Trichlorobiphenyls	57	45	21	1	<1%
Tetrachlorobiphenyls	22	31	49	15	<1%
Pentachlorobiphenyls	<1%	10	27	53	12
Hexachlorobiphenyls	<1%	<1%	2	26	42
Heptachlorobiphenyls	<1%	<1%	<1%	4	38
Octachlorobiphenyls	<1%	<1%	<1%	<1%	7
Nonachlorobiphenyls	<1%	<1%	<1%	<1%	1
Decachlorobiphenyl	<1%	<1%	<1%	<1%	<1%

*Adapted from PCBs: Cancer Dose-Response Assessment and Application to Environmental Mixtures, EPA/600/P-96/001F, September 1996.

2.1.3 Regulatory Background

PCB production and export in the U.S. was halted in October 1977 under the auspices of the Toxic Substances Control Act (TSCA). Use and import of PCBs were banned in Japan in 1972. In addition to the production ban instituted under TSCA, EPA regulates PCBs, as Aroclors, under a wide range of environmental statutes. For example, Aroclors are regulated in effluent guidelines developed under the Clean Water Act and administered through the National Pollutant Discharge Elimination System (NPDES). The Office of Water has established water quality criteria (WQC) for freshwater and marine systems. The freshwater chronic WQC is 0.014 µg/L of total Aroclor. The marine chronic WQC is 0.030 µg/L. The WQC for human health is 4.5×10^{-5} µg/L. Under the Safe Drinking Water Act, EPA has established a maximum contaminant limit (MCL) of 0.50 µg/L for total Aroclor. Under the auspices of the Resource Conservation and Recovery Act (RCRA) EPA has placed Aroclors on Appendix VIII (hazardous substances) and Appendix IX (groundwater monitoring), and has established a Universal Treatment Standard (UTS) of 1 mg/kg of Aroclors in non-wastewaters and 0.10 mg/L in wastewaters. PCBs are included in the Toxics Release Inventory (TRI) developed under the Emergency Planning and Community Right to Know Act (EPCRA).

2.1.4 Fate and Effects

The fate and effects of PCBs in the environment are driven by the physical properties of the individual PCB congeners. In general, PCBs are hydrophobic and lipophilic. Therefore, they are more likely to be found in soils, sediments, and tissues, than dissolved in water. PCBs found in water are likely to be associated with the particulate phase, with some of the lower chlorinated congeners present in the dissolved phase.

Baker and Eisenreich (1990) examined the behavior of PCBs in Lake Superior, finding that PCBs volatilize when river inputs to the lake are relatively high in PCBs. They calculated volatilization rates for PCBs that are approximately equal to the rate of atmospheric deposition into the lake. These findings support a model of PCB cycling proposed by Mackay and Patterson (1986) in which PCBs dissolved in rain or sorbed onto air particulates are transported to surface water. This input results in a fugacity

gradient that favors volatilization from the water into the atmosphere, where the PCBs are dissolved in rain water or sorbed onto particulates again, thus repeating the cycle.

2.1.5 Biological Transformations

PCBs can be degraded by microorganisms by several mechanisms, including both aerobic and anaerobic processes. Although PCBs are generally resistant to aerobic breakdown, Rochkind *et al.* (1986) found that microorganisms of the genera *Acetobacter*, *Alcaligenes*, and *Pseudomonas* are capable of degrading PCBs under aerobic conditions. However, the rates of degradation are greatly influenced by the chlorine substitution pattern in each congener. Rochkind *et al.* found that:

- higher chlorinated PCBs degrade more slowly under aerobic conditions than those with fewer chlorine atoms;
- PCBs with chlorines on only one ring are metabolized more rapidly than PCBs in the same level of chlorination, but with the chlorine atoms distributed on both rings;
- the ring with fewer chlorines will be hydroxylated first, and;
- chlorine atoms attached at the *ortho* position (2 or 6 on the ring) significantly inhibit degradation.

In anaerobic environments, PCBs will undergo reductive dechlorination (loss of chlorine), with the degradation rate related to the number of chlorine atoms on the PCB. As a result, the more highly chlorinated congeners are more readily dechlorinated under anaerobic conditions. Fiedler *et al.* (1994) found that the chlorines in the *meta* and *para* positions (3, 4, and 5 on the ring) were more readily lost by reductive dechlorination, resulting in an apparent increase in the prevalence of the *ortho*-substituted PCBs in the environment.

PCBs are lipophilic, concentrating in fatty tissues of organisms. As a result, PCBs are not readily excreted from organisms as intact chlorinated biphenyls. The metabolic transformation of PCBs requires that the molecule undergo hydroxylation to make it more polar, and thus more water soluble. In higher organisms, PCBs are hydroxylated through a metabolic pathway involving the hepatic monooxygenase system mediated by the enzyme Cytochrome P-450. As with other transformations of PCBs, the rates are related to the level of chlorination and the substitution patterns.

As a result of both their lipophilic nature and their low rates of biodegradation, PCBs accumulate, or bioconcentrate, to higher concentrations in each subsequent trophic level of an ecosystem. Fiedler *et al.* (1994) has shown that both the total PCB concentrations and the concentrations of the "toxic" or "dioxin-like" PCBs (see Section 2.1.6) increase in typical aquatic systems consisting of phytoplankton, zooplankton, plankton-eating fish, piscivorous fish, and piscivorous birds.

2.1.6 Toxicity

EPA has classified PCBs as carcinogens. Other human health effects include disruption of endocrine systems. Effects of short-term exposures in humans include chloracne, changes in skin pigmentation, numbness of the limb and general weakness. Long-term exposures have been associated with changes in liver function, irritations of the nose, throat and intestinal tract, fertility problems, birth defects, premature births, and neurological and developmental problems in newborns.

Many of these health effects of PCBs are similar to those related to exposures to polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) and are believed to result from the actions of a subset of the 209 possible PCB congeners known as the "coplanar" PCBs. The coplanar PCBs have structures that resemble the 2,3,7,8-substituted PCDDs/PCDFs, in which the two aromatic rings lie in one plane and are believed to be more readily transported across cell membranes. The World

Health Organization (WHO) has classified 12 PCB congeners as the “toxic” PCBs, or the “dioxin-like” PCBs, based on structure-activity relationships (see Table 2-4 and Van den Berg *et al.*, 1998). However, for reasons discussed in Section 2.6, the toxic PCBs were not the primary focus of the LMMB Study.

Table 2-4. World Health Organization Toxic PCB Congeners

Congener Number	PCB Congener	Structural Group
77	3,3',4,4'-Tetrachlorobiphenyl	Non- <i>ortho</i> substituted PCB
81	3,4,4',5-Tetrachlorobiphenyl	Non- <i>ortho</i> substituted PCB
126	3,3',4,4',5-Pentachlorobiphenyl	Non- <i>ortho</i> substituted PCB
169	3,3',4,4',5,5'-Hexachlorobiphenyl	Non- <i>ortho</i> substituted PCB
105	2,3,3',4,4'-Pentachlorobiphenyl	Mono- <i>ortho</i> substituted PCB
114	2,3,4,4',5-Pentachlorobiphenyl	Mono- <i>ortho</i> substituted PCB
118	2,3',4,4',5-Pentachlorobiphenyl	Mono- <i>ortho</i> substituted PCB
123	2',3,4,4',5-Pentachlorobiphenyl	Mono- <i>ortho</i> substituted PCB
156	2,3,3',4,4',5-Hexachlorobiphenyl	Mono- <i>ortho</i> substituted PCB
157	2,3,3',4,4',5'-Hexachlorobiphenyl	Mono- <i>ortho</i> substituted PCB
167	2,3',4,4',5,5'-Hexachlorobiphenyl	Mono- <i>ortho</i> substituted PCB
189	2,3,3',4,4',5,5'-Heptachlorobiphenyl	Mono- <i>ortho</i> substituted PCB

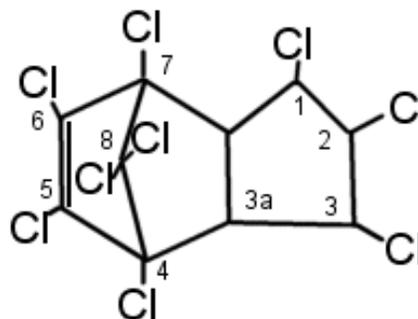
The term “*ortho*” in Table 2-4 refers to the position of the chlorines attached to the phenyl ring structure, relative to the carbon-carbon bond between the two rings. Chlorines attached at the 2, 2', 6, or 6' positions of the biphenyl structure (see Figure 2-1) are in the “*ortho*” position. A “non-*ortho*” congener does not have any chlorines in the 2, 2', 6, or 6' positions, while a “mono-*ortho*” congener has a chlorine attached at one of those positions.

2.2 *trans*-Nonachlor Introduction

2.2.1 Physical/Chemical Properties

trans-Nonachlor is the common name for 1,2,3,4,5,6,7,8,8-nona-chloro-3a,4,7,7a-tetrahydro-4,7-methanoindan, a member of the class of cyclodiene pesticides. *trans*-Nonachlor is a component of the pesticide formulation “technical chlordane,” comprising about 1.1% of that mixture of at least 140 related compounds. *trans*-Nonachlor differs from the two structural isomers of the compound chlordane (*cis*- and *trans*-chlordane) by the addition of one additional chlorine atom, in the number 3 position of the molecule (see Figures 2-2 and 2-3).

Figure 2-2. Generalized 2-D Structure of *trans*-Nonachlor



Compared to the two isomers of chlordane, there is very little published physical-chemical data for *trans*-nonachlor. For example, Mackay *et al.* (1992) do not list *trans*-nonachlor at all. The general properties of *trans*-nonachlor can be inferred from those of chlordane. The addition of one more chlorine atom to the chlordane structure increases the melting and boiling points for *trans*-nonachlor, decreases the water solubility, and decreases the vapor pressure. *trans*-Nonachlor has low solubility in water, but is readily soluble in organic solvents. It has a melting point above 100°C and a boiling point above 175°C.

In the LMMB Study, *trans*-nonachlor serves as a model for the cyclodiene pesticides.

2.2.2 *trans*-Nonachlor Production

trans-Nonachlor was not produced as a pure compound, but was one of the major components of technical chlordane mixtures. Chlordane is produced through the chlorination of cyclopentadiene to form hexachloropentadiene. This intermediate product is condensed to form chlordene, which undergoes additional chlorination to produce *cis*- and *trans*-chlordane, plus *trans*-nonachlor, heptachlor, and several other major components. Chlordane mixtures were first produced in the U.S. in 1948 and various formulations of chlordane were widely used as pesticides on food crops and lawns, and for termite control from 1948 to 1988. In April 1988, all commercial uses in the U.S. were banned (USEPA, 1988).

Since 1988, the only U.S. domestic manufacturer of chlordane has been the Velsicol Chemical Company of Memphis, TN. Production data for chlordane are difficult to obtain, but EPA estimated that 3.5 to 4 million pounds of chlordane were distributed in 1986. Data from the Toxics Release Inventory for 1990 indicate that 100,000 to 1 million pounds of chlordane were produced that year.

EPA estimated that more than 7.5 million pounds of chlordane were used for home, lawn, and garden purposes in the U.S. in 1974 (USEPA, 1975). Other sources estimate total production in 1974 was on the order of 21 million pounds, suggesting that over 13 million pounds of chlordane were exported that year (WHO, 1988).

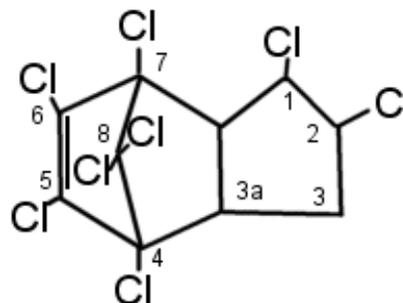
2.2.3 Regulatory Background

trans-Nonachlor has been regulated in the U.S. as a component of chlordane. Beginning in 1975, EPA ordered a halt to the use of chlordane and the related pesticide heptachlor for most household and agricultural uses, citing an imminent human cancer hazard. The 1975 action limited the use of chlordane to underground injection for termite control and treatment of the roots and tops of non-food plants. From July 1983 to April 1988, EPA further restricted the use of chlordane to underground injection for termite control. In April 1988, EPA canceled all commercial uses of chlordane in the U.S.

Regulation of *trans*-nonachlor has typically been accomplished by analogy to chlordane. Thus, the maximum contaminant limit (MCL) established under the Safe Drinking Water Act is 2 µg/L for *trans*-nonachlor, the same MCL used for chlordane. Similarly, the water quality criteria developed under the Clean Water Act for *trans*-nonachlor have the same values as were developed for chlordane.

Chlordane has been banned in 47 countries, including the U.S., and 14 additional countries have severely restricted its use.

Figure 2-3. Generalized 2-D Structure of *trans*-Chlordane



2.2.4 Fate and Effects

All of the components of chlordane have been found to bioaccumulate, with *trans*-nonachlor the most bioaccumulative of the components. In general, *trans*-nonachlor is hydrophobic and lipophilic. Therefore, it is more likely to be found in soils, sediments, and tissues than dissolved in water. When found in water, *trans*-nonachlor is likely to be associated with the particulate phase, rather than actually dissolved in water.

2.2.5 Toxicity

As with other aspects of *trans*-nonachlor, the majority of the data on toxicity has been determined for either technical chlordane mixtures or the predominant chlordane isomers. To date, the data from human studies have not provided sufficient evidence to conclude that either chlordane or *trans*-nonachlor is a human carcinogen. However, mice fed low levels of chlordane in food developed liver cancer. Therefore, *trans*-nonachlor is considered to be a probable human carcinogen. Other human health effects include neurological effects, blood dyscrasia, hepatotoxicity, immunotoxicity, and endocrine system disruption.

2.3 Study Design

2.3.1 Description

PCBs and *trans*-nonachlor were chosen for analysis in the LMMB Study as representatives of the persistent, bioaccumulative chlorinated compounds. PCB congeners and *trans*-nonachlor were measured in vapor, precipitation, particulates, atmospheric dry deposition, water in the open lake, tributaries, sediment, lower pelagic food web organisms, and fish. The data generated from this study were used to estimate an overall mass balance of PCBs and *trans*-nonachlor in Lake Michigan (see Section 1.4).

2.3.2 Scope

To develop a mass balance of PCBs and *trans*-nonachlor in Lake Michigan, all significant sources and stores of PCBs and *trans*-nonachlor in the environment were measured. Significant sources and stores included tributary inputs, atmospheric inputs from the vapor phase, particulate phase, and precipitation, sediment, lower pelagic food web organisms, and fish. The specific components that were studied are shown in Table 2-5.

Field sampling was conducted from February 1994 through October 1995, with an additional sampling cruise in May 1996 to retrieve sediment traps and collect samples at Stations LM94-11, LM94-17, LM94-18, LM94-21S and LM94-32.

2.3.3 Organization/Management

The responsibility for collecting and analyzing PCBs and *trans*-nonachlor samples from the various components was divided among multiple principal investigators (Table 2-5). Each principal investigator developed a Quality Assurance Project Plan (QAPP) that was submitted to EPA's Great Lakes National Program Office. The QAPPs detailed the project management, study design, and sampling and analysis procedures that would be used in the study and the quality control elements that would be implemented to protect the integrity of the data. The LMMB Quality assurance program is further discussed in Section 2.6, and detailed information on the quality assurance activities and data quality assessment specific to each ecosystem component are discussed in Chapters 3-5.

Table 2-5. Components Sampled by Principal Investigators

Ecosystem Compartment	Component	Principal Investigator
Atmosphere	Vapor Particulate Precipitation	Clyde Sweet , Illinois State Water Survey (Sleeping Bear Dunes from 4/94 to 7/94 and all other sites)
	Vapor Particulate Precipitation	Ron Hites and Ilora Basu , Indiana University (Sleeping Bear Dunes <i>only</i> , from 8/94 to 10/95)
	Dry deposition	Steve Eisenreich , University of Minnesota Gray Freshwater Biological Institute and Rutgers University
Tributary	Dissolved Total	William Sonzogni , University of Wisconsin, Wisconsin State Lab of Hygiene
Open Lake	Dissolved Total	Eric Crecelius , Battelle Sequim
Sediment	Surficial Resuspended	Patricia Van Hoof and Brian Eadie , Great Lakes Environmental Research Laboratory, National Oceanic and Atmospheric Administration
Lower Pelagic Food Web Organisms	Mysis Diporeia Zooplankton Phytoplankton	Deborah Swackhamer , University of Minnesota
Fish	Lake Trout Slimy sculpin Deepwater sculpin Coho salmon Alewife Bloater chub Smelt	Robert Hesselberg and James Hickey , United States Geological Survey, Biological Resources Discipline (formerly National Biological Service)

2.4 Sampling Locations

2.4.1 Atmospheric Components

Atmospheric samples were collected at eight shoreline sampling stations and 16 open-lake sampling stations within Lake Michigan and two open-lake sampling stations in Green Bay. In addition, three out-of-basin land-based sampling stations were established as regional background sites to represent air coming over Lake Michigan during periods of southwest or northwest prevailing winds. The sampling locations and sampling frequencies for the LMMB Project were selected through discussions with experts in the field during several workshops, including the Great Lakes Mass Balance Planning Workshop in April 1992 and the LMMB Planning Meeting in September 1993. Site-selection criteria considered predominant annual wind directions, source areas, and episodic summer events. In general, sites were selected to be regionally representative of land-use categories and to represent the different potential sources of pollutants in this study (e.g., releases associated with population centers versus applications of agricultural activities). The sampling frequencies were designed to capture the expected variability at the sites (e.g., more frequent sampling in urban areas versus less frequent sampling in remote areas and more frequent sampling in spring summer, and fall months).

The shoreline atmospheric sampling stations include those specific to the LMMB Study as well as several that are part of the Integrated Atmospheric Deposition Network (IADN). Samples were collected from

the land-based IADN stations at the Brule River, Eagle Harbor, and Bondville from April 1994 through October 1995. Sampling at these IADN stations was governed by study design and quality assurance programs specific to IADN, but generally similar to those in the LMMB Study, so the data have been incorporated into the LMMB database. The locations of the shoreline atmospheric PCB sampling stations within the Lake Michigan basin are shown in Figure 2-4. The site classifications, planned sampling frequencies, and types of vapor-phase and particulate-phase samples are shown in Table 2-6. These frequencies were generally followed as sampling schedules permitted and except in cases of sampler malfunction, lack of precipitation, or when circumstances prevented retrieval of a sample.

Table 2-6. Site Classifications, Planned Frequencies, and Types of Vapor-phase and Particulate-phase Samples Collected at Shoreline and Out-of-basin Stations

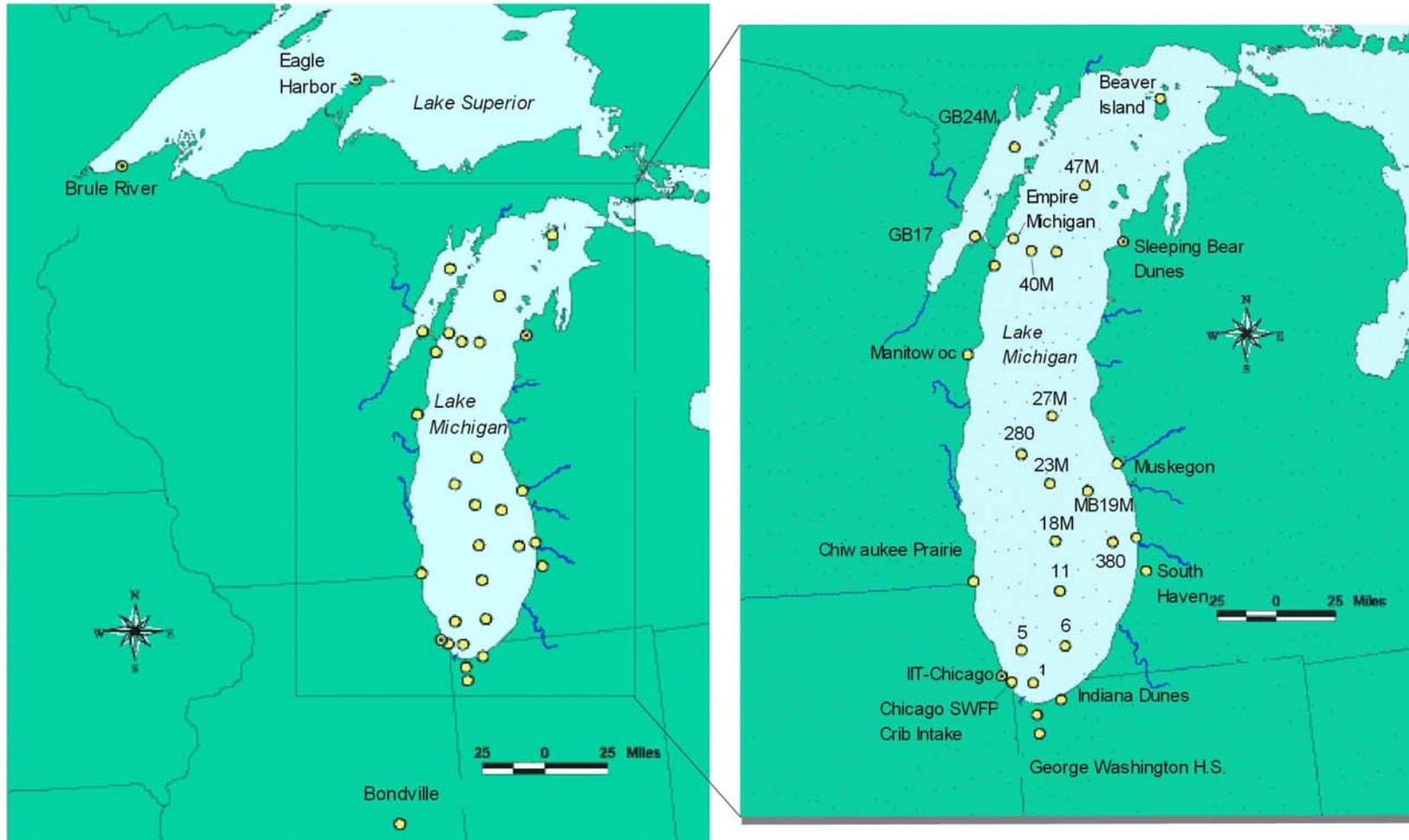
Site Classification	Planned Frequency	Site Names	Sample Type
Urban - Major urban sources within 1 km	One 24-h composite collected every 3 days	IIT Chicago	Multiple 24-h samples composited to represent 1 sample per month
Urban-influenced - Major urban sources within 10 km	One 24-h composite collected every 3 days	Chiwaukee Prairie	Multiple 24-h samples composited to represent 1 sample per month
		Indiana Dunes	
		Manitowoc	
		Muskegon	
Rural - Urban sources generally 10 to 50 km away, but agricultural sources within 1 km	One 24-h composite collected every 6 days	Bondville	Multiple 24-h samples composited to represent 1 sample per month
		South Haven	
Remote - No urban areas or major sources of air pollutants within 50 km	One 24-h composite collected every 12 days	Beaver Island	Multiple 24-h samples composited to represent 1 sample per month
		Brule River	
		Eagle Harbor	
		Sleeping Bear Dunes	Individual 24-h samples analyzed and mathematically composited to represent 1 sample per month

PCBs and *trans*-nonachlor were measured in vapor, particulates, and precipitation samples collected at 16 locations in Lake Michigan during seven cruises of the *Research Vessel Lake Guardian* between April 1994 and October 1995 and at two stations in Green Bay. Because these open-lake samples were collected on board the ship, they are single-day samples, and were not composited by month.

Monthly integrated dry deposition samples were collected from the following stations: 68th Street Crib, Sleeping Bear Dunes, Harrison Crib, IIT Chicago and South Haven. In addition, two 4-day composite dry deposition samples were collected on the ship in July 1994.

Figure 2-4. Atmospheric Sampling Stations

Atmospheric Stations ● IADN Stations ⊙



2.4.2 Tributaries

Tributary samples were collected from 11 rivers that flow into Lake Michigan (Figure 2-5). These tributaries included the Menominee, Fox, Sheboygan, and Milwaukee Rivers in Wisconsin; the Grand Calumet River in Indiana; and the St. Joseph, Kalamazoo, Grand, Muskegon, Pere Marquette, and Manistique Rivers in Michigan. With the exception of the Pere Marquette River, these tributaries were selected for the LMMB Study because of elevated concentrations of contaminants in resident fish. The Pere Marquette River was selected because it has a fairly large and pristine watershed. Samples collected from the Pere Marquette River can be used to estimate loads from the small portion of the Lake Michigan watershed that was not monitored in this study. The 11 monitored tributaries represent greater than 90% of the total river flow into Lake Michigan and an even higher percentage of the total tributary load of pollutants into Lake Michigan.

Table 2-7 describes specific watershed characteristics and impairment information for each of the monitored tributaries. Of the 11 tributaries, 6 (the Kalamazoo, Manistique, Menominee, Fox, Sheboygan, and Grand Calumet Rivers) are classified as Great Lakes areas of concern (AOCs). Areas of concern are severely degraded geographic areas within the Great Lakes Basin. They are defined by the US-Canada Great Lakes Water Quality Agreement (Annex 2 of the 1987 Protocol) as “geographic areas that fail to meet the general or specific objectives of the agreement where such failure has caused or is likely to cause impairment of beneficial use or the area’s ability to support aquatic life.” Most of the eleven tributaries are also listed on the Clean Water Act Section 303(d) list of impaired water bodies due to contamination from mercury, PCBs, and other pollutants.

Figure 2-5. Tributary Sampling Stations



Table 2-7. Watershed Characteristics for Tributaries Monitored in the LMMB Study

Tributary	Watershed area (mi ²)	Total river miles in watershed	Riparian Habitat		IWI Score ^a	Impaired for ^b	Area of Concern
			Forested	Agricultural/Urban			
St. Joseph	4685	3743	25-50%	>50%	3- less serious problems, low vulnerability	<i>E. coli</i> , mercury, PCBs, pathogens, macro-invertebrate community	
Kalamazoo	2047	1560	25-50%	>50%	3- less serious problems, low vulnerability	Mercury, PCBs	X
Grand (lower)	2003	2014	25-50%	>50%	5- more serious problems, low vulnerability	PCBs, pathogens	
Muskegon	2686	1886	25-50%	>50%	5- more serious problems, low vulnerability		
Pere Marquette	2644	1356	25-50%	>50%	3- less serious problems, low vulnerability	Mercury, PCBs	
Manistique	1464	1061	>75%	20-50%	1- better quality, low vulnerability	Mercury, PCBs, pathogens	X
Menominee	2306	1660	>75%	20-50%	1- better quality, low vulnerability	Dioxin, PCBs, mercury, pathogens	X
Fox (lower)	442	700	25-50%	>50%	6- more serious problems, high vulnerability	PCBs, organic enrichment, dissolved oxygen	X
Sheboygan	2201	1699	25-50%	>50%	5- more serious problems, low vulnerability	PCBs, mercury	X
Milwaukee	864	802	25-50%	>50%	5- more serious problems, low vulnerability	PCBs	
Grand Calumet	1039	760	25-50%	>50%	5- more serious problems, low vulnerability	PCBs, pesticides, lead, mercury, dissolved oxygen, cyanide, chlorides, impaired biotic community, oil and grease, copper	X

^aEPA's Index of Watershed Indicators Score for assessing the health of aquatic resources.

^bBased on 1998 listing of Clean Water Act Section 303(d) impaired waters.

2.4.3 Open Lake

Open-lake water column samples were collected from 38 sampling locations on Lake Michigan, 2 sampling locations in Green Bay, and 1 sampling location on Lake Huron (Figure 2-6). Open-lake samples were collected during eight cruises of the *R/V Lake Guardian* between April 1994 and September 1995. Due to field conditions and other considerations, samples were not collected at all 41 stations during each cruise. The dates of the eight cruises and the total number of stations occupied are shown in Table 2-8.

The stations used in the LMMB Study and shown in Figure 2-6 include many historical stations used by GLNPO and other programs. Stations established specifically for the LMMB Study are shown in Figure 2-6 with identifiers that begin with "MB." The identifier for the station in Lake Huron begins with "LH," as seen in the upper right corner of Figure 2-6. The identifiers for the two stations in Green Bay begin with "GB," as seen in the upper left portion of Figure 2-6. Some of the stations are those specified by GLNPO as "Master" stations that are used for various purposes beyond the LMMB Study. The identifiers for those master stations end in "M."

The first survey occurred in the early spring just after "ice out" in April 1994. The second survey was in early summer (June 1994) after the onset of stratification and following the spring runoff period of agricultural chemicals from crop land. The third survey was in late summer (August 1994) during later stages of stratification. The fourth and fifth surveys, conducted in October 1994 and January 1995, sampled only a few of the Lake Michigan sites. The sixth survey occurred in March 1995 just after ice out. The seventh and eighth surveys occurred in August and September 1995, during stratification.

Figure 2-6. Open-Lake Water Column Sampling Stations

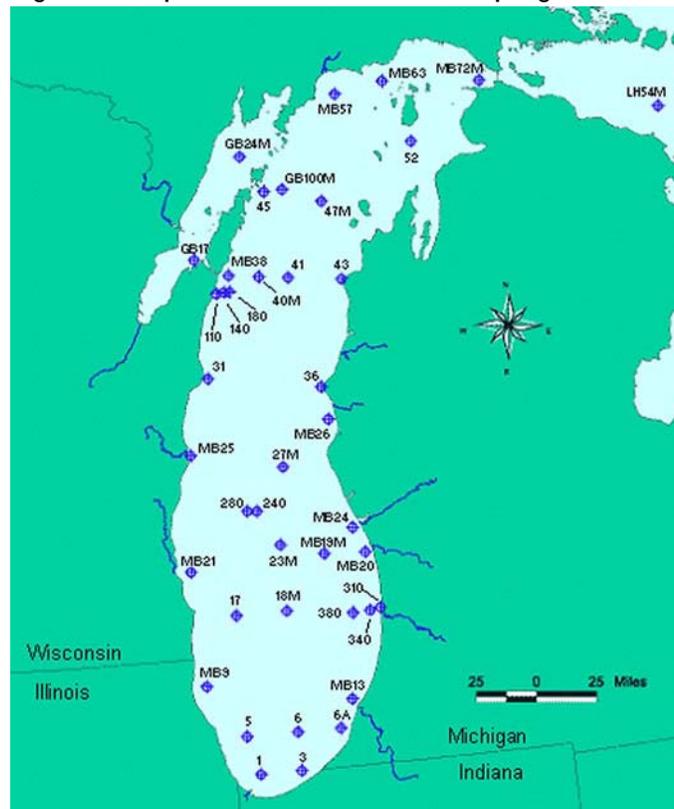


Table 2-8. Open-lake Cruise Dates and Number of Stations Occupied

Cruise Date	Number of Stations Occupied
April 1994	39
June 1994	14
August 1994	41
October 1994	37
January 1995	4
March 1995	40
August 1995	19
September 1995	41

2.4.4 Sediment

In 1994 and 1995, 117 sediment samples were collected from Lake Michigan and 6 samples were collected from Green Bay, by box coring, Ponar dredge, and gravity coring. The sediment sampling locations were selected to help define the three depositional zones (depositional, transitional, and non-depositional). The locations and the sampling device used at each location are shown in Figure 2-7.

In addition, sediment traps were deployed at eight locations in Lake Michigan (see Figure 2-8). However, samples could not be retrieved from the traps at two of those locations. Sample retrieval was successful at trap locations 1, 2, 5, 6, 7, and 8.

Figure 2-7. Sediment Sampling Stations

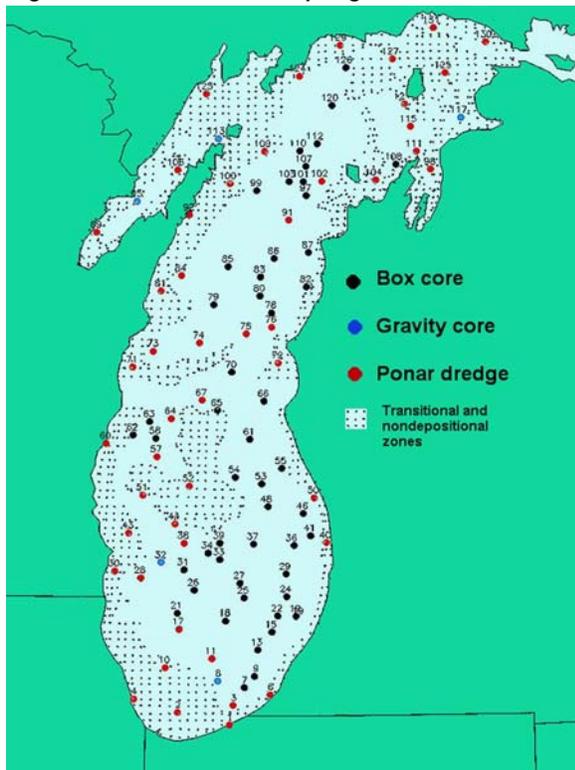


Figure 2-8. Sediment Trap Locations



2.4.5 Lower Pelagic Food Web Organisms

Plankton sampling locations were selected by GLNPO and the PIs in advance of sampling. The sites included eight stations in three biological sampling areas or “biota boxes” (Stations 110, 140, 180, 240, 280, 310, 340, and 380), three master stations (18M, 27M, and 47M), and a fourth biota box centered around Station 5, near Chicago. The four biota boxes are outlined in red in Figure 2-9. Samples were collected on seven occasions, from June 1994 to September 1995. In addition, zooplankton were collected from Station 19M in January 1995 and phytoplankton were collected from Stations 23M and 41 in June 1994. A total of 72 zooplankton and 71 phytoplankton samples were collected during the study.

In addition to the plankton samples, samples of *Mysis* and *Diporeia* were to be collected at the stations where lake trout were collected (near biota boxes 1-3) and at one site NE of Chicago. *Mysis* and *Diporeia* samples were collected from stations 140, 180, 240, 280, 340, 380, 47M and 5. Samples of *Mysis* also were collected at stations 27M and 18M. A total of 53 *Mysis* samples and 39 *Diporeia* samples were

collected. *Mysis* feed on both phytoplankton and zooplankton, while *Diporeia* feed to detritus and phytoplankton (see Figure 7-5 in Chapter 7).

2.4.6 Fish

Specimens of lake trout, coho salmon, bloater chub, alewife, smelt, deepwater sculpin, and slimy sculpin were collected using various means. Two subsets of alewife and bloater chub were differentiated, based on total length (see Table 2-9). Coho salmon were differentiated into three subsets by age (hatchery, yearling, and adult). In their adult stages, the lake trout and Coho salmon are piscivorous fish, while the other fish species collected are forage fish that generally feed on plankton and detritus (see Figure 7-5 in Chapter 7).

Where possible, five fish were composited for analysis. Fish were collected during the spring, summer, and fall of 1994, and the spring and fall of 1995, from three of the four biota boxes in Figure 2-9 (fish were *not* collected from the biota box at Station 5, near Chicago).

Additional fish were collected from locations throughout the lake by means ranging from gill nets to hook-and-line angling. Table 2-9 contains a summary of the numbers of individual fish collected, the total number of locations from which they were collected, and the total number of samples submitted for analysis, by species. Table 2-10 contains a summary of the sample collection techniques used, by species.

Figure 2-9. Sampling Stations for Lower Pelagic Food Web Organisms and Fish

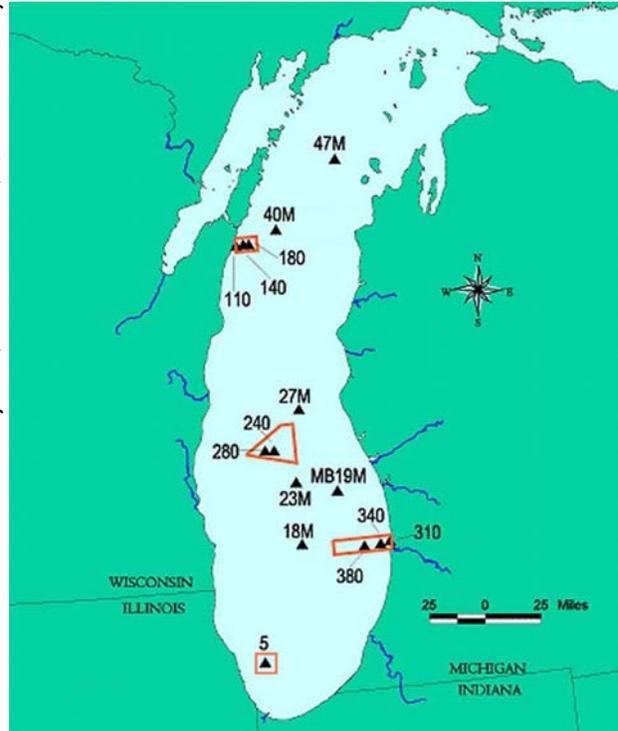


Table 2-9. Number of Fish Collected by Species and Location

Species	Total Number of Individual Fish Collected	Number of Locations	Number of Composite Samples Created
Lake Trout	1087	3	246
Slimy sculpin	315	3	69
Deepwater sculpin	325	3	74
Smelt	365	3	73
Coho salmon - adult	238	79	54
Coho salmon - yearling	38	22	8
Coho salmon - hatchery	25	1	5
Alewife >120 mm	347	3	70
Alewife <120 mm	298	3	60
Bloater chub >160 mm	334	3	67
Bloater chub <160 mm	348	3	70

Table 2-10. Number of Fish Collected by Technique

Species	Number of Fish Collected by Technique				
	Hook and Line	Gill Net	Bottom Trawl	Harvest Weir	Dip Net
Lake Trout	-	1029	58	-	-
Slimy sculpin	-	25	290	-	-
Deepwater sculpin	-	-	325	-	-
Smelt	-	25	340	-	-
Coho salmon - adult	235	3	-	-	-
Coho salmon - yearling	29	-	-	9	-
Coho salmon - hatchery	-	-	-	-	25
Alewife >120 mm	-	-	347	-	-
Alewife < 120 mm	-	-	298	-	-
Bloater chub >160 mm	-	-	334	-	-
Bloater chub <160 mm	-	-	348	-	-

2.5 Sampling Methods

Full details of the sampling methods used in the LMMB Study have been published by EPA in a Methods Compendium (USEPA, 1997d and USEPA, 1997e). A brief summary is provided below.

2.5.1 Atmospheric Components

Each shoreline site had a 10-meter meteorological tower and a number of meteorological instruments including wind speed and wind direction sensors at a height of 10 m (Met-One, Grants Pass, OR), a solar radiation sensor (LI-Cor, model LI 200S, Lincoln, NE), temperature and relative humidity sensors (Campbell Scientific, Logan, UT), and a standard Belfort rain gauge (Belfort Instrument, Baltimore, MD) with a Nipher wind shield. All of the meteorological sensors were automatically recorded every 6 seconds using a datalogger (Campbell Scientific, model 21X, Logan, UT).

2.5.1.1 Vapor Fraction

Airborne semivolatile organic contaminants, which include PCBs and *trans*-nonachlor, were collected using high-volume (Hi-Vol) samplers for organics, modified to include an aluminum tube behind the filter holder that accommodated a vapor trap consisting of a stainless steel cartridge of XAD-2[®] resin. The samplers were operated for a 24-hour period at a flow rate of 34 m³ per hour. The frequencies of sampling depended on the nature of the site (e.g., urban versus remote), as described in Section 2.4.1. The samplers were checked each week for proper functioning, to collect a sample, or to set up for the next collection. Samples from shoreline sites, except those collected at Sleeping Bear Dunes, were physically composited to yield one sample per site representing the entire month. Samples from Sleeping Bear Dunes were not composited, but analyzed separately. The results for each sample at Sleeping Bear Dunes were mathematically composited to yield one result for the entire month.

The samples collected aboard the *R/V Lake Guardian* were not composited, but were analyzed individually, because there was at most one sample per station in any given month and not all stations were sampled on every cruise. In addition, the results for a small number of samples could not be tied to

specific locations or master stations (e.g., the samples were collected while the *R/V Lake Guardian* steamed between stations). The locations of these samples are listed as “unrecorded.”

2.5.1.2 Particulate Fraction

Airborne particulate organic contaminants were collected on 20.3 x 25.4 cm pre-fired quartz fiber filters using high-volume samplers for organics. The samplers were operated for a 24-hour period at a flow rate of 34 m³ per hour. The frequencies of sampling depended on the nature of the site (e.g., urban versus remote), as described in Section 2.4.1. The samplers were checked each week for proper functioning, to collect a sample, or to set up for the next collection. Samples from shoreline sites, except those collected at Sleeping Bear Dunes, were physically composited to yield one sample per site representing the entire month. Samples from Sleeping Bear Dunes were not composited, but analyzed separately. The results for each sample at Sleeping Bear Dunes were mathematically composited to yield one result for the entire month.

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2.5.1.3 Precipitation Fraction

A MIC sampler (Meteorological Instruments of Canada) with a 0.212 m² stainless steel catch basin was used for collecting precipitation samples for analysis of PCBs and *trans*-nonachlor. The sampler was modified for all-weather operation by enclosing and insulating the space underneath the sampler. The temperature in the enclosure was maintained at 10 to 15°C during the winter using a small space heater. The collector also was fitted with a precipitation sensor and a retractable cover. The catch basin remained covered to prevent evaporation until precipitation was detected by the sensor.

During sample collection, precipitation passed through a column containing XAD-2[®] resin that adsorbed PCBs and *trans*-nonachlor in the precipitation sample. Glass wool plugs inserted on either side of the XAD-2[®] resin trapped any particles in the sample. The sampler was in operation continuously for four-week periods in order to collect the required 5 L of precipitation, and was checked each week to ensure proper functioning and sample collection. The XAD columns were sealed with PTFE caps, transported to the testing laboratory, and stored in air-tight containers at -18°C until analysis. In the laboratory, the precipitation collection funnel was rinsed with water and wiped with a piece of clean quartz fiber filter paper to remove adhering particles. The filter paper and rinsings were included as part of the sample.

2.5.1.4 Dry Deposition

Dry particle deposition was measured using deposition plates. Strips of Mylar[®] (approximately 5.7 cm by 1.8 cm) were coated with a layer of Apeizon[®] L grease about 5 µm thick to keep particles from bouncing off the surface of the strip. This approach was designed to address concerns that traditional sampling methods such as high volume samplers may underestimate the deposition of large particles (>10 µm).

The strips were attached to plates made from polyvinyl chloride (PVC). The leading edge of each PVC plate was tapered at about a 10° angle to provide a laminar flow of air over the plate and reduce turbulence. The deposition plates were mounted in an Eagle II automatic dry deposition collector at each site. Each collector contained two deposition plates. A wind vane on the collector points the leading

edge of the plates into the wind and a moisture sensor activates a motorized cover that protects the plates from rain or snow. A timer monitored the total time that the plates were exposed.

The plates were exposed to dry deposition for periods ranging from 4 to 97 days. The total length of time over which samples were collected represented 20 to 30% of the duration of the LMMB Study. The longer exposures (e.g., 97 days) were required in rural areas where particle deposition rates were low.

Completed sample strips were weighed in the field, transferred to clean wide-mouth jars, frozen, and shipped to the laboratory for analysis.

2.5.2 Tributaries

The number and timing of sampling events were dependent upon the stability of the tributaries and the timing of increased flow events. Tributaries with greater stability (i.e., those that are less responsive to precipitation events) were sampled less frequently than those that were more variable. Sampling was timed to collect approximately one-third of the samples during base flow conditions (i.e., when flows were below the 20th percentile of the historic flow regime) and approximately two-thirds of the samples when flows were above the 20th percentile.

Tributary samples were collected as near to river mouths as possible without being subject to flow reversals that are common near river mouths in Lake Michigan. Composite samples were obtained using the USGS quarter-point sampling procedure. In this procedure, the stream is visually divided into three equal flow areas. At the center of each flow area, samples were collected from 0.2 and 0.8 times the depth. All six samples were then composited and pumped (using a peristaltic pump) through a 0.7- μ m glass fiber filter. Filters were removed, folded in quarters, and wrapped in aluminum foil for particulate PCB analysis. The filtrate was then passed through a 250-g XAD-2[®] resin column at a flow rate of 500-1000 mL per minute to trap dissolved organics. Samples were chilled and delivered to the testing laboratory for analysis.

2.5.3 Open Lake

Open-lake samples were collected from various depths depending upon the stratification conditions. During stratification, open-lake stations were sampled at the mid-epilimnion and mid-hypolimnion. During non-stratified periods, samples were collected at mid-water column depth and two meters below the surface. At master stations, during times of non-stratification, were sampled at mid water column, one meter below the surface, and two meters off the bottom. During times of stratification, master stations were sampled at one meter below the surface, mid-epilimnion, mid-hypolimnion, and two meters off the bottom. In addition, Stations 18M and 41 were sampled at the thermocline and 2 meters below the surface during stratification.

Water samples were collected using an onboard sampling and filtration system on the *R/V Lake Guardian*. Samples were drawn with a peristaltic pump through a hose held overboard at a specific depth. A volume of water ranging from 100 to 1000 L was pumped through a "Pentaplate" filtration apparatus holding up to five glass-fiber filters in parallel. The filtered water was discharged into glass carboys and subsequently pumped through a column containing 250 g of XAD-2[®] resin at a flow rate of 500-1000 mL per minute to trap dissolved organics. The total volume of water passed through the filtration and XAD-2[®] systems was measured in the glass carboys and recorded.

After sampling was complete, the filters and the XAD-2[®] resin column were removed from the sampling apparatus. The filters were frozen onboard the ship, and transferred to the laboratory for analysis while still frozen. The resin columns were cooled to 4°C and transferred to the laboratory for analysis.

2.5.4 Sediment

Sediment samples were collected using three types of equipment. A modified Soutar box corer was used to retrieve cores approximately 60 cm in length, with well-preserved sediment-water interfaces. Samples also were collected using a gravity corer and a Ponar dredge, depending on the nature of the lake bottom at the collection point. Surficial sediment samples were collected from the cores by sectioning the cores into intervals ranging from 0.5 to 1.5 cm thick. The sections were transferred to glass containers, frozen onboard the ship, and transferred to the laboratory while still frozen.

Sediment trap samples were collected and split while still wet. The 60-mL trap bottles were allowed to settle for 25 hours, under refrigeration. The overlying water (~25 mL) was poured off into a beaker, and the remaining trap sample was poured into the splitter reservoir through a 700- μ m screen. The sample was split into four subsamples and washed through the splitter using the overlying water in the beaker and distilled water. The subsamples were transferred to glass containers, frozen onboard the ship, and transferred to the laboratory while still frozen.

2.5.5 Lower Pelagic Food Web Organisms

Phytoplankton were collected using a device called a phytovibe. This device was specially designed and constructed for GLNPO for collecting large volumes of plankton for analysis of chemical contaminants such as mercury and PCBs. The phytovibe consists of a pair of inverted pyramids constructed of stainless steel mesh lined with 10- μ m Nitex netting. Water is pumped by a submersible pump through nylon tubing into the top of the device, which has an opening that is 1 m². The end of the nylon tubing is covered with 100- μ m netting to remove zooplankton. In order to prevent plugging of the netting with plankton, the phytovibe is shaken by a motor. The samples were washed down into a detachable sampling cup with lake water and collected for processing. Sampling times ranged from 6 to 14 hours, depending on plankton concentration in the water and sample size needed for a particular analysis.

The depth of collection was chosen based on interpretations of the temperature, fluorescence, and bathymetric profiles from the ship, with the objective of choosing a depth that maximized the occurrence of phytoplankton that were being grazed. This generally corresponded to the epilimnion or the subthermocline chlorophyll maximum in stratified conditions.

Zooplankton were collected in nested Nitex nets of two different mesh sizes (102- μ m and 500- μ m) during standard vertical tows, from near the bottom to the surface. The 500- μ m nets were used to exclude larger organisms, including small fish, from the zooplankton samples. The number of tows performed was dependent on the mass of sample collected per tow. *Diporeia* spp. were collected in benthic tows, and *Mysis* spp. were collected in vertical and benthic tows.

Plankton samples were transferred to glass containers, frozen onboard the ship, and transferred to the laboratory while still frozen.

2.5.6 Fish

Whole fish were collected intact, with all body fluids and no incisions, except lake trout, which had their stomachs removed. Fish were wrapped in aluminum foil, placed in polyethylene bags, tagged, and frozen onboard the vessel. The fish were aged by checking for coded wire tags on the head and for fin clips. Fish were then composited by age, location, species, and size range. Samples were homogenized at the laboratory using a 40-qt vertical cutter mixer for large fish, 12-qt Stephan Machinery vertical cutter for medium-sized fish, or a high-speed 2-qt Robot Coupe for small fish. Additional information on the numbers of fish collected and the composite samples that were created can be found in Section 2.4.6.

2.6 Analytical Methods

Full details of the analytical methods used in the LMMB Study have been published by EPA in a methods compendium (USEPA, 1997d and USEPA 1997e). The general considerations in the choice of methods are discussed in Section 2.6.1. The convention for the data presented in this report is discussed in Section 2.6.2, and brief summaries of the specifics of the analyses for each lake component are provided in Sections 2.6.3 to 2.6.7.

2.6.1 General Analytical Considerations

Three significant, and interrelated aspects of the analytical methods for the PCBs and *trans*-nonachlor used in this study were the selection of analytical instrumentation, the selection of specific PCB congeners of interest, and the provision of a common set of analytical standards to all of the investigators. The vast majority of the commonly used analytical techniques for PCB analysis employ gas chromatography as a means of separating the PCB congeners. Traditionally, methods for the analysis of Aroclor mixtures have employed an electron capture detector (ECD) and produce chromatographic data that require that the analyst look for patterns of chromatographic peaks that resemble those in an authentic standard of each Aroclor. However, as a result of the changes that can occur in environmental samples (e.g., “weathering”), the pattern of peaks present in an environmental sample often changes enough to make it difficult or impossible to identify a pattern attributable to a specific Aroclor mixture.

Given these difficulties with Aroclor analysis, the most common alternative is to perform analyses for the individual PCB congeners. At present, there are no gas chromatography columns that can completely separate all 209 individual PCBs. Many of the congeners pass through the gas chromatograph at the same time, a phenomenon called “coelution.” Using an electron capture detector, it is not possible to distinguish between two PCB congeners that coelute. Using a mass spectrometer as a detector permits the analyst to distinguish some coeluting congeners because the mass spectrometer can differentiate the masses of the individual compounds. Therefore, if two congeners coelute but have different molecular weights (e.g., a tetrachlorobiphenyl and a pentachlorobiphenyl), the mass spectrometer can distinguish between them. However, even the combination of gas chromatography and mass spectrometry (GC/MS) cannot separate all 209 congeners. The costs of GC/MS analyses are substantially higher than those for GC/ECD. For this reason and others described below, GC/ECD was chosen as the primary analytical technique for the PCBs. GC/ECD also is applicable to the analysis of *trans*-nonachlor, and the *trans*-nonachlor results often were determined from the same analyses as the PCB congeners. The combination of gas chromatography and negative ion chemical ionization mass spectrometry was used for the analysis of PCB congeners in fish tissues.

A critical aspect of any analytical procedure is the availability of authentic standards of the analytes of interest. PCB analyses present a significant challenge in this regard because Aroclors were produced on an industrial scale as mixtures of PCB congeners, with some degree of variation between production lots over time. The commercial production of those Aroclors was outlawed over 20 years ago, but EPA has issued a small number of permits for the manufacture of Aroclors for use as analytical standards. Although the manufacturers of the standards go to great lengths to ensure that their standards resemble the original commercial mixtures, some differences are expected, and those differences can affect the end results of the analyses.

In order to address the concerns about methods and standards for the PCBs, EPA developed an approach to selecting appropriate PCB congeners for analysis and for providing common analytical standards to all of the investigators in the LMMB. Michael Mullin of EPA developed a mixture of specific proportions of Aroclors 1232, 1248, and 1262 that was designed to contain all of the Aroclor-derived congeners that are

likely to be found in environmental samples. That mixture is known as the “Mullin mix” and was provided to all of the investigators in the LMMB for use as a common reference standard.

In addition, information on the specific PCB congeners contained in the Mullin mix was used to focus the LMMB PCB analyses on those congeners that represent a significant portion of mass of Aroclors that may have been released into the environment. This is a critical aspect of the LMMB Study. Although the toxic effects of PCBs are certainly of interest in Lake Michigan, the purpose of the LMMB Study is to develop a mass balance for the anthropogenic pollutants described in Chapter 1. Therefore, the investigators focused on PCB congeners that occur in relatively high concentrations in the Aroclors that may have been released into the environment.

The majority of the toxic effects of PCB exposure are associated with the 12 WHO toxic congeners. However, not all of these congeners can be readily separated by GC methods and most of the toxic congeners are present in environmental samples at concentrations that require very sensitive analytical methods (e.g. high resolution mass spectrometry). Data on the composition of congeners in the Mullin mix were used to select those congeners that represent a significant portion of the mass of Aroclors 1232, 1248, and 1262 and that the investigators were able to detect reliably. Table 2-11 contains a list of the 45 PCB congeners that constitute at least 1% of the mass of the Mullin mix of the three Aroclors.

Collectively, these 45 congeners contribute 77.31% of the mass of the Mullin mix. There are 77 additional congeners that have been identified in the Mullin mix, each of which contributes 0.01% to 0.99% of the total mass. Collectively, these 77 congeners contribute 22.69% of the mass of the Mullin mix.

Data for the Mullin mix indicate that 10 of the 12 WHO toxic congeners are present in the mix at concentrations that could be measured. Seven of those 10 toxic congeners can be separated from all the other congeners and represent 1.17% of the mass of the Mullin mix. PCB 118 is the toxic congener with the highest concentration, representing 0.6% of the mass in the Mullin mix. Collectively, the 10 toxic congeners that are present and the other 5 coeluting congeners represent 5.50% of the mass.

The data in Table 2-11 demonstrate why looking for *just* the toxic PCB congeners would make it difficult to develop a robust mass balance for Lake Michigan, since such an approach would ignore 95 to 99% of the mass of PCBs present in Aroclors.

The use of the Mullin mix as a common analytical standard across all of the laboratories provides an important control mechanism in the analysis of the PCBs and provided a mechanism with which to select a basic set of PCB congeners of interest for the LMMB Study. Differences in the study requirements and specific instruments used in each laboratory, matrix-specific sample preparation and extraction techniques, and other factors enabled each of the laboratories to report results for additional PCB congeners. However, different numbers of additional congeners or coeluting groups of congeners being reported in each of the laboratories. The maximum number of congeners reported for each laboratory is shown in Table 2-12.

The “total” PCB concentrations also were determined for each sample in the study. The totals are simply the sum of all of the PCB congeners that were found in the sample. However, each PI determined the total PCB concentrations based on the specific congeners determined in that laboratory and some adjustments were made when interferences from non-PCB analytes were apparent.

Table 2-11. PCB Congeners that Contribute at Least 1% of the Mass of the Mullin Mix

PCB Congener	Concentration in Mullin Mix (ng/mL)	% of Total Mass in Mullin Mix
PCB-008+005	15	7.71
PCB-001	14	7.20
PCB-031+028	12	6.17
PCB-003	8.5	4.37
PCB-066	7.1	3.65
PCB-180	6.6	3.39
PCB-044	5.0	2.57
PCB-052	5.0	2.57
PCB-132+153+105	4.8	2.47
PCB-203+196	4.6	2.36
PCB-015+017	4.5	2.31
PCB-018	4.4	2.26
PCB-056+060	4.4	2.26
PCB-201	4.4	2.26
PCB-033	4.2	2.16
PCB-070+076	3.9	2.00
PCB-022	3.6	1.85
PCB-187+182	3.6	1.85
PCB-163+138	3.5	1.80
PCB-004+010	3.4	1.75
PCB-123+149	3.3	1.70
PCB-174	3.2	1.64
PCB-041+071	2.8	1.44
PCB-049	2.8	1.44
PCB-074	2.6	1.34
PCB-032	2.5	1.29
PCB-016	2.4	1.23
PCB-064	2.2	1.13
PCB-194	2.1	1.08
PCB-095	2.0	1.03
PCB-170+190	2.0	1.03

+ indicates congeners that typically coelute

Table 2-12. Maximum Number of PCB Congeners Reported, by Laboratory

Laboratory	Maximum Number of PCB Congeners or Groups of Coeluting Congeners
Battelle, Sequim	105
Indiana University	108
University of Wisconsin, Wisconsin State Lab of Hygiene	65 (78)*
University of Minnesota	110
National Oceanic and Atmospheric Administration	105
Rutgers University	86
Illinois State Water Survey	107
United States Geological Survey, Biological Resources Discipline	80

*The figure in parentheses represents the number of congeners reported in analyses conducted after a change in the laboratory's standard operating procedure that was instituted in November 1994.

2.6.2 Data Presented in this Report

As noted in Section 2.1, there are 209 possible PCB congeners, and the investigators in this study reported results for 65 to 110 of these congeners, depending on the capabilities of each laboratory (Table 2-12). Given the hundreds of samples that were collected for some media, it is impractical to present *all* of the PCB congener results for any of the media in this report, let alone the entire LMMB Study. This report seeks to strike a balance between the depth of the data presentation and a desire to limit the report to a manageable size. Therefore, except as noted below, throughout the remainder of this report, summaries are presented for the results for the following analytes:

- PCB congener 33 (2',3,4-trichlorobiphenyl)
- PCB congener 118 (2,3',4,4',5-pentachlorobiphenyl)
- PCB congener 180 (2,2',3,4,4',5,5'-heptachlorobiphenyl)
- Total PCBs
- *trans*-nonachlor

The three PCB congeners were selected for presentation for the following reasons:

- These congeners do not coelute with any other congeners that were abundant in the Aroclors in any of the LMMB media (thus allowing presentation and data interpretation across all media in the LMMB report),
- They were reported by all but one of the investigators in the LMMB, thus enabling direct comparisons across all media (except dry deposition),
- They represent different levels of chlorination of the parent biphenyl structure and thus should represent a variety of environmental fates for PCBs,
- None were used as surrogates in the analysis,
- All three congeners are present in the "Mullin mix" standard of Aroclors used for the LMMB Study, and
- PCB 118 represents one of the coplanar congeners currently deemed "toxic" because of its biological activity, while PCBs 33 and 180 currently are *not* classified in the "toxic" group.

The only exception to this approach occurs in Chapter 6, on the sediment analyses, where the principal investigator found that PCB 33 coeluted with the organochlorine pesticide heptachlor. As a result, the presence of heptachlor in the sediment samples lead to high recoveries of PCB 33 in matrix spike

samples. Therefore, the principal investigator provided detailed graphics for the coeluting PCB congener pair 28+31 and not PCB 33. The coelution with heptachlor was not evident in the matrix spike recoveries from samples of other matrices, and other matrices would not be expected to retain heptachlor from historical sources to the extent that may occur in sediments.

2.6.3 Atmospheric Components

The preparation and analysis of three of the four fractions of the atmospheric samples followed similar procedures. Soxhlet extraction was used to extract the PCBs and *trans*-nonachlor from:

- XAD-2[®] resin used to collect the vapor phase samples,
- Glass fiber filters used to collect the particulate samples, and
- XAD-2[®] resin used to collect the precipitation samples.

Hexane:acetone (50:50) was used for all three Soxhlet extractions and the extracts were concentrated by rotary evaporation.

For all fractions, interfering compounds were removed and analytes were fractionated with silica gel. The hexane fraction contained all of the PCBs and the second fraction (40% dichloromethane, 60% hexane) contained *trans*-nonachlor. PCBs and *trans*-nonachlor were determined by capillary gas chromatography with electron-capture detection.

The dry deposition samples were prepared by extracting the Mylar[®] strips with dichloromethane and hexane in an ultrasonic bath. The extracts were subjected to a cleanup procedure that employed deactivated silica gel and deactivated alumina which removed most of the Apeizon[®] L grease from the extracts. PCBs and *trans*-nonachlor were determined by capillary gas chromatography with electron-capture detection. Because some grease remained in the concentrated extracts, a 1-m glass capillary pre-column was attached to the front end of the GC column and the remaining grease was deposited on the pre-column. Half of the 1-m pre-column was cut off after 3 to 5 sample injections and the pre-column was replaced after 6 to 10 injections. Combined with frequent maintenance and replacement of the glass injector liners in the GC, the pre-column prevented the residual grease from compromising the resolution of the GC column.

To minimize the potential effects of sorption of PCBs and *trans*-nonachlor from the gas phase onto the grease strips, the deposition of PCBs onto the field blank associated with each sample was used to correct the sample results, based on the mass of PCBs normalized to the surface area of the sample.

2.6.4 Tributaries and Open Lake

The XAD-2[®] resins and glass fiber filters used to collect tributary samples were extracted separately with a sequence of Soxhlet extractions, followed by volume reductions and rinses. Florisil and silica gel column chromatography were used to cleanup tributary sample extracts prior to analysis, allowing fractionation of the PCBs from *trans*-nonachlor and the majority of the other organochlorine pesticide compounds in the samples. Following this fractionation, PCB congeners and *trans*-nonachlor were then determined by the analyses of separate extracts using capillary gas chromatography with electron-capture detection.

The XAD-2[®] resins and glass fiber filters used to collect open-lake samples were extracted separately with a sequence of Soxhlet extractions, followed by volume reductions and rinses, in a fashion similar to that for the tributary samples. For the open-lake samples, cleanup procedures included the use of acidified silica gel and alumina to remove polar interferences from the sample extracts. Subsequent to the

start of the study, the laboratory performing the analyses of the open-lake samples adjusted their extract cleanup procedures and included a second acidified silica gel cleanup, in an attempt to overcome potential interferences that were present on the XAD-2[®] resin used to collect water samples. As a result of those changes, the laboratory did not obtain separate cleanup fractions containing the PCBs and *trans*-nonachlor, but analyzed the sample extracts on two dissimilar GC columns (DB-5 and DB-1701). While the DB-1701 column provided clear chromatographic separation of any *trans*-nonachlor in the sample, this analyte coeluted with PCB 99 on the DB-5 column. As a result of the potential coelution, the reported concentrations of PCB 99 in open-lake samples are probably biased by any *trans*-nonachlor present in the samples.

2.6.5 Sediment

Approximately 15-30 g of thawed wet sediment was extracted with dichloromethane in an ultrasonic bath held at 30°C. The extracts were dried over sodium sulfate and passed through a cleanup column. PCBs were separated from pesticides and polyaromatic hydrocarbons by column chromatography fractionation. PCBs and *trans*-nonachlor were determined by capillary gas chromatography with electron-capture detection.

2.6.6 Lower Pelagic Food Web Organisms

Lower pelagic food web organism samples were thawed, rinsed with methanol, then extracted by a Soxhlet procedure (four hours with methanol; then 16-24 hours with dichloromethane). The methanol fraction was back-extracted with hexane. The hexane fraction containing the PCBs was combined with the dichloromethane fraction and concentrated by rotary evaporation. Lipids were removed from the extracts, and the extracts were cleaned up and eventually reduced to 200-300 µL prior to analysis. PCBs were determined by capillary gas chromatography with electron-capture detection. *trans*-Nonachlor was analyzed by electron capture negative ionization (ECNI) gas chromatography/mass spectrometry (GC/MS) with selected ion monitoring (SIM), using methane as the reagent gas.

2.6.7 Fish

Homogenized fish tissue samples were thawed and then extracted with a 90/10 mixture of petroleum ether/ethyl acetate. Extracts were concentrated and the lipid content was determined from an aliquot of the concentrated extract. The extracts were then prepared for analysis by separation and removal of lipids using a gel permeation chromatography system. PCBs and *trans*-nonachlor were determined by electron capture negative ionization (ECNI) gas chromatography/mass spectrometry (GC/MS) with selected ion monitoring (SIM), using methane as the reagent gas.

2.7 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB quality assurance (QA) program prescribed minimum standards to which all organizations collecting data were required to adhere. The goal of the QA program was to ensure that all data gathered during the LMMB Study met defined standards of quality with specified levels of confidence. Data quality was defined, controlled, and assessed through activities that included development of study QAPPs, use of SOPs, and data verification. These activities are described in detail in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b).

Specific quality control elements implemented in the sampling and analysis of PCB and *trans*-nonachlor included:

- use of standard operating procedures and trained personnel for field sampling and laboratory analysis;
- determination of method sensitivity through calculation of method detection limits;
- preparation and analysis of a variety of blanks to characterize contamination associated with specific sample handling, storage, and analysis processes including field blanks, lab reagent blanks, bottle blanks, trip blanks, and lab solvent blanks;
- collection and analysis of field or laboratory duplicate samples;
- preparation and analysis of a variety of quality control samples including standard reference samples and performance standards;
- use of internal and surrogate standards for all field samples;
- use of a standardized data reporting format; and
- preparation and analysis of matrix spike samples to characterize the applicability of the analytical method to the study sample matrices.

In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data. Prior to data submission, each researcher submitted electronic test files containing field and analytical data according to the LMMB data reporting standard. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers.

An intercomparison study for the PCB analyses was conducted among all PIs and the EPA ORD laboratory in Duluth, Minnesota. A detailed discussion of the intercomparison study is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b).

Because all of the PIs were analyzing different types of samples, such as vapor, fish, and sediment, and employing sample-specific preparation procedures, the intercomparison study focused on the instrumental analysis portion of the study. Each of the PIs was provided with two solutions of PCB congeners prepared by Ultra Scientific in consultation with Dr. Mike Mullin of EPA ORD. The solutions included PCB congeners with retention times and response factors covering the ranges observed in environmental samples as well as congeners that are known to be difficult to resolve.

The results submitted by each PI were evaluated by comparison to: 1) the gravimetric true value of the solution as prepared and 2) the 95% confidence intervals for specific congeners based on the full set of results from the study. A goal of 30 percent bias from the true gravimetric mean was established for the intercomparison study.

This goal was not always met. Comparison of the results from each PI to the gravimetric true mean indicated a high bias for some congeners and low bias for others. With few exceptions, results that exhibited more than 30% bias from the true value were associated with coeluting congeners. The results from all of the PIs were within the 95% confidence intervals calculated for the PCB congeners, indicating that none of the results were likely to be outliers. However, the relatively low number of degrees of freedom (i.e., eight laboratory participants) limit the statistical power of this evaluation.

The variability of the analytical results among PIs also was evaluated by calculating the relative standard deviation (RSD) among results for each congener or group of coeluting congeners. Although the RSD values for the majority of the congeners were less than 30%, the results for congeners 37, 77, 77+110, 81, and 123+149 in one of the two solutions in the intercomparison study exceeded 30% RSD. Coelution is a problem for all of these six congeners. However, these congeners represent only a small portion of the

total mass of PCBs. Only the coeluting pair of 123+149 is present in the Mullin mix at greater than 1%, and PCB-77 and PCB-81 represent only 0.15% and 0.08% of the Mullin mix, respectively. Therefore, the RSD results greater than 30% for these congeners in the intercomparison study are not likely to have a large influence on the study goal of developing a mass balance of PCBs for Lake Michigan.

Overall, the results of the intercomparison study suggest the PIs were successfully employing analytical procedures consistent with what is expected for determination of PCB congeners in environmental samples and did not indicate any major analytical difficulties associated with any of the labs in the study.

Prior to sample collection, Quality Assurance Project Plans (QAPPs) were developed by the PIs and submitted to GLNPO for review. In the QAPPs, the PIs defined MQOs in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. The MQOs were designed to control various phases of the measurement process and to ensure that the total measurement uncertainty was within the ranges prescribed by the DQOs. The MQOs for PCBs and *trans*-nonachlor are listed in Section 7 of *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b).

The PI-defined MQOs also were used in the data verification process. GLNPO conducted data verification through the LMMB QA Workgroup. The workgroup was chaired by GLNPO's Quality Assurance Manager and consisted of quality control coordinators that were responsible for verifying the quality of specific data sets. Data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. If the results failed to meet MQOs and corrective actions were not feasible, the results were flagged to inform data users of the failure. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. In addition, a wide variety of flags were applied to the data to provide detailed information to data users. For example, the flag LAC (laboratory accident, no result reported) was applied to sample results to document that a sample was collected, but no result was reported due to a laboratory accident. The frequencies of flags applied to PCB and *trans*-nonachlor study data are provided in the Quality Implementation Sections of each of the following chapters. The flag summaries include the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but do not include all flags applied to the data to document sampling and analytical information (such as LAC). In order to provide detailed quality information to data users, the study data are maintained in the GLENDA database with all applied flags. Detailed definitions of the flags can be found in the *Allowable Codes Table* on GLNPO's web site at www.epa.gov/glnpo under *Result Remark, List of QC flags* (lab_rmrk).

Comparability of the data from the various PIs was enhanced by the use of standardized reporting units for samples from similar matrices. In addition, the analyses of PCBs incorporated the use of surrogate compounds that were added to the sample before extraction. These surrogates provide an estimate of the efficiency of the entire sample preparation, extraction, cleanup, and analysis process, as applied to each sample. The recoveries of the surrogates were used by most of the investigators to correct the results of the target PCBs for any apparent losses or gains of the surrogates. The dry deposition PCB data were *not* corrected for surrogate recoveries, but were corrected for the potential contribution of PCBs absorbed into the Apeizon[®] L grease directly from the vapor phase, using field blank results.

For *trans*-nonachlor analyses, the PIs had difficulty identifying a surrogate compound that worked well for those matrices analyzed by gas chromatography with electron-capture detection (GC/ECD). The analyses of lower pelagic food web organisms and fish were performed by GC/MS techniques, which permitted the use of a stable ¹³C-labeled form of *trans*-chlordane as a surrogate. Therefore, the lower pelagic food web and fish results were corrected for surrogate recoveries.

Of the GC/ECD analyses for *trans*-nonachlor, *only* the data from the atmospheric samples collected at Sleeping Bear Dunes were corrected for surrogate recoveries. As with the PCB results, the dry deposition *trans*-nonachlor data were *not* corrected for surrogate recoveries, but were corrected for the potential contribution of *trans*-nonachlor absorbed into the Apeizon[®] L grease directly from the vapor phase, using field blank results.

The PIs participating in the study also conducted real-time data verification. PIs applied best professional judgement during sampling, analysis, and data generation, based on their experience monitoring PCB and *trans*-nonachlor in the environment. In most cases, when sample results were questionable, the PI reanalyzed the sample or clearly documented the data quality issues in the database through the application of data quality flags or by including comments in the database field, "Exception to Method, Analytical." Because the flags and comments are maintained in the database for each sample result, data users are fully informed of data quality and can evaluate quality issues based on their intended use of the data. The level of documentation that GLNPO is maintaining in the study database is unprecedented for a database of this size and will serve as a model for future efforts.

GLNPO also conducted data quality assessments in terms of four of the six attributes used as the basis for the MQOs, specifically sensitivity, precision, and bias. For example, system precision was estimated as the mean relative percent difference (RPD) between results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between results for laboratory duplicate pairs. Bias was estimated using the mean recovery of spiked field samples or other samples of known concentration such as laboratory performance standards. A summary of data quality assessments is provided for the PCB and *trans*-nonachlor study data in the Quality Implementation Section of each of the following chapters.

Chapter 3

PCBs/trans-Nonachlor in Atmospheric Components

3.1 Results

Atmospheric samples were collected from November 1993 to October 1995 at nine sampling stations on the shoreline of Lake Michigan, three stations outside of the Lake Michigan basin, 17 stations in the open lake (over-water), and two stations in Green Bay, and analyzed for PCB congeners (Table 3-1) and *trans*-nonachlor (Table 3-2). Results for “total PCBs” were determined by summing the results for the individual PCB congeners. These analytes were measured in four separate atmospheric media or phases: vapor (pg/m³), particulates (pg/m³), precipitation (pg/L), and dry deposition (pg/m²). In total, 306 vapor-phase samples, 235 particulate samples, 209 precipitation samples, and 42 dry deposition samples were collected and analyzed for PCBs. For *trans*-nonachlor, 303 vapor-phase samples, 220 particulate samples, 206 precipitation samples, and 40 dry deposition samples were collected and analyzed. Eighteen of the particulate samples analyzed for PCBs and *trans*-nonachlor were collected while the *R/V Lake Guardian* was steaming between stations. Because these samples were not collected at fixed locations, they are considered spatial composites and are listed as such in Tables 3-1 and 3-2.

As noted in Chapter 2, there are 209 possible PCB congeners, and the investigators in this study reported results for 65 to 110 of these congeners, depending on the capabilities of each laboratory. For the purposes of this report, we are presenting summaries of the results for the following subset of analytes:

- PCB congener 33
- PCB congener 118
- PCB congener 180
- Total PCBs
- *trans*-nonachlor

Table 3-1. Number of Atmospheric Samples Collected and Analyzed for PCB Congeners and Total PCBs

Sampling Station	Sampling Dates	Vapor Samples Analyzed	Particulate Samples Analyzed	Dry Deposition Samples Analyzed	Precipitation Samples Analyzed	Total Samples Analyzed	
Shoreline Atmospheric Stations	Beaver Island	03/15/94 to 09/26/95	19	18	0	20	57
	Chicago SWFP Crib Intake	07/01/94 to 10/03/95	0	0	9	0	9
	Chiwaukee Prairie	03/15/94 to 10/02/95	21	21	0	20	62
	IIT Chicago	12/06/93 to 10/02/95	25	25	13	17	80
	Indiana Dunes	03/15/94 to 10/20/95	31	30	0	21	82
	Manitowoc	03/12/94 to 10/08/95	19	19	0	20	58
	Muskegon	03/15/94 to 10/13/95	18	16	0	20	54
	Sleeping Bear Dunes	11/23/93 to 10/07/95	35	15	8	16	74
	South Haven	11/23/93 to 10/08/95	22	19	11	21	73
Out-of-Basin Atmospheric Stations	Bondville	03/15/94 to 10/20/95	21	21	0	21	63
	Brule River	04/01/94 to 10/08/95	19	18	0	19	56
	Eagle Harbor	04/01/94 to 07/31/94	8	4	0	4	16
Over-Water Atmospheric Stations	Spatial composites	04/30/94 to 10/11/95	0	18	0	0	18
	Empire Michigan	04/01/94 to 07/29/94	10	4	0	4	18
	GB17	04/12/95 to 04/12/95	0	0	0	1	1
	GB24M	10/17/94 to 09/20/95	4	2	0	1	7
	Harrison Crib	08/11/94 to 08/11/94	0	0	1	0	1
	1	05/10/94 to 10/11/95	5	1	0	1	7
	5	05/11/94 to 10/10/95	6	3	0	1	10
	6	08/25/94 to 10/12/95	4	1	0	0	5
	110	04/08/95 to 09/23/95	3	0	0	0	3

Sampling Station		Sampling Dates	Vapor Samples Analyzed	Particulate Samples Analyzed	Dry Deposition Samples Analyzed	Precipitation Samples Analyzed	Total Samples Analyzed
Over-Water Atmospheric Stations	18M	05/06/94 to 10/09/95	5	0	0	0	5
	23M	05/04/94 to 10/03/95	4	0	0	1	5
	27M	05/02/94 to 09/27/95	5	0	0	0	5
	280	10/26/94 to 10/01/95	4	0	0	0	4
	310	03/28/95 to 10/08/95	3	0	0	0	3
	380	10/31/94 to 01/23/95	1	0	0	1	2
	40M	10/18/94 to 09/25/95	4	0	0	0	4
	41	04/30/94 to 08/12/94	2	0	0	0	2
	47M	08/07/94 to 09/19/95	5	0	0	0	5
	MB19M	01/24/95 to 01/24/95	1	0	0	0	1
	11M	05/08/94 to 05/08/94	2	0	0	0	2
Total			306	235	42	209	792

Table 3-2. Number of Atmospheric Samples Collected and Analyzed for *trans*-Nonachlor

Sampling Station	Sampling Dates	Vapor Samples Analyzed	Particulate Samples Analyzed	Dry Deposition Samples Analyzed	Precipitation Samples Analyzed	Total Samples Analyzed	
Shoreline Atmospheric Stations	Beaver Island	03/15/94 to 09/26/95	18	17	0	20	55
	Chicago SWFP Crib Intake	07/01/94 to 10/03/95	0	0	9	0	9
	Chiwaukee Prairie	03/15/94 to 10/02/95	21	21	0	20	62
	IIT Chicago	12/06/93 to 10/02/95	25	25	13	17	80
	Indiana Dunes	03/15/94 to 10/20/95	31	29	0	21	81
	Manitowoc	03/12/94 to 10/08/95	19	18	0	20	57
	Muskegon	03/15/94 to 10/13/95	18	16	0	19	53
	Sleeping Bear Dunes	11/23/93 to 10/07/95	34	4	8	14	60
	South Haven	11/23/93 to 10/08/95	22	18	10	21	71
Out-of-Basin Atmospheric Stations	Bondville	03/15/94 to 10/20/95	21	21	0	21	63
	Brule River	04/01/94 to 10/08/95	18	18	0	19	55
	Eagle Harbor	04/01/94 to 07/31/94	8	4	0	4	16
Over-Water Atmospheric Stations	Spatial composites	04/30/94 to 10/11/95	0	18	0	0	18
	Empire Michigan	04/01/94 to 07/29/94	10	4	0	4	18
	GB17	04/12/95 to 04/12/95	0	0	0	1	1
	GB24M	10/17/94 to 09/20/95	4	2	0	1	7
	1	05/10/94 to 10/11/95	5	1	0	1	7
	5	05/11/94 to 10/10/95	6	3	0	1	10
	6	08/25/94 to 10/12/95	4	1	0	0	5
	110	04/08/95 to 09/23/95	3	0	0	0	3
	18M	05/06/94 to 10/09/95	5	0	0	0	5

Sampling Station	Sampling Dates	Vapor Samples Analyzed	Particulate Samples Analyzed	Dry Deposition Samples Analyzed	Precipitation Samples Analyzed	Total Samples Analyzed	
Over-Water Atmospheric Stations	23M	05/04/94 to 10/03/95	4	0	0	1	5
	27M	05/02/94 to 09/27/95	5	0	0	0	5
	280	10/26/94 to 10/01/95	4	0	0	0	4
	310	03/28/95 to 10/08/95	3	0	0	0	3
	380	10/31/94 to 01/23/95	1	0	0	1	2
	40M	10/18/94 to 09/25/95	4	0	0	0	4
	41	04/30/94 to 08/12/94	2	0	0	0	2
	47M	08/07/94 to 09/19/95	5	0	0	0	5
	MB19M	01/24/95 to 01/24/95	1	0	0	0	1
	11M	05/08/94 to 05/08/94	2	0	0	0	2
Total		303	220	40	206	769	

3.1.1 Vapor Fraction

Vapor-phase PCB congeners were detected in the vast majority of the samples collected from all LMMB Study stations. Vapor-phase PCB 33 was detected in all but two samples (Table 3-3), vapor-phase PCB 118 was detected in all but one sample (Table 3-4), and vapor-phase PCB 180 was detected in all but five samples (Table 3-5). Tables 3-3 to 3-6 present the results for the monthly composite vapor samples from this study. As discussed in Chapter 2, the composite results represent either: 1) the physical compositing of several individual samples collected during a calendar month to create one sample for analysis, or 2) mathematical composites of the results from the analysis of the individual samples collected over a calendar month. In some instances, both physical and mathematical composites were prepared within a month. In these instances, the reported result is a mathematical composite based on both the physical composite samples and the individual samples. The total number of composite results is shown for each station as “N,” along with the mean concentration, range, standard deviation, and relative standard deviation (RSD). Tables 3-3 to 3-6 also indicate the percent of the *individual* sample results that were below the sample-specific detection limit, (as opposed to the percent of the composite results). The mean concentrations were calculated using the results reported by each laboratory (substitution of the detection limit or other value was not used for results below the sample-specific detection limits).

Monthly composite vapor-phase PCB congener concentrations ranged from 0 pg/m³ for PCB 180 at the Sleeping Bear Dunes and Brule Rivers stations and open-water station 27M, to 290 pg/m³ for PCB 33 at the IIT Chicago sampling station (Tables 3-3 to 3-5). Monthly composite concentrations of vapor-phase total PCBs ranged from 0 pg/m³ at Beaver Island and Brule River stations to 6300 pg/m³ at the IIT

Chicago station (Table 3-6). Mean monthly composite concentrations of vapor-phase PCBs ranged from 0.24 pg/m³ for PCB 180 at Sleeping Bear Dunes to 2600 pg/m³ for total PCBs at the IIT Chicago site.

The variability of the monthly composite concentrations differed among both stations and congeners, with RSD values ranging from 32% to 150% for PCB 33, from 15% to 170% for PCB 118, and 45% to 160% for PCB 180. Except for vapor-phase results for PCBs 118 and 180 at Indiana Dunes, and the PCB 33 results at Sleeping Bear Dunes, many of the highest RSD values are associated with sampling stations with small numbers of total samples, particularly for the over-water stations and the remote shore-based site at Eagle Harbor, suggesting that one of the monthly composite results may be driving the variability.

For stations with greater than 10 samples over the course of the study, the variability for vapor-phase PCB 33 was greatest at Sleeping Bear Dunes (RSD = 120%) and greatest for PCB 118 and PCB 180 at Indiana Dunes (RSDs of 140% and 150%, respectively).

Vapor-phase *trans*-nonachlor was detected much less frequently than PCB congeners (Table 3-7). Vapor-phase *trans*-nonachlor was not detected in the samples from two over-water stations. Of the 28 sampling stations, 13 stations had 13% to 50% of the individual samples below detection limits. Only one sample was collected at Stations 380 and MB19M and each had a result of zero.

Concentrations of vapor-phase *trans*-nonachlor ranged from 0 pg/m³ at over-water stations 380 and MB19M to 118 pg/m³ at Bondville. Non-zero mean monthly composite concentrations of *trans*-nonachlor for each sampling station ranged from 2.1 pg/m³ measured at Brule River to 43 pg/m³ measured at Bondville.

Table 3-3. Monthly Composite Concentrations of Vapor-phase PCB 33 Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station	N	Mean (pg/m ³)	Range (pg/m ³)	SD (pg/m ³)	RSD (%)	% Below DL*	
Shoreline Atmospheric Stations	Beaver Island	18	20	2.1 to 54	17	83	0
	Chiwaukee Prairie	19	14	2.0 to 35	9.3	66	0
	IIT Chicago	19	130	24 to 290	87	69	0
	Indiana Dunes	19	39	4.6 to 120	30	76	0
	Manitowoc	19	16	2.4 to 48	13	80	0
	Muskegon	18	21	2.6 to 71	17	83	0
	Sleeping Bear Dunes	11	10	2.0 to 44	12	120	0
	South Haven	19	17	3.4 to 37	11	64	0
Out-of-Basin Atmospheric Stations	Bondville	19	41	4.0 to 130	33	80	10
	Brule River	18	6.1	0.62 to 21	5.7	94	0
	Eagle Harbor	4	4.9	0.89 to 12	5.0	100	0
Over-Water Atmospheric Stations	Empire Michigan	4	6.4	4.3 to 8.7	2.2	34	0
	GB24M	3	27	3.5 to 72	39	150	0
	1	3	31	8.0 to 51	22	70	0
	5	4	37	20 to 55	14	38	0
	6	3	25	16 to 30	7.8	32	0
	110	3	20	2.1 to 54	29	140	0
	18M	3	43	7.8 to 100	53	120	0
	23M	2	31	23 to 40	12	37	0
	27M	3	19	6.0 to 34	14	76	0
	280	3	20	7.0 to 45	22	110	0
	310	3	26	10 to 53	23	91	0
	380	1	10	NA	NA	NA	0
	40M	3	13	2.0 to 28	13	100	0
	47M	3	22	4.6 to 51	25	110	0
	MB19M	1	10	NA	NA	NA	0
	11M	1	33	NA	NA	NA	0

* Value represents the percent of the individual samples collected and analyzed, not of the monthly composite samples prepared from the individual samples.
NA = Not applicable

Table 3-4. Monthly Composite Concentrations of Vapor-Phase PCB 118 Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m ³)	Range (pg/m ³)	SD (pg/m ³)	RSD (%)	% Below DL*
Shoreline Atmospheric Stations	Beaver Island	18	19	1.2 to 70	21	110	0
	Chiwaukee Prairie	19	2.2	0.24 to 5.8	1.5	71	0
	IIT Chicago	19	29	3.5 to 66	22	77	0
	Indiana Dunes	19	6.8	0.58 to 33	9.2	140	0
	Manitowoc	19	2.2	0.25 to 5.0	1.5	67	0
	Muskegon	18	6.6	1.1 to 21	6.5	99	0
	Sleeping Bear Dunes	11	1.2	0.29 to 2.7	0.75	62	3.8
	South Haven	19	1.8	0.35 to 5.2	1.3	73	0
Out-of-Basin Atmospheric Stations	Bondville	19	1.6	0.43 to 2.9	0.78	50	0
	Brule River	18	0.83	0.075 to 2.8	0.85	100	0
	Eagle Harbor	4	2.9	0.20 to 9.9	4.7	170	0
Over-Water Atmospheric Stations	Empire Michigan	4	1.2	0.59 to 1.7	0.50	43	0
	GB24M	3	5.2	1.1 to 13	6.4	120	0
	1	3	39	1.3 to 110	61	160	0
	5	4	6.5	5.4 to 7.9	1.0	16	0
	6	3	42	2.2 to 120	67	160	0
	110	3	5.7	0.78 to 15	8.4	150	0
	18M	3	6.2	2.0 to 14	7.1	120	0
	23M	2	6.5	5.7 to 7.4	1.2	18	0
	27M	3	4.1	0.64 to 6.4	3.1	74	0
	280	3	4.2	1.5 to 7.1	2.8	67	0
	310	3	3.9	2.3 to 6.1	2.0	51	0
	380	1	1.0	NA	NA	NA	0
	40M	3	2.4	0.48 to 4.9	2.2	95	0
	47M	3	3.2	1.2 to 6.3	2.8	87	0
	MB19M	1	1.0	NA	NA	NA	0

* Value represents the percent of the individual samples collected and analyzed, not of the monthly composite samples prepared from the individual samples.
 NA = Not applicable

Table 3-5. Monthly Composite Concentrations of Vapor-Phase PCB 180 Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station	N	Mean (pg/m ³)	Range (pg/m ³)	SD (pg/m ³)	RSD (%)	% Below DL*	
Shoreline Atmospheric Stations	Beaver Island	18	11	0.53 to 27	9.8	92	0
	Chiwaukee Prairie	19	0.54	0.076 to 1.2	0.32	59	0
	IIT Chicago	19	4.3	0.44 to 9.2	3.3	75	0
	Indiana Dunes	19	1.6	0.13 to 8.3	2.3	150	0
	Manitowoc	19	0.47	0.059 to 1.1	0.32	68	0
	Muskegon	18	1.0	0.13 to 2.7	0.93	90	0
	Sleeping Bear Dunes	11	0.24	0.00 to 0.57	0.20	84	35
	South Haven	19	0.47	0.059 to 1.3	0.38	87	0
Out-of-Basin Atmospheric Stations	Bondville	19	0.52	0.13 to 1.1	0.30	57	0
	Brule River	18	0.27	0.00 to 0.80	0.23	87	11
	Eagle Harbor	4	0.33	0.065 to 0.81	0.33	100	13
Over-Water Atmospheric Stations	Empire Michigan	4	0.36	0.015 to 0.50	0.16	45	0
	GB24M	3	0.73	0.24 to 1.6	0.79	110	0
	1	3	16	0.90 to 45	25	160	0
	5	4	2.4	1.6 to 4.3	1.3	52	0
	6	3	15	1.1 to 43	24	160	0
	110	3	0.93	0.16 to 2.4	1.3	140	0
	18M	3	1.8	0.57 to 4.0	1.9	100	0
	23M	2	1.6	0.69 to 2.5	1.3	80	0
	27M	3	1.0	0.00 to 2.0	0.99	96	33
	280	3	1.4	0.43 to 3.1	1.5	110	0
	310	3	1.1	0.36 to 1.6	0.64	60	0
	380	1	0.47	NA	NA	NA	0
	40M	3	0.67	0.087 to 1.4	0.69	100	0
	47M	3	0.75	0.17 to 1.6	0.77	100	0
	MB19M	1	0.46	NA	NA	NA	0
11M	1	55	NA	NA	NA	0	

* Value represents the percent of the individual samples collected and analyzed, not of the monthly composite samples prepared from the individual samples.

NA = Not applicable

Table 3-6. Monthly Composite Concentrations of Vapor-Phase Total PCBs Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m ³)	Range (pg/m ³)	SD (pg/m ³)	RSD (%)
Shoreline Atmospheric Stations	Beaver Island	19	970	0 to 2400	880	90
	Chiwaukee Prairie	19	320	47 to 810	230	72
	IIT Chicago	19	2600	460 to 6300	1900	72
	Indiana Dunes	19	680	88 to 2000	580	85
	Manitowoc	19	350	49 to 830	260	74
	Muskegon	18	490	68 to 1300	410	84
	Sleeping Bear Dunes	15	380	54 to 2000	550	150
	South Haven	19	400	54 to 1400	360	89
Out-of-Basin Atmospheric Stations	Bondville	19	250	44 to 590	150	60
	Brule River	19	110	0.00 to 390	110	99
	Eagle Harbor	4	260	29 to 800	370	140
Over-Water Atmospheric Stations	Empire Michigan	4	170	87 to 260	77	46
	GB24M	4	940	7.8 to 3400	1600	180
	1	5	990	6.0 to 3600	1500	150
	5	6	670	9.8 to 1500	590	88
	6	4	1200	52 to 3900	1800	140
	110	3	810	84 to 2200	1200	150
	18M	5	560	7.6 to 2200	930	170
	23M	4	490	21 to 1300	600	120
	27M	5	360	9.6 to 1000	410	120
	280	4	480	4.9 to 1300	570	120
	310	3	650	380 to 1200	430	67
	380	1	290	NA	NA	NA
	40M	4	340	7.6 to 1000	460	140
	41	2	21	16 to 25	6.4	31
	47M	5	410	8.5 to 1500	630	150
	MB19M	1	280	NA	NA	NA
11M	2	2200	8.9 to 4300	3100	140	

NA = Not applicable

Table 3-7. Monthly Composite Concentrations of Vapor-Phase *trans*-Nonachlor Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station	N	Mean (pg/m ³)	Range (pg/m ³)	SD (pg/m ³)	RSD (%)	% Below DL*	
Shoreline Atmospheric Stations	Beaver Island	18	3.9	0.10 to 20	4.9	130	6
	Chiwaukee Prairie	19	9.3	0.30 to 25	8.1	86	0
	IIT Chicago	19	29	1.5 to 80	22	77	0
	Indiana Dunes	19	19	1.0 to 61	16	84	0
	Manitowoc	19	7.5	0 to 19	6.0	81	21
	Muskegon	18	14	0.40 to 51	16	110	0
	Sleeping Bear Dunes	15	5.3	0.98 to 15	4.8	86	26
	South Haven	19	10	0 to 33	8.8	86	4.5
Out-of-Basin Atmospheric Stations	Bondville	19	43	1.9 to 120	37	87	0
	Brule River	18	2.1	0 to 12	2.9	140	28
	Eagle Harbor	4	3.7	1.0 to 6.2	2.1	58	13
Over-Water Atmospheric Stations	Empire Michigan	4	8.8	5.5 to 21	3.6	41	0
	GB24M	4	2.9	0.00 to 5.1	2.3	79	25
	1	5	13	1.1 to 39	15	110	0
	5	6	14	1.8 to 28	11	81	0
	6	4	12	1.1 to 34	15	130	0
	110	3	5.2	0.0 to 14	8.0	150	33
	18M	5	8.3	0 to 31	13	150	20
	23M	4	14	3.8 to 25	10	74	0
	27M	5	5.6	0 to 14	5.2	93	20
	280	4	5.8	0 to 19	8.6	150	25
	310	3	6.8	1.9 to 16	7.6	110	0
	380	1	0	NA	NA	NA	100
	40M	4	6.6	0.20 to 14	6.2	94	0
	41	2	3.2	0 to 6.5	4.6	140	50
	47M	5	7.2	0 to 14	5.8	80	20
	MB19M	1	0	NA	NA	NA	100
Station 11M	2	4.3	3.8 to 4.7	0.69	16	0	

* Value represents the percent of the individual samples collected and analyzed, not of the monthly composite samples prepared from the individual samples.
NA = Not applicable

3.1.1.1 Temporal Variation

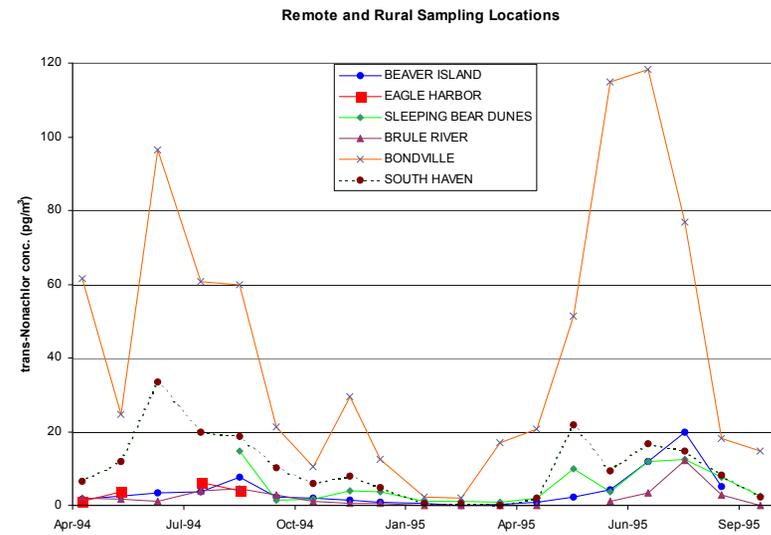
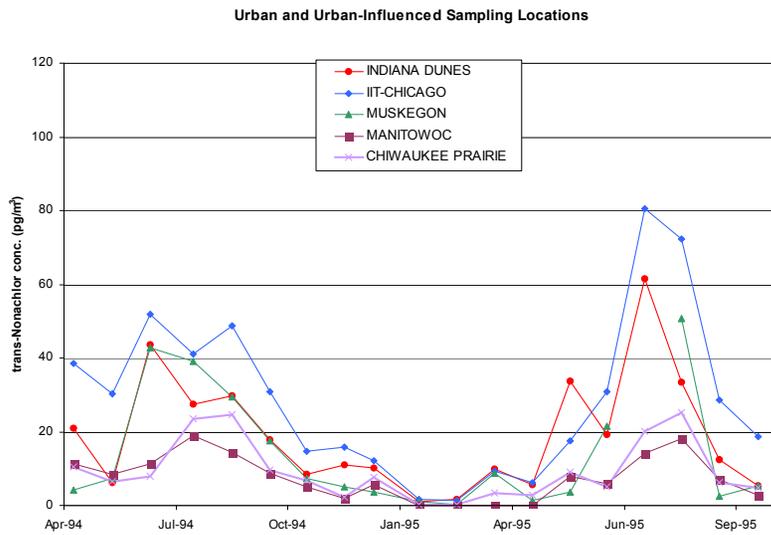
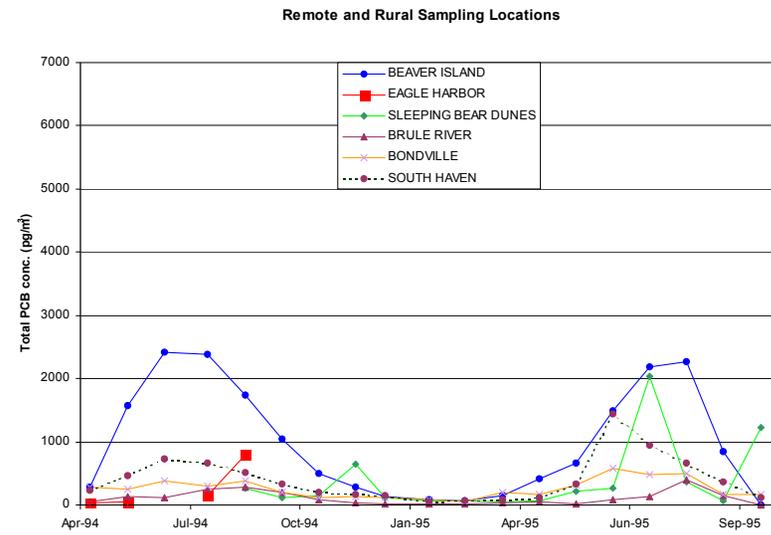
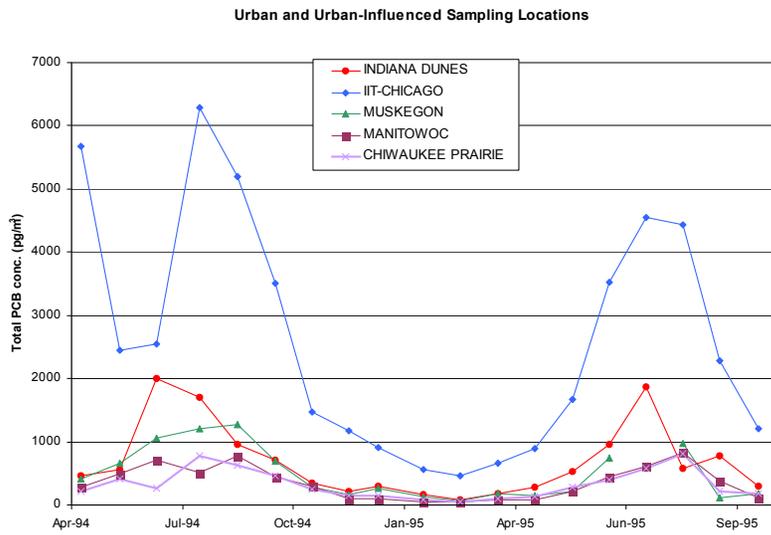
Vapor-phase PCB results exhibited a seasonal trend, with higher concentrations occurring in summer months and lower concentrations occurring in winter months (Figure 3-1). This seasonal variation has often been reported for semivolatile compounds (Hoff *et al.*, 1992, Burgoyne and Hites, 1993, and Cortes *et al.*, 1998) and may be a result of the interaction of the vapor pressures of the PCBs and the increased temperatures during summer months. The results for each monthly composite sample were plotted using the mid-point of the compositing period as the date (e.g., the date midway between the start of the collection of the first individual sample in the composite and the end of the collection of the last individual sample in the composite).

All of the sites exhibited similar trends in vapor phase total PCB concentrations, with higher concentrations generally occurring in the summer and lower concentrations in the winter, despite differences between sites of an order of magnitude or more. For example, concentrations of vapor-phase total PCBs measured at the urban-influenced site, Manitowoc, were 49 pg/m³ in February 1995 and were 17 times higher in August 1995 at 830 pg/m³. For the remote site, Beaver Island, vapor-phase total PCB concentrations were 72 pg/m³ in February 1995 and were 31 times higher in August 1995, at 2300 pg/m³.

Vapor-phase *trans*-nonachlor results showed an even stronger seasonal variation than the vapor-phase PCB results. All of the sites exhibited similar trends in vapor phase *trans*-nonachlor concentrations, with higher concentrations generally occurring in the summer and lower concentrations in the winter, despite differences between sites of an order of magnitude or more. For the urban site IIT Chicago, concentrations of vapor-phase *trans*-nonachlor were 1.5 pg/m³ in February 1995 and were 50 times higher in July 1995, at 80 pg/m³. For the rural Bondville station, vapor-phase *trans*-nonachlor was 2 pg/m³ in February 1995 and was 60 times higher in July 1995 at 120 pg/m³.

Temporal variability could not be evaluated for the over-water stations because of the limited number of composite samples (1 to 4 at any given over-water station) that do not represent either all four seasons in any one year, or the entire time-span of the LMMB Study.

Figure 3-1. Temporal Variations of Total Vapor-Phase PCB (top) and *trans*-Nonachlor (bottom) Concentrations Measured at Lake Michigan Shoreline and Out-of-Basin Stations from April 1994 to October 1995

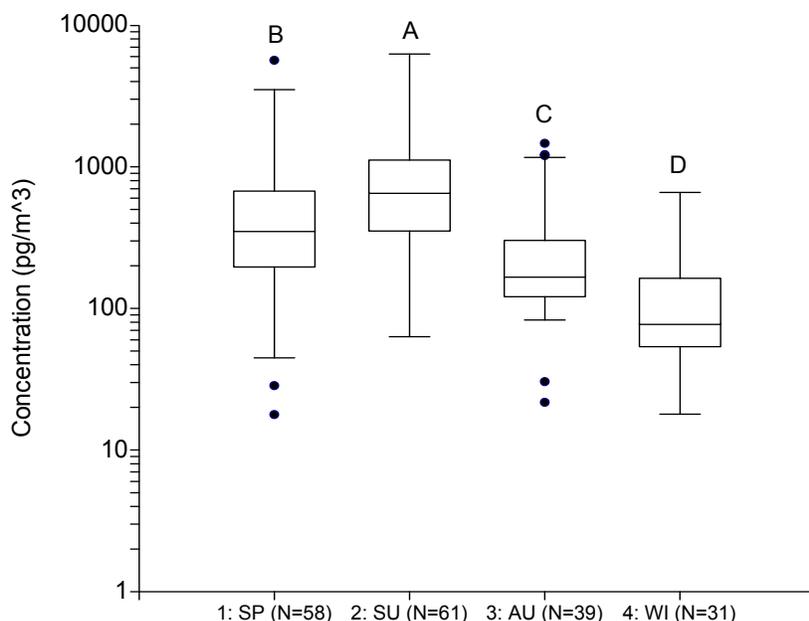


PCB congener and total PCB concentrations were significantly different among the four seasons. Seasons were defined as:

- Spring (SP) = March 20 to June 20,
- Summer (SU) = June 21 to September 22,
- Autumn (AU) = September 23 to December 21, and
- Winter (WI) = December 22 to March 19

As illustrated in Figure 3-2, the concentrations of total PCBs measured at shoreline and out-of-basin stations differed significantly between seasons ($p < 0.0001$, two-way ANOVA with a Tukey pairwise comparison, total PCB concentrations were log-transformed prior to conducting the test). Concentrations of vapor-phase total PCBs are significantly higher in the summer and the seasons can be ranked in order of decreasing monthly composite vapor-phase total PCB concentration as: Summer > Spring > Autumn > Winter. Concentrations of PCB 118 and 180 also were significantly different for all seasons in the same pattern as the total PCBs.

Figure 3-2. Seasonal Differences in Vapor-phase Total PCB Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from April 1994 and October 1995

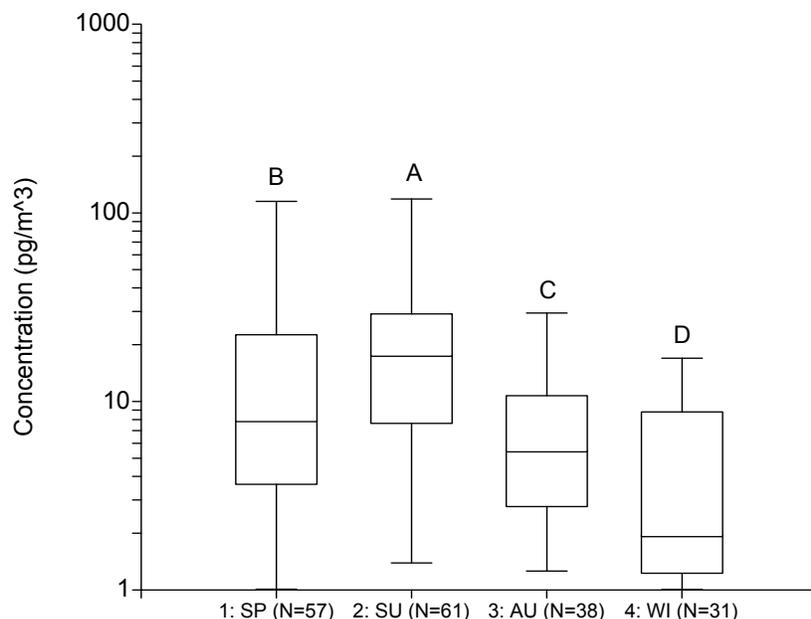


Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The letters (A - D) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Concentration is plotted on a log scale.

For PCB 33, there was a statistically significant interaction between season and station, indicating that the variations among seasons differed for the stations. The out-of-basin stations at Bondville and Eagle Harbor and the shoreline stations at Muskegon and Sleeping Bear Dunes did not have a significant difference for vapor-phase PCB 33 among seasons. The results for all other stations exhibited some significant difference among seasons, with the same general trend as total PCBs, PCB 118 and PCB 180, in which the mean concentrations were highest in summer and lowest in winter. At Eagle Harbor, the lack of a seasonal difference likely was due to the lack of composite samples collected in autumn and winter at this remote site.

For *trans*-nonachlor, concentrations differed significantly among seasons ($p < 0.0001$, two-way ANOVA with a Tukey pairwise comparison, *trans*-nonachlor concentrations were log-transformed prior to conducting the test). Mean concentrations of vapor-phase *trans*-nonachlor are significantly higher in the summer and the seasons can be ranked in order of decreasing monthly composite vapor-phase total PCB concentration as: Summer > Spring > Autumn > Winter.

Figure 3-3. Seasonal Differences in *trans*-Nonachlor Concentrations Measured at Lake Michigan Shoreline and Out-of-Basin Stations from April 1994 to October 1995



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Letters above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at $\alpha = 0.05$). Concentration is plotted on a log scale.

3.1.1.2 Geographical Variation

Vapor-phase PCB congener and total PCB concentrations varied by sampling station (Table 3-9). Urban and urban-influenced sites had higher mean monthly composite concentrations for the duration of the study period than rural sites. For example, the mean vapor-phase total PCB concentrations were 2600, 460, and 400 pg/m^3 , respectively, for the urban, urban-influenced, and rural stations. A similar pattern was observed for PCB 118 (Table 3-8). These data are consistent with what is expected, given that urban and urban-influenced areas contain significant sources of vapor-phase PCBs. However, the mean concentrations for total PCBs and PCB 118 at the remote sites are higher than those at the urban and urban-influenced sites. The higher mean concentration for the remote sites is largely due to the high concentration of PCBs at the Beaver Island station (Figure 3-4). The results for PCBs at Beaver Island suggest the presence of an unknown source for PCBs at this station.

The mean concentration of vapor-phase total PCBs at over-water stations was 640 pg/m^3 (Table 3-8), which is higher than the mean concentrations for the urban-influenced, out-of-basin, and rural stations (460, 190, and 400 pg/m^3 , respectively). The mean concentration of vapor-phase PCB 118 at over-water stations was also higher than the other station types (Table 3-8). However, the mean concentrations of

PCB at the over-water stations may be driven by the relatively high concentrations observed at Stations 1,5,6, and 11M (Tables 3-3 to 3-6), which are all fairly close to shore in the area near Chicago.

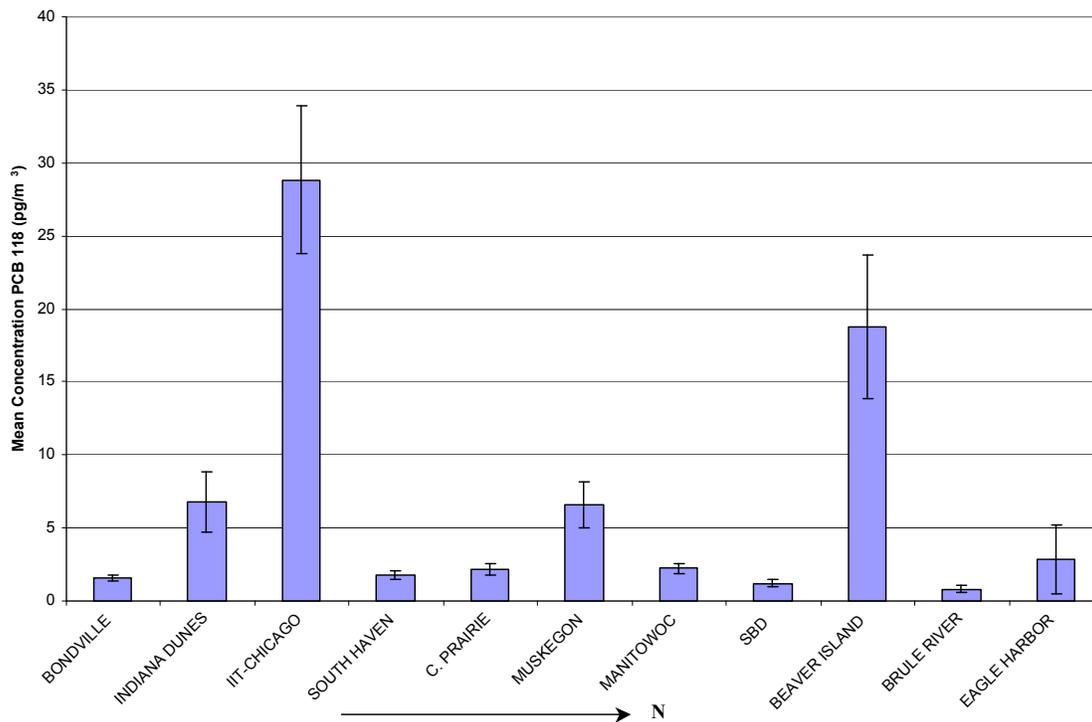
The mean concentration of vapor-phase *trans*-nonachlor at over-water stations was 8.1 pg/m³, which is lower than the mean concentrations at all other types of stations except the remote stations.

Table 3-8. Mean Monthly Composite Concentrations of Vapor-Phase Total PCBs, PCB 118, and *trans*-Nonachlor at LMMB Study Sampling Stations in and around Lake Michigan from April 1994 to October 1995

Vapor-phase parameter	Sampling Station Type		N	Mean (pg/m ³)	Range (pg/m ³)	RSD (%)
Total PCBs	Shoreline	Urban	19	2600	460 to 6300	72
		Urban-Influenced	75	460	47 to 2000	90
		Rural	19	400	54 to 1400	89
		Remote	34	710	0.0 to 2400	110
		Overall	147	790	0.0 to 6300	140
	Over-water		62	640	4.0 to 4300	160
	Out-of-Basin		42	190	0.0 to 800	93
PCB 118	Shoreline	Urban	19	29	3.5 to 66	77
		Urban-Influenced	75	4.4	0.24 to 33	140
		Rural	19	1.8	0.35 to 5.2	73
		Remote	29	12	0.29 to 70	150
		Overall	142	8.9	0.24 to 70	170
	Over-water		43	13	0.48 to 150	250
	Out-of-Basin		41	1.4	0.075 to 9.9	120
<i>trans</i> -Nonachlor	Shoreline	Urban	19	29	1.5 to 80	77
		Urban-Influenced	75	12	0.0 to 61	100
		Rural	19	10	0.0 to 33	86
		Remote	33	4.6	0.10 to 20	100
		Overall	146	13	0.0 to 80	120
	Over-water		62	8.1	0.0 to 39	110
	Out-of-Basin		41	21	0.0 to 120	150

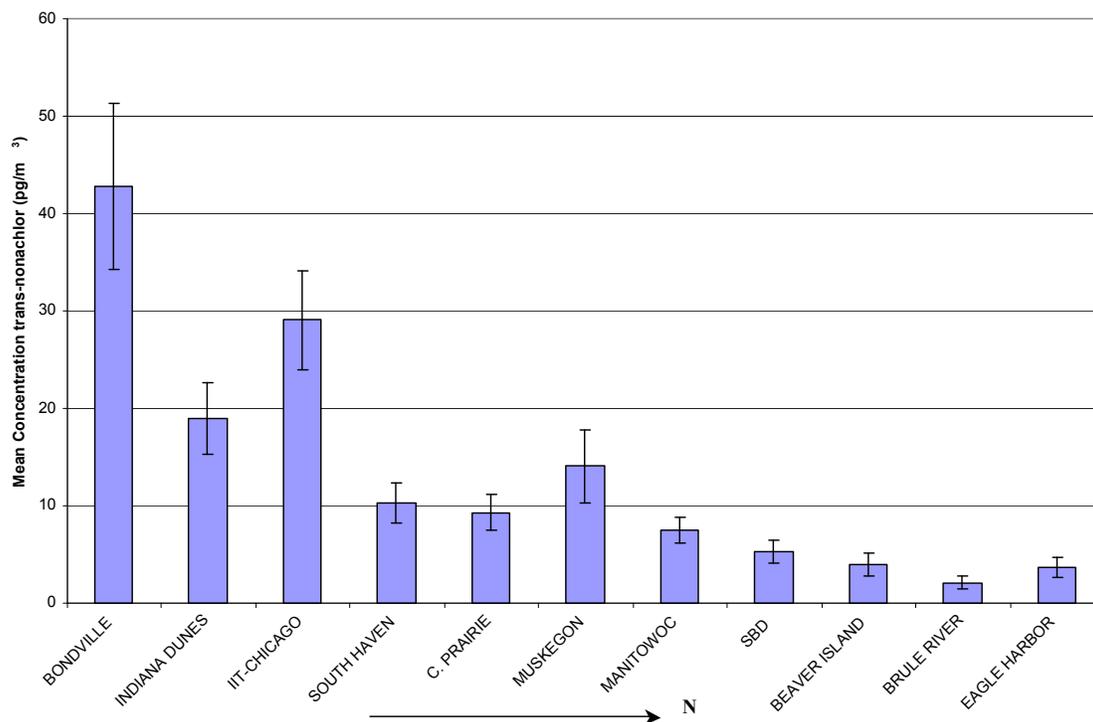
Vapor-phase PCB concentrations varied by station, with the highest mean concentrations generally at the urban IIT Chicago station and the remote Beaver Island station. However, there is no clear trend of concentrations and latitude (Figure 3-4).

Figure 3-4. Vapor-phase PCB 118 Concentrations Measured at Shoreline and Out-of-basin Sampling Stations around Lake Michigan from April 1994 to October 1995



Vapor-phase *trans*-nonachlor concentrations also varied by sampling station. The mean monthly composite sample results for *trans*-nonachlor in Table 3-8 exhibit a general trend of decreasing concentrations from urban stations to remote stations. In addition, the *trans*-nonachlor data exhibit a trend of increasing concentrations moving south across Lake Michigan (Figure 3-5).

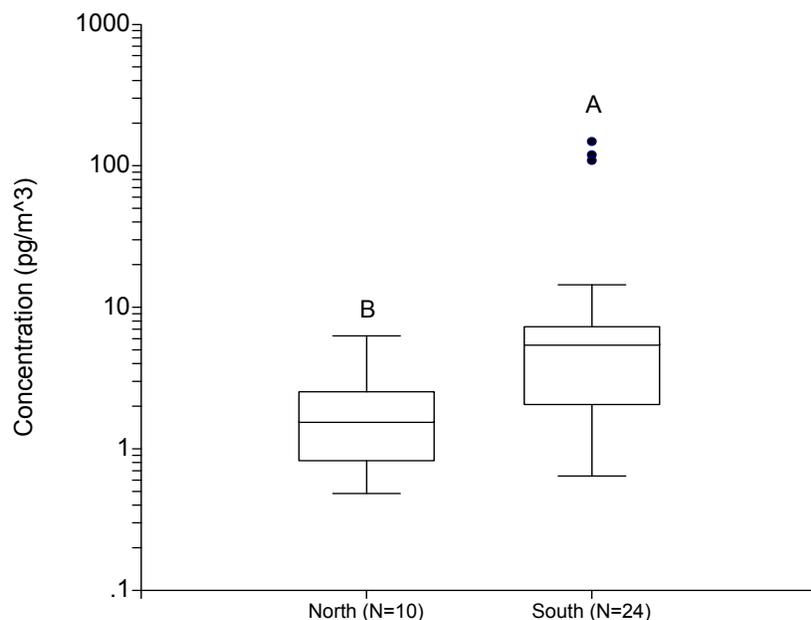
Figure 3-5. Vapor-phase *trans*-Nonachlor Concentrations Measured at Sampling Stations around Lake Michigan from April 1994 to October 1995



Concentrations of vapor-phase PCB congeners in samples collected at over-water sampling locations also differed among stations. Figure 3-6 illustrates a significant difference between sampling stations in Southern Lake Michigan (sites south of 43° latitude) and stations in Northern Lake Michigan (sites north of 43° latitude) for PCB 118. PCB 118 concentrations observed at southern sampling stations were significantly higher than concentrations observed at northern sampling stations.

For vapor-phase *trans*-nonachlor and total PCBs, a significant difference between over-water sampling stations in southern Lake Michigan (sites south of 43° latitude) compared to stations in northern Lake Michigan did *not* occur.

Figure 3-6. Concentrations of PCB 118 in Vapor Measured in Over-water Samples Collected in the Northern and Southern Areas of Lake Michigan



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Letters above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Northern sites are those north of 43° latitude.

3.1.2 Particulate Fraction

Particulate-phase PCB congeners were detected in the majority of the samples collected from all LMMB Study stations. Tables 3-9 to 3-12 present the results for the monthly composite particulate-phase samples from this study. As discussed in Chapter 2, the composite results represent either: 1) the physical compositing of several individual samples collected during a calendar month to create one sample for analysis, or 2) mathematical composites of the results from the analysis of the individual samples collected over a calendar month. In some instances, both physical and mathematical composites were prepared within a month. In these instances, the reported result is a mathematical composite based on both the physical composite samples and the individual samples. The total number of composite results is shown for each station as “N,” along with the mean concentration, range, standard deviation, and relative standard deviation (RSD). Tables 3-9 to 3-11 also indicate the percent of the *individual* sample results that were below the sample-specific detection limit, not the percent of the composite results. The mean concentrations were calculated using the results reported by each laboratory (substitution of the detection limit or other value was not used for results below the sample-specific detection limits).

Particulate-phase PCB congener concentrations ranged from 0 pg/m³ for PCB 180 at the Manitowoc and Sleeping Bear Dunes sampling stations to 8.7 pg/m³ for PCB 118 at the IIT Chicago sampling station (Tables 3-9 to 3-11). Concentrations of particulate-phase total PCBs ranged from 0 pg/m³ at the Beaver Island station to 250 pg/m³ at the IIT Chicago station (Table 3-12). The mean particulate-phase PCB concentrations ranged from 0.10 pg/m³ for PCB 180 at Sleeping Bear Dunes to 3.2 pg/m³ at the IIT Chicago station. Mean particulate-phase total PCB concentrations ranged from 0.37 pg/m³ at over-water Station 6 to 91 pg/m³ at the IIT Chicago station.

The variability of the PCB concentrations differed among both stations and congeners, with RSD values for PCB 33 ranging from 24% to 77%, from 26% to 190% for PCB 118, and 35% to 210% for PCB 180. In contrast to the vapor-phase results, the greatest RSD values tend to be associated with the stations with larger numbers of samples, while the lowest RSD values occur at the two stations with only four samples, Eagle Harbor and Empire Michigan. However, the low RSD values at these two stations may be due to a lack of seasonal variability since the results for these stations are only from one season. Over-water stations 5 and GB24M have only one sample, therefore, no RSD can be calculated. For stations with greater than 10 samples over the course of the study, the variability for particulate-phase PCB 33 was greatest at IIT Chicago (RSD = 72%) and greatest for PCB 118, PCB 180, and total PCBs at Sleeping Bear Dunes (RSDs of 190%, 210%, and 110%, respectively).

Particulate-phase *trans*-nonachlor was detected much less frequently than PCB congeners in the samples. Except for the samples collected at the Empire Michigan station, *trans*-nonachlor was reported as being below the sample-specific detection limit in 20 to 100% of the particulate-phase samples from the other 16 stations (Table 3-13). Concentrations of particulate-phase *trans*-nonachlor ranged from 0 pg/m³ at 12 stations to 2.6 pg/m³ at Bondville. Mean monthly composite concentrations of *trans*-nonachlor for each sampling station ranged from 0.16 pg/m³ measured at GB24M to 1.2 pg/m³ measured at IIT Chicago, with a concentration of 1.8 pg/m³ for the only sample collected at over-water Station 1.

Table 3-9. Monthly Composite Concentrations of Particulate-Phase PCB 33 Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m ³)	Range (pg/m ³)	SD (pg/m ³)	RSD (%)	% Below DL*
Shoreline Atmospheric Stations	Beaver Island	17	0.52	0.21 to 1.4	0.26	50	0
	Chiwaukee Prairie	19	0.52	0.20 to 0.82	0.16	31	0
	IIT Chicago	19	1.7	0.67 to 5.3	1.2	72	0
	Indiana Dunes	19	0.63	0.28 to 1.4	0.29	46	3
	Manitowoc	19	0.43	0.17 to 0.83	0.17	40	5
	Muskegon	16	0.38	0.032 to 0.67	0.19	51	25
	Sleeping Bear Dunes	14	0.59	0.16 to 1.4	0.40	68	7
Out-of-Basin Atmospheric Stations	South Haven	17	0.58	0.32 to 1.1	0.20	34	11
	Bondville	19	0.66	0.24 to 1.1	0.22	33	0
	Brule River	18	0.46	0.18 to 1.0	0.21	47	0
Over-water Atmospheric Stations	Eagle Harbor	4	0.32	0.20 to 0.58	0.18	56	0
	Empire Michigan	4	0.30	0.20 to 0.35	0.071	24	0
	GB24M	1	0.34	NA	NA	NA	100
	5	1	1.3	NA	NA	NA	0

* Value represents the percent of the individual samples collected and analyzed, not of the monthly composite samples prepared from the individual samples.
NA = Not applicable

Table 3-10. Monthly Composite Concentrations of Particulate-phase PCB 118 Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m ³)	Range (pg/m ³)	SD (pg/m ³)	RSD (%)	% Below DL*
Shoreline Atmospheric Stations	Beaver Island	17	1.7	0.51 to 4.0	0.95	56	0
	Chiwaukee Prairie	19	0.47	0.19 to 0.83	0.18	40	0
	IIT Chicago	19	3.2	1.5 to 8.7	1.7	54	0
	Manitowoc	19	0.48	0.20 to 1.3	0.26	54	0
	Muskegon	16	0.67	0.17 to 1.6	0.46	69	0
	Sleeping Bear Dunes	14	0.24	0.023 to 1.8	0.46	190	43
	South Haven	17	0.49	0.20 to 1.9	0.39	80	11
	Indiana Dunes	19	0.77	0.35 to 1.7	0.31	41	0
Out-of-Basin Atmospheric Stations	Bondville	91	0.40	0.19 to 0.89	0.17	44	5
	Brule River	18	0.50	0.14 to 1.4	0.27	53	0
	Eagle Harbor	4	0.22	0.14 to 0.28	0.067	30	0
Over-water Atmospheric Stations	Empire Michigan	4	0.34	0.25 to 0.44	0.089	26	0
	GB24M	1	0.14	NA	NA	NA	100
	5	1	0.61	NA	NA	NA	0
	Spatial Composites	12	0.56	0.065 to 2.0	0.54	96	8

* Value represents the percent of the individual samples collected and analyzed, not of the monthly composite samples prepared from the individual samples.

NA = Not applicable

Table 3-11. Monthly Composite Concentrations of Particulate-Phase PCB 180 Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m ³)	Range (pg/m ³)	SD (pg/m ³)	RSD (%)	% Below DL*
Shoreline Atmospheric Stations	Beaver Island	17	1.0	0.26 to 2.6	0.71	69	0
	Chiwaukee Prairie	19	0.21	0.067 to 0.34	0.075	36	10
	IIT Chicago	19	1.9	0.97 to 4.6	0.84	45	0
	Indiana Dunes	19	0.36	0.10 to 0.71	0.16	45	0
	Manitowoc	19	0.22	0.0 to 0.74	0.15	69	5
	Muskegon	16	0.38	0.14 to 0.83	0.22	59	0
	Sleeping Bear Dunes	14	0.10	0.0 to 0.82	0.21	210	57
	South Haven	17	0.29	0.046 to 1.5	0.34	120	17
Out-of-Basin Atmospheric Stations	Bondville	19	0.26	0.078 to 1.3	0.28	110	14
	Brule River	18	0.18	0.00 to 0.69	0.15	82	6
	Eagle Harbor	4	0.090	0.046 to 0.13	0.034	37	25
Over-Water Atmospheric Stations	Empire Michigan	4	0.11	0.065 to 0.15	0.037	35	0
	GB24M	1	0.11	NA	NA	NA	100
	5	1	0.21	NA	NA	NA	100
	Spatial Composites	12	0.27	0.047 to 0.71	0.20	74	33

* Value represents the percent of the individual samples collected and analyzed, not of the monthly composite samples prepared from the individual samples.

NA = Not applicable

Table 3-12. Monthly Composite Concentrations of Particulate-phase Total PCBs Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m ³)	Range (pg/m ³)	SD (pg/m ³)	RSD (%)
Shoreline Atmospheric Stations	Beaver Island	18	52	0.0 to 110	29	56
	Chiwaukee Prairie	19	22	7.7 to 31	6.1	28
	IIT Chicago	19	91	46 to 250	48	53
	Indiana Dunes	19	33	18 to 66	12	36
	Manitowoc	19	26	8.6 to 110	22	84
	Muskegon	16	24	7.7 to 51	12	49
	Sleeping Bear Dunes	15	18	0.0 to 69	21	110
	South Haven	18	23	0.0 to 47	12	52
Out-of-Basin Atmospheric Stations	Bondville	19	25	9.6 to 58	14	54
	Brule River	18	21	5.8 to 71	14	66
	Eagle Harbor	4	14	8.2 to 20	4.7	33
Over-Water Atmospheric Stations	Spatial Composites	18	19	0.18 to 77	21	110
	Empire Michigan	4	14	8.9 to 18	4.0	29
	GB24M	2	3.9	0.26 to 7.6	5.2	130
	1	1	2.6	NA	NA	NA
	5	3	17	0.25 to 48	27	160
	6	1	0.37	NA	NA	NA

NA = Not applicable

Table 3-13. Monthly Composite Concentrations of Particulate-Phase *trans*-Nonachlor Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m ³)	Range (pg/m ³)	SD (pg/m ³)	RSD (%)	% Below DL*
Shoreline Atmospheric Stations	Beaver Island	17	0.35	0.0 to 0.72	0.22	62	29
	Chiwaukee Prairie	19	0.48	0.0 to 1.0	0.25	53	24
	IIT Chicago	19	1.2	0.0 to 2.5	0.68	58	20
	Indiana Dunes	18	0.64	0.0 to 1.6	0.45	70	34
	Manitowoc	18	0.58	0.075 to 1.4	0.42	73	22
	Muskegon	16	0.47	0.0 to 1.4	0.39	84	31
	Sleeping Bear Dunes	4	0.30	0.0 to 1.1	0.55	190	75
	South Haven	17	0.46	0.0 to 1.2	0.32	71	33
Out-of-Basin Atmospheric Stations	Bondville	19	0.81	0.0 to 2.6	0.89	110	48
	Brule River	18	0.43	0.0 to 1.1	0.31	71	39
	Eagle Harbor	4	0.24	0.051 to 0.49	0.20	84	50
Over-Water Atmospheric Stations	Empire Michigan	4	0.34	0.17 to 0.51	0.14	41	0
	GB24M	2	0.16	0.0 to 0.32	0.23	140	100
	1	1	1.8	NA	NA	NA	0
	5	3	0.36	0.0 to 1.0	0.55	150	67
	6	1	0.74	NA	NA	NA	100
	Spatial Composites	18	0.41	0.0 to 1.6	0.46	110	61

* Value represents the percent of the individual samples collected and analyzed, not of the monthly composite samples prepared from the individual samples.

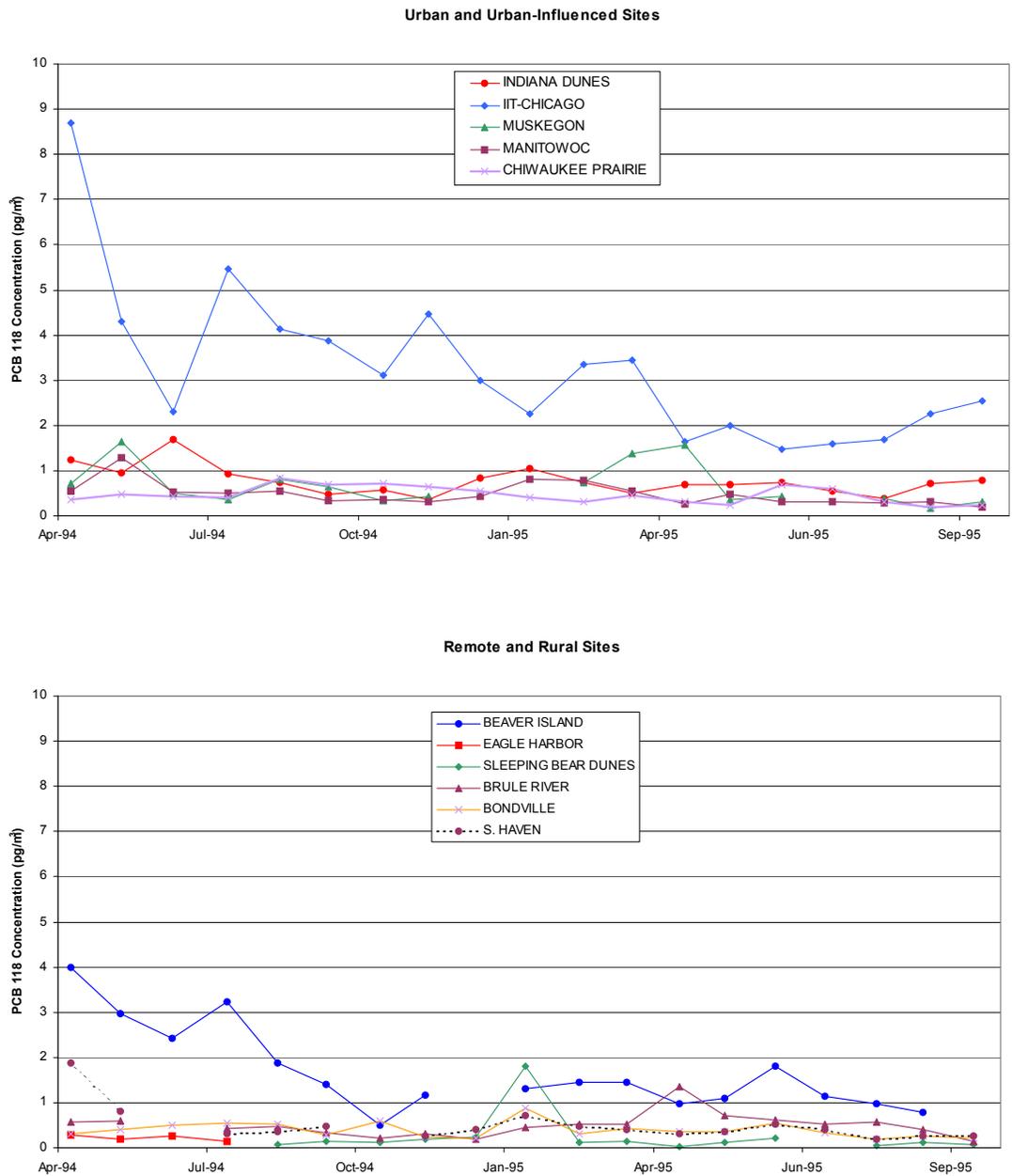
NA = Not applicable

3.1.2.1 Temporal Variation

Particulate-phase PCB congener and total PCB results exhibited different temporal trends among congeners and also among stations. Season did not have a significant effect on particulate-phase PCB 33 concentrations, but did have a significant effect on particulate-phase total PCBs ($p < 0.0001$, two-way ANOVA, PCB concentrations were log-transformed prior to conducting the test). For particulate-phase PCB 118 and PCB 180 concentrations, there was a significant interaction between station and season ($p < 0.0361$, two-way ANOVA, PCB concentrations were log-transformed prior to conducting the test). The relationship between season and concentration differed for PCBs 118 and 180 at different stations. Figure 3-7 illustrates the interaction between station and season for PCB 118.

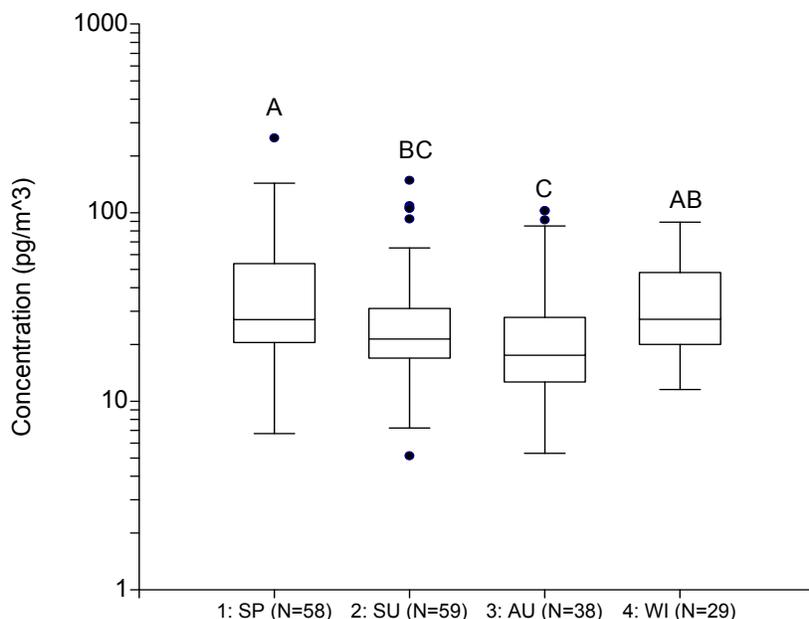
The particulate-phase results for PCB 118 at the Beaver Island and IIT Chicago stations are highest in April 1994 and generally decrease by September 1995, and variable in between. While some of the urban and urban-influenced stations exhibit their highest concentrations of PCB 118 in May 1994 (e.g., Muskegon, Manitowoc, and Indiana Dunes), the overall decrease seen at Beaver Island and IIT Chicago is not apparent at the other stations. The rural and remote stations other than Beaver Island do not show a temporal trend in particulate-phase PCB 118 concentrations. The highest result at Sleeping Bear Dunes occurred in January 1995 (1.8 pg/m³). However, this result may be due to contamination, as evidenced by the field duplicate composite sample that had a concentration of only 0.19 pg/m³. The highest result at IIT Chicago in April 1994 is especially striking, given that the other samples collected from this station during April 1995 had lower results than the neighboring months.

Figure 3-7. Temporal Variations in Particulate-phase PCB 118 Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from April 1994 to October 1995



The particulate-phase total PCB concentrations were significantly higher in Spring compared to Autumn and Summer (two-way ANOVA, with Tukey pairwise comparisons) and significantly higher in Winter than Autumn (Figure 3-8).

Figure 3-8. Seasonal Differences in Particulate-phase Total PCB Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from April 1994 to October 1995

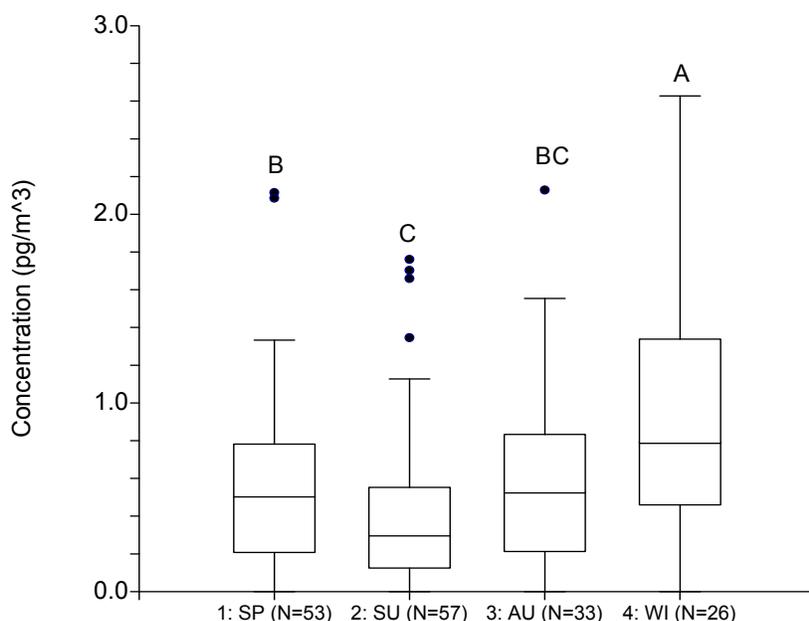


Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The letters (A - D) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Concentration is plotted on a log scale.

The seasonal differences evident in Figure 3-8 were apparent even when the high April 1994 results were removed from the data set. Given that the data were log-transformed before the comparisons, it is not unexpected that removing the April 1994 results did not change the seasonal patterns.

For *trans*-nonachlor, concentrations measured in particulate-phase samples also were significantly different among seasons, with mean concentrations highest in winter and lowest in summer (two-way ANOVA, with Tukey pairwise comparisons, see Figure 3-9). However, the pattern of seasonal differences was not the same as exhibited in the particulate-phase total PCB results.

Figure 3-9. Seasonal Differences in Particulate-phase *trans*-Nonachlor Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from April 1994 to October 1995



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The letters (A - D) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

Temporal variability could not be evaluated for the over-water stations because of the limited number of composite samples (1 to 4 at any given over-water station) that do not represent either all four seasons in any one year, or the entire time-span of the LMMB Study.

3.1.2.2 Geographical Variation

Particulate-phase PCB congener and total PCB concentrations varied by sampling station (Table 3-14). As was noted for the vapor-phase results, urban and urban-influenced sites had higher mean monthly composite concentrations for the duration of the study period than rural sites, consistent with the hypothesis that urban and urban-influenced areas contain significant sources of particulate-phase PCBs. As also noted for the vapor-phase results, the results for total PCBs and PCB 33 at the remote sites fall between the urban and urban-influenced sites, suggesting the presence of an unknown source for PCBs at the remote sites, likely near Beaver Island (see Figures 3-7 and 3-10).

Table 3-14. Mean Monthly Composite Concentrations of Particulate-phase Total PCBs, PCB 33, and *trans*-Nonachlor at LMMB Study Sampling Stations in and around Lake Michigan between April 1994 and October 1995

Particulate-phase parameter	Sampling Station Type	N	Mean (pg/m ³)	Range (pg/m ³)	RSD(%)	
Total PCBs	Shoreline	Urban	19	91	46 to 250	53
		Urban-Influenced	73	26	7.7 to 110	55
		Rural	18	23	0 to 47	52
		Remote	33	37	0 to 110	83
		Overall	143	37	0 to 250	90
	Over-Water		29	16	0.18 to 77	120
	Out-of-Basin		41	22	5.8 to 71	60
PCB 33	Shoreline	Urban	19	1.7	0.67 to 5.3	72
		Urban-Influenced	73	0.50	0.032 to 1.4	46
		Rural	17	0.58	0.32 to 1.1	34
		Remote	31	0.55	0.16 to 1.4	59
		Overall	140	0.68	0.032 to 5.3	93
	Over-Water		18	0.60	0 to 1.6	79
	Out-of-Basin		41	0.54	0.18 to 1.1	45
<i>trans</i> -Nonachlor	Shoreline	Urban	19	1.2	0 to 2.5	58
		Urban Influenced	71	0.54	0 to 1.6	70
		Rural	17	0.46	0 to 1.2	71
		Remote	21	0.34	0 to 1.1	85
		Overall	128	0.59	0 to 2.5	82
	Over-Water		29	0.43	0 to 1.8	110
	Out-of-Basin		41	0.59	0 to 2.6	110

There was no apparent relationship between the particulate-phase concentration of PCB 118 and latitude (see Figure 3-10).

There is an apparent relationship between the particulate-phase concentration of *trans*-nonachlor and latitude (Figure 3-11). Except for the high mean particulate-phase concentration observed at the urban IIT Chicago site, the mean concentration of *trans*-nonachlor generally decreases moving from south to north across Lake Michigan.

Figure 3-10. Particulate-phase PCB 118 Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from April 1994 to October 1995

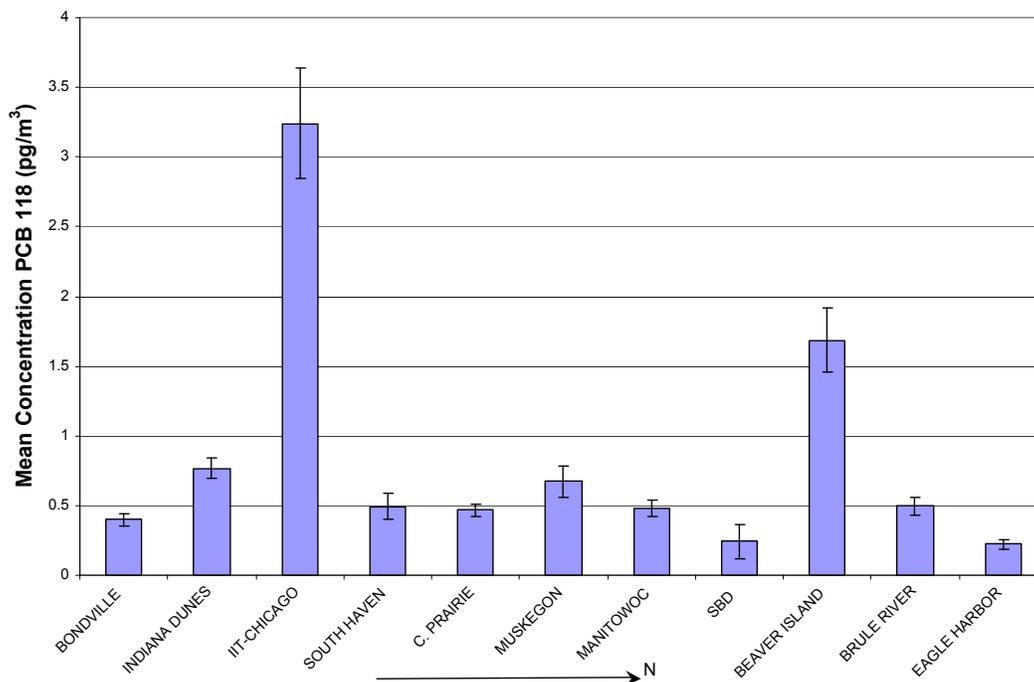
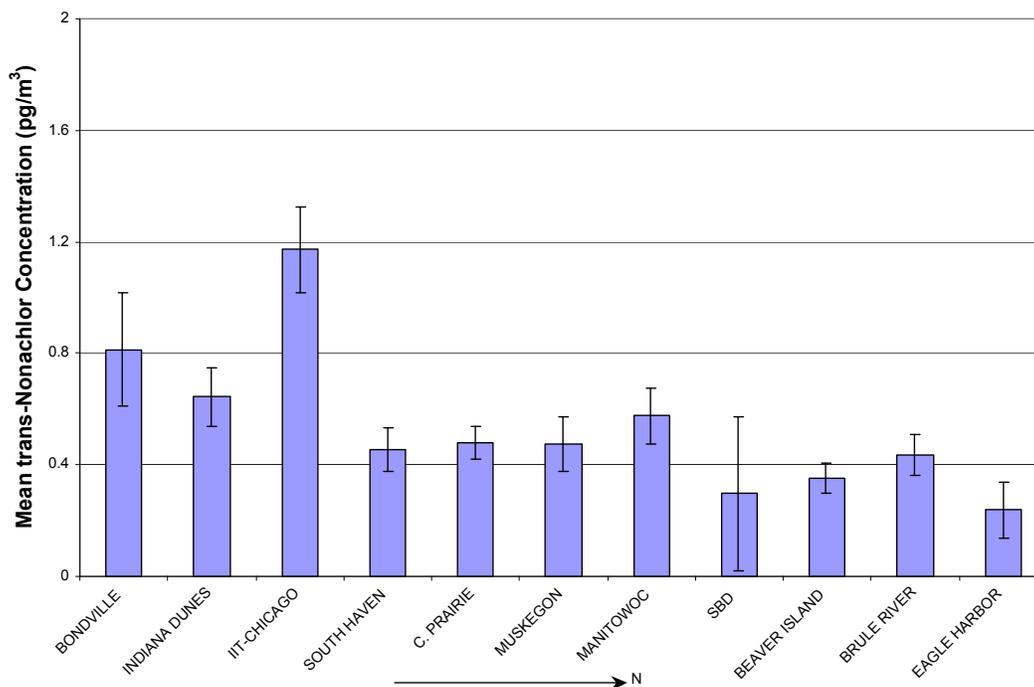


Figure 3-11. Particulate-phase *trans*-Nonachlor Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from April 1994 to October 1995



3.1.3 Precipitation Fraction

PCB congeners were detected in many of the precipitation samples collected from the LMMB Study stations. However, the overall frequency of occurrence of PCBs in the precipitation samples was lower than for the vapor-phase and particulate-phase samples. The frequency of precipitation samples with results below the sample-specific detection limit was greatest for PCB 33 compared to either PCB 118 or 180.

The precipitation samples were collected as described in Chapter 2. The samples collected from the shoreline and out-of-basin stations represent true 28-day composite samples. The precipitation samples collected from the over-water stations represent single-day composite results. Tables 3-15 to 3-18 present the results for the composite precipitation samples from this study. The total number of composite results is shown for each station as “N,” along with the mean concentration, range, standard deviation, relative standard deviation (RSD), and the percent of the sample results that were below the sample-specific detection limit. In calculating these summary statistics, the analytical results for each sample were volume-weighted to account for differences in the total volume of precipitation that fell during each 28-day period. The mean concentrations were calculated using the results reported by each laboratory (substitution of the detection limit or other value was not used for results below the sample-specific detection limits).

Precipitation PCB concentrations ranged from 0 pg/L for PCB 33 at 10 of the 12 shoreline and out-of-basin sampling stations (see Table 3-15) to 5,500 pg/L for PCB 118 at Muskegon (Table 3-16). Mean precipitation PCB concentrations ranged from 2.2 pg/L for PCB 33 at the Empire Michigan station to 470 pg/L for PCB 33 at the IIT Chicago station. For total PCBs, the mean concentrations in precipitation ranged from 290 pg/L at the Eagle Harbor station to 16,000 pg/L at the IIT Chicago station. The precipitation samples collected at the IIT Chicago site had the highest volume-weighted mean concentrations of PCBs 33, 180, and total PCBs, while PCB 118 had highest volume-weighted mean concentration at the Muskegon site (see Tables 3-15 to 3-18).

Many of the summary statistics for the precipitation samples collected from the over-water stations could not be calculated because only one precipitation sample was collected at most of these stations.

trans-Nonachlor was detected even less frequently than the PCB congeners in the precipitation samples (Table 3-19). Except for the samples collected at the IIT Chicago station, *trans*-nonachlor was reported as being below the sample-specific detection limit in 75 to 100% of the precipitation samples from all stations. The concentrations of *trans*-nonachlor in the precipitation samples ranged from 0 pg/L at every site to a high of 630 pg/L at the Chiwaukee Prairie site. The mean concentrations of *trans*-nonachlor in precipitation samples ranged from 0 pg/L at three over-water stations to 120 pg/L at the IIT Chicago station. Similarly, the volume-weighted mean concentrations ranged from 0 pg/L at three over-water stations to 100 pg/L at the IIT Chicago site.

As with the PCB results, many of the summary statistics for the precipitation samples collected from the over-water station could not be calculated because only one precipitation sample was collected at most of these stations.

Table 3-15. Monthly Composite Concentrations of PCB 33 Measured in Precipitation Samples Collected around Lake Michigan from April 1994 to October 1995

Sampling Station		N	VW Mean (pg/L)	Mean (pg/L)	Range (pg/L)	SD (pg/L)	RSD (%)	% Below DL
Shoreline Atmospheric Stations	Beaver Island	19	45	42	0.0 to 450	100	240	68
	Chiwaukee Prairie	17	18	19	0.0 to 83	26	130	59
	IIT Chicago	16	270	470	15 to 3200	800	170	6
	Indiana Dunes	20	39	38	0.0 to 160	38	100	50
	Manitowoc	18	36	51	0.0 to 350	85	170	50
	Muskegon	18	37	67	0.0 to 470	120	180	50
	Sleeping Bear Dunes	14	58	83	13 to 300	72	86	7
	South Haven	19	47	74	0.0 to 620	150	210	47
Out-of-basin Atmospheric Stations	Bondville	20	45	71	0.0 to 310	84	120	30
	Brule River	18	15	32	0.0 to 310	78	240	72
	Eagle Harbor	3	21	16	0.0 to 47	27	170	67
Over-water Atmospheric Stations	Empire Michigan	4	3.0	2.2	0.0 to 8.8	4.4	200	100
	GB17	1	33	33	NA	NA	NA	100
	GB24M	1	10	10	NA	NA	NA	100
	1	1	6.9	6.9	NA	NA	NA	100
	5	1	36	36	NA	NA	NA	100
	23M	1	7.6	7.6	NA	NA	NA	100
	380	1	8.5	8.5	NA	NA	NA	100

NA = Not applicable

Table 3-16. Monthly Composite Concentrations of PCB 118 Measured in Precipitation Samples Collected around Lake Michigan from April 1994 to October 1995

Sampling Station		N	VW Mean (pg/L)	Mean (pg/L)	Range (pg/L)	SD (pg/L)	RSD (%)	% Below DL
Shoreline Atmospheric Stations	Beaver Island	19	41	53	5.5 to 250	67	130	11
	Chiwaukee Prairie	16	26	38	10 to 79	23	61	13
	IIT Chicago	16	230	440	48 to 2300	710	160	0
	Indiana Dunes	20	34	41	8.2 to 230	48	120	0
	Manitowoc	17	46	81	6.3 to 880	210	250	18
	Muskegon	17	240	360	13 to 5500	1300	360	0
	Sleeping Bear Dunes	14	11	16	3.4 to 37	9.7	59	50
	South Haven	19	35	110	6.2 to 1600	350	320	5
Out-of-basin Atmospheric Stations	Bondville	20	24	34	11 to 93	25	74	0
	Brule River	18	67	61	0.0 to 770	180	290	39
	Eagle Harbor	3	5.8	4.9	0.0 to 11	5.8	120	67
Over-water Atmospheric Stations	Empire Michigan	3	7.7	5.7	0.0 to 17	9.9	170	67
	GB17	1	76	76	NA	NA	NA	0
	GB24M	1	23	23	NA	NA	NA	0
	1	1	27	27	NA	NA	NA	0
	5	1	45	45	NA	NA	NA	100
	23M	1	12	12	NA	NA	NA	0
	380	1	17	17	NA	NA	NA	0

NA = Not applicable

Table 3-17. Monthly Composite Concentrations of PCB 180 Measured in Precipitation Samples Collected around Lake Michigan from April 1994 to October 1995

Sampling Station		N	VW Mean (pg/L)	Mean (pg/L)	Range (pg/L)	SD (pg/L)	RSD (%)	% Below DL
Shoreline Atmospheric Stations	Beaver Island	19	23	33	2.5 to 160	42	130	21
	Chiwaukee Prairie	17	24	41	7.8 to 150	39	95	18
	IIT Chicago	16	180	320	14 to 1900	520	160	0
	Indiana Dunes	20	30	38	4.6 to 210	47	120	10
	Manitowoc	18	16	35	0.0 to 210	53	150	33
	Muskegon	18	22	25	0.0 to 50	12	48	17
	Sleeping Bear Dunes	14	5.5	7.7	0.0 to 17	6.3	82	93
	South Haven	19	18	37	5.6 to 370	81	220	32
Out-of-basin Atmospheric Stations	Bondville	20	12	18	0.0 to 80	18	100	40
	Brule River	18	12	14	0.0 to 45	13	93	50
	Eagle Harbor	3	2.5	3.2	0.0 to 7.4	3.8	120	100
Over-water Atmospheric Stations	Empire Michigan	4	9.2	11	2.2 to 20	8.1	73	75
	GB17	1	29	29	NA	NA	NA	100
	GB24M	1	8.5	8.5	NA	NA	NA	100
	1	1	14	14	NA	NA	NA	0
	5	1	19	19	NA	NA	NA	100
	23M	1	3.5	3.5	NA	NA	NA	100
	380	1	6.9	6.9	NA	NA	NA	100

NA = Not applicable

Table 3-18. Monthly Composite Concentrations of total PCBs Measured in Precipitation Samples Collected around Lake Michigan from April 1994 to October 1995

Sampling Station	N	Mean (pg/L)	Range (pg/L)	SD (pg/L)	RSD (%)	
Shoreline Atmospheric Stations	Beaver Island	20	1900	0.0 to 11000	2800	150
	Chiwaukee Prairie	20	1800	0.0 to 4700	1200	66
	IIT Chicago	17	16000	0.0 to 110000	28000	180
	Indiana Dunes	21	1500	0.0 to 7200	1500	100
	Manitowoc	20	2600	0.0 to 18000	4200	160
	Muskegon	20	2600	0.0 to 19000	4000	150
	Sleeping Bear Dunes	16	1300	0.0 to 2800	880	66
	South Haven	21	3800	0.0 to 48000	10000	280
Out-of-basin Atmospheric Stations	Bondville	21	1700	0.0 to 4200	1100	69
	Brule River	19	1700	0.0 to 13000	2900	170
	Eagle Harbor	4	290	0.0 to 700	300	100
Over-water Atmospheric Stations	Empire Michigan	4	2000	520 to 4800	2000	100
	GB17	1	2300	NA	NA	NA
	GB24M	1	680	NA	NA	NA
	1	1	750	NA	NA	NA
	5	1	1500	NA	NA	NA
	23M	1	360	NA	NA	NA
	380	1	510	NA	NA	NA

NA = Not applicable

Table 3-19. Monthly Composite Concentrations of *trans*-Nonachlor Measured in Precipitation Samples Collected around Lake Michigan from April 1994 to October 1995

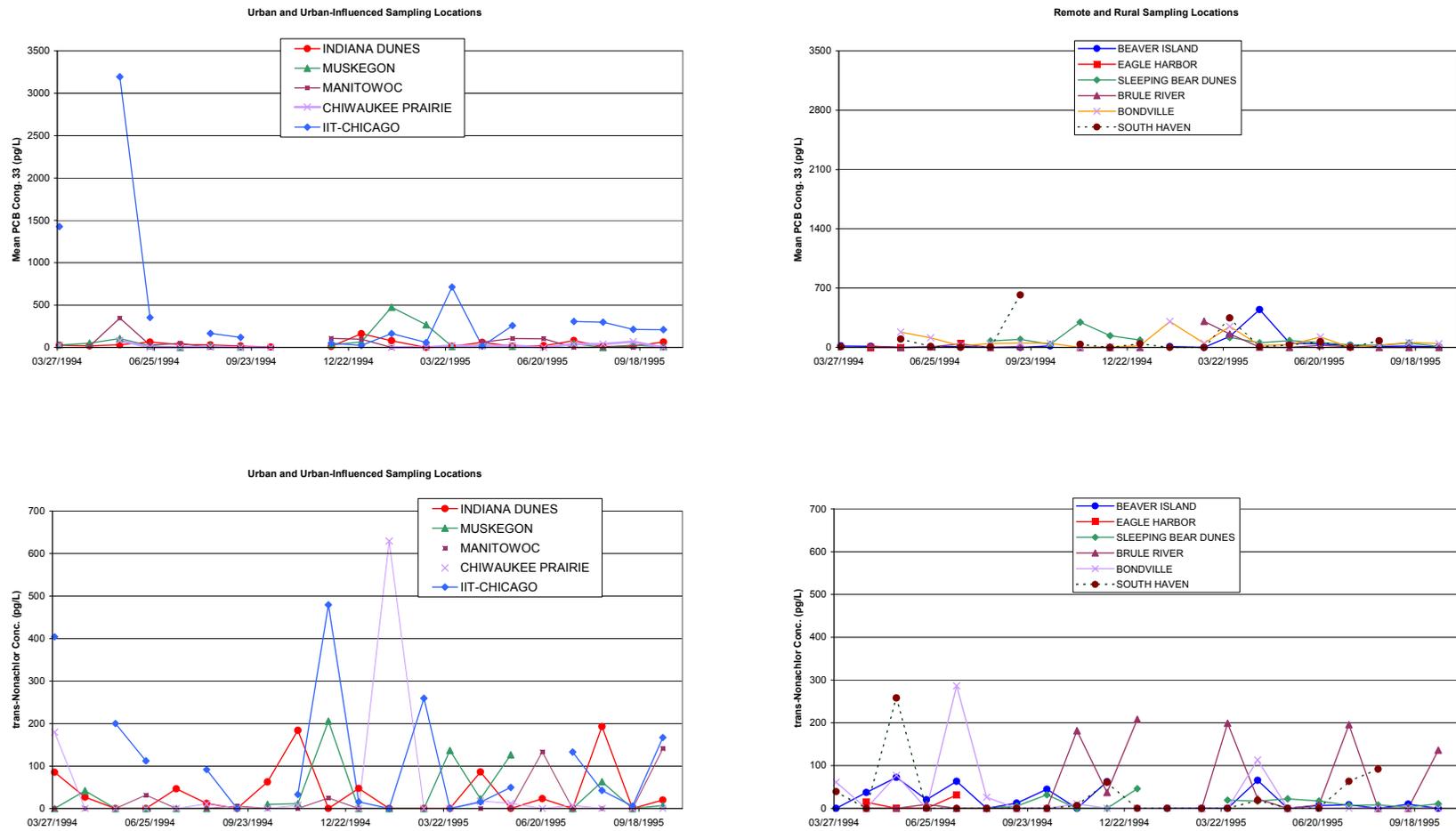
Sampling Station		N	VW Mean (pg/L)	Mean (pg/L)	Range (pg/L)	SD (pg/L)	RSD (%)	% Below DL
Shoreline Atmospheric Stations	Beaver Island	20	18	20	0.0 to 73	27	130	80
	Chiwaukee Prairie	20	11	43	0.0 to 630	140	330	90
	IIT Chicago	17	100	120	0.0 to 480	140	120	41
	Indiana Dunes	21	26	37	0.0 to 190	58	150	76
	Manitowoc	20	17	17	0.0 to 140	42	250	90
	Muskegon	19	27	33	0.0 to 210	59	180	79
	Sleeping Bear Dunes	14	12	13	0.0 to 46	13	100	100
	South Haven	21	13	26	0.0 to 260	59	230	76
Out-of-basin Atmospheric Stations	Bondville	21	29	27	0.0 to 290	67	250	76
	Brule River	19	37	53	0.0 to 210	82	160	79
	Eagle Harbor	4	14	11	0.0 to 31	15	130	75
Over-water Atmospheric Stations	Empire Michigan	4	16	39	0.0 to 130	62	160	100
	GB17	1	0.0	0.0	NA	NA	NA	100
	GB24M	1	0.0	0.0	NA	NA	NA	100
	1	1	20	20	NA	NA	NA	100
	5	1	69	69	NA	NA	NA	100
	23M	1	13	13	NA	NA	NA	100
	380	1	0.0	0.0	NA	NA	NA	100

NA = Not applicable

3.1.3.1 Temporal Variation

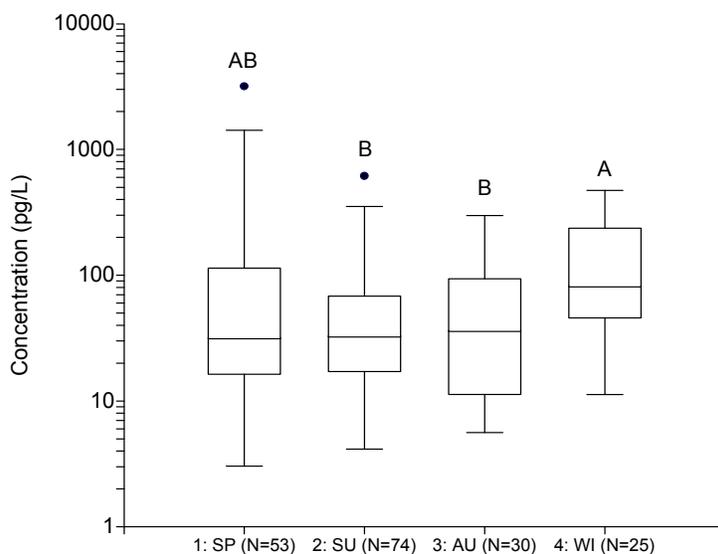
The PCB congeners and total PCBs exhibited no clear temporal trends in the precipitation samples collected at any of the stations. Figure 3-12 presents the results for PCB 33 and *trans*-nonachlor over the course of the LMMB Study, by station, differentiating the urban and urban-influenced stations from the rural and remote stations. The results for PCB 33 at the IIT Chicago site in May 1994 are 5 - 10 times higher than any other result for this congener throughout the study. Although there are several results for *trans*-nonachlor that are higher than those from the IIT Chicago site in May 1994, the results for *trans*-nonachlor exhibit the same sharp decline from May 1994 to June 1994 as was seen for the PCB 33 results at the same site.

Figure 3-12. Temporal Variation in Precipitation PCB 33 (top) and *trans*-Nonachlor (bottom) Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from March 1994 to October 1995



There is a significant difference in the concentrations of PCB 33 in precipitation among seasons ($p=0.0248$, ANOVA, with Tukey pairwise comparisons) (Figure 3-13). Concentrations are significantly higher in winter than in summer and autumn. The variability during all four seasons is large enough that there is considerable overlap in the box plots.

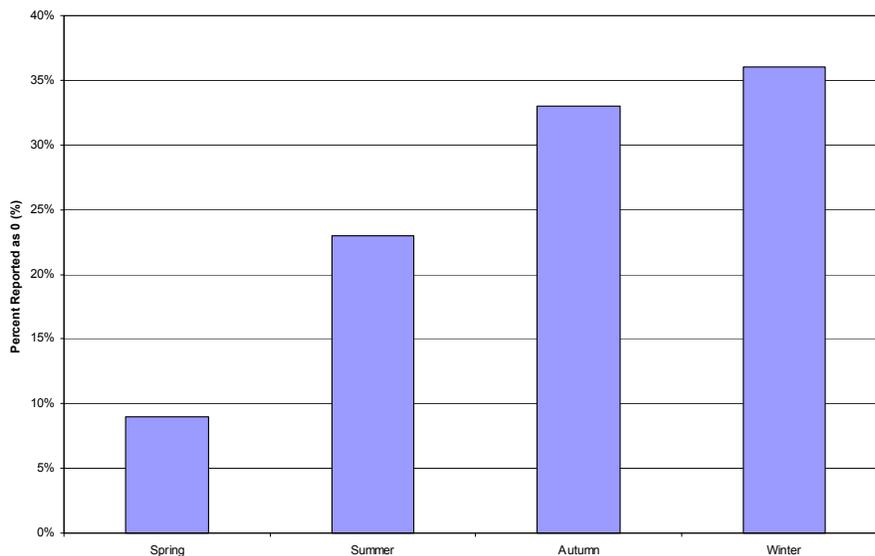
Figure 3-13. Seasonal Patterns of PCB 33 Concentrations in Precipitation Measured at Lake Michigan Shoreline and Out-of-basin Stations from March 1994 to October 1995



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range ($IQR=75th-25th$ percentile) away from the nearest edge of the box. Circles represent results beyond $1.5 \times IQR$ from the box. The letters (A - D) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at $\alpha = 0.05$). Concentration is plotted on a log scale.

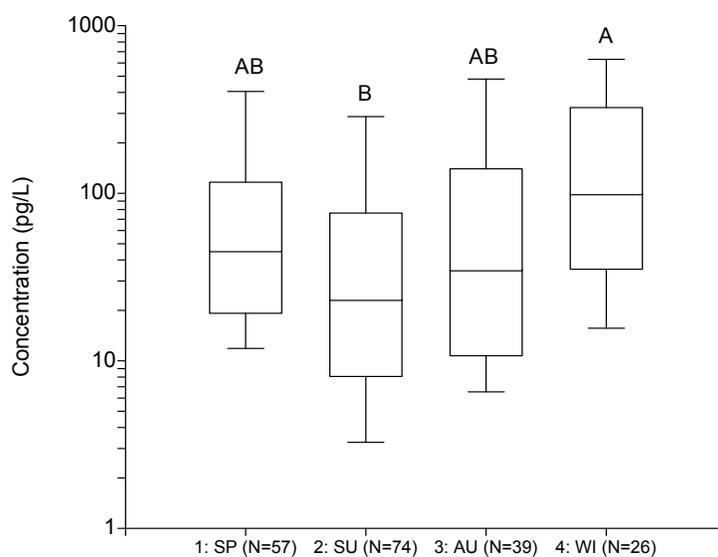
Additionally, there is difference for the seasons in the percentage of samples with results for PCB 33 reported as zero (Figure 3-14). There is a clear and substantial increase in the percent of such samples from spring to winter. These differences were significant based on a Chi-square test at $\alpha=0.05$ ($p=0.0201$). This is notable, given that the concentration of PCB 33 is significantly higher in winter than summer and autumn, even though more winter samples were reported as zero.

Figure 3-14. Percent of Precipitation PCB 33 Sample Results Reported as Zero, by Season



The concentrations of *trans*-nonachlor also showed a significant difference among seasons (Figure 3-15). The winter concentrations of *trans*-nonachlor are significantly higher than the summer concentrations. Spring and Autumn concentrations are not significantly different from one another, or from either winter or summer.

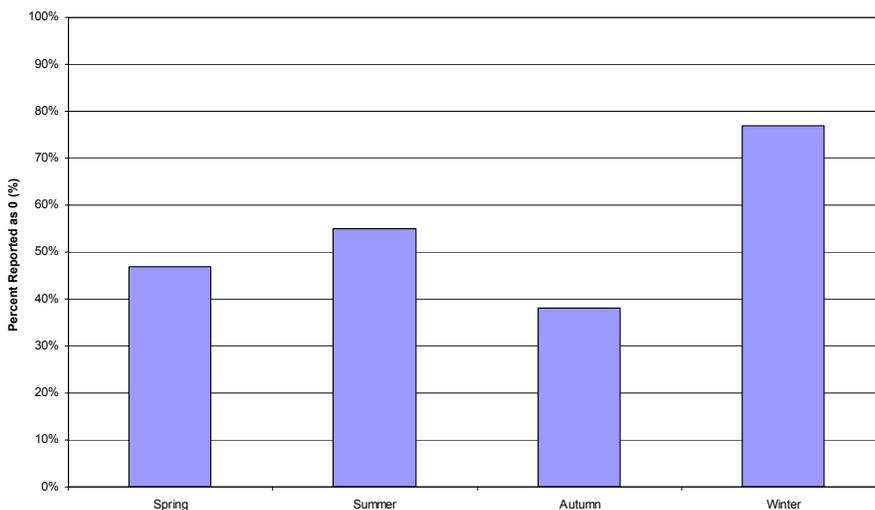
Figure 3-15. Seasonal Patterns of *trans*-Nonachlor Concentrations in Precipitation Measured at Lake Michigan Shoreline and Out-of-basin Stations from March 1994 to October 1995



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The letters (A - D) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Concentration is plotted on a log scale.

The overall percentage of samples reported as zero for *trans*-nonachlor is much higher than for PCB 33. Figure 3-16 shows the relationship with season, which is not as clear as for PCB 33. These differences were significant, based on a Chi-square test at $\alpha=0.05$ ($p=0.0173$).

Figure 3-16. Percent of Precipitation *trans*-Nonachlor Sample Results Reported as Zero, by Season



3.1.3.2 Geographical Variation

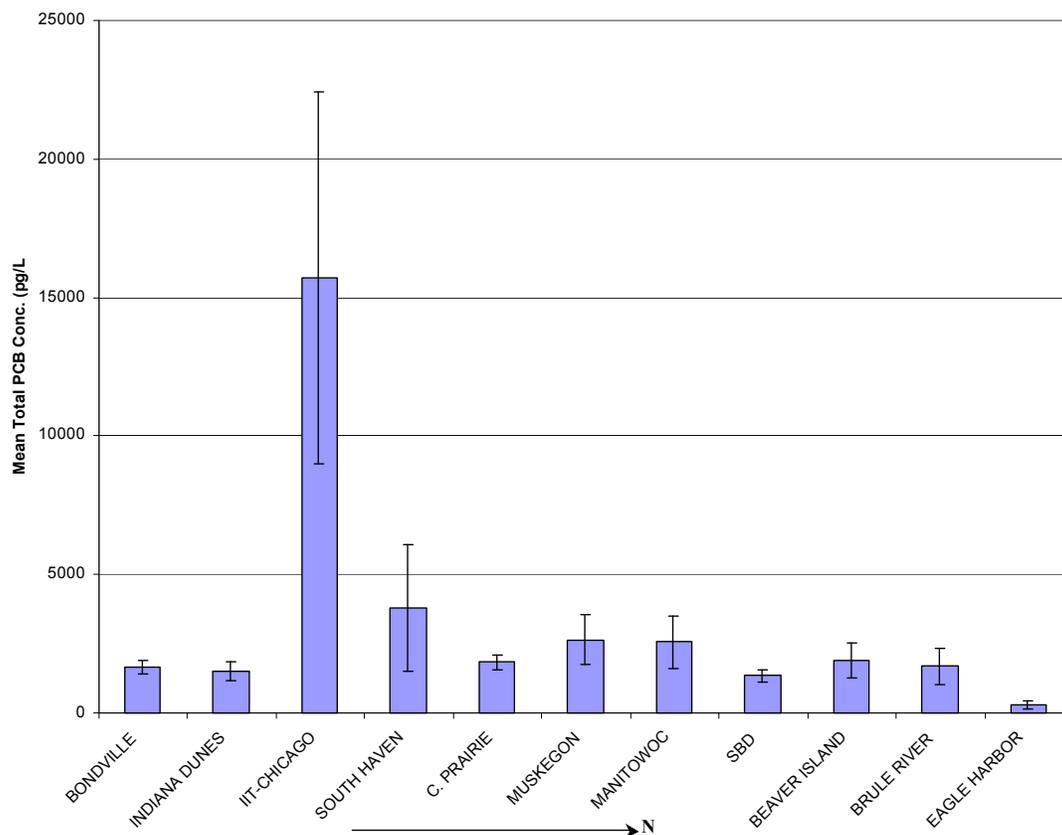
Precipitation PCB congener and total PCB concentrations varied by sampling station. Table 3-20 provides the mean composite sample concentration, the range, and the RSD, for the precipitation samples collected in the LMMB Study. The urban and urban-influenced sites had higher mean monthly composite concentrations for the duration of the study period than remote sites, consistent with the hypothesis that urban and urban-influenced areas contain significant sources of PCBs. However, the mean results for total PCBs and PCB 33 in the precipitation samples from the rural sites are higher than those for both the remote and the urban-influenced sites. The results for precipitation differ from those for the vapor-phase and particulate-phase, where the remote sites showed higher than anticipated concentrations of PCBs, suggesting that the unknown source near the Beaver Island site did not have an effect on PCB concentrations in precipitation.

Table 3-20. Mean Precipitation Concentrations of Total PCB, PCB 33 and *trans*-Nonachlor at LMMB Study Sampling Stations in and around Lake Michigan between March 1994 and October 1995

Precipitation Parameter	Sampling Station Type		N	Mean (pg/L)	Range (pg/L)	RSD (%)
Total PCBs	Shoreline	Urban	17	15800	0.0 to 110,000	180
		Urban-influenced	81	2100	0.0 to 19,000	140
		Rural	21	3800	0.0 to 48,000	280
		Remote	36	1600	0.0 to 11,000	130
		Overall	155	3700	0.0 to 110,000	290
	Over-water		10	1400	361 to 4,800	100
	Out-of-basin		44	1500	0.0 to 13,000	130
PCB 33	Shoreline	Urban	16	470	15 to 3,200	170
		Urban-influenced	73	44	0.0 to 4,700	170
		Rural	19	74	0 to 620	210
		Remote	33	60	0.0 to 450	150
		Overall	141	100	0.0 to 3,200	310
	Over-water		10	11	0.0 to 36	120
	Out-of-basin		41	50	0.0 to 310	160
<i>trans</i> -Nonachlor	Shoreline	Urban	17	120	0.0 to 480	120
		Urban-influenced	80	33	0.0 to 630	260
		Rural	21	26	0.0 to 260	230
		Remote	34	17	0.0 to 73	130
		Overall	152	38	0.0 to 630	230
	Over-water		10	26	0.0 to 130	170
	Out-of-basin		44	37	0.0 to 290	200

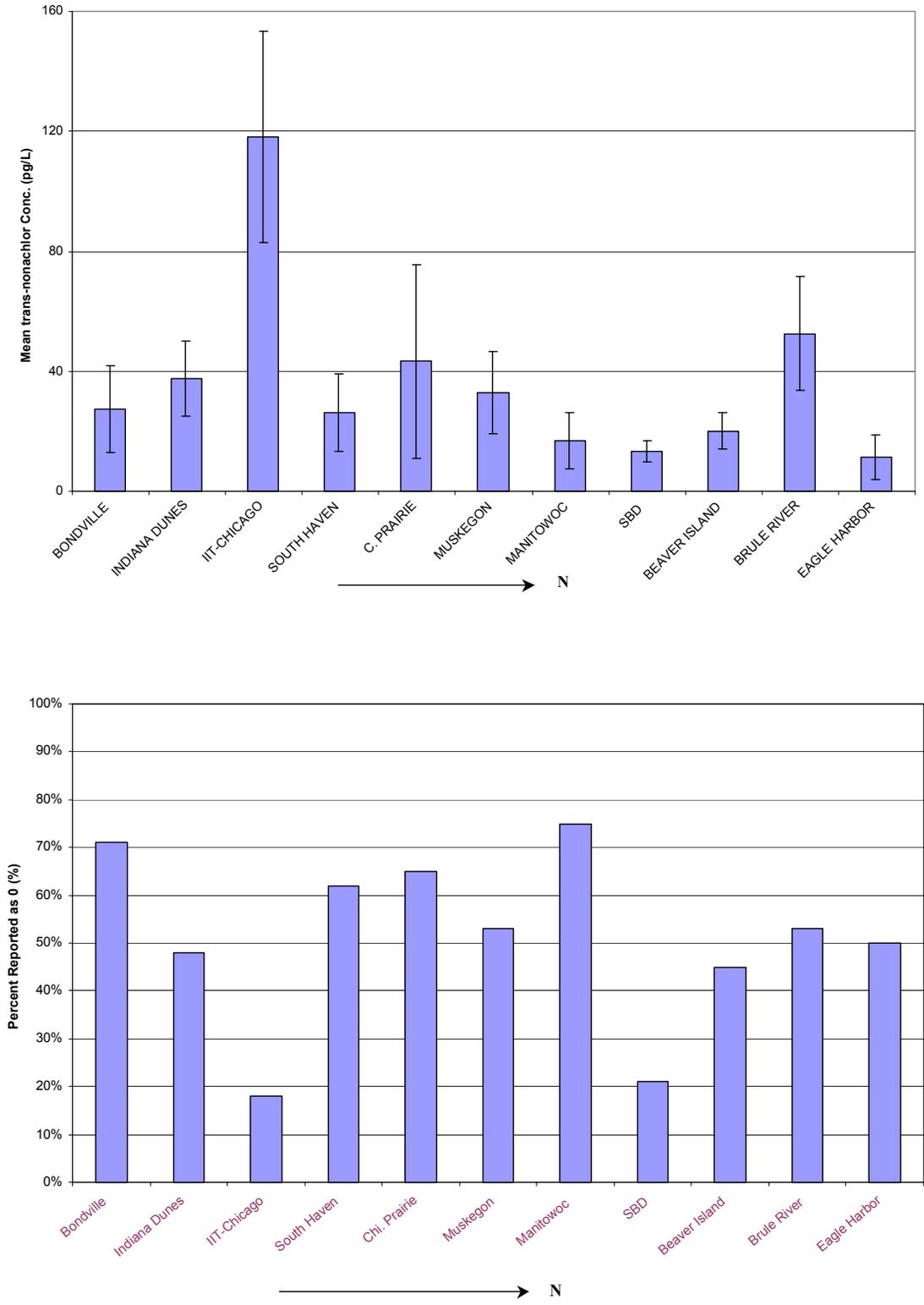
Although there is a general decrease in precipitation total PCB concentrations moving north from the high concentrations observed at the IIT Chicago site, the variability in the data for the stations does not reveal a clear trend (Figure 3-17).

Figure 3-17. Precipitation-phase Total PCB Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from March 1994 to October 1995



The top portion of Figure 3-18 is a similar plot of *trans*-nonachlor concentrations in precipitation by station. Again, aside from the general decrease in the concentrations north of the IIT Chicago site, there is not a prominent trend by latitude. The bottom portion of Figure 3-18 presents the percentage of precipitation samples in which *trans*-nonachlor was reported as zero. In general, the sites with lower mean concentrations of *trans*-nonachlor in precipitation had higher percentages of sample reported as zero. Conversely, the IIT Chicago site had the highest mean concentration in precipitation and the lowest percentage of results reported as zero. The Sleeping Bear Dunes site also had a low percentage of results reported as zero, although it had one of the lowest mean concentrations in this study.

Figure 3-18. Precipitation-phase *trans*-Nonachlor Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from March 1994 to October 1995 (top) and the Percent of Sample Results Reported as Zero for each Sampling Location (bottom)



3.1.4 Dry Deposition

Dry deposition samples were collected from a limited number of sites during the LMMB Study using the procedures described in Chapter 2. The frequencies of occurrence of the PCB congeners varied greatly. Table 3-21 presents the results for the dry deposition samples from this study. The total number of samples is shown for each station as “N,” along with the mean concentration, range, standard deviation, and relative standard deviation (RSD). The mean concentrations were calculated using the results reported by each laboratory (substitution of the detection limit or other value was not used for results below the sample-specific detection limits).

Note that the units for the dry deposition samples differ significantly from those for the vapor-phase and particulate-phase samples. Based on the manner in which the samples are collected, dry deposition results are reported here in terms of mass per unit area, in ng/m^2 , not the mass per unit volume units of pg/m^3 used for the other phases. Also, PCB 33 was not measured in the dry deposition samples.

Dry-deposition PCB congener concentrations ranged from 140 ng/m^2 for PCB 118 at the IIT Chicago sampling station to over 3 million ng/m^2 for PCB 180 at the South Haven sampling station. Total PCBs in the dry deposition samples exhibited a similar range. Mean concentrations for PCBs in dry deposition ranged from 450 ng/m^2 at the IIT Chicago station to 1.5 million ng/m^2 at the South Haven station. Mean concentration for dry deposition total PCBs ranged from 1800 ng/m^2 at the Chicago SWFP crib intake to 320,000 ng/m^2 at the South Haven station.

The analysis of the dry deposition samples presented more difficulties than the other phases studied. As a result, a larger proportion of data for the dry deposition samples were qualified or found invalid, thereby complicating the summary statistics shown in Table 3-21. In some cases, only one sample had valid results for a specific PCB congener, such that a range and standard deviation could not be determined. In addition the very high concentrations of PCB 180 observed in a few samples at the South Haven station significantly skew the mean, range, and standard deviations reported in Table 3-21 for this congener and for the total PCBs.

The frequencies at which the PCB congeners were found above the sample-specific detection limits also varied greatly by congener. PCB 118 was found below the detection limit in 33 to 100% of the dry deposition samples, while there were fewer valid results for PCB 180 above the detection limit (Table 3-21).

trans-Nonachlor was reported in many of the dry deposition samples, but generally at lower concentrations than the PCBs (Table 3-21). The concentration of *trans*-nonachlor in dry deposition samples ranged from 0 ng/m^2 at South Haven to 209 ng/m^2 at the Chicago SWFP Crib Intake. Most of the results for *trans*-nonachlor were reported as being below the sample-specific detection limits (e.g., 60 to 100%).

Table 3-21. Monthly Composite Concentrations of PCBs and *trans*-Nonachlor Measured in Dry Deposition

Parameter	Sampling Station	N	Mean (ng/m ³)	Range (ng/m ³)	SD (ng/m ³)	RSD (%)	% Below DL
PCB 118	Chicago SWFP Crib Intake	2	604	534 to 674	99.0	16	50
	IIT Chicago	7	453	144 to 919	296	65	100
	Sleeping Bear Dunes	3	745	524 to 1160	360	48	33
PCB 180	IIT Chicago	1	3220	NA	NA	NA	0
	Sleeping Bear Dunes	1	884	NA	NA	NA	0
	South Haven	2	1,580,000	5240 to 3,160,000	2,230,000	141	0
Total PCBs	Chicago SWFP Crib Intake	9	1830	324 to 5150	1710	94	NC
	Harrison Crib	1	5400	NA	NA	NA	NC
	IIT Chicago	13	7060	1720 to 23,500	6480	92	NC
	Sleeping Bear Dunes	8	6120	48.6 to 19,600	7940	130	NC
	South Haven	11	315,000	109 to 3,380,000	1,020,000	323	NC
<i>trans</i> -Nonachlor	Chicago SWFP Crib Intake	9	78.2	34.8 to 209	52.0	66	89
	IIT Chicago	5	64.8	0.00 to 100	40.6	63	60
	Sleeping Bear Dunes	3	39.4	18.2 to 55.2	19.1	48	100
	South Haven	4	25.7	0.00 to 58.5	30.0	118	75

NA = Not applicable. Only one result was reported.

NC = Not calculated. The total PCB concentration is the sum of the results for the individual PCB congeners, each of which has a sample-specific detection limit. However, detection limits are not additive, so there is no meaningful way to specify a detection limit for total PCBs.

3.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the PCBs and *trans*-nonachlor monitoring portion of the study are further described in Section 2.7 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in the Lake Michigan Mass Balance Study Quality Assurance Report (USEPA, 2001b). A brief summary of data quality issues for the atmospheric PCBs and *trans*-nonachlor data is provided below.

As discussed in Section 2.5, because data comparability was important to the successful development of the mass balance model, the PIs used similar sample collection, extraction, and analysis methods for the PCB and *trans*-nonachlor monitoring in this study. For a small portion of the study (June 15, 1994 to September 22, 1994), a revision to the silica gel clean-up procedure for the determination of PCBs in precipitation and particulate phases resulted in coelution of PCB 99 with *trans*-nonachlor. Affected sample results are qualified with the high bias flag (HIB) in the database.

The PIs used surrogate spikes to monitor the bias of the analytical procedure. Analytical results for PCBs in vapor, precipitation, and particulate phases were corrected for surrogate recoveries. Analytical results for PCBs in dry deposition were *not* corrected for surrogate recoveries because the recoveries of the surrogates (PCB 14 and PCB 65) were subject to chromatographic interferences. The PI noted that the recoveries were too erratic to be used as reliable indicators of method accuracy. Sample results for PCBs

associated with surrogate recoveries outside the MQO limits were qualified with the failed surrogate spike flag (FSS).

Analytical results for *trans*-nonachlor were not corrected for surrogate recoveries, except for those collected and analyzed by Indiana University (Sleeping Bear Dunes site August 1994 to October 1995). Analytical results were considered invalid (INV) and qualified when surrogate recoveries were less than 10%. Some PCB data were found to be invalid for this reason, but the *trans*-nonachlor surrogate recoveries were never below 10%.

Laboratory matrix spike samples also were used to monitor the bias of the analytical procedure. For the dry deposition analyses, a spiked laboratory solvent blank also was prepared and analyzed. Analytical results associated with matrix spike samples with recoveries below the MQO limits were qualified with the failed matrix spike and low bias flags (FMS and LOB) and results associated with matrix spike samples with recoveries higher than the MQO limits were qualified with the failed matrix spike and high bias flags (FMS and HIB). Analytical results were considered invalid (INV) and qualified when the analyte was undetected and recoveries for associated matrix spike samples were less than 10%. Some PCB data were found to be invalid for this reason, but the *trans*-nonachlor surrogate recoveries were never below 10%.

To characterize contamination associated with field and analytical activities, field blanks were obtained for precipitation, particulate, and vapor samples at a subset of monitoring stations, and for dry deposition strips. For precipitation, particulate, and vapor samples, filters and/or absorbent were installed in the samplers for the normal sampling period but were not exposed to precipitation or air flow. The precipitation field blank included a water rinse of the collector surfaces to check for contamination by dry-deposited material that might have penetrated the cover and seal on the precipitation collector. Field blanks were not collected at all stations and potential station-specific contamination associated with these sites cannot be evaluated. However, contamination associated with sample collection, sampling equipment, sample processing, shipping, storing, and analysis can be evaluated based on the field blanks collected throughout the study.

PCB congeners were detected in all field blanks in all sample phases. This is not unexpected given the ubiquitous nature of PCBs in the environment. For *trans*-nonachlor determinations, 80% of the field blank results contained detectable concentrations of *trans*-nonachlor. When field blank concentrations were within a factor of five of the concentration in an associated sample, the sample result was qualified with the failed field blank flag (FFR) and also with the high bias flag (HIB). When sample concentrations were indistinguishable from the associated field blank concentration, samples were determined to be invalid and were qualified as such (INV). For PCBs in dry deposition, 30% of sample results were qualified as invalid, based on field blank contamination. For *trans*-nonachlor, 23% of the sample results for all phases were qualified as invalid, based on field blank contamination. Due to contaminated field blanks and variable sample results for field duplicates, many of the PCB results for samples collected from the bow of the *R/V Lake Guardian* in 1994 were determined to be invalid and are qualified as such, based on the potential for a shipboard source of PCB contamination (Miller, 1999). Samples collected from the yardarm of the *R/V Lake Guardian* and samples collected in 1995 were not affected.

For dry deposition samples, field blanks were collected with each sample and exposed to ambient conditions only for the length of time (<30 minutes) required to set up the routine dry deposition samples. Once the strips for the routine samples were set up, the field blank strips were returned to their sealed containers for the duration of the routine sampling episode. Because each sample had an associated field blank, the surface-area-normalized deposition of PCBs was subtracted from the corresponding field sample to minimize artifacts associated with sorption of gas-phase organic chemicals to the grease coating the deposition strips. When normalized to exposed surface area, the field blanks for land sites (n=35)

averaged 5100 ng/m² for total PCBs and the blanks for over-water sites (n=11) averaged 4700 ng/m² (Franze *et al.*, 1998).

Laboratory blanks were prepared and analyzed for PCBs and *trans*-nonachlor in all phases. PCB congeners were detected in all laboratory blanks in all sample phases. For example, all results reported for PCB 1 for samples analyzed at Illinois Water Survey were determined to be invalid by the PI, based on erratic laboratory background. Thus, the PCB 1 results were not included in the reported total PCB concentrations. When laboratory blank contamination was greater than the method detection limit, all of the associated results were qualified with failed blank sample (FBS) and high bias (HIB). No laboratory blanks contained *trans*-nonachlor above the method detection limit.

As discussed in Section 2.7, data verification was performed by comparing all field and QC sample results produced by each PI with the MQOs and with overall LMMB Study objectives. Analytical results were qualified when pertinent QC sample results did not meet the acceptance criteria defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Tables 3-22 to 3-24 summarize the flags applied to the atmospheric PCB and *trans*-nonachlor data generated by each of the PIs involved in the analysis of atmospheric samples. Table 3-23 addresses data generated at the Illinois Water Survey. Table 3-23 addresses data generated at Indiana University. Table 3-24 addresses data generated for dry deposition samples. Qualifier flags were not applied to the data for total PCBs because they were the results of calculations rather than laboratory analyses.

The summary tables include the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but do not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.7. As noted throughout this report, given the large number of PCB congeners that were determined by the investigators in this study, it is not practical to summarize the results for every congener.

As illustrated in Tables 3-23 and 3-24 and discussed in previous sections, PCB congeners and *trans*-nonachlor were not detected in a substantial portion of precipitation samples. Particulate and vapor samples more frequently contained PCB congeners and *trans*-nonachlor above detection limits than precipitation samples. Fifty-one percent of precipitation samples analyzed at Illinois Water Survey (Table 3-22) contained PCB 33 below detection limits and were qualified with the MDL flag (less than method detection limit) and 25% were qualified with the UND flag (analyte not detected). Sixty-four percent of precipitation samples analyzed at Indiana University (Table 3-23) contained PCB 180 below detection limits and were qualified with the MDL flag and PCB 180 was not detected in 21% of precipitation samples.

Of the three PCB congeners, PCB 33 was most frequently below detection limits for precipitation samples analyzed at Illinois Water Survey, whereas PCB 180 was most frequently below detection limits for precipitation samples analyzed at Indiana University.

Table 3-22. Field Sample Flags Applied to Select PCB Congeners and *trans*-Nonachlor Results in Atmospheric Samples Analyzed at Illinois Water Survey

Analyte	Fraction	Flags										
		Sensitivity		Contamination		Holding Time	Precision	Bias				Invalid
		MDL	UND	FFR	FBS	EHT	FFD	FPC	FSS	FMS	HIB	INV
PCB 33	Particulate	5% (11)	0.5% (1)	0.5% (1)	0	0.5% (1)	0	2% (5)	0.5% (1)	4% (8)	0	5% (11)
	Precipitation	51% (91)	25% (44)	0	0	46% (82)	1% (2)	0	1% (2)	5% (9)	0	0
	Vapor	0.8% (2)	0.8% (2)	0	3% (8)	5% (13)	0.4% (1)	6% (16)	0.8% (2)	0	0	8% (19)
PCB 118	Particulate	2% (5)	0	1% (3)	0	0.5% (1)	0	2% (5)	0.5% (1)	0	0	5% (11)
	Precipitation	11% (20)	0.6% (4)	0	5% (8)	46% (81)	0.6% (1)	0	0.6% (1)	0	0	0
	Vapor	0	0	0	16% (42)	5% (13)	1% (4)	6% (16)	1% (3)	0	0	7% (19)
PCB 180	Particulate	8% (18)	0.9% (2)	0.5% (1)	11% (23)	0.5% (1)	0	2% (5)	0.5% (1)	0	0	5% (11)
	Precipitation	28% (50)	5% (8)	0	10% (18)	46% (82)	0.6% (1)	0	0.6% (1)	0	0	0
	Vapor	1% (4)	1% (3)	0.4% (1)	34% (91)	5% (13)	1% (3)	6% (16)	1% (3)	0	0.4% (1)	7% (19)
<i>trans</i> -nonachlor	Particulate	35% (75)	16% (34)	0	0	0.5% (1)	0	0	0	0	0	0
	Precipitation	78% (151)	55% (106)	0	0	0.5% (1)	0	0	0	14% (27)	0	0
	Vapor	8% (21)	7% (19)	0.7% (2)	0	0.7% (2)	0.7% (2)	0	0	3% (8)	0	0

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

MDL = Less than method detection limit (Analyte produced an instrument response but reported value is below the calculated method detection limit. Validity of reported value may be compromised.)

UND = Analyte not detected (Analyte produced no instrument response above noise.)

FFR = Failed field blank (A field blank sample, type unknown, associated with this analysis failed the acceptance criteria. It is unknown whether the blank that failed was a field blank or a lab blank. Validity of reported value may be compromised.)

FBS = Failed blank sample (A blank sample associated with this analysis failed the acceptance criteria. It is unknown whether the blank that failed was a field blank or a lab blank. Validity of reported value may be compromised.)

EHT = Exceeded holding time (Sample or extract was held longer than the approved amount of time before analysis. Validity of reported value may be compromised.)

FFD = Failed field duplicate (A field duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)

FPC = Failed performance check (A laboratory performance check sample associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)

FSS = Failed surrogate (Surrogate recoveries associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)

FMS = Failed matrix spike (A matrix spike associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)

HIB = Likely biased high (Reported value is probably biased high as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery, blank contamination, or other internal lab QC data. Reported value is not considered invalid.)

INV = Reported value is deemed invalid by the QC Coordinator.

Table 3-23. Field Sample Flags Applied to Select PCB Congener and *trans*-Nonachlor Results in Atmospheric Samples Analyzed at Indiana University

Analyte	Fraction	Flags										
		Sensitivity		Contamination		Holding Time	Precision	Bias				Invalid
		MDL	UND	FFR	FBS	EHT	FFD	FPC	FSS	FMS	LOB	HIB
PCB 33	Particulate	7% (1)	0	21% (3)	0	0	0	NA	0	0	0	0
	Precipitation	7% (1)	0	7% (1)	14% (2)	0	7% (1)	NA	0	0	7% (1)	0
	Vapor	0	0	19% (5)	62% (16)	0	0	NA	0	0	4% (1)	19% (5)
PCB 118	Particulate	43% (6)	0	14% (2)	1	0	0	NA	0	0	0	0
	Precipitation	57% (8)	0	7% (1)	1	0	0	NA	0	0	7% (1)	0
	Vapor	4% (1)	0	23% (6)	6	0	12% (3)	NA	0	0	4% (1)	12% (3)
PCB 180	Particulate	21% (3)	36% (5)	0	7% (1)	0	0	NA	0	0	0	0
	Precipitation	64% (9)	21% (3)	7% (1)	7% (1)	0	7% (1)	NA	0	0	7% (1)	0
	Vapor	4% (1)	31% (8)	12% (3)	8% (2)	0	23% (6)	NA	0	8% (2)	4% (1)	0
<i>trans</i> -nonachlor	Particulate	25% (1)	50% (2)	0	0	0	0	NA	25% (1)	0	0	0
	Precipitation	79% (11)	21% (3)	7% (1)	0	0	0	NA	0	29% (4)	7% (1)	0
	Vapor	26% (9)	0	0	0	3% (1)	0	NA	15% (5)	5	3% (1)	6% (2)

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

- MDL = Less than method detection limit (Analyte produced an instrument response but reported value is below the calculated method detection limit. Validity of reported value may be compromised.)
- UND = Analyte not detected (Analyte produced no instrument response above noise.)
- FFR = Failed field blank (A field blank sample, type unknown, associated with this analysis failed the acceptance criteria. It is unknown whether the blank that failed was a field blank or a lab blank. Validity of reported value may be compromised.)
- FBS = Failed blank sample (A blank sample associated with this analysis failed the acceptance criteria. It is unknown whether the blank that failed was a field blank or a lab blank. Validity of reported value may be compromised.)
- EHT = Exceeded holding time (Sample or extract was held longer than the approved amount of time before analysis. Validity of reported value may be compromised.)
- FFD = Failed field duplicate (A field duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- FPC = Failed performance check (A laboratory performance check sample associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- FSS = Failed surrogate (Surrogate recoveries associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- FMS = Failed matrix spike (A matrix spike associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- LOB = Likely biased low (Reported value is probably biased low as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery or other internal lab QC data. Reported value is not considered invalid.)
- HIB = Likely biased high (Reported value is probably biased high as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery, blank contamination, or other internal lab QC data. Reported value is not considered invalid.)
- NA = This flag was not applied to this data set or this type of QC sample was not prepared and analyzed.

Table 3-24. Field Sample Flags Applied to Select PCB Congener and *trans*-Nonachlor Results in Dry Deposition Atmospheric Samples

Analyte	Flags									
	Sensitivity		Contamination		Holding Time	Precision	Bias			Invalid
	MDL	UND	FFB	EHT	FFD	FMS	FSS	HIB	FPC	INV
PCB118	37% (15)	0	68% (28)	2% (1)	0	49% (20)	0	27% (11)	0	68% (28)
PCB180	0	0	90% (38)	2% (1)	0	48% (20)	0	48% (20)	0	90% (38)
<i>trans</i> -nonachlor	70% (28)	8% (3)	48% (19)	3% (1)	0	10% (4)	0	0	0	48% (19)

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

- MDL = Less than method detection limit (Analyte produced an instrument response but reported value is below the calculated method detection limit. Validity of reported value may be compromised.)
- UND = Analyte not detected (Analyte produced no instrument response above noise.)
- FFB = A field matrix blank associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.
- EHT = Exceeded holding time (Sample or extract was held longer than the approved amount of time before analysis. Validity of reported value may be compromised.)
- FFD = Failed field duplicate (A field duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- FMS = Failed matrix spike (A matrix spike associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- FSS = Failed surrogate (Surrogate recoveries associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- HIB = Likely biased high (Reported value is probably biased high as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery, blank contamination, or other internal lab QC data. Reported value is not considered invalid.)
- FPC = Failed performance check (A laboratory performance check sample associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- INV = Reported value is deemed invalid by the QC Coordinator.

Note: PCB 33 was not determined in the dry deposition samples.

For dry deposition samples, 37% contained PCB 118 below detection limits and were qualified with the MDL flag. However, PCB 118 was detected in all of the samples (i.e., none of the sample results were qualified with the undetected flag). For *trans*-nonachlor, 78% of the precipitation samples analyzed at Illinois Water Survey contained *trans*-nonachlor below detection limits and were qualified the MDL flag and in 55% of precipitation samples *trans*-nonachlor was not detected. Seventy-nine percent of precipitation samples analyzed at Indiana University contained *trans*-nonachlor below detection limits and were qualified the MDL flag and in 21% of samples *trans*-nonachlor was not detected. Seventy percent of dry deposition samples contained *trans*-nonachlor below detection limits and in 8% of dry deposition samples, *trans*-nonachlor was not detected.

A substantial portion of precipitation samples were flagged for exceeding sample holding times for determination of PCB congeners. For example, 46% of precipitation samples analyzed for PCB congeners at Illinois Water Survey exceeded the established holding time. However, the holding times for PCBs and many other environmental pollutants are not well-established and the effects on the sample results generally are not known. PCBs are highly stable compounds and loss or degradation is considered minimal even after 12 months if the samples are stored frozen. Loss or degradation rates may vary among congeners, depending on the mechanism (e.g., biological transformation, evaporative loss, or photolysis).

To characterize contamination associated with field and analytical activities, field blanks were obtained for precipitation, particulate, and vapor samples at a subset of monitoring stations, and for dry deposition strips.

For the analyzed at Illinois Water Survey, 1% or less of sample results for PCBs and *trans*-nonachlor were associated with field blanks that showed significant contamination and were qualified with the failed field blank flag. A single result for PCB 180 in a vapor sample also was qualified with the high bias flag due to this contamination. For the vapor samples analyzed at Indiana University, 23 % or less of sample results were associated with field blanks that showed significant contamination and were qualified with the failed field blank and high bias flags. Laboratory blanks also showed contamination for PCB congeners in all phases. Vapor samples were most frequently flagged for laboratory blank contamination with 62% of vapor sample results for PCB 33 generated at Indiana University being qualified with the failed laboratory blank flag and 34% of sample results for PCB 180 generated at Illinois Water Survey being qualified with the failed laboratory blank flag. As a result of contamination, 19% of the vapor sample results for PCB 33 also were qualified the high bias flag.

Contamination was a significant issue for PCB congeners and *trans*-nonachlor in dry deposition samples. The majority of dry deposition sample results are flagged for contamination and invalidated. Invalid sample results will not be used in the LMMB model. Due to the ubiquitous nature of PCBs, contamination can be an issue when analyzing samples with concentrations close to the method detection limit. Overall, the large majority of sample results were not affected by contamination.

Field duplicates were collected and analyzed for all phases. Although field duplicates were not planned for dry deposition, one field duplicate was collected. However, the dry deposition field duplicate was not used to evaluate study data. For the samples analyzed at Illinois Water Survey, less than 1% of all the field samples had associated duplicates with results outside the MQO limit and thus were qualified with the failed field duplicate flag. For the samples analyzed at Indiana University, 23% of vapor samples analyzed for PCB 180 had associated field duplicates with results outside the MQO limit and were qualified with the failed field duplicate flag. Only one precipitation sample for PCB 180 and one for PCB 33 had an associated field duplicate outside the MQO limit.

Matrix spike samples results showed acceptable results for the large majority of study samples in all phases, except for dry deposition. For samples analyzed at Illinois Water Survey, all of the spike

recoveries for all sample results for PCB 118 and PCB 180 in all phases were within MQO limits. For *trans*-nonachlor, 14% of the precipitation sample results were qualified with the failed matrix spike flag for samples analyzed at Illinois Water Survey. For samples analyzed at Indiana University, all of the spike recoveries for all sample results for PCB 33 and PCB 118 in all phases were within MQO limits. For *trans*-nonachlor, 29% of precipitation sample results were qualified with the failed matrix spike flag for samples analyzed at Indiana University. For analysis of PCBs and *trans*-nonachlor in dry deposition samples, matrix effects presented analytical difficulties and 48% of the sample results were qualified with the failed matrix spike flag for PCB 180 and 10% for *trans*-nonachlor.

Surrogate recoveries indicated acceptable results for the large majority of study samples. Of the results for PCBs 33, 118, and 180 generated at the Illinois Water Survey, at most 1% of the vapor, precipitation, and particulate samples were qualified with the failed surrogate spike flag (FSS). None of the *trans*-nonachlor results generated at the Illinois Water Survey failed the surrogate recovery limits. None of the results for PCBs 33, 118, or 180 analyzed at Indiana University failed the surrogate recovery limits, but 15% of the vapor samples and 25% of the particulate-phase samples analyzed there for *trans*-nonachlor failed the surrogate recovery limits. As noted earlier in this section, the surrogate recoveries for the dry deposition results were erratic and subject to interferences. As a result, no results for dry deposition samples were qualified due to surrogate recovery problems and no surrogate recovery correction was applied to the dry deposition results for any analyte.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived its data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean relative percent difference (RPD) between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean relative percent difference (RPD) between the results for laboratory duplicate pairs. Tables 3-25 to 3-28 provide summaries of data quality assessments for several of these attributes for the data for atmospheric PCB congener 33, 118, and 180 and *trans*-nonachlor.

Data quality assessments were conducted for two separate sets of results: those sample results that are above 5 times the sample specific detection limits and those sample results that are below 5 times the sample specific detection limits. Performing separate assessment illustrates the expected differences in data quality for these sample groups that are due to increased variability in the analytical results when sample concentrations are close to the detection limit of the analytical method. In addition, MQOs often were set and applied differently for sample results that are greater than 5 times the detection limit versus those results that are less than five times the method detection limit.

As discussed in this chapter, a significant number of sample results were below the calculated analytical sample specific method detection limits. Seven percent of precipitation samples analyzed at Indiana University were reported below the MDL and 51% of precipitation samples analyzed at Illinois Water Survey were reported as below the MDL. For PCB 180, 86% of precipitation samples analyzed at Indiana University were below the sample specific detection limits. For study samples that are below detection limits, the variability of sample results is expected to be greater than for sample results that are significantly above the detection limit and in the middle of the calibration range of the analytical method. Data quality assessments based on field duplicates and laboratory duplicates also will reflect increased variability because the sample concentrations are close to or below the detection limits.

System precision, estimated as the mean RPD between field duplicate results, varied by fraction. For example, for PCB 118 particulate-phase samples analyzed at Illinois Water Survey, with results greater than 5 times their associated sample specific MDL, had a mean RPD of 21% and vapor samples analyzed at Illinois Water Survey, with results greater than 5 times their associated sample specific MDL, had a mean RPD of 54%. System precision also varied by the relationship of sample concentrations to the

sample specific detection limits. For example, for vapor-phase samples analyzed at Indiana University for PCB 180, the mean RPD was 42% for sample results less than 5 times the sample specific detection limit and was 22% for sample results greater than 5 times the sample specific detection limit. Similarly, for vapor-phase samples analyzed at Indiana University for *trans*-nonachlor, the mean RPD was 53% for sample results less than 5 times the sample specific detection limit and was 16% for sample results greater than 5 times the sample specific detection limit.

In some cases, the system precision was unexpectedly greater for sample results at higher concentrations. For example, for vapor samples analyzed at Illinois Water Survey, the mean RPD was 21% for sample results less than 5 times the sample specific detection limit and was 40% for sample results greater than 5 times the sample specific detection limit. System precision also varied by congener, although a pattern among congeners was not evident. For example, for precipitation samples analyzed at Indiana University, the mean RPD was 34% for PCB 118 and was 53% for PCB 180, whereas for particulate samples, the mean RPD was 55% for PCB 118 and was 23% for PCB 180. Duplicate pair samples with a reported concentration of zero for either one of both samples could not be used in this assessment. Because of the large number of results reported as zero, the system precision estimate is based on only a small number of field duplicates and may not accurately reflect the system.

Analytical precision, estimated as the mean RPD between laboratory duplicates, only could be estimated for a single particulate sample analyzed at Indiana University (a small number of laboratory duplicates prepared and analyzed for these analytes in the study because of the large expense of these analyses). The RPD between laboratory duplicates of particulate sample was 13% for PCB 33 and 34% for PCB 118. This analytical precision for particulate samples was lower than the mean RPD for system precision, where the mean RPD was 31% for PCB 33 and 55% for PCB 118.

Evaluation of matrix spike sample (LMS) recoveries shows a slight low bias overall for all PCB congeners for phases of atmospheric samples, except dry deposition. For vapor samples, the mean LMS recovery for PCB 33 was 93% for samples analyzed at Indiana University and at the Illinois Water Survey. For PCB 180 in vapor samples, the mean LMS recovery was 94% for samples analyzed at Illinois Water Survey and 96% for samples analyzed at Indiana University. For precipitation samples, the mean LMS recovery for PCB 33 was 86% for samples analyzed at Illinois Water Survey and 91% for samples analyzed at Indiana University. For *trans*-nonachlor, the low bias was more pronounced. For example, for vapor samples, the mean LMS recovery was 80% for samples analyzed at Illinois Water Survey and 70% for samples analyzed at Indiana University.

For dry deposition, a significant high bias was observed based on results of the LMS samples. For PCBs 118 and 180, the mean LMS recoveries were 626% and 10,798 % . For *trans*-nonachlor, the bias was much less extreme, with a mean LMS recovery of 126%. Sample results associated with LMS results that were outside the MQO were qualified with the failed matrix spike and high bias flags. As discussed above, a significant portion of sample results for dry deposition were determined to be invalid based on results of LMS and other QC samples. For the majority of PCB and *trans*-nonachlor results, the PI and QC coordinator determined that the bias demonstrated by results for the LMS and other QC samples was not strong enough to warrant flagging the data as either HIB or LOB. As discussed above, the sample results that are flagged HIB are due, in part, to contamination in field and laboratory blanks.

Table 3-25. Data Quality Assessment for PCB 33 in Atmospheric Samples

Fraction (Lab)	Number of Routine Samples Analyzed	System Precision Mean Field Duplicate RPD (%)		Analytical		
		< 5 * MDL	> 5 * MDL	Precision	Bias	Sensitivity
				Mean Lab Duplicate RPD < 5* MDL	Mean LMS Recovery (%)	Samples reported as < MDL (%)
Vapor (Illinois)	251	(0)	34% (14)	(0)	93% (33)	0.80%
Precipitation (Illinois)	179	72% (3)	(0)	(0)	86% (23)	51%
Particulate (Illinois)	208	31% (10)	(0)	(0)	82% (28)	4.8%
Vapor (Indiana)	26	(0)	16% (13)	(0)	93% (14)	(0)
Precipitation (Indiana)	14	23% (11)	(0)	(0)	91% (14)	7.1%
Particulate (Indiana)	14	31% (8)	(0)	13% (1)	90% (13)	7.1%

The number of QC samples used in the assessment is provided in parentheses.
 RPD= Relative percent difference
 LMS= Laboratory matrix spike

Table 3-26. Data Quality Assessment for PCB 118 in Atmospheric Samples

Fraction (Lab)	Number of Routine Samples Analyzed	System Precision Mean Field Duplicate RPD (%)		Analytical		
		< 5 * MDL	> 5 * MDL	Precision	Bias	Sensitivity
				Mean Lab Duplicate RPD < 5* MDL	Mean LMS Recovery (%)	Samples reported as < MDL (%)
Vapor (Illinois)	251	(0)	54% (14)	(0)	97% (34)	0
Precipitation (Illinois)	179	43% (8)	(0)	(0)	94% (23)	11%
Particulate (Illinois)	208	28% (8)	21% (2)	(0)	94% (28)	2.4%
Vapor (Indiana)	26	45% (7)	34% (6)	(0)	96% (14)	3.9%
Precipitation (Indiana)	14	34% (11)	(0)	(0)	93% (14)	57%
Particulate (Indiana)	14	55% (8)	(0)	34% (1)	95% (13)	43%
Dry deposition	13	(0)	(0)	(0)	626% (5)	69%

The number of QC samples used in the assessment is provided in parentheses.
 RPD= Relative percent difference
 LMS= Laboratory matrix spike

Table 3-27. Data Quality Assessment for PCB 180 in Atmospheric Samples

Fraction (Lab)	Number of Routine Samples Analyzed	System Precision Mean Field Duplicate RPD (%)		Analytical		
		< 5 * MDL	> 5 * MDL	Precision	Bias	Sensitivity
				Mean Lab Duplicate RPD < 5* MDL	Mean LMS Recovery (%)	Samples reported as < MDL (%)
Vapor (Illinois)	251	21%(3)	40% (11)	(0)	94% (34)	1.6%
Precipitation (Illinois)	179	47% (9)	(0)	(0)	93% (23)	29%
Particulate (Illinois)	208	33% (9)	10% (1)	(0)	97% (28)	8.2%
Vapor (Indiana)	26	42% (3)	22% (2)	(0)	96% (14)	35%
Precipitation (Indiana)	14	53% (7)	(0)	(0)	92% (14)	86%
Particulate (Indiana)	14	23%(5)	(0)	(0)	95% (13)	57%
Dry deposition	13	(0)	(0)	(0)	10,798% (5)	0

The number of QC samples used in the assessment is provided in parentheses.

RPD= Relative percent difference

LMS= Laboratory matrix spike

Table 3-28. Data Quality Assessment for *trans*-Nonachlor in Atmospheric Samples

Fraction (Lab)	Number of Routine Samples Analyzed	System Precision Mean Field Duplicate RPD (%)		Analytical		
		< 5 * MDL	> 5 * MDL	Precision	Bias	Sensitivity
				Mean Lab Duplicate RPD < 5* MDL	Mean LMS Recovery (%)	Samples reported as < MDL (%)
Vapor (Illinois)	270	all results = 0	24% (23)	(0)	80% (36)	7.8%
Precipitation (Illinois)	193	all results = 0	(0)	(0)	73% (23)	78%
Particulate (Illinois)	217	52% (10)	(0)	(0)	75% (28)	34%
Vapor (Indiana)	34	53% (10)	16% (2)	(0)	70% (18)	27%
Precipitation (Indiana)	14	66% (8)	(0)	(0)	75% (14)	100%
Particulate (Indiana)	4	all results = 0	(0)	54% (1)	70% (13)	75%
Dry deposition	21	(0)	(0)	(0)	126% (5)	81%

The number of QC samples used in the assessment is provided in parentheses.

RPD= Relative percent difference

LMS= Laboratory matrix spike

3.3 Data Interpretation

3.3.1 Atmospheric Sources

Atmospheric sources of PCBs and *trans*-nonachlor to Lake Michigan can include exchange of contaminants from the vapor phase to the water, deposition of contaminants associated (e.g., bound or sorbed) with particulates, and contaminants in precipitation. This report summarizes the concentrations of PCB congeners, total PCBs, and *trans*-nonachlor reported during the LMMB Study in each of these atmospheric phases: vapor, particulate, dry deposition, and precipitation. The data for these phases will be used in the LMMB modeling efforts to evaluate the fluxes and loads of contaminants from each of these sources.

PCBs and *trans*-nonachlor were detected in samples from all four atmospheric phases. PCBs were detected above the sample-specific detection limits most frequently in the vapor-phase samples, followed by the particulate-phase samples, and least often in the precipitation samples. This is consistent with the findings of researchers that have estimated the atmospheric fluxes of PCB from the vapor and particulate phase as much higher than from wet deposition (Franz *et al.*, 1998).

While PCBs were detected in all four atmospheric phases, the frequency of occurrence and magnitude of concentrations differed among the PCB congeners and among the four phases. Figure 3-19 shows the mean percentage of individual PCB congeners that contributed to the total PCB concentration in vapor, particulate, and precipitation phases. In the vapor phase, the lower molecular weight, less-chlorinated congeners predominated, while particulate and precipitation phases contained a more diverse mixture of PCB congeners, including higher molecular weight congeners. Baker and Eisenreich (1990) also found that the more volatile tri- and tetrachlorobiphenyl congeners dominated the distribution of PCBs in the atmospheric gas phase. The higher vapor pressures of these less-chlorinated PCB congeners favor volatilization from the particulate and dissolved phases to the vapor phase. The differences in vapor pressures among the PCB congeners may explain some of the differences in the frequencies of occurrence of PCB congeners in the various phases. For example, the more volatile PCB 33 was less often detected in the precipitation phase than the less volatile, more chlorinated PCB 180 (Figure 3-20).

To statistically evaluate the contribution of the various PCB congeners, the proportion of the total PCB concentration attributed to the higher chlorinated (high molecular weight) congeners was calculated for vapor-phase, particulate-phase, and precipitation samples. For the purposes of this evaluation, the higher chlorinated congeners include the hexachloro-, heptachloro-, octachloro-, and nonachlorobiphenyl congeners, while the lower chlorinated congeners include the dichloro-, trichloro-, tetrachloro-, and pentachlorobiphenyl congeners. Neither the three monochlorobiphenyl congeners nor the one decachlorobiphenyl congener were reported by all laboratories in all phases, so they were not included in this calculation.

The high molecular weight proportion was calculated as:

$$\text{High molecular weight proportion} = \frac{\sum(\text{Cl}_6 + \text{Cl}_7 + \text{Cl}_8 + \text{Cl}_9)}{\sum(\text{Cl}_2 + \text{Cl}_3 + \text{Cl}_4 + \text{Cl}_5 + \text{Cl}_6 + \text{Cl}_7 + \text{Cl}_8 + \text{Cl}_9)}$$

Figure 3-19. Mean Percentage of Individual PCB Congener's Contribution to Total PCB Concentrations

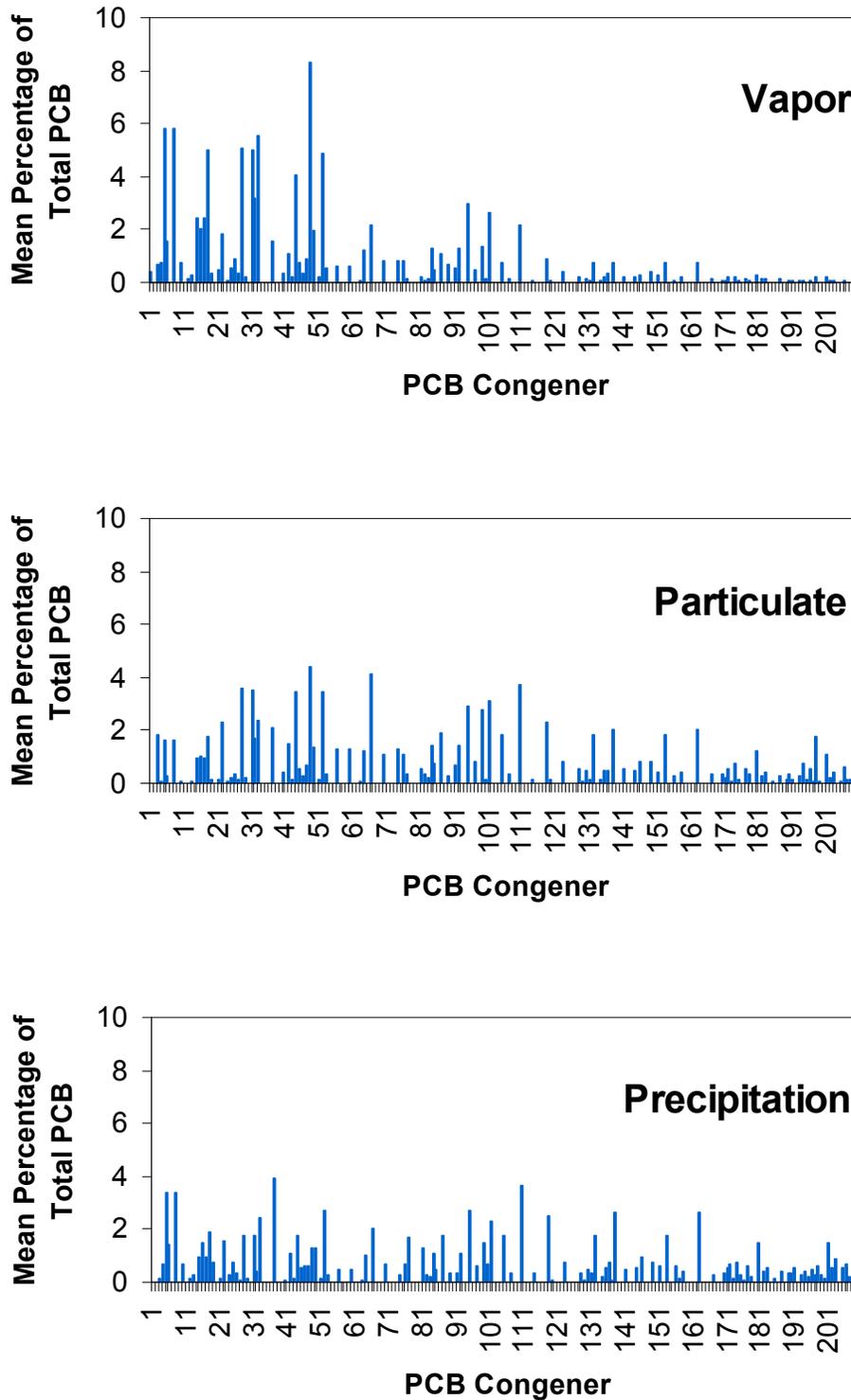
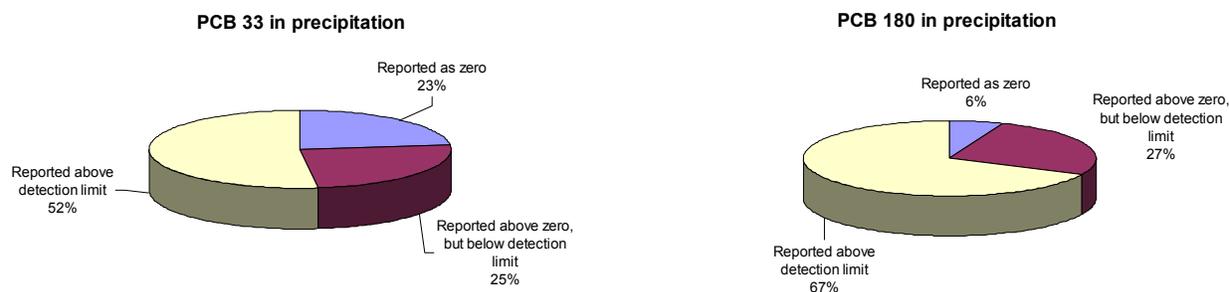


Figure 3-20. Percentages of PCBs 33 and 180 in Precipitation Samples Reported as Zero, Below the Detection Limits, and Above the Detection Limits



There were three instances in which two or more congeners in the two categories coeluted and could not be reported separately (PCBs 123 and 149; PCBs 111 and 131; and PCBs 105, 132, and 153), therefore, none of the results for these congeners were used to calculate the proportions.

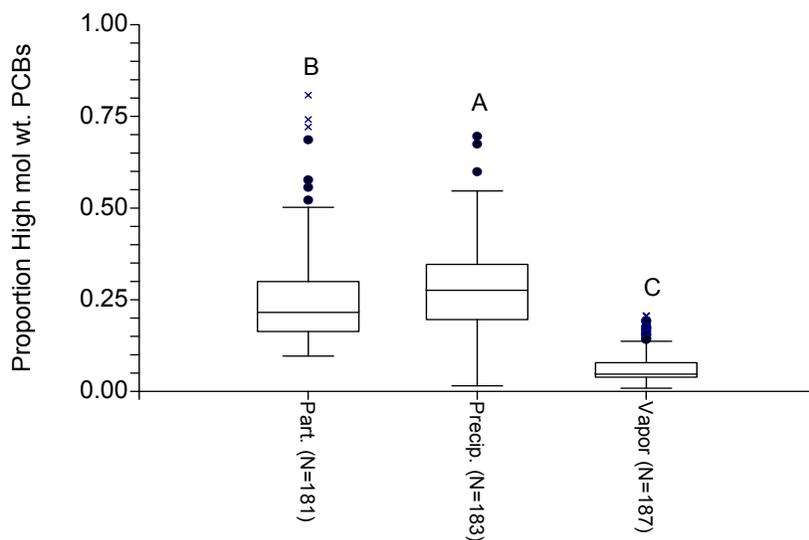
Based on a comparison of high molecular weight proportions in over 180 vapor, particulate, and precipitation samples, there was a significant difference among the three phases (Figure 3-21). Precipitation samples had the highest proportion of high molecular weight PCB congeners, followed by particulate-phase samples. Vapor-phase samples contained the lowest proportion of high molecular weight PCB congeners, consistent with the lower vapor pressures of the higher molecular weight congeners.

Similarly to the low molecular weight PCB congeners, *trans*-nonachlor, which has a high vapor pressure also was more prevalent in the vapor phase than in precipitation or the particulate phase. Mean vapor-phase concentrations of *trans*-nonachlor were approximately 10 to 20 times higher than the particulate-phase concentrations at the same sampling stations (see Tables 3-7 and 3-13). *trans*-Nonachlor was even less common in precipitation samples. With the exception of the IIT Chicago site, 75 to 100% of precipitation samples from the various LMMB sampling stations contained *trans*-nonachlor below the sample-specific detection limit.

3.3.2 Atmospheric Concentrations

In this study, total PCB concentrations in the vapor phase ranged from 0 to 6300 pg/m³ at shoreline sampling stations surrounding Lake Michigan. Average monthly composite concentrations of total PCBs ranged from 320 to 2600 pg/m³ at these stations. These concentrations are comparable to vapor-phase total PCB concentrations measured by other researchers over large water bodies near urban influences. Brunciak *et al.* (2001) measured average vapor-phase total PCB concentrations of 1180 pg/m³ near Baltimore, MD and 550 pg/m³ over the Northern Chesapeake Bay. Similarly, vapor-phase total PCB concentrations ranged from 210 to 4780 pg/m³ over Galveston Bay, TX (Park *et al.*, 2001). The lower PCB concentrations measured at the more remote out-of-basin sampling stations in the LMMB Study (averaging 110 to 260 pg/m³) were comparable to concentrations measured by other researchers at remote sites across the northern hemisphere. Iwata *et al.* (1993) measured average vapor-phase total PCB concentrations of 93, 130, 130, 320, and 290 pg/m³ over the Bering Sea, Gulf of Alaska, North Pacific Ocean, Caribbean Sea, and North Atlantic Ocean, respectively.

Figure 3-21. Proportion of High Molecular Weight PCB Congeners in the Vapor Phase, Particulate Phase, and Precipitation



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The ^s represent results beyond 3*IQR from the box. The letters (A - D) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Proportions were transformed by calculating the arcsine of the square root of the proportion prior to testing.

The range of vapor-phase total PCB concentrations measured in the LMMB Study during 1994 and 1995 also are relatively consistent with PCB concentrations historically measured in the Great Lakes region. Baker and Eisenreich (1990) reported average atmospheric PCB concentrations over the Great Lakes of 300 to 3200 pg/m³ with no discernable trend from 1977 through 1986. Baker and Eisenreich (1990) concluded that PCB concentrations have remained relatively constant in the atmosphere over this period. In 1986, Baker and Eisenreich (1990) measured an average PCB concentration of 1200 pg/m³ over Lake Superior. Hoff *et al.* (1992) measured monthly averages of 55 to 823 pg/m³ over Southern Ontario in 1988 to 1989. Also in 1989, Hornbuckle *et al.* (1993) measured average total PCB concentrations of 670 to 2200 pg/m³ over southern Green Bay, and 160 to 520 pg/m³ over northern Green Bay in 1989. From 1991 to 1993, Hornbuckle *et al.* (1995) measured 30 to 400 pg/m³ of total PCB in air samples collected at the Sleeping Bear Dunes site. PCB concentrations measured in the LMMB Study during 1994 and 1995 are consistent with the range of previous measurements and do not clearly suggest trends of increasing or decreasing PCB concentrations in the vapor phase, however, as Hoff *et al.* (1992) noted, such long-term trends may be difficult to detect due to the large amplitude of seasonal cycles and due to differences in sampling locations and analytical methodologies in the various studies. Using longer-term monitoring data and consistent IADN (Integrated Atmospheric Deposition Network) monitoring stations, Simcik *et al.* (1999) were able to detect decreases in vapor-phase total PCB concentrations from 1991 to 1997 over Lake Michigan and Lake Erie, with half-lives of 2.8 to 3.3 years.

Total PCB concentrations in precipitation averaged 1.3 to 16 ng/L at shoreline sampling stations and 0.29 to 1.7 ng/L at out-of-basin stations during the LMMB Study. These values also were relatively consistent with total PCB concentrations measured in precipitation over other large water bodies across the U.S. Leister and Baker (1994) measured a volume-weighted mean total PCB concentration of 1.6 ng/L in

precipitation over the Chesapeake Bay, and Park *et al.* (2001) measured total PCB concentrations of 0.08 to 3.34 ng/L in precipitation over Galveston Bay, TX. Total PCB concentrations in snowfall at Lake Tahoe ranged from 4.8 to 5.1 ng/L (Datta *et al.*, 1998). In the Great Lakes region, Simcik *et al.* (2000) reported lower PCB concentrations in precipitation over Lake Michigan and Lake Erie than over Lake Huron and Lake Ontario. Simcik *et al.* (2000) also reported significant decreases in PCB concentrations in precipitation over Lake Michigan from 1991 to 1997, with a half life of 6.9 years.

3.3.3 Seasonality

Concentrations of PCBs in the vapor phase were highly influenced by season (Figure 3-2). Total PCB concentrations and individual congeners (PCB 118 and PCB 180) in the vapor phase peaked in mid summer and reached minimum values in the winter. The mean total PCB concentration during the summer at shoreline and out-of-basin stations was eight times higher than in the winter. *trans*-Nonachlor followed the same trend, with vapor-phase mean concentrations in summer ten times higher than in the winter. This finding is consistent with other researchers who have measured PCBs and chlordanes over annual cycles (Hoff *et al.*, 1992; Green *et al.*, 2000). Hoff *et al.* (1992) concluded that this seasonal pattern was due to volatilization and the effects of temperature and vapor pressures on the distribution of these organic contaminants in the vapor phase. As temperature increases, distribution of these organic contaminants within the atmosphere favors the vapor phase. Fluxes of PCBs from Lake Michigan to the atmospheric vapor phase also may increase vapor-phase PCB concentrations during the summer (Hornbuckle *et al.*, 1993).

In contrast, the particulate-phase total PCB concentrations exhibited a different seasonal pattern than the vapor-phase results (Figure 3-8). Particulate-phase total PCB concentrations were higher in spring and winter than in summer and autumn. The particulate-phase *trans*-nonachlor concentrations exhibited a different pattern than the corresponding vapor-phase results (Figure 3-9), and slightly different from the pattern for the particulate-phase total PCBs, with the highest concentrations in the winter. These patterns for total PCBs and *trans*-nonachlor also are consistent with the effects of temperature and vapor pressures, in that at the lower temperatures during winter, the contaminants are less likely to volatilize off of the surface of particulates into the vapor phase.

3.3.4 Regional Considerations

Atmospheric sampling stations in the LMMB Study were grouped into the following categories based on their proximity to urban areas: urban, urban-influenced, rural, and remote (see Table 2-6 in Chapter 2). Mean total PCB concentrations at urban sites were six times higher than at urban-influenced sites, seven times higher than at rural sites, and four times higher than at remote sites. The highest total PCB concentrations were at the IIT Chicago site (mean of 2600 pg/m³), which is expected since various combustion sources and other sources are likely to be present in a large urban area. The second highest total PCB concentrations were at the remote Beaver Island location (mean of 970 pg/m³), which was not anticipated and suggests an unknown source near this otherwise relatively remote site in northern Lake Michigan. The Beaver Island location had the highest concentrations of PCB 180 (mean of 11 pg/m³), a highly chlorinated and relatively high molecular weight congener. Mean PCB 180 concentrations at Beaver Island were 3 times higher than at the IIT Chicago site and 33 to 46 times higher than at any other remote station. The high concentrations of relatively high molecular weight PCB congeners at the Beaver Island site suggest a nearby source, rather than long-range transport of PCBs from distant sources. However, a review of land use maps, literature sources, and other information was conducted during the preparation of this report. That review did not uncover any obvious sources. Therefore, rather than speculate about possible sources, the anomalous PCB results at Beaver Island are simply reported here.

Results were similar for particulate phase PCB concentrations, with the highest concentrations at the IIT Chicago and Beaver Island sites. Total PCB concentrations in precipitation also were highest at the IIT Chicago site, but precipitation-phase PCBs at Beaver Island were comparable to other remote sites.

The results from this study demonstrate that the urban source of PCBs from the Chicago area significantly influence PCB concentrations over Lake Michigan. A statistically significant difference in the vapor-phase concentrations of PCB 118 between over-water stations north and south of 43° latitude (Figure 3-6) was observed in this study. PCB concentrations over the southern portion of Lake Michigan, and particularly near Chicago, were significantly higher than concentrations over northern Lake Michigan. PCB 118 concentrations at over-water stations 1 and 6, near Chicago, were 6 to 39 times higher than at any other over-water station. PCB 118 concentrations at these two stations also were higher than at the IIT Chicago site.

Other researchers have noted a similar influence on atmospheric PCB concentrations over Lake Michigan due to the urban Chicago area. As a part of the AEOLUS (Atmospheric Exchange Over Lakes and Oceans) Project, Simcik *et al.* (1997) determined that gas-phase PCB concentrations over southern Lake Michigan were highly influenced by the urban/industrial area from Evanston, IL to Gary, IN. Emissions from these urban areas increased the average coastal atmospheric concentration above the continental background by a factor of four. Gas-phase PCB concentrations ranged from 0.14 ng/m³ to 1.1 ng/m³ over the lake and from 0.27 to 14 ng/m³ in the urban area. Total PCB concentrations in rain measured by Offenberg and Baker (1997) over southern Lake Michigan ranged from 4.1 to 189 ng/L and were from 2 to 400 times higher than the measured regional background concentrations. Offenberg and Baker (1997) concluded that the “urban plume” of Chicago increases PCB wet deposition loadings over southern Lake Michigan by 50 to 400%.

In contrast to the PCB results, the vapor-phase *trans*-nonachlor concentrations suggest that there is a significant source in the rural, agricultural area near Bondville, with generally decreasing concentrations in more northern stations (Figure 3-5). *trans*-Nonachlor concentrations in the vapor phase were highest at the Bondville station followed by the IIT Chicago station. Although *trans*-nonachlor is no longer produced in the U.S., nor applied in agricultural practice, this apparent trend from south to north may indicate the effects of historical agricultural applications, with lesser contributions from other historical uses in urban areas such as Chicago.

Chapter 4

PCBs/*trans*-Nonachlor in Tributaries

4.1 Results

A total of 354 samples were collected from 11 tributaries that flow into Lake Michigan or Green Bay and analyzed for PCBs and *trans*-nonachlor. The samples were collected as described in Section 2.5.2, by pumping 80 to 160 L of river water through a cartridge packed with 250 g of XAD-2[®], a macroreticular resin that traps hydrophobic organic contaminants. A “pentaplate” filter was installed in the sampling train front of the XAD-2[®] cartridge to collect the particulate matter suspended in the sample. Separate analyses were performed on the XAD-2[®] resin and the filtered particulates from each sampling effort, yielding results for operationally defined “dissolved” and “particulate” PCBs (Table 4-1) and *trans*-nonachlor (Table 4-2). Interferences and laboratory accidents reduced the number of *trans*-nonachlor results to 338 dissolved results and 350 particulate results.

As noted in Chapter 2, there are 209 possible PCB congeners, and the investigators in this study reported results for 65 to 110 of these congeners, depending on the capabilities of each laboratory. From March 1994 through October 1994, the analyses performed at the University of Wisconsin, Wisconsin State Lab of Hygiene determined results for 65 congeners or co-eluting congeners. In November 1994, the laboratory instituted a change in their standard operating procedure that allowed them to report the results for 78 congeners or coeluting congeners. For the purposes of this report, we are presenting summaries of the results for the following subset of all of the analytes:

- PCB congener 33
- PCB congener 118
- PCB congener 180
- Total PCBs
- *trans*-nonachlor

Table 4-1. Number of Tributary Samples Analyzed for Dissolved and Particulate PCB Congeners and Total PCBs

Tributary	Sampling Dates	Dissolved PCBs	Particulate PCBs	Total Samples
Fox River	04/07/94 to 10/12/95	39	39	78
Grand Calumet	08/04/94 to 10/18/95	15	15	30
Grand River	04/11/94 to 10/31/95	47	47	94
Kalamazoo	04/12/94 to 10/30/95	38	38	76
Manistique	04/11/94 to 10/26/95	28	28	56
Menominee	04/13/94 to 10/11/95	24	24	48
Milwaukee	03/29/94 to 10/06/95	38	38	76
Muskegon	04/14/94 to 12/05/95	28	28	56
Pere Marquette	04/05/94 to 10/18/95	28	28	56
Sheboygan	04/06/94 to 10/24/95	36	36	72
St. Joseph	04/06/94 to 10/27/95	33	33	66
Total		354	354	708

Table 4-2. Number of Tributary Samples Analyzed for Dissolved and Particulate *trans*-Nonachlor

Tributary	Sampling Dates	Dissolved <i>Trans</i> -Nonachlor	Particulate <i>Trans</i> -Nonachlor	Total Samples
Fox River	04/07/94 to 10/12/95	38	38	76
Grand Calumet	08/04/94 to 10/18/95	15	15	30
Grand River	04/11/94 to 10/31/95	34	47	81
Kalamazoo	04/12/94 to 10/30/95	38	37	75
Manistique	04/11/94 to 10/26/95	28	27	55
Menominee	04/13/94 to 10/11/95	24	24	48
Milwaukee	03/29/94 to 10/06/95	36	38	74
Muskegon	04/14/94 to 12/05/95	28	28	56
Pere Marquette	04/05/94 to 10/18/95	28	27	55
Sheboygan	04/06/94 to 10/24/95	36	36	72
St. Joseph	04/06/94 to 10/27/95	33	33	66
	Total	338	350	688

The 11 tributaries were chosen for sampling by the Lake Michigan Tributary Coordinating Committee, comprised of representatives from EPA, the Wisconsin Department of Natural Resources, the Michigan Department of Natural Resources, and the U.S. Geological Survey offices in Wisconsin and Michigan. The 11 sites represent the variety of types of river that drain into the Lake Michigan basin. Ten of the eleven rivers were chosen because elevated concentrations of contaminants previously observed in fish collected from these tributaries suggest that these rivers are contributing the highest contaminant loadings to the lake. The exception was the Pere Marquette River in Michigan. This tributary was chosen as the “background” site, with little anthropogenic input. The samples from the Pere Marquette River will be used to estimate loads from the small portion of the Lake Michigan watershed that was not monitored in this study. The 11 monitored tributaries represent greater than 90% of the total river flow into Lake Michigan and an even higher percentage of the total tributary load of pollutants into Lake Michigan (see Section 2.4.2).

The committee classified the tributaries into three categories, based on their “event responsiveness,” meaning the degree to which their physical and hydrological characteristics respond to the flow changes associated with precipitation events. The categories were: variable, stable, and super stable. The classifications were used to establish the sampling frequency for each tributary (Table 4-3). All tributaries were to be sampled monthly during the winter and during base (low) flow conditions, with additional samples collected after precipitation events that increased the tributary flow by at least 20%. The planned sampling frequencies were met for all but four of the tributaries (Grand Calumet, Menominee, Milwaukee, and Sheboygan Rivers).

Table 4-3. Tributary Classifications Relative to Responsiveness to Precipitation Events

Tributary	Event Responsiveness	Number of Planned Sampling Events	
		High Flow	Low Flow
Fox River	Stable	18	8
Grand Calumet	Super Stable	16	
Grand River	Stable	24	12
Kalamazoo	Stable	18	8
Manistique	Stable	16	
Menominee	Stable	18	8
Milwaukee	Variable	30	15
Muskegon	Stable	16	
Pere Marquette	Super Stable	11	5
Sheboygan	Variable	30	15
St. Joseph	Stable	18	8

4.1.1 Temporal Variation

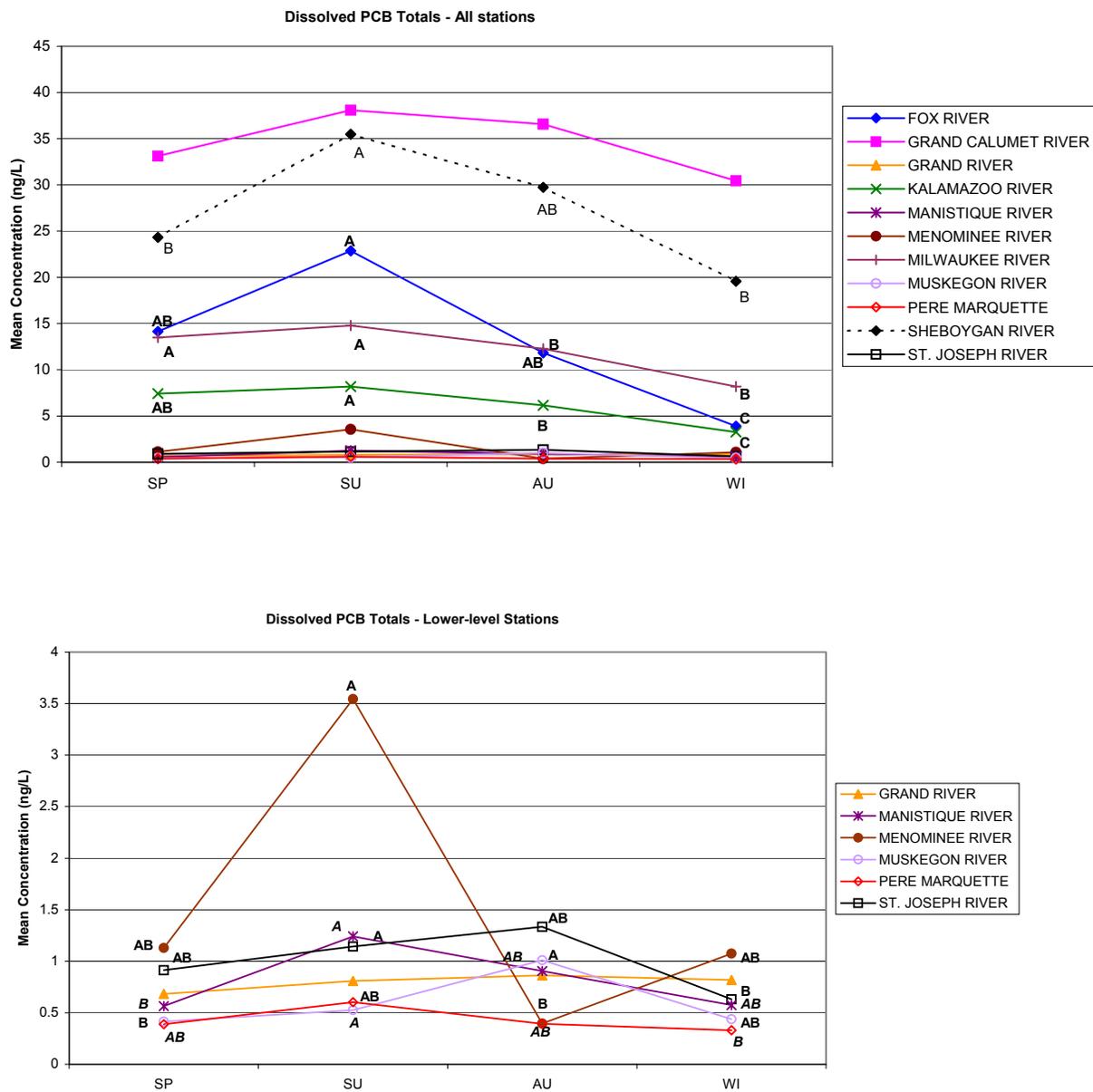
Many of the tributary samples were collected in response to precipitation events and these events may not have occurred simultaneously across the entire Lake Michigan basin. As a result, the collection dates of the samples sometimes vary greatly across the tributaries. Therefore, the tributary results were examined by season, where the seasons were defined as:

- Spring (SP) = March 20 to June 20,
- Summer (SU) = June 21 to September 22,
- Autumn (AU) = September 23 to December 21, and
- Winter (WI) = December 22 to March 19

The concentrations of dissolved and particulate total PCBs exhibited a seasonal trend for many of the tributaries, with higher mean concentrations occurring in summer months and lower mean concentrations occurring in winter months. There were significant differences between seasons for the dissolved total PCB concentrations in nine of the eleven tributaries, and significant differences between season for the particulate total PCB concentration in six of the eleven tributaries. However, the trend was not consistent across all of the tributaries. Based on F-tests of log-transformed concentration data, there were significant interactions between tributary and season. The temporal variations in the dissolved and particulate concentrations of individual PCB congeners did not exhibit trends that were consistent across all tributaries, based on F-tests of log-transformed concentration data.

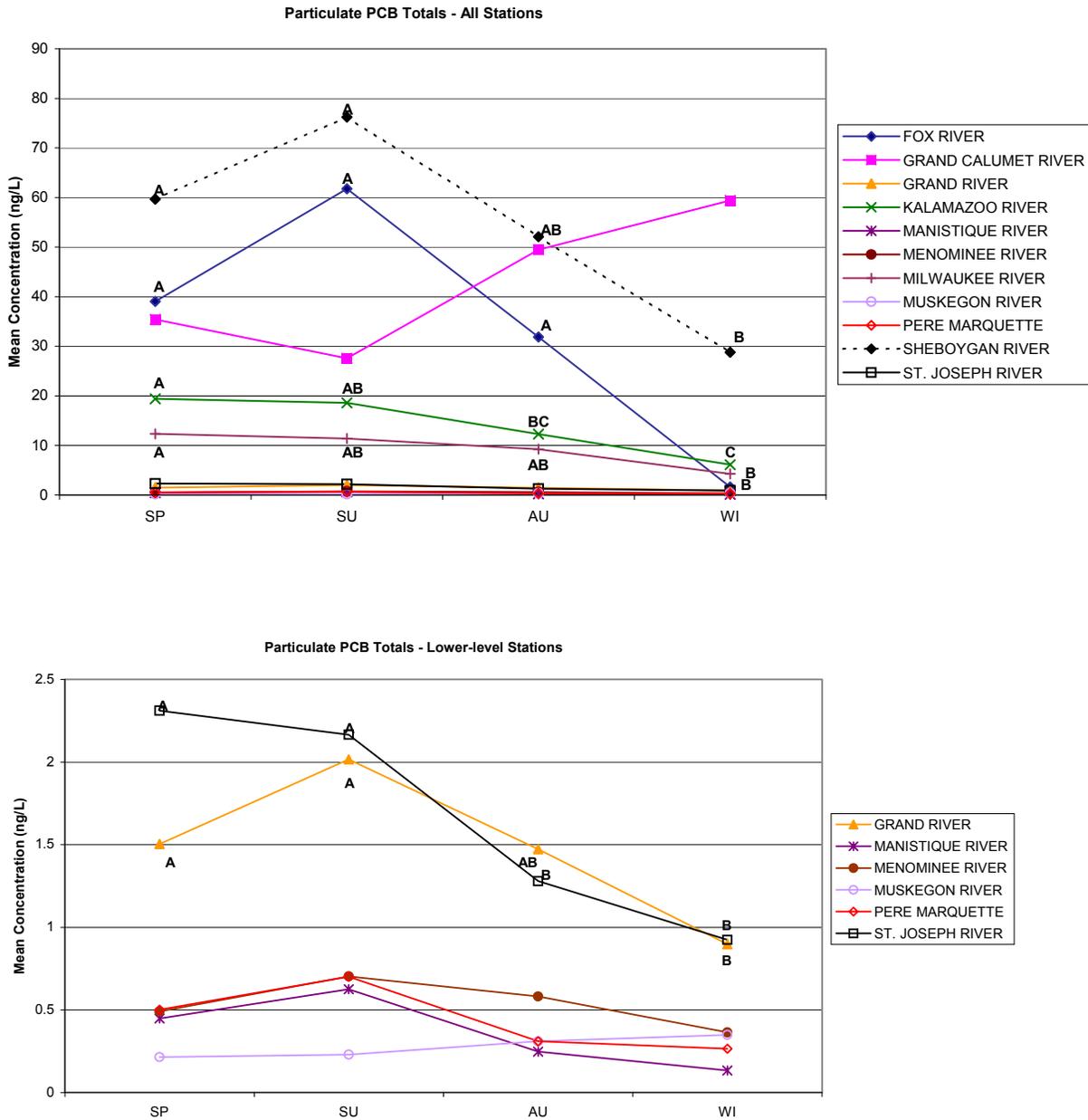
The mean seasonal concentrations of dissolved and particulate total PCBs across all 11 tributaries span at least two orders of magnitude. The tributaries can be visually divided into two groups, based on PCB concentration. Specifically, six of the eleven tributaries exhibit dissolved and particulate total PCB mean concentrations that are less than 4 ng/L, and often less than 1 ng/L, across all four seasons. The results are plotted separately for dissolved total PCBs (Figure 4-1) and particulate total PCBs (Figure 4-2).

Figure 4-1. Temporal Variation in Total Dissolved PCB Concentrations Measured in Lake Michigan Tributaries



Note: The letters (A - C) represent the results of the analysis of variance and multiple comparisons test. Points with the same letter were not statistically different (at alpha = 0.05). Tributaries without letters are those where there were no significant differences between seasons.

Figure 4-2. Temporal Variation in Total Particulate PCB Concentrations Measured in Lake Michigan Tributaries



Note: The letters (A - B) represent the results of the analysis of variance and multiple comparisons test. Points with the same letter were not statistically different (at alpha = 0.05). Tributaries without letters are those where there were no significant differences between seasons.

The mean dissolved total PCB concentrations appear to peak in summer in three of the tributaries (Fox, Menominee, and Sheboygan), while they appear to peak in the autumn for three other tributaries (Grand River, Muskegon, and St. Joseph). However, for many of the tributaries, the results do not show significant differences between seasons and those apparent peaks are not significantly different from the mean concentrations of the adjacent seasons. For example, the seasonal mean dissolved total PCB concentrations in the Grand Calumet River and the Grand River are not statistically significant different

between any of the seasons. For Fox River and Kalamazoo River, the mean concentrations in spring and summer are not significantly different, but the mean concentration in summer is significantly higher than in autumn, which is significantly higher than in winter.

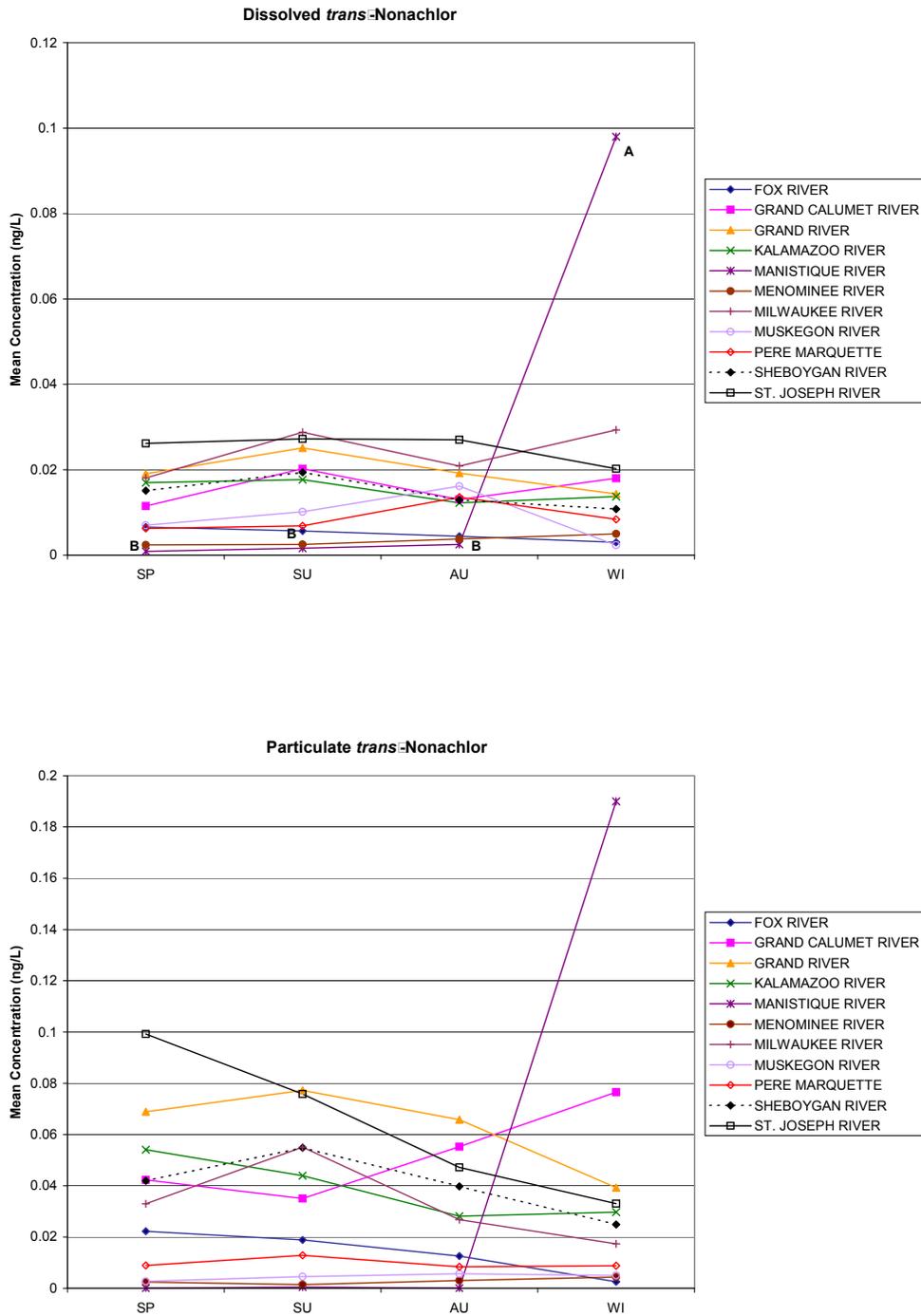
The summer mean concentration of dissolved total PCBs in the Menominee River is significantly different from the autumn mean concentration, but neither the summer nor the autumn mean is significantly different from the spring and winter means. The large increase in concentration that is visible in Figure 4-1 is driven by one of the four summer results for this tributary, with a dissolved total PCB result of 10.6 ng/L. There is no unambiguous evidence that indicates this high result for total dissolved PCBs is due to contamination in the field or the laboratory, thus the result was not excluded from the database. However, examination of the data qualifiers applied to the individual PCB congener results by both the PI who produced the results and the data reviewers suggest some increased uncertainty with this specific sample (e.g., PCB 33 was associated with a field blank that did not meet the acceptance criteria and PCB 180 was reported with the suspected contamination flag), but these concerns did not affect a large number of other congeners. Were this result excluded from the calculation of the mean seasonal results, the mean summer result for dissolved total PCBs at the Menominee River would be on the order of 1.1 ng/L, a value well in line with the other low-level stations.

The mean particulate total PCB concentrations appear to peak in either spring or summer in 9 of the 11 tributaries, with the lowest mean concentrations in the winter. However, the significance of the seasonal differences varies by tributary. For example, in the Sheboygan River, the mean spring and summer particulate total PCB concentrations are not significantly different from one another, but both are significantly different from the winter mean concentration. In the Fox River, mean spring, summer, and autumn particulate total PCB concentrations are not significantly different from one another, but all are significantly different from the mean winter concentration. For the Kalamazoo, Milwaukee, Grand, and St. Joseph Rivers, the spring mean particulate total PCB concentrations are never the lowest concentrations of the four seasons and the winter concentrations are never the highest of the four seasons.

Despite the apparent increase in the mean total particulate PCB concentrations from summer to winter in Figure 4-2 for the Grand Calumet River, there is no statistically significant difference across all four seasons in this tributary. Among the six low-level tributaries, there are no significant differences among the seasons for the mean particulate total PCB concentrations in the Manistique, Menominee, Muskegon, and Pere Marquette Rivers.

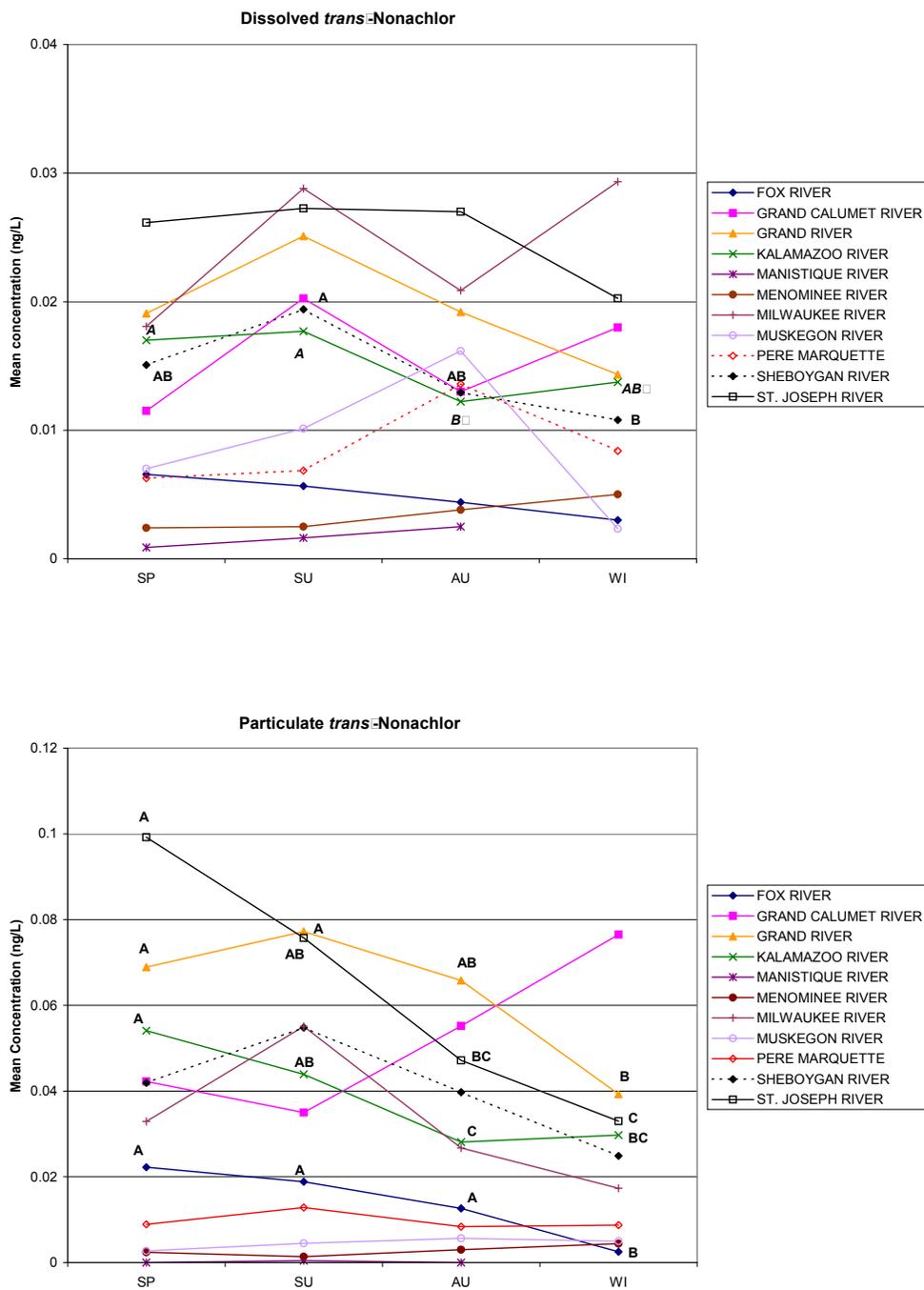
The mean concentrations of dissolved and particulate *trans*-nonachlor show fewer significant differences than the total PCB results (Figure 4-3). Eight of the eleven tributaries (Fox, Grand Calumet, Grand, Menominee, Milwaukee, Muskegon, Pere Marquette, and St. Joseph) exhibit no statistically significant differences in mean dissolved *trans*-nonachlor concentrations among the seasons. Of the other three tributaries, the mean dissolved *trans*-nonachlor in the Kalamazoo River is never the lowest in spring or summer, and never the highest in autumn, while in the Sheboygan River, mean dissolved *trans*-nonachlor is never the lowest in the summer, or the highest in the winter. The dissolved *trans*-nonachlor results for the Manistique River are characterized by a very high mean concentration in the winter which is significantly different from the other three seasons, which in turn, are not significantly different from one another. The very high winter mean concentration is repeated in the particulate *trans*-nonachlor results in this tributary. Figure 4-4 illustrates the seasonal trends for dissolved and particulate *trans*-nonachlor in the tributaries after removing the very high winter mean result for the Manistique River.

Figure 4-3. Temporal Variation in Total Dissolved (top) and Particulate (bottom) *trans*-Nonachlor Concentrations Measured in Lake Michigan Tributaries



Note: The letters (A - B) represent the results of the analysis of variance and multiple comparisons test. Points with the same letter were not statistically different (at alpha = 0.05). Tributaries without letters are those where there were no significant differences between seasons.

Figure 4-4. Temporal Variation in Total Dissolved (top) and Particulate (bottom) *trans*-Nonachlor Concentrations Measured in Lake Michigan Tributaries without the Winter Mean for the Manistique River



Note: The letters (A - B) represent the results of the analysis of variance and multiple comparisons test. Points with the same letter were not statistically different (at alpha = 0.05). Tributaries without letters are those where there were no significant differences between seasons.

Six of the tributaries (Grand Calumet, Menominee, Milwaukee, Muskegon, Pere Marquette, and Sheboygan) exhibited no statistically significant differences in the particulate *trans*-nonachlor concentrations across seasons. The Manistique River had one non-zero result in summer and one non-zero result in winter, and all other results were reported as zero. As seen in the dissolved *trans*-nonachlor result, the winter mean particulate concentration in the Manistique River was much higher than for any other tributary. The bottom portion of Figure 4-4 shows the results for the tributaries without this high mean particulate result.

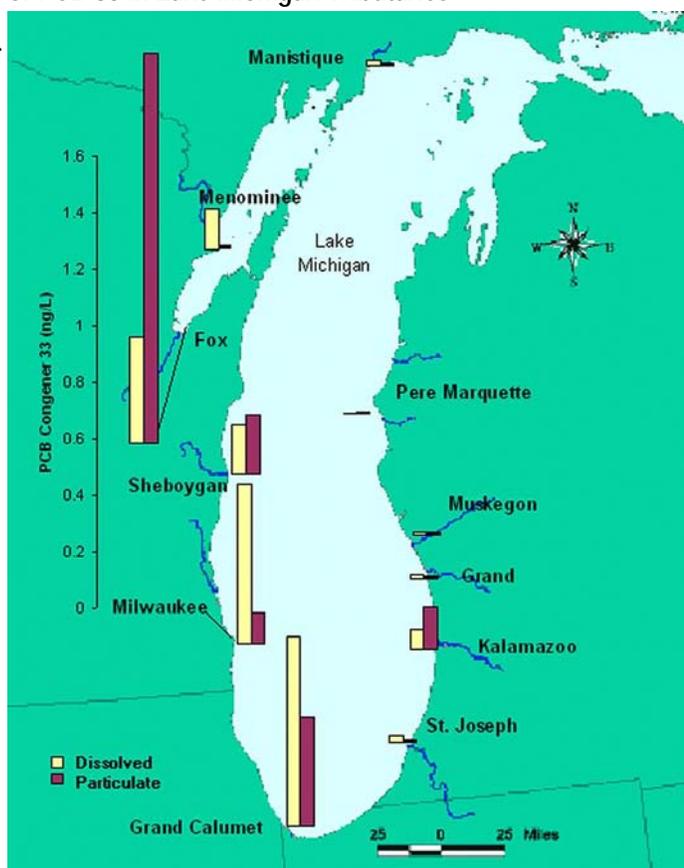
The trends for the other four tributaries are such that the mean particulate *trans*-nonachlor concentrations in the spring were never the lowest, and the winter mean concentrations were never the highest.

4.1.2 Geographical Variation

The concentrations of dissolved and particulate PCBs and *trans*-nonachlor varied by tributary over the course of the study (Tables 4-4 through 4-8). For example, the concentration of dissolved PCB 33 ranged from 0 to 1.1 ng/L and the concentration of particulate PCB 33 ranged from 0 to 4.2 ng/L. The mean dissolved concentrations of PCB 33 ranged from 0.0067 ng/L in the Pere Marquette River to 0.76 ng/L in the Grand Calumet River, while the mean particulate concentration of PCB 33 ranged from 0.00042 ng/L in the Pere Marquette River to 1.5 ng/L in the Fox River (Figure 4-5). (The particulate PCB 33 results were reported as zero for all 27 samples from the St. Joseph River).

Other PCB congeners exhibited ranges and mean concentrations similar to those observed for PCB 33. The dissolved total PCB concentrations ranged from 0 ng/L in four tributaries to 48 ng/L in the Grand Calumet, while particulate total PCB concentrations ranged from 0 ng/L in four tributaries to 120 ng/L in the Sheboygan River. Mean dissolved total PCB concentrations ranged from 0.43 ng/L in the Pere Marquette River to 35 ng/L in the Grand Calumet, while mean particulate concentration ranged from 0.25 ng/L in the Muskegon River to 55 ng/L in the Sheboygan River.

Figure 4-5. Mean Dissolved and Particulate Concentrations of PCB 33 in Lake Michigan Tributaries



For PCB 33, the mean dissolved concentrations are higher than the mean particulate concentrations in eight of the eleven tributaries (Figure 4-5), while the particulate concentrations are higher in the Fox, Kalamazoo, and Sheboygan Rivers. The distribution between the dissolved and particulate fractions appears to change for the higher molecular weight congeners (e.g., see Figure 4-6 for the mean concentrations of PCB 180). For PCB 118, the mean concentrations of the particulate samples were markedly higher than the dissolved concentrations in 9 of the 11 tributaries and essentially equal in the

Menominee and Muskegon Rivers (Table 4-5). For PCB 180, the mean concentrations of the particulate samples were markedly higher than the dissolved concentrations in all 11 tributaries.

Concentrations of dissolved *trans*-nonachlor ranged from 0 in seven tributaries to 0.19 ng/L in the Manistique River, while particulate *trans*-nonachlor ranged from 0 in five tributaries to 0.38 ng/L in the Manistique River (Table 4-9). (Note: The maximum dissolved and particulate *trans*-nonachlor concentrations occurred in the same sample from the Manistique River, which is otherwise relatively uncontaminated. These two values may be the result of contamination of the sample during collection).

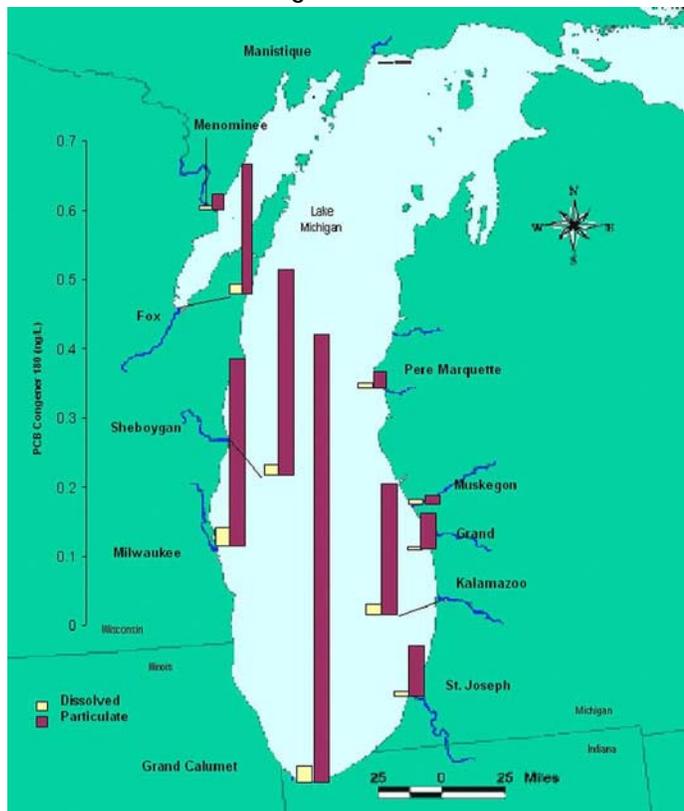
Mean dissolved *trans*-nonachlor concentrations ranged 0.0033 ng/L in the Menominee River to 0.026 ng/L in the St. Joseph River, while mean particulate *trans*-nonachlor concentrations ranged from 0.0028 ng/L in the Menominee River to 0.074 ng/L in the St. Joseph River.

There are statistically significant differences among the mean concentrations of dissolved and particulate PCBs in the 11 tributaries. The differences in the mean dissolved concentrations of total PCBs are shown in Figure 4-7. The mean dissolved total PCB concentrations in the Grand Calumet and Sheboygan Rivers were significantly higher than in all other tributaries. The mean dissolved total PCB concentrations in the Pere Marquette River were significantly lower than in all other tributaries except the Muskegon River. There is a statistically significant interaction between tributary and year for the particulate total PCB results ($p=0.0118$, two-way ANOVA, total PCB concentrations were log-transformed prior to conducting the test). Therefore, the mean particulate total PCB concentrations for all of the tributaries are presented separately for 1994 and 1995 (Figure 4-8, top and bottom, respectively).

There was a statistically significant difference between the particulate total PCB concentrations from 1994 and 1995 at three of the 11 tributaries (Fox, Grand, and Muskegon Rivers), based on two-sample *t*-tests of log-transformed PCB data. The mean particulate total PCB concentrations were significantly higher in 1994 than in 1995 in the Fox and Grand Rivers, while in the Muskegon River, the 1995 mean concentration was higher than in 1994. The differences between the results in 1994 and 1995 in these three tributaries may be a function of the unequal distribution of samples across calendar years (e.g., there are no 1994 data before April and no 1995 data after October), or the differences may be the result of some other factors.

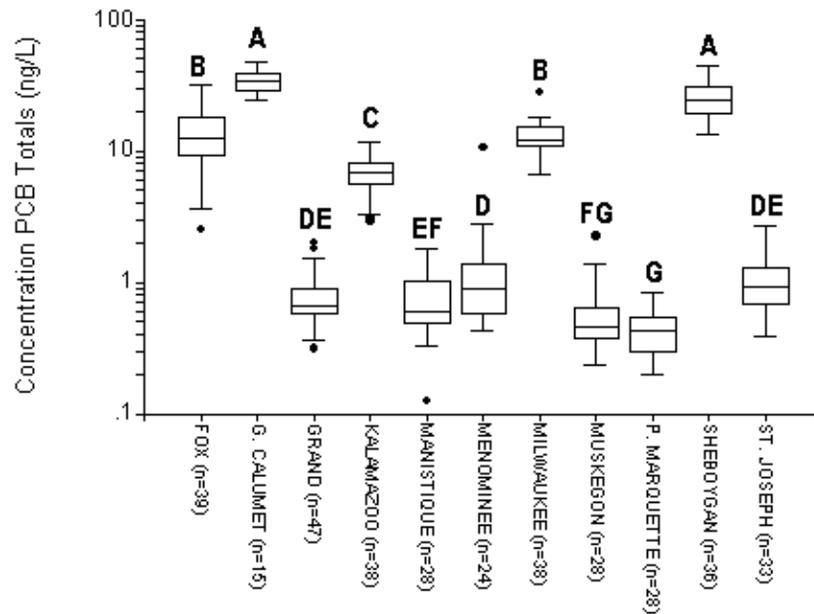
The distinction of the “lower-level” tributaries shown in Figure 4-2 also holds true when the same dissolved and particulate total PCB results were used in Figures 4-7 and 4-8. The six tributaries with relatively low concentrations of dissolved and particulate PCBs (Grand, Manistique, Menominee, Muskegon, Pere Marquette, and St. Joseph) in Figure 4-2 can also be distinguished from the five

Figure 4-6. Mean Dissolved and Particulate Concentrations of PCB 180 in Lake Michigan Tributaries



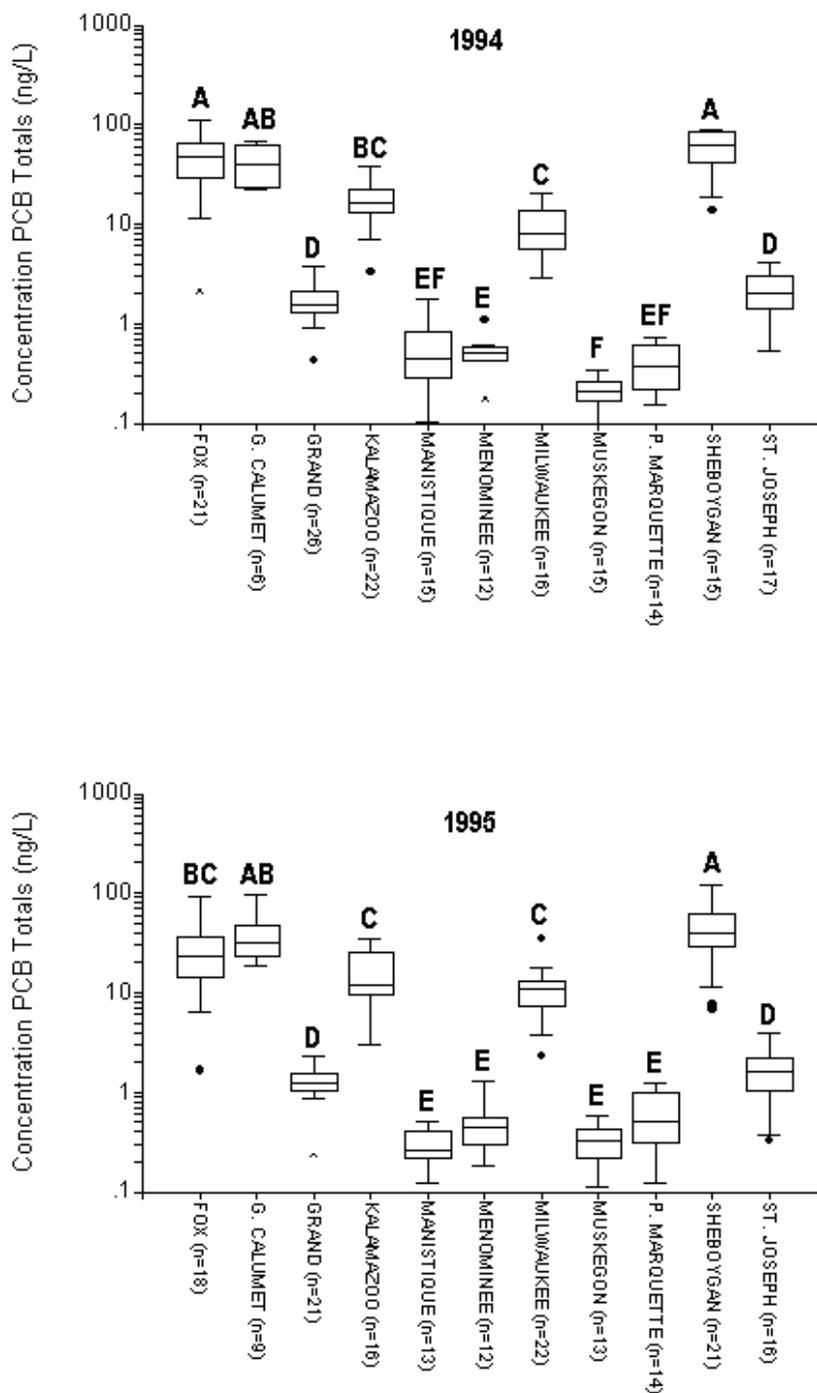
tributaries with much higher mean concentrations (Fox, Grand Calumet, Kalamazoo, Milwaukee, and Sheboygan) in Figures 4-7 and 4-8.

Figure 4-7. Mean Dissolved Total PCB Concentrations in Lake Michigan Tributaries



Concentration is plotted on a log scale. Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond $1.5 \times \text{IQR}$ from the box. The letters (A - G) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at $\alpha = 0.05$).

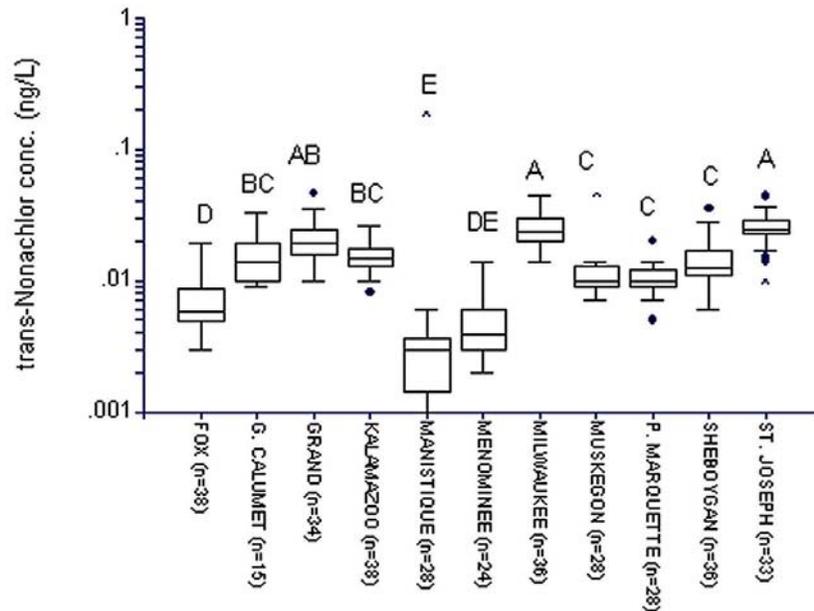
Figure 4-8. Mean Particulate Total PCB Concentrations in Lake Michigan Tributaries in 1994 (top) and 1995 (bottom)



Concentration is plotted on a log scale. Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The ^s represent results beyond 3*IQR from the box. The letters (A - F) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

The results for *trans*-nonachlor exhibited less distinct geographical variations, compared to the PCB results (Figure 4-9). For example, the concentrations of dissolved *trans*-nonachlor did not exhibit the distinction of the “lower-level” tributaries shown in Figure 4-2 for the PCB results. Only two of those six “lower-level” tributaries had statistically lower dissolved *trans*-nonachlor concentrations: the Manistique and Menominee Rivers. In marked contrast to the dissolved PCB results, the dissolved *trans*-nonachlor results for the Fox River were the third lowest of the 11 tributaries.

Figure 4-9. Mean Dissolved *trans*-Nonachlor Concentrations in Lake Michigan Tributaries

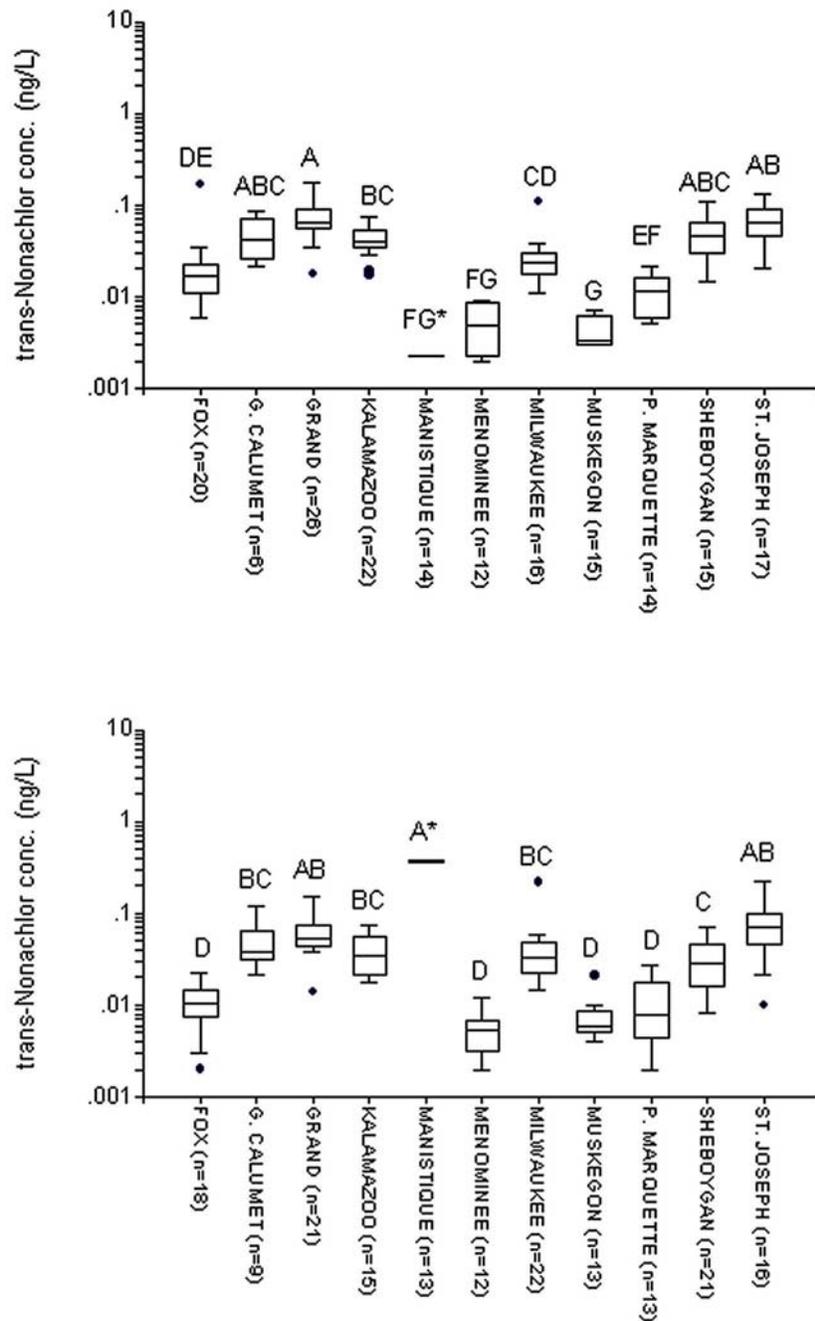


Concentration is plotted on a log scale. Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The ^s represent results beyond 3*IQR from the box. The letters (A - E) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

As with the particulate PCB results, there is a statistically significant interaction between tributary and year for the particulate *trans*-nonachlor results ($p=0.0001$, two-way ANOVA, *trans*-nonachlor concentrations were log-transformed prior to conducting the test). Therefore, the mean particulate *trans*-nonachlor concentrations for all of the tributaries are presented separately for 1994 and 1995 (Figure 4-10, top and bottom, respectively).

However, unlike the particulate PCB results, the distinctions between rivers with relatively low or relatively high concentrations of particulate *trans*-nonachlor are not as clear, nor as consistent between the two years. For example, the particulate *trans*-nonachlor results for the Fox River are not statistically different from those in the Pere Marquette River in either 1994 or 1995. The concerns about the anomalous particulate *trans*-nonachlor in the Manistique River are evident in the top and bottom portions of Figure 4-10, where the 1994 mean result is among the lowest of all 11 tributaries, while the 1995 mean result is the highest of all 11 tributaries.

Figure 4-10. Mean Particulate *trans*-Nonachlor Concentrations in Lake Michigan Tributaries in 1994 (top) and 1995 (bottom)



Concentration is plotted on a log scale. Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The *s represent instances where all but one observation was zero (0) and the log of 0 is indeterminate. The letters (A - G) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

Table 4-4. Concentrations of PCB Congener 33 Measured in Tributaries

Fraction	Tributary	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
Dissolved	Fox River	39	0.43	0.066 to 0.93	0.23	55	0.0
	Grand Calumet	15	0.76	0.39 to 1.1	0.27	36	0.0
	Grand River	35	0.018	0.0 to 0.043	0.0099	55	23
	Kalamazoo	36	0.095	0.035 to 0.17	0.032	34	0.0
	Manistique	24	0.0099	0.0 to 0.028	0.0098	99	50
	Menominee	15	0.082	0.015 to 0.56	0.14	170	20
	Milwaukee	37	0.27	0.094 to 0.94	0.14	52	0.0
	Muskegon	24	0.010	0.0 to 0.067	0.018	170	71
	Pere Marquette	27	0.0067	0.0 to 0.025	0.0087	129	93
	Sheboygan	28	0.20	0.12 to 0.31	0.058	29	0.0
	St. Joseph	28	0.020	0.0 to 0.052	0.015	74	50
Particulate	Fox River	39	1.5	0.067 to 4.2	0.99	64	0.0
	Grand Calumet	15	0.46	0.18 to 1.1	0.26	57	0.0
	Grand River	25	0.0033	0.0 to 0.026	0.0070	210	84
	Kalamazoo	34	0.16	0.023 to 0.38	0.092	56	0.0
	Manistique	27	0.0016	0.0 to 0.0090	0.0029	180	100
	Menominee	24	0.00076	0.0 to 0.018	0.0037	490	100
	Milwaukee	34	0.12	0.032 to 0.36	0.068	56	0.0
	Muskegon	28	0.00088	0.0 to 0.012	0.0027	310	100
	Pere Marquette	28	0.00042	0.0 to 0.0083	0.0017	400	100
	Sheboygan	16	0.25	0.048 to 0.46	0.12	47	0.0
	St. Joseph	27	0.0	0.0 to 0.0	0.0	--	100

Table 4-5. Concentrations of PCB Congener 118 Measured in Tributaries

Fraction	Tributary	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
Dissolved	Fox River	39	0.044	0.014 to 0.14	0.022	51	7.7
	Grand Calumet	15	0.14	0.083 to 0.25	0.044	31	0.0
	Grand River	45	0.013	0.0 to 0.028	0.0052	41	31
	Kalamazoo	38	0.058	0.026 to 0.14	0.023	39	0.0
	Manistique	27	0.0039	0 to 0.011	0.0034	88	93
	Menominee	22	0.014	0.0058 to 0.040	0.0074	51	91
	Milwaukee	37	0.072	0.037 to 0.19	0.026	36	0.0
	Muskegon	28	0.0068	0.0 to 0.019	0.0064	94	100
	Pere Marquette	27	0.0062	0.0 to 0.028	0.0065	110	96
	Sheboygan	36	0.19	0.084 to 0.31	0.058	30	0.0
St. Joseph	32	0.021	0.0095 to 0.039	0.0082	38	50	
Particulate	Fox River	39	0.43	0.014 to 1.2	0.26	60	2.6
	Grand Calumet	15	0.83	0.20 to 1.7	0.46	55	0.0
	Grand River	47	0.065	0.0045 to 0.14	0.026	40	2.1
	Kalamazoo	36	0.47	0.088 to 0.98	0.24	51	0.0
	Manistique	27	0.010	0.0 to 0.032	0.0080	78	63
	Menominee	23	0.015	0.0 to 0.030	0.0076	51	70
	Milwaukee	38	0.20	0.030 to 0.60	0.13	62	0.0
	Muskegon	28	0.0068	0.0 to 0.014	0.0035	51	100
	Pere Marquette	28	0.017	0.0 to 0.046	0.013	74	64
	Sheboygan	36	1.9	0.22 to 4.2	1.1	57	0.0
St. Joseph	32	0.083	0.0 to 0.2	0.045	54	9.4	

Table 4-6. Concentrations of PCB Congener 180 Measured in Tributaries

Fraction	Tributary	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
Dissolved	Fox River	38	0.013	0.0 to 0.044	0.0088	69	68
	Grand Calumet	14	0.022	0.0 to 0.081	0.019	86	36
	Grand River	42	0.0029	0.0 to 0.010	0.0026	90	95
	Kalamazoo	37	0.014	0.0 to 0.056	0.010	66	57
	Manistique	28	0.0015	0.0 to 0.014	0.0029	190	96
	Menominee	21	0.0052	0.0 to 0.024	0.0060	110	100
	Milwaukee	38	0.023	0.011 to 0.11	0.016	70	21
	Muskegon	28	0.0076	0.0 to 0.023	0.0070	93	89
	Pere Marquette	28	0.0054	0.0 to 0.020	0.0059	110	96
	Sheboygan	36	0.016	0.0 to 0.055	0.011	67	50
St. Joseph	32	0.0065	0.0 to 0.023	0.0068	110	91	
Particulate	Fox River	39	0.20	0.011 to 0.50	0.12	58	5.1
	Grand Calumet	15	0.66	0.32 to 1.5	0.33	50	0.0
	Grand River	44	0.049	0.0093 to 0.13	0.023	46	0.0
	Kalamazoo	36	0.19	0.046 to 0.36	0.086	45	0.0
	Manistique	25	0.0031	0.0 to 0.010	0.0031	100	92
	Menominee	24	0.026	0.0 to 0.12	0.025	95	42
	Milwaukee	38	0.28	0.086 to 1.1	0.17	61	0.0
	Muskegon	27	0.012	0.0 to 0.027	0.0070	61	85
	Pere Marquette	26	0.018	0.0 to 0.063	0.015	84	58
	Sheboygan	36	0.30	0.045 to 0.91	0.18	59	0.0
St. Joseph	31	0.074	0.016 to 0.15	0.032	43	6.5	

Table 4-7. Concentrations of Total PCBs Measured in Tributaries

Fraction	Tributary	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)
Dissolved	Fox River	39	14	2.5 to 32	7.6	53
	Grand Calumet	15	35	24 to 48	6.5	19
	Grand River	47	0.76	0.0 to 2.0	0.35	47
	Kalamazoo	38	6.9	2.9 to 12	2.1	30
	Manistique	28	0.76	0.13 to 1.8	0.39	52
	Menominee	24	1.4	0.0 to 11	2.1	150
	Milwaukee	38	13	6.7 to 28	4.0	30
	Muskegon	28	0.58	0.23 to 2.2	0.40	69
	Pere Marquette	28	0.43	0.0 to 0.83	0.19	45
	Sheboygan	36	26	13 to 45	8.3	32
	St. Joseph	33	1.0	0.0 to 2.7	0.53	52
Particulate	Fox River	39	39	1.6 to 110	25	64
	Grand Calumet	15	41	19 to 96	22	53
	Grand River	47	1.6	0.24 to 3.7	0.63	40
	Kalamazoo	38	16	0.0 to 38	9.6	59
	Manistique	28	0.41	0.046 to 1.8	0.37	90
	Menominee	24	0.52	0.18 to 1.3	0.27	53
	Milwaukee	38	11	2.3 to 35	6.2	58
	Muskegon	28	0.25	0.0 to 0.59	0.14	54
	Pere Marquette	28	0.47	0.0 to 1.2	0.32	67
	Sheboygan	36	55	6.9 to 120	31	56
	St. Joseph	33	1.9	0.0 to 4.1	0.98	52

Table 4-8. Concentrations of *trans*-Nonachlor Measured in Tributaries

Fraction	Tributary	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
Dissolved	Fox River	38	0.0056	0.0 to 0.019	0.0050	89	97
	Grand Calumet	15	0.015	0.0090 to 0.033	0.0067	44	67
	Grand River	34	0.020	0.0 to 0.046	0.0083	40	2.9
	Kalamazoo	38	0.016	0.0080 to 0.026	0.0040	26	74
	Manistique	28	0.0083	0.0 to 0.19	0.036	430	96
	Menominee	24	0.0033	0.0 to 0.014	0.0036	110	100
	Milwaukee	36	0.023	0.0 to 0.044	0.0093	41	25
	Muskegon	28	0.0094	0.0 to 0.046	0.0088	94	96
	Pere Marquette	28	0.0081	0.0 to 0.020	0.0054	67	96
	Sheboygan	36	0.015	0.0060 to 0.035	0.0057	39	81
	St. Joseph	33	0.026	0.010 to 0.045	0.0071	28	15
Particulate	Fox River	38	0.018	0.0 to 0.17	0.026	145	74
	Grand Calumet	15	0.049	0.021 to 0.12	0.028	56	0.0
	Grand River	47	0.067	0.014 to 0.18	0.030	44	0.0
	Kalamazoo	37	0.042	0.017 to 0.076	0.016	39	2.7
	Manistique	27	0.014	0.0 to 0.38	0.073	520	96
	Menominee	24	0.0028	0.0 to 0.012	0.0035	130	100
	Milwaukee	38	0.037	0.011 to 0.22	0.035	96	18
	Muskegon	28	0.0041	0.0 to 0.021	0.0047	110	96
	Pere Marquette	27	0.0098	0.0 to 0.027	0.0075	76	85
	Sheboygan	36	0.040	0.0082 to 0.11	0.024	58	19
	St. Joseph	33	0.074	0.010 to 0.23	0.043	57	3.0

4.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the PCBs and *trans*-nonachlor monitoring portion of the study are further described in Section 2.7 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in the Lake Michigan Mass Balance Study Quality Assurance Report (USEPA, 2001b). A brief summary of data quality issues for the tributary PCBs and *trans*-nonachlor data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being

analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.5, because data comparability was important to the successful development of the mass balance model, the PIs used similar sample collection, extraction, and analysis methods for the PCB and trans-nonachlor monitoring in this study. However, as noted earlier in this section, after the study began, changes were made to the procedures used for cleaning the XAD-2[®] resin and for the analyses of the tributary samples. The first 35 field samples were analyzed on an older GC/ECD system and were quantified against the Aroclor mixture prepared in 1985 by Dr. Mike Mullin at the EPA-Grosse Ile laboratory. These samples are identified in the data set with the text "Method 1293-11/11/94" in the Exception to Method text field. After mid-November 1994, analyses were performed on a new GC/ECD system that resulted in resolution of more PCB congeners (78 vs. 65) and lower method detection limits (MDLs) than in the earlier analyses. In addition, samples analyzed after mid-November 1994 were quantified against the 1994 version of the Mullin mix standard prepared exclusively for the LMMB Study. These analytical changes were implemented after November 12, 1994, but affect all the tributary samples collected from May 1994 to the end of the LMMB Study.

As discussed in Section 2.7, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 4-9 provides a summary of flags applied to the tributary PCB and *trans*-nonachlor data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.7. Compared to other matrices, the percentage of results that were qualified for these criteria is relatively small.

PIs used surrogate spikes to monitor the bias of the analytical procedure. The PCB results were corrected for the recoveries of the surrogates. The *trans*-nonachlor results were *not* surrogate-corrected. Only 0.6% of the results of the tributary samples analyzed for dissolved PCB 33 (2 samples) were qualified for surrogate recovery problems (Table 4-9).

Laboratory matrix spike samples also were used to monitor the bias of the analytical procedure. The laboratory matrix spike samples were prepared from unexposed filters and XAD-2[®] cartridges that were spiked with PCBs and *trans*-nonachlor. The results for the matrix spike samples were compared to the MQO for spike recoveries (50 - 125%). Analytical results associated with matrix spike samples with recoveries below the MQO limits were flagged with failed matrix spike and low bias and results associated with matrix spike samples with recoveries higher than the MQO limits were flagged with failed matrix spike and high bias. Analytical results were considered invalid and flagged as such when the analyte was undetected and recoveries for associated matrix spike samples were less than 10%. No tributary *trans*-nonachlor samples failed the matrix spike MQOs. Overall, only 1.4% of the samples were associated with a matrix spike samples that failed the MQOs for a given PCB congener. None of the results for PCBs 33, 118, or 180 were flagged as failing the matrix spike MQOs.

Field blanks were collected for PCBs and *trans*-nonachlor. When field blank contamination was greater than 3.3 times the method detection limit, all of the associated results were flagged with the failed field blank sample code (FRB). Field blanks were not collected at all stations, so potential station-specific contamination associated with these sites cannot be evaluated. However, contamination associated with sample collection and sampling equipment and sample processing, shipping, storing, and analyzing can be evaluated based on the field blanks collected throughout the study. For dissolved PCB 33, 3% of the field

samples were associated with a field blank in which this congener was reported above the sample-specific detection limit (Table 4-9). None of the field samples results for *trans*-nonachlor were qualified because of field blank results.

Two types of laboratory blanks were prepared and analyzed for PCBs and *trans*-nonachlor. One type of laboratory blank (LRB) consisted of an unexposed resin cartridge and filter that were extracted like a field sample. Another type of laboratory blank (LDB) consisted of a volume of solvent processed through an empty Soxhlet apparatus in the same fashion used to extract the field samples. After extraction, the solvent was concentrated and analyzed like a field sample. The results for both types of laboratory blanks were handled in the same fashion. When laboratory blank contamination was greater than the method detection limit, all of the associated results were flagged. None of the field samples results for *trans*-nonachlor were qualified because of laboratory blank results.

PCB congeners were reported detected in all of the laboratory blanks that were analyzed. The following PCB congeners were detected in LDB (empty Soxhlet) blanks above the MDL: 15+17, 18, 87, 170+190, 180, and 206. The following PCB congeners were detected in LRB (unused resin cartridge and filter) blanks above the MDL: 28+31, 41+71+64, 44, 49, 52, 87, 95, 101, 170+190, 180, 194, 208+195, 201 and 206. The differences between the results for these two types of laboratory blanks provide an indication of the congeners that are contributed by the resin and filter, as opposed to the laboratory glassware. The resin and the filter appear to contribute congeners 28+31, 41+71+64, 44, 49, 52, 95, 101, 194, 208+195, and 201.

Trip blanks were prepared and analyzed for PCBs and *trans*-nonachlor. When trip blank contamination was greater than 3.3 times the method detection limit, all of the associated results were flagged with failed trip blank sample code (FFT). For dissolved PCB 33, 7% of the field samples were associated with a trip blank in which this congener was reported above 3.3 times the method detection limit (Table 4-9). None of the field samples were associated with a trip blank that contained *trans*-nonachlor above 3.3 times the method detection limit.

Field duplicates were to be collected at a frequency of 5%. Duplicate samples collected within 5 minutes of each other were considered field duplicates. However, an examination of the field collection records indicated that some of the planned field duplicates were not collected within that 5-minute time frame as a result of problems with equipment mobilization or the time required to pump the sample through the filter and resin cartridge. Those “duplicates” that were collected more than 5 minutes apart were considered “sequential field duplicates” and the data were labeled accordingly (e.g., SDF1 vs. FD1). Combining the field duplicates and sequential field duplicates, the actual rate of collection of duplicates was 4.2%.

The results from the original field sample and the associated duplicate were compared on the basis of the relative percent difference (RPD). The RPD value for each PCB congener and *trans*-nonachlor was compared to the MQO for field duplicate precision. Only 0.3% of the field samples results for PCBs 33 and 180 were qualified because of the field duplicate precision (FFD) concerns (Table 4-9). None of the *trans*-nonachlor results were qualified.

Table 4-9. Summary of Routine Field Sample Flags Applied to Select PCB Congeners and *trans*-Nonachlor in Tributary Samples

Analyte	Fraction	Flags								
		Sensitivity		Contamination		Precision	Bias			
		MDL	UND	FFR	FFT	FFD	FSS	FMS	LOB	HIB
PCB 33	Dissolved	9% (28)	17% (52)	3% (10)	7% (23)	0.3% (1)	0.6% (2)	0	0	0
	Particulate	5% (16)	47% (141)	0	0	0	0	0	0	0
PCB 118	Dissolved	30% (103)	9% (31)	0	0	0	0	0	0	0
	Particulate	21% (72)	4% (14)	0	0	0	0	0	0	0
PCB 180	Dissolved	47% (163)	25% (86)	0	0	0.3% (1)	0	0	0	0
	Particulate	18% (61)	5% (16)	0	0	0	0	0	0	0
<i>trans</i> -Nonachlor	Dissolved	52% (176)	14% (49)	0	0	0	0	0	0	0
	Particulate	26% (93)	15% (53)	0	0	0	0	0	0	0

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

- MDL = Less than method detection limit (Analyte produced an instrument response but reported value is below the calculated method detection limit. Validity of reported value may be compromised.)
- UND = Analyte not detected (Analyte produced no instrument response above noise.)
- FFR = Failed field blank (A field blank sample, type unknown, associated with this analysis failed the acceptance criteria. It is unknown whether the blank that failed was a field blank or a lab blank. Validity of reported value may be compromised.)
- FFT = A trip blank associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.
- FFD = Failed field duplicate (A field duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- FSS = Failed surrogate (Surrogate recoveries associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- FMS = Failed matrix spike (A matrix spike associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- LOB = Likely biased low (Reported value is probably biased low as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery or other internal lab QC data. Reported value is not considered invalid.)
- HIB = Likely biased high (Reported value is probably biased high as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery, blank contamination, or other internal lab QC data. Reported value is not considered invalid.)

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean relative percent difference (RPD) between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean relative percent difference (RPD) between the results for laboratory duplicate pairs. Table 4-10 provides a summary of data quality assessments for several of these attributes for the tributary PCB and *trans*-nonachlor data.

Because the relative variability of most measurement techniques increases as one approaches the detection limit of the technique, the assessment of the field duplicate results were divided into two concentration regimes. One measure of system precision was calculated for those field duplicate results that were less than 5 times the method detection limit (MDL) of the analyte and a separate measure was calculated for those field duplicate results that were greater than 5 times the MDL.

For PCBs 33 and 118, the dissolved measurements were much more precise for those samples above 5 times the MDL, compared to those samples below 5 times the MDL. The mean relative percent difference (RPD) between the field duplicates decreased from 45% for dissolved PCB 33 field duplicates below 5 times the MDL to 12% for the field duplicates above 5 times the MDL. For PCB 118, the mean RPD dropped from 27% to 3.7% for the dissolved results. There were no field duplicate pairs with dissolved concentrations of PCB 180 or *trans*-nonachlor that were above 5 times the MDL, so a similar comparison is not possible for these two analytes. The precision of the particulate measurements varied much less than that of the dissolved measurements. For particulate PCB 33 in field duplicates, the mean RPD actually increased from 13% for samples below 5 times the MDL to 15% for those duplicates above 5 times the MDL. For PCB 118, the mean RPD decreased from 15% to 10%. For particulate PCB 180, the mean RPDs were 14% and 13% , and they decreased from 13% to 8.6% for particulate *trans*-nonachlor.

Analytical bias was assessed using the results from matrix spike samples. Because it is not practical to prepare a sufficiently large volume (80 - 160 L) of water spiked with known amounts of both dissolved and particulate analytes, the matrix spike samples were prepared in the laboratory by adding known amounts of the PCBs and *trans*-nonachlor to a filter and XAD-2[®] resin cartridge that had never been exposed in the field and then extracting the filter and the resin using the sample techniques employed for the field samples. The mean recoveries of the analytes were excellent for the PCBs, ranging from 97% to 103% for the PCB congeners in Table 4-10, with no appreciable difference between the dissolved and particulate fractions. The mean recoveries for *trans*-nonachlor were very good, at 86% and 87% for the dissolved and particulate fractions respectively.

Thus, these results demonstrate that the analytical techniques applied to the field samples introduce little or no bias into the PCB results, and a slight low bias into the *trans*-nonachlor results. However, it is not possible to directly assess the capabilities of the sampling techniques to collect the dissolved and particulate analytes from the field samples themselves, a problem that was discussed at length in the quality assurance project plan for the LMMB Study (e.g., it is not practical to prepare large volumes (80 - 160 L) of water containing known concentrations the analytes of interest for routine use as reference samples).

Analytical sensitivity was assessed on the basis of the percentage of study samples that were reported with concentrations below the sample-specific detection limit (SSDL). The sensitivity varied by congener for the PCBs, partly as a function of the analytical instrumentation and its response to the individual congeners.

Table 4-10. Data Quality Assessment for Select PCB Congeners and *trans*-Nonachlor in Tributary Samples

Analyte/Number Field Samples	Parameter	Number of QC samples		Assessment	
		Dissolved	Particulate	Dissolved	Particulate
PCB 33 - 309 Dissolved 297 Particulate	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	9 field duplicate pairs	4 field duplicate pairs	45%	13%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	13 field duplicate pairs	10 field duplicate pairs	12%	15%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	64 Matrix Spikes	64 Matrix Spikes	98%	97%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	-	24%	53%
PCB 118 - 346 Dissolved 349 Particulate	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	22 field duplicate pairs	10 field duplicate pairs	27%	15%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	5 field duplicate pairs	19 field duplicate pairs	3.7%	10%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	64 Matrix Spikes	64 Matrix Spikes	101%	101%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	-	37%	24%
PCB 180 - 342 Dissolved 341 Particulate	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	24 field duplicate pairs	11 field duplicate pairs	27%	14%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	0 field duplicate pairs	18 field duplicate pairs	-	13%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	64 Matrix Spikes	64 Matrix Spikes	103%	103%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	-	69%	22%
<i>trans</i> -Nonachlor - 338 Dissolved 350 Particulate	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	26 field duplicate pairs	22 field duplicate pairs	19%	13%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	0 field duplicate pairs	5 field duplicate pairs	-	8.6%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	65 Matrix Spikes	65 Matrix Spikes	86%	88%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	-	66%	41%

PCB congeners and *trans*-nonachlor were not detected in substantial portions of the dissolved and particulate samples from the tributaries ("UND" flag in Table 4-9). These analytes were detected below the sample-specific detection limits in substantial portions of the samples as well ("MDL" flag in Table 4-9). For the three congeners listed in Table 4-9, the percentage of the samples with results reported below the sample-specific detection limits increases with the congener number (e.g., with molecular weight), suggesting that solubility may play a role in the distribution.

However, other factors affect this assessment of sensitivity, including both the extent of PCB contamination in Lake Michigan and the expected partitioning of analytes between the dissolved and particulate fractions. For example, only 24% of the dissolved PCB 33 results were below the SSDL, while 69% of the dissolved PCB 180 results were below the SSDL. In contrast, 53% of the particulate PCB 33 results were below the SSDL, while only 22% of the particulate PCB 180 results were below the SSDL. These differences between PCB 33 and PCB 180 may reflect the physical properties of the two congeners which indicate that PCB 33 is likely to be more soluble in water than PCB 180 and that PCB 180 is more likely to sorb to particulates. Conversely, the analytical sensitivities reported here may reflect the fact that the mean concentrations of PCB 33 in the tributaries are generally higher than the mean concentrations of either PCBs 118 or 180, thus fewer samples will contain PCB 33 below the SSDL.

The sensitivity for *trans*-nonachlor was similar to that for PCB 180, with 66% of the dissolved results below the SSDL and 41% of the particulate results below the SSDL.

4.3 Data Interpretation

4.3.1 Comparison to Historical Studies

There appear to be relatively few historical data on PCBs and *trans*-nonachlor available for the tributaries in the LMMB Study. Much of the published data focuses on the open lake, not the tributaries. Data for the Fox River are available from the Wisconsin Department of Natural Resources (DNR) based on their efforts to remediate PCB contamination in 39 miles of the lower Fox River emptying into Green Bay.

Those data are a combination of data collected in 1989 and 1990 and the data collected in the Fox River as part of the LMMB Study in 1994 and 1995. The results are for total PCBs, without any fractionation between dissolved and particulate phases. The individual results from each sample collected in 1989 and 1990 are not available in the DNR report, so no formal statistical comparisons could be made. The results are presented in a graph in the DNR report, in which the total PCB concentrations appear to range from near 0 to 120 ng/L in the 1989 - 1990 study, and from near 0 to 130 ng/L for the 1994 - 1996 data (collected as part of the LMMB Study). Moreover, DNR concluded that "*the Lower Fox River is the source of 95% of the PCB load to Green Bay and is the single largest tributary load to Lake Michigan.*"

The data from the LMMB Study presented in Section 4.2 show that the mean concentrations of PCB congeners and total PCBs in the Fox River are among the highest of the 11 tributaries in this study. When combined with the flow data from the LMMB Study, these concentration data can be transformed into loads that can be compared to the loads from the other tributaries, and ultimately compared to the conclusions of the DNR report.

PCB data collected from large volume samples similar to those in the LMMB Study were reported from the Detroit River, which connects Lake Huron and Lake Erie (Froese *et al.* 1997). The samples were collected on eight occasions between March and October 1995 and on one occasion in May 1996. The investigators in that study reported that dissolved total PCB concentrations ranged from less than 5 ng/L

to 13 ng/L, while particulate total PCB concentrations ranged from less than 5 ng/L to 22 ng/L, with a mean particulate concentration of 10 ng/L. Those results fall within the same general ranges as the dissolved and particulate results for the Fox, Grand Calumet, Kalamazoo, Milwaukee, and Sheboygan Rivers in this study, and are higher than the results for many of the other Lake Michigan tributaries.

Another earlier study addressed PCB concentrations in 14 major tributaries that discharge into Lake Michigan. Marti and Armstrong (1990) reported the results from between three and eight samples collected from each of the 14 tributaries from 1980 to 1983. The 14 tributaries in that study included 10 of the 11 tributaries in the LMMB Study (only the Grand Calumet River was not included). The sample volumes were approximately 16 liters, and were filtered and processed through a column of XAD-2[®] resin, in a fashion similar to that used in the LMMB Study.

As with the WDNR data, the results were reported for “total PCBs,” however, in addition to the total PCB concentration (e.g., dissolved and particulate), Marti and Armstrong reported the percentage that represent the particulate PCBs. Where possible, they also assigned the PCBs to one of three Aroclors or Aroclor mixtures (1242 + 1248, 1254, and 1260).

For the 10 LMMB tributaries, Marti and Armstrong reported mean total PCB concentrations ranging from 9 to 103 ng/L, with the extreme values ranging from 4 to 262 ng/L in those 10 tributaries. Marti and Armstrong attributed from 53% to 83% of the “total PCB” concentrations to particulate-phase PCBs. In contrast, the sum of the mean dissolved and mean particulate total PCB concentrations in the LMMB Study ranged from 0.8 to 76 ng/L, while the percentage of the total PCBs attributable to the particulates ranges from 27% to 74%. Marti and Armstrong found the highest total PCB concentration in the Fox River (262 ng/L). The three highest mean concentrations were reported for the Sheboygan, Fox, and Milwaukee Rivers, at 103, 98, and 97 ng/L, respectively. The sums of the mean dissolved and particulate total PCB results from the LMMB Study for these same three tributaries are 81, 53, and 24 ng/L, suggesting that total PCB concentrations in these three tributaries decreased by 21% to 71% from 1980 to 1995.

Data from the study also suggest that PCB concentrations are influenced by river flows as well as sediment PCB concentrations. Under low-flow conditions, total PCB concentrations in the Fox River were relatively high, possibly the result of the release of PCBs from sediments into the river water. As rivers flow increased, the total PCB concentrations decreased to the point of mean flow, and then increased again at higher flows. The total PCB concentration increase with increased flow is believed to be indicative of resuspension of PCB-contaminated sediments.

Marti and Armstrong also reported the results for 20 blanks processed through the filtration and extraction procedures applied to the tributary samples. The mean PCB concentration in the XAD-2 resin blanks was 1.1 ng/L \pm 1.4 ng/L. The mean total PCB concentration for the filter blanks was 0.81 ng/L \pm 0.76 ng/L. Therefore, although the Marti and Armstrong data from 1980-1983 suggest that there may have been significant decreases in PCB concentrations by the time of the LMMB Study, the results for the blanks in the Marti and Armstrong data are as large or larger than the LMMB Study total PCB results for at least five of the LMMB tributaries, complicating the evaluation of any historical trends, especially for the less polluted tributaries.

4.3.2 Regional Considerations

The results from this study generally support the assumptions used to design the study – namely that there are several tributaries that contribute large amounts of PCBs and *trans*-nonachlor to Lake Michigan and that there are other tributaries that have much lower concentrations (Figure 4-11). The tributaries that contribute the largest amounts of PCBs and *trans*-nonachlor are those near the Chicago metropolitan area and on the western shore of Lake Michigan (e.g., Grand Calumet, Milwaukee, Sheboygan, and Fox).

As these results are converted into pollutant loads to the lake, management decisions can focus on those tributaries where reductions are most practical and on those that will have the greatest impact on the overall concentrations of contaminants in Lake Michigan.

4.3.3 Other Interpretations and Perspectives

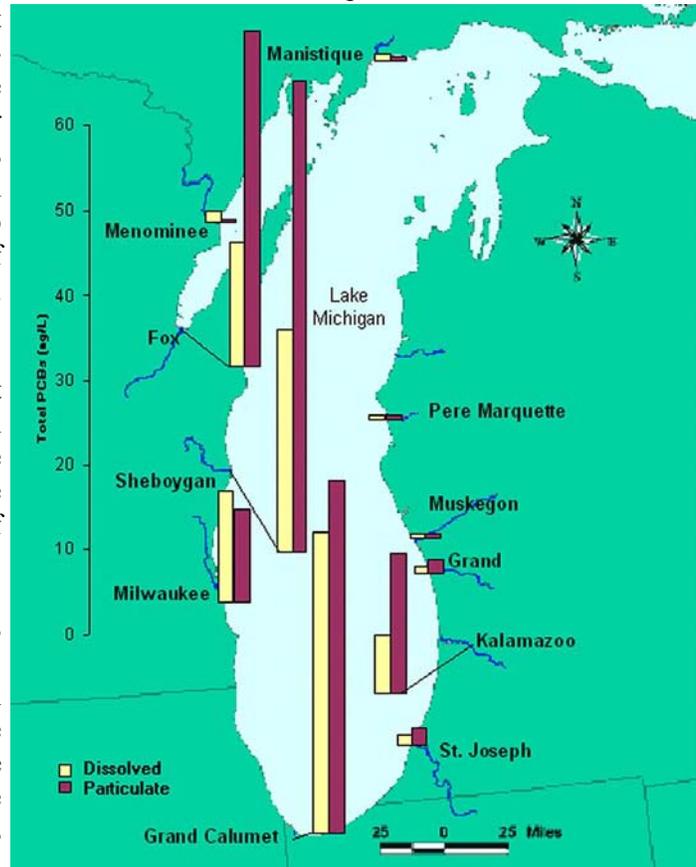
In the Wisconsin DNR study of the lower Fox River described in Section 4.3.1, the investigators noted a correlation between the concentrations of chlorophyll *a* and particulate PCBs in the Fox River. That relationship was subsequently investigated in the Milwaukee and Manitowoc rivers with similar results (Fitzgerald and Steuer, 1996).

The possible relationship between particulate PCB concentrations and chlorophyll *a* was examined using the LMMB Study data. The particulate PCB results for 39 samples from the Fox River demonstrate a strong correlation with chlorophyll *a* for both individual PCB congeners and total PCBs, while the correlations in the Milwaukee River are not as strong (Table 4-11).

Table 4-11. Correlation of Particulate PCB and *trans*-Nonachlor Concentrations with Chlorophyll *a* in the Fox and Milwaukee Rivers

Particulate-Phase Analyte	Correlation with Chlorophyll <i>a</i> (r)	
	Fox River (n=39)	Milwaukee River (n=37)
PCB 33	0.845	0.343
PCB 118	0.901	0.625
PCB 180	0.884	0.595
Total PCBs	0.873	0.627
<i>trans</i> -Nonachlor	0.642	0.596

Figure 4-11. Mean Dissolved and Particulate Total PCB Concentrations in Lake Michigan Tributaries



Fitzgerald and Steuer attribute the correlation to a combination of the low solubility of PCBs, and thus their affinity for particle surfaces, and active uptake of PCBs by algal cells. As a result, they consider PCBs in the particulate phase to be subdivided into the abiotic fraction, comprised of the PCBs associated with suspended particles including resuspended river sediments, and the biotic fraction, comprised of algae that have incorporated PCBs into their cells. This biotic fraction is the lowest link in the incorporation of PCBs into the food web.

Given the differences observed between the Fox and Milwaukee Rivers in Table 4-11, the correlations between particulate total PCBs and chlorophyll *a* were examined for all 11 tributaries in the LMMB Study (Table 4-12). The r-values for the correlations range from -0.180 to 0.895, with the strongest correlations in the Sheboygan, Kalamazoo, and Fox Rivers. The correlations do not appear to be related to overall particulate PCB concentrations because some relatively clean rivers have high correlations (e.g., St. Joseph), while some rivers with much higher PCB concentrations show very low or even negative correlations (e.g., Grand Calumet and Muskegon).

Data were collected for “total solids” during the LMMB Study. Total solids include both the suspended solids and the dissolved solids and therefore, the total solids results will overestimate the concentration of solid particles in the sample. However, there are strongly positive correlations between particulate total PCBs and total solids in many of the tributaries (Table 4-12). The correlations with total solids generally are similar to the correlations with chlorophyll *a* in most of the tributaries. The exceptions are the Grand Calumet and Muskegon Rivers. The correlation with total solids is very strong in the Grand Calumet River, while the correlation with chlorophyll *a* is very low. This suggests that the particulate PCBs in this tributary are almost exclusively “abiotic.” In the Muskegon, both correlations are very low, and with different signs.

Table 4-12. Correlation of Particulate Total PCB Concentrations with Chlorophyll *a* and Total Solids in Lake Michigan Tributaries

Tributary	Correlation with Particulate Total PCBs (r)	
	Chlorophyll <i>a</i>	Total Solids
Fox River	0.873	0.848
Grand Calumet	0.094	0.841
Grand River	0.619	0.892
Kalamazoo	0.877	0.849
Manistique	0.443	0.354
Menominee	0.274	0.495
Milwaukee	0.627	0.826
Muskegon	-0.180	0.056
Pere Marquette	0.613	0.591
Sheboygan	0.895	0.859
St. Joseph	0.718	0.786

Chapter 5

PCBs/trans-Nonachlor in Open-lake Water

5.1 Results

Open-lake samples were collected from 38 sampling stations in Lake Michigan, 2 stations in Green Bay, and 1 station in Lake Huron. A total of 350 samples were collected and analyzed for PCBs and *trans*-nonachlor. Samples were collected as described in Section 2.5.3, by pumping 100 to 1000 L of lake water through a column packed with 250 g of XAD-2[®], a macroreticular resin that traps hydrophobic organic contaminants. A “pentaplate” filter was installed in the sampling train in front of the XAD-2[®] column to collect the particulate matter suspended in the sample. Separate analyses were performed on the XAD-2[®] resin and the filtered particulates from each sampling effort, yielding results for operationally defined “dissolved” and “particulate” PCBs (Table 5-1) and *trans*-nonachlor (Table 5-2).

The results from two samples collected at Station MB63 in September 1995 are not included in the summary tables. The results for these two samples were several orders of magnitude higher than any other samples collected in the LMMB Study and were removed from consideration based on a consensus of the LMMB modeling team, leaving 348 samples from the rest of the study. Interferences and laboratory accidents further reduced the number of dissolved PCB results to 347 and reduced the number of *trans*-nonachlor results to 341 dissolved results and 347 particulate results.

Of the 38 sampling stations in Lake Michigan, 25 are “permanent” monitoring stations used by GLNPO and other investigators for a variety of studies. One additional permanent station is located in Lake Michigan near the mouth of Green Bay (GB100M) and two permanent stations are located in Green Bay itself (GB17 and GB24M). Twelve stations were established for the purposes of the Lake Michigan Mass Balance Study (the “MB” stations in Figure 5-1) and the one station in Lake Huron (LH54M) serves as a means to assess the flux of contaminants from Lake Michigan into Lake Huron. The station locations are shown in Figure 5-1.

As noted in Chapter 2, there are 209 possible PCB congeners, and the investigators in this study reported results for 65 to 110 of these congeners, depending on the capabilities of each laboratory. Battelle Marine Sciences Laboratory determined results for 105 congeners or co-eluting congeners.

For the purposes of this report, we are presenting summaries of the results for the following subset of all of the analytes:

- PCB congener 33
- PCB congener 118
- PCB congener 180
- Total PCBs
- *trans*-nonachlor

Figure 5-1. Open-lake Sampling Stations

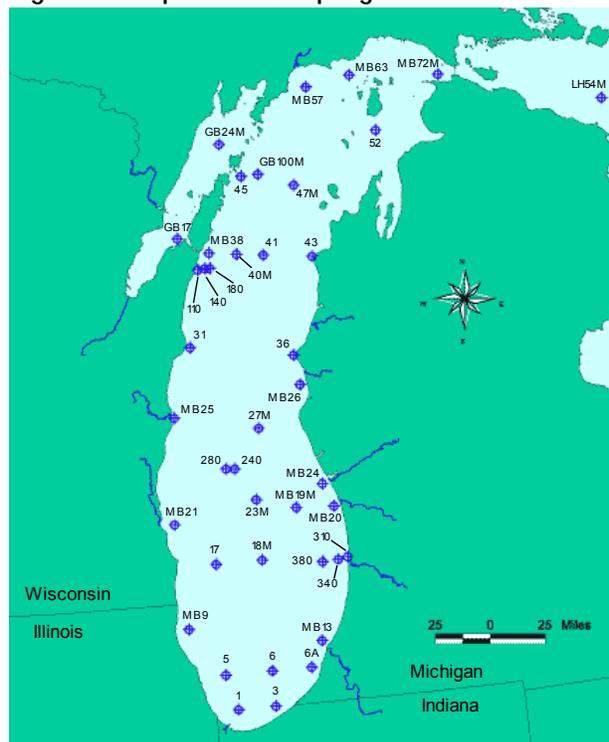


Table 5-1. Numbers of Open-lake Samples Analyzed for Dissolved and Particulate PCB Congeners and Total PCBs

Sampling Station	Sampling Dates	Dissolved PCBs	Particulate PCBs	Total Samples
1	05/10/94 to 10/11/95	5	5	10
3	05/10/94 to 10/13/95	5	5	10
5	05/11/94 to 10/10/95	11	11	22
6	05/09/94 to 10/12/95	6	6	12
6A	05/09/94 to 10/13/95	5	5	10
9	05/11/94 to 10/10/95	6	6	12
13	05/09/94 to 10/13/95	5	5	10
17	05/07/94 to 10/09/95	8	8	16
18M	05/07/94 to 10/09/95	17	17	34
19M	05/05/94 to 10/05/95	11	11	22
20	05/05/94 to 10/06/95	6	6	12
21	05/07/94 to 10/04/95	9	9	18
23M	05/04/94 to 10/03/95	17	17	34
24	05/05/94 to 10/05/95	5	5	10
25	05/03/94 to 09/29/95	6	5	11
26	05/02/94 to 09/27/95	3	4	7
27M	05/02/94 to 09/28/95	16	16	32
31	05/02/94 to 09/28/95	5	5	10
36	05/01/94 to 09/27/95	4	4	8
38	04/28/94 to 09/22/95	6	6	12
40M	04/30/94 to 09/26/95	11	11	22
41	05/01/94 to 09/27/95	9	9	18
43	05/01/94 to 09/26/95	5	5	10
45	04/26/94 to 09/20/95	5	5	10
47M	04/26/94 to 09/20/95	13	13	26
52	04/26/94 to 09/19/95	8	8	16
57	04/25/94 to 09/18/95	5	5	10
63	04/25/94 to 09/18/95	5	5	10
72M	04/25/94 to 09/17/95	8	8	16
110	06/19/94 to 09/24/95	6	6	12
140	04/28/94 to 09/23/95	10	10	20
180	06/18/94 to 09/22/95	11	11	22
240	05/04/94 to 10/02/95	10	11	21
280	05/04/94 to 10/02/95	14	14	28
310	05/06/94 to 10/08/95	7	7	14
340	05/06/94 to 10/07/95	11	11	22
380	05/06/94 to 10/06/95	13	13	26
GB17	04/27/94 to 09/22/95	8	8	16
GB24M	04/27/94 to 09/21/95	10	9	19
GB100M	04/26/94 to 09/20/95	9	10	19
LH54M	04/24/94 to 09/17/95	13	13	26
	Total	347	348	695

Table 5-2. Number of Open-lake Samples Analyzed for Dissolved and Particulate *trans*-Nonachlor

Sampling Station	Sampling Dates	Dissolved <i>trans</i> -Nonachlor	Particulate <i>trans</i> -Nonachlor	Total Samples
1	05/10/94 to 10/11/95	5	5	10
3	05/10/94 to 10/13/95	5	5	10
5	05/11/94 to 10/10/95	10	11	21
6	05/09/94 to 10/12/95	6	6	12
6A	05/09/94 to 10/13/95	5	5	10
9	05/11/94 to 10/10/95	6	6	12
13	05/09/94 to 10/13/95	5	5	10
17	05/07/94 to 10/09/95	8	8	16
18M	05/07/94 to 10/09/95	16	17	33
19M	05/05/94 to 10/05/95	11	11	22
20	05/05/94 to 10/06/95	5	6	11
21	05/07/94 to 10/04/95	9	9	18
23M	05/04/94 to 10/03/95	17	17	34
24	05/05/94 to 10/05/95	5	5	10
25	05/03/94 to 09/29/95	5	5	10
26	05/02/94 to 09/27/95	3	4	7
27M	05/02/94 to 09/28/95	16	16	32
31	05/02/94 to 09/28/95	5	5	10
36	05/01/94 to 09/27/95	4	4	8
38	04/28/94 to 09/22/95	6	6	12
40M	04/30/94 to 09/26/95	11	11	22
41	05/01/94 to 09/27/95	9	9	18
43	05/01/94 to 09/26/95	5	5	10
45	04/26/94 to 09/20/95	5	5	10
47M	04/26/94 to 09/20/95	13	13	26
52	04/26/94 to 09/19/95	8	8	16
57	04/25/94 to 09/18/95	5	5	10
63	04/25/94 to 09/18/95	5	5	10
72M	04/25/94 to 09/17/95	8	7	15
110	06/19/94 to 09/24/95	6	6	12
140	04/28/94 to 09/23/95	10	10	20
180	06/18/94 to 09/22/95	11	11	22
240	05/04/94 to 10/02/95	10	11	21
280	05/04/94 to 10/02/95	12	14	26
310	05/06/94 to 10/08/95	7	7	14
340	05/06/94 to 10/07/95	11	11	22
380	05/06/94 to 10/06/95	13	13	26
GB17	04/27/94 to 09/22/95	8	8	16
GB24M	04/27/94 to 09/21/95	10	9	19
GB100M	04/26/94 to 09/20/95	9	10	19
LH54M	04/24/94 to 09/17/95	13	13	26
Total		341	347	688

5.1.1 Temporal Variation

Temporal variation was assessed by examining the mean concentrations of dissolved and particulate total PCBs across seven cruises of the *R/V Lake Guardian* (Figures 5-2 and 5-3). The data from the January 1995 cruise were not included in this assessment because winter lake conditions only permitted the collection of samples at four stations. In general, the mean dissolved and particulate concentrations of total PCBs show little variation over time, with no discernable temporal or seasonal trends. An analysis of variance found no differences between the concentrations by cruise. In the context of a mass balance, the concentrations of PCBs and *trans*-nonachlor in the open lake reflect a large number of inputs, internal processes, and outputs of a complex ecosystem. The observed total PCB concentrations in the open lake over the course of this study may reflect competing temporal trends among those inputs, outputs, and processes. However, the apparent lack of temporal trends shown in these figures is complicated by concerns about contamination of the XAD-2[®] resin. Those concerns are discussed in detail in Section 5.2.3.

Figure 5-2. Dissolved Total PCB by Cruise

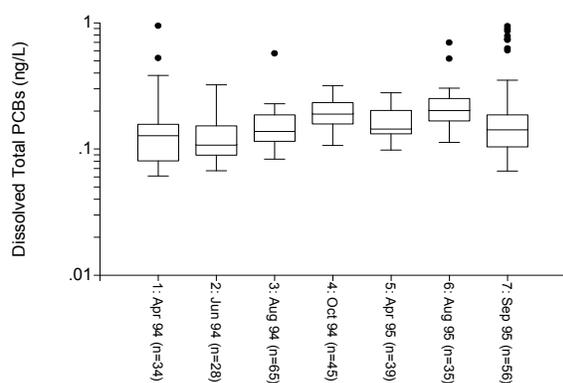
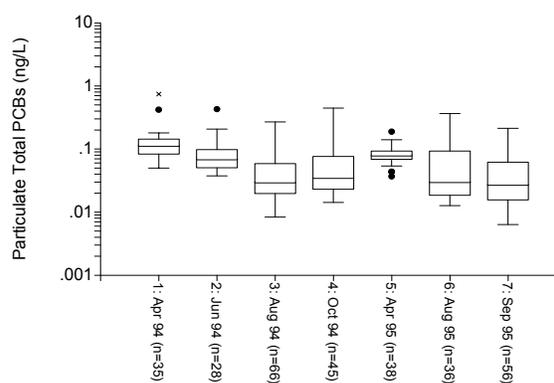


Figure 5-3. Particulate Total PCB by Cruise



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The Xs represent results beyond 3*IQR from the box. Concentration is plotted on a log scale and the scales for the two figures are different.

5.1.2 Geographical Variation

The concentrations of dissolved and particulate PCBs and *trans*-nonachlor varied by station over the course of the study (Tables 5-3 through 5-12). EPA researchers at the Large Lakes Research Station in Grosse Ile, Michigan, used the data from the LMMB Study to prepare “contour plots” of the lake where similar concentrations of PCBs and *trans*-nonachlor are indicated using a color scale. Examples of such plots are shown in Figures 5-4 to 5-11 for the dissolved and particulate concentrations of PCBs 33, 118, and 180, and *trans*-nonachlor. Similar plots for dissolved total PCBs and particulate total PCBs are shown in Figures 5-12 and 5-13.

The data in these tables and figures include all of the valid data from open lake samples, except the two samples at Station MB63 discussed in Section 5.1. The use and interpretation of the results in these tables and figures is complicated by concerns about contamination of the XAD-2[®] resin. Those concerns are discussed in detail in Section 5.2.3.

Table 5-3. Concentrations of Dissolved PCB Congener 33 Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
1	5	0.00748	0.00392 to 0.0122	0.00304	41	0
3	5	0.00622	0.00418 to 0.00742	0.00137	22	0
5	11	0.0187	0.00217 to 0.0975	0.0303	163	0
6	6	0.0101	0.00349 to 0.0235	0.00750	74	0
6A	5	0.00630	0.00516 to 0.00909	0.00166	26	0
9	6	0.0684	0.00234 to 0.206	0.0987	144	0
13	5	0.00718	0.00567 to 0.00981	0.00164	23	0
17	8	0.00639	0.00358 to 0.00826	0.00159	25	0
18M	17	0.00617	0.00240 to 0.00991	0.00231	37	0
19M	11	0.00624	0.00487 to 0.00958	0.00136	22	0
20	5	0.00749	0.00571 to 0.0120	0.00268	36	0
21	9	0.00660	0.00331 to 0.0152	0.00350	53	0
23M	17	0.0107	0.00400 to 0.0853	0.0193	180	0
24	5	0.00727	0.00585 to 0.0106	0.00202	28	0
25	6	0.00445	0.00302 to 0.00611	0.00127	28	0
26	3	0.00584	0.00451 to 0.00722	0.00136	23	0
27M	16	0.00416	0.00191 to 0.00830	0.00202	49	0
31	5	0.00562	0.00349 to 0.0112	0.00324	58	0
36	4	0.0296	0.00382 to 0.100	0.0472	160	0
38	6	0.00535	0.00398 to 0.00730	0.00112	21	0
40M	10	0.00514	0.00332 to 0.00947	0.00178	35	0
41	9	0.00306	0.00237 to 0.00438	0.000671	22	0
43	5	0.00448	0.00247 to 0.00785	0.00216	48	0
45	5	0.00528	0.00290 to 0.00918	0.00244	46	0
47M	12	0.00460	0.00123 to 0.00700	0.00184	40	0
52	7	0.00510	0.00344 to 0.00658	0.00117	23	0
57	5	0.00374	0.00278 to 0.00459	0.000742	20	0
63	5	0.00338	0.00252 to 0.00499	0.00094	28	0
72M	8	0.00366	0.00270 to 0.00469	0.000785	21	0
110	6	0.00894	0.00277 to 0.0337	0.0121	136	0
140	10	0.00373	0.00 to 0.00530	0.00158	42	10
180	11	0.00717	0.00325 to 0.0335	0.00876	122	0
240	10	0.00496	0.00346 to 0.00763	0.00114	23	0
280	14	0.0307	0.00250 to 0.194	0.0651	212	0
310	7	0.00787	0.00590 to 0.0118	0.00212	27	0
340	11	0.00585	0.00305 to 0.00899	0.00174	30	0
380	13	0.00590	0.00202 to 0.0114	0.00219	37	0
GB17	8	0.0127	0.00287 to 0.0254	0.00709	56	0
GB24M	10	0.00512	0.00335 to 0.00806	0.00154	30	0
GB100M	8	0.00421	0.00228 to 0.00707	0.00170	41	0
LH54M	13	0.00398	0.00116 to 0.0122	0.00270	68	0

Table 5-4. Concentrations of Particulate PCB Congener 33 Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
1	5	0.00148	0.00 to 0.00530	0.00218	147	20
3	5	0.00113	0.00 to 0.00375	0.00151	133	20
5	11	0.000634	0.00 to 0.00361	0.00100	158	10
6	6	0.000413	0.00 to 0.00133	0.000501	121	33
6A	5	0.00205	0.00 to 0.00770	0.00320	156	20
9	6	0.000694	0.000129 to 0.00126	0.000421	61	0
13	5	0.00208	0.00 to 0.00698	0.00286	137	20
17	8	0.000550	0.00 to 0.00194	0.000619	113	25
18M	17	0.000573	0.00 to 0.00233	0.000788	138	29
19M	11	0.000605	0.00 to 0.00244	0.000898	149	27
20	6	0.00101	0.000193 to 0.00195	0.000694	69	0
21	9	0.000593	0.00 to 0.00158	0.000497	84	11
23M	17	0.000615	0.00 to 0.00382	0.000942	153	18
24	5	0.000793	0.000188 to 0.00225	0.000853	108	0
25	5	0.000676	0.000142 to 0.00157	0.000627	93	0
26	4	0.000910	0.0000872 to 0.00285	0.00131	144	25
27M	16	0.000497	0.00 to 0.00166	0.000519	104	13
31	5	0.000842	0.00 to 0.00290	0.00120	143	20
36	4	0.00476	0.00 to 0.0180	0.00884	185	25
38	6	0.000438	0.00 to 0.00168	0.000633	145	33
40M	11	0.000207	0.00 to 0.000649	0.000258	125	55
41	9	0.000302	0.00 to 0.00202	0.000666	220	67
43	5	0.000740	0.00 to 0.00305	0.00130	175	20
45	5	0.000446	0.000117 to 0.00145	0.000566	127	0
47M	13	0.000360	0.00 to 0.00236	0.000681	189	62
52	8	0.000441	0.00 to 0.00238	0.000798	181	25
57	5	0.000732	0.00 to 0.00332	0.00145	198	60
63	5	0.00123	0.00 to 0.00516	0.00220	178	40
72M	7	0.000112	0.00 to 0.000285	0.000135	121	57
110	6	0.000214	0.00 to 0.000648	0.000238	111	33
140	10	0.000566	0.00 to 0.00268	0.000789	139	30
180	11	0.000351	0.00 to 0.000833	0.000315	90	27
240	11	0.000466	0.00 to 0.00204	0.000615	132	36
280	13	0.000349	0.00 to 0.000890	0.000281	80	23
310	7	0.00331	0.000611 to 0.0100	0.00330	100	0
340	11	0.00147	0.00 to 0.00414	0.00132	90	18
380	13	0.000825	0.00 to 0.00266	0.000692	84	15
GB17	8	0.0283	0.0130 to 0.0578	0.0131	46	0
GB24M	9	0.00108	0.000209 to 0.00340	0.000977	90	0
GB100M	10	0.000237	0.00 to 0.000714	0.000249	105	40
LH54M	13	0.000245	0.00 to 0.00125	0.000377	154	54

Table 5-5. Concentrations of Dissolved PCB Congener 118 Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
1	5	0.00117	0.00 to 0.00183	0.000747	64	20
3	5	0.00129	0.00 to 0.00252	0.00109	85	40
5	11	0.00306	0.00 to 0.00974	0.00302	99	18
6	6	0.00227	0.000869 to 0.00407	0.00130	57	0
6A	5	0.000921	0.00 to 0.00250	0.000978	106	60
9	6	0.00356	0.00 to 0.00802	0.00297	84	33
13	5	0.00167	0.000797 to 0.00232	0.000636	38	0
17	8	0.00318	0.00 to 0.0128	0.00405	127	25
18M	17	0.00330	0.00 to 0.0125	0.00331	100	6
19M	11	0.00363	0.000223 to 0.0119	0.00359	99	18
20	5	0.00245	0.00 to 0.00745	0.00305	124	40
21	9	0.00328	0.000858 to 0.0142	0.00426	130	0
23M	17	0.00218	0.000394 to 0.00555	0.00149	69	6
24	5	0.00275	0.00 to 0.00896	0.00362	132	40
25	6	0.00253	0.000616 to 0.00948	0.00346	137	33
26	3	0.000825	0.000377 to 0.00120	0.000417	50	33
27M	16	0.00142	0.000338 to 0.00522	0.00109	77	6
31	5	0.00260	0.00 to 0.0104	0.00439	169	40
36	4	0.00426	0.000273 to 0.0142	0.00663	156	25
38	6	0.00363	0.000216 to 0.0139	0.00520	143	33
40M	10	0.00256	0.0000681 to 0.0115	0.00338	132	40
41	9	0.000788	0.00 to 0.00208	0.000635	81	44
43	5	0.00174	0.000159 to 0.00396	0.00146	84	20
45	5	0.00171	0.000626 to 0.00353	0.00132	77	40
47M	12	0.00258	0.000269 to 0.00994	0.00342	132	33
52	7	0.000790	0.00 to 0.00207	0.000670	85	57
57	5	0.00173	0.000202 to 0.00453	0.00192	111	60
63	5	0.00088	0.00039 to 0.00166	0.00056	63	60
72M	8	0.000760	0.00 to 0.00208	0.000676	89	63
110	6	0.00230	0.000255 to 0.00846	0.00320	139	33
140	10	0.00219	0.0000899 to 0.00912	0.00294	134	30
180	11	0.00265	0.000228 to 0.00991	0.00274	103	18
240	10	0.00254	0.000738 to 0.00823	0.00259	102	0
280	14	0.00420	0.00 to 0.0183	0.00580	138	14
310	7	0.00352	0.00144 to 0.00552	0.00167	47	0
340	11	0.00286	0.00 to 0.00867	0.00268	94	18
380	13	0.00272	0.00 to 0.0111	0.00328	121	15
GB17	8	0.00406	0.00195 to 0.00727	0.00183	45	0
GB24M	10	0.00218	0.000302 to 0.00729	0.00206	94	10
GB100M	8	0.00218	0.000422 to 0.00798	0.00249	114	13
LH54M	13	0.00163	0.0000737 to 0.00947	0.00254	156	38

Table 5-6. Concentrations of Particulate PCB Congener 118 Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
1	5	0.00252	0.000610 to 0.00730	0.00282	112	0
3	5	0.00223	0.000269 to 0.00683	0.00264	118	20
5	11	0.00195	0.000315 to 0.00450	0.00134	69	0
6	6	0.00203	0.00 to 0.00402	0.00198	98	17
6A	5	0.00358	0.00 to 0.0136	0.00567	158	40
9	6	0.00194	0.000354 to 0.00441	0.00154	79	0
13	5	0.00378	0.00 to 0.0131	0.00537	142	20
17	8	0.00255	0.000111 to 0.00420	0.00176	69	13
18M	17	0.00215	0.00 to 0.0139	0.00376	174	29
19M	11	0.00272	0.0000860 to 0.0124	0.00352	130	9
20	6	0.00307	0.00111 to 0.00504	0.00156	51	0
21	9	0.00275	0.000704 to 0.00816	0.00236	86	0
23M	17	0.00284	0.00 to 0.0129	0.00325	114	12
24	5	0.00245	0.000849 to 0.00510	0.00173	71	0
25	5	0.00172	0.000476 to 0.00288	0.000914	53	0
26	4	0.00218	0.00109 to 0.00352	0.00120	55	0
27M	16	0.00224	0.000109 to 0.00702	0.00224	100	13
31	5	0.00162	0.000527 to 0.00258	0.000934	58	0
36	4	0.00254	0.000722 to 0.00457	0.00177	70	0
38	6	0.00136	0.000543 to 0.00267	0.000841	62	0
40M	11	0.000581	0.00 to 0.00162	0.000494	85	18
41	9	0.000553	0.000229 to 0.000942	0.000300	54	22
43	5	0.00130	0.000407 to 0.00239	0.000957	74	0
45	5	0.00133	0.000450 to 0.00241	0.000777	58	0
47M	13	0.000618	0.00 to 0.00166	0.000556	90	31
52	8	0.00104	0.00 to 0.00270	0.000927	89	13
57	5	0.00114	0.00 to 0.00232	0.00106	93	20
63	5	0.00141	0.00 to 0.002550	0.00118	83	20
72M	7	0.000637	0.00 to 0.00136	0.000495	78	29
110	6	0.00121	0.000398 to 0.00204	0.000723	60	0
140	10	0.00140	0.000267 to 0.00280	0.000988	71	0
180	11	0.00141	0.0000435 to 0.00273	0.00104	74	9
240	11	0.00176	0.0000510 to 0.00368	0.00149	85	18
280	13	0.00214	0.0000664 to 0.00411	0.00148	69	15
310	7	0.0101	0.00240 to 0.0263	0.00852	84	0
340	11	0.00436	0.0000385 to 0.0122	0.00388	89	18
380	13	0.00371	0.0000735 to 0.00660	0.00228	61	8
GB17	8	0.0157	0.00 to 0.0326	0.0116	74	25
GB24M	9	0.00233	0.000283 to 0.00410	0.00121	52	11
GB100M	10	0.00119	0.00 to 0.00226	0.000806	68	10
LH54M	13	0.000839	0.00 to 0.00230	0.000821	98	38

Table 5-7. Concentrations of Dissolved PCB Congener 180 Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
1	5	0.000340	0.00 to 0.00156	0.000684	201	80
3	5	0.000143	0.00 to 0.00228	0.000208	175	70
5	11	0.00311	0.00 to 0.000747	0.00880	153	89
6	6	0.000400	0.00 to 0.000345	0.000692	133	83
6A	5	0.000371	0.00 to 0.00405	0.000694	208	80
9	6	0.000882	0.00 to 0.000347	0.00191	159	100
13	5	0.000486	0.00 to 0.0295	0.000921	283	64
17	8	0.000383	0.00 to 0.00160	0.000748	187	80
18M	17	0.000258	0.00 to 0.00309	0.000642	223	83
19M	11	0.000314	0.00 to 0.00211	0.000605	190	80
20	5	0.000289	0.00 to 0.000381	0.000411	189	90
21	9	0.000263	0.00 to 0.00211	0.000455	195	75
23M	17	0.000119	0.00 to 0.000563	0.000260	158	91
24	5	0.000757	0.00 to 0.00258	0.00146	249	82
25	6	0.000555	0.00 to 0.000882	0.000855	142	60
26	3	0.000518	0.00 to 0.00139	0.000580	173	78
27M	16	0.000294	0.00 to 0.000891	0.000516	218	88
31	5	0.000535	0.00 to 0.00223	0.00116	154	50
36	4	0.00262	0.00 to 0.0124	0.00481	236	71
38	6	0.0000565	0.00 to 0.00261	0.0000637	217	80
40M	10	0.000107	0.00 to 0.00144	0.000181	259	82
41	9	0.000165	0.00 to 0.00982	0.000252	183	50
43	5	0.000228	0.00 to 0.000128	0.000316	113	100
45	5	0.000148	0.00 to 0.00346	0.000145	218	69
47M	12	0.0000981	0.00 to 0.000518	0.000131	170	80
52	7	0.000151	0.00 to 0.000630	0.000246	138	60
57	5	0.000858	0.00 to 0.000291	0.00179	98	100
63	5	0.000183	0.00 to 0.00060	0.00024	133	100
72M	8	0.0000796	0.00 to 0.0479	0.000127	172	57
110	6	0.000556	0.00 to 0.000458	0.00124	146	80
140	10	0.0000667	0.00 to 0.00177	0.000126	173	67
180	11	0.000116	0.00 to 0.00476	0.000183	217	67
240	10	0.000414	0.00 to 0.00196	0.000724	192	73
280	14	0.00145	0.00 to 0.00334	0.00343	193	60
310	7	0.000712	0.00 to 0.00114	0.00151	112	33
340	11	0.000170	0.00 to 0.00209	0.000441	175	69
380	13	0.000445	0.00 to 0.00404	0.000970	212	71
GB17	8	0.00109	0.00 to 0.00699	0.00240	220	63
GB24M	10	0.000296	0.00 to 0.00186	0.000568	192	80
GB100M	8	0.000137	0.00 to 0.000282	0.000117	85	100
LH54M	13	0.000121	0.00 to 0.000527	0.000175	144	85

Table 5-8. Concentrations of Particulate PCB Congener 180 Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
1	5	0.000974	0.00 to 0.00248	0.00128	132	40
3	5	0.000943	0.00 to 0.00364	0.00121	170	55
5	11	0.000807	0.00 to 0.00103	0.000343	300	89
6	6	0.00115	0.00 to 0.00168	0.000488	145	46
6A	5	0.00160	0.00 to 0.00288	0.00123	173	40
9	6	0.000654	0.00 to 0.00125	0.000485	181	71
13	5	0.00162	0.00 to 0.00246	0.000864	107	36
17	8	0.00111	0.00 to 0.00568	0.00238	149	40
18M	17	0.000929	0.00 to 0.000577	0.000283	128	50
19M	11	0.00123	0.00 to 0.00531	0.00219	135	40
20	6	0.00178	0.00 to 0.00168	0.000534	146	50
21	9	0.00110	0.00 to 0.00278	0.00104	93	38
23M	17	0.00112	0.00 to 0.000954	0.000373	135	55
24	5	0.00143	0.00 to 0.00547	0.00151	162	47
25	5	0.000415	0.0000299 to 0.00371	0.00144	81	17
26	4	0.000919	0.00 to 0.00241	0.000886	80	22
27M	16	0.000729	0.00 to 0.00407	0.00122	109	29
31	5	0.000553	0.00 to 0.00183	0.000800	193	60
36	4	0.00115	0.00 to 0.00183	0.000663	88	31
38	6	0.000329	0.00 to 0.00161	0.000664	120	40
40M	11	0.000200	0.00 to 0.00586	0.00189	86	18
41	9	0.000114	0.00 to 0.00332	0.00157	137	50
43	5	0.000581	0.00 to 0.00197	0.000805	245	83
45	5	0.000552	0.00 to 0.00477	0.00139	77	15
47M	13	0.000336	0.00 to 0.00139	0.000455	227	82
52	8	0.000532	0.00 to 0.00232	0.00100	173	60
57	5	0.000709	0.00 to 0.00164	0.000710	129	40
63	5	0.00093	0.00 to 0.00207	0.000913	98	60
72M	7	0.000268	0.00 to 0.00207	0.000833	115	29
110	6	0.000221	0.00 to 0.00276	0.00119	126	40
140	10	0.000365	0.00 to 0.00276	0.00135	118	50
180	11	0.000277	0.00 to 0.00142	0.000511	78	17
240	11	0.000708	0.00 to 0.00477	0.00167	135	45
280	13	0.000751	0.00 to 0.00516	0.00218	152	20
310	7	0.00431	0.00 to 0.00296	0.00140	153	50
340	11	0.00219	0.00 to 0.00307	0.000902	124	38
380	13	0.00180	0.000761 to 0.0117	0.00399	93	0
GB17	8	0.00644	0.00415 to 0.0142	0.00332	52	0
GB24M	9	0.000627	0.00 to 0.00238	0.000840	134	44
GB100M	10	0.000593	0.00 to 0.00199	0.000730	123	50
LH54M	13	0.000314	0.00 to 0.00111	0.000428	136	62

Table 5-9. Concentrations of Dissolved Total PCBs Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)
1	5	0.172	0.0796 to 0.227	0.0616	36
3	5	0.187	0.107 to 0.137	0.0566	13
5	11	0.303	0.0758 to 0.574	0.282	85
6	6	0.168	0.0864 to 0.165	0.0447	26
6A	5	0.169	0.138 to 0.200	0.0271	16
9	6	0.364	0.0613 to 0.898	0.360	99
13	5	0.199	0.0713 to 0.865	0.0493	93
17	8	0.180	0.103 to 0.788	0.0285	102
18M	17	0.166	0.0932 to 0.528	0.0636	73
19M	11	0.169	0.142 to 0.219	0.0450	16
20	6	0.181	0.0791 to 0.248	0.106	39
21	9	0.189	0.0669 to 0.304	0.0600	38
23M	17	0.174	0.0996 to 0.232	0.0652	27
24	5	0.207	0.00 to 0.319	0.0594	59
25	6	0.140	0.101 to 0.352	0.0557	38
26	3	0.121	0.170 to 0.312	0.0151	29
27M	16	0.131	0.0789 to 0.274	0.0474	40
31	5	0.144	0.0722 to 0.253	0.0531	36
36	4	0.299	0.185 to 0.949	0.292	75
38	6	0.185	0.123 to 0.243	0.104	23
40M	11	0.145	0.113 to 0.384	0.0720	56
41	9	0.104	0.128 to 0.270	0.0216	26
43	5	0.142	0.00 to 0.269	0.0550	50
45	5	0.232	0.0692 to 0.126	0.197	21
47M	13	0.133	0.0806 to 0.216	0.0761	39
52	8	0.115	0.00 to 0.272	0.0503	57
57	5	0.121	0.00 to 0.167	0.0318	44
63	5	0.107	0.0731 to 0.156	0.3058	31
72M	8	0.118	0.0682 to 0.204	0.0500	42
110	6	0.257	0.108 to 0.243	0.262	30
140	10	0.178	0.100 to 0.209	0.130	27
180	11	0.164	0.157 to 0.280	0.0641	25
240	10	0.159	0.0920 to 0.249	0.0629	32
280	14	0.245	0.100 to 0.247	0.239	40
310	7	0.373	0.0673 to 0.944	0.280	97
340	11	0.179	0.0992 to 0.219	0.0421	37
380	13	0.182	0.116 to 0.734	0.0465	98
GB17	8	0.653	0.290 to 1.52	0.420	64
GB24M	10	0.166	0.0844 to 0.247	0.0602	36
GB100M	9	0.289	0.00 to 0.634	0.256	89
LH54M	13	0.129	0.0526 to 0.209	0.0556	43

Table 5-10. Concentrations of Particulate Total PCBs Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)
1	5	0.100	0.0334 to 0.270	0.102	101
3	5	0.0830	0.0344 to 0.144	0.0867	65
5	11	0.0699	0.0259 to 0.0877	0.0490	51
6	6	0.0563	0.0159 to 0.137	0.0445	92
6A	5	0.140	0.0217 to 0.449	0.174	124
9	6	0.0728	0.0222 to 0.126	0.0349	48
13	5	0.138	0.0196 to 0.170	0.165	70
17	8	0.0707	0.0161 to 0.0774	0.0416	56
18M	17	0.0652	0.0224 to 0.0996	0.0712	54
19M	11	0.0757	0.0131 to 0.124	0.0783	59
20	6	0.103	0.0141 to 0.0814	0.0573	52
21	9	0.0910	0.0113 to 0.264	0.0479	109
23M	17	0.0754	0.00836 to 0.269	0.0620	103
24	5	0.0870	0.0355 to 0.181	0.0653	55
25	5	0.0522	0.0129 to 0.245	0.0203	82
26	4	0.0843	0.0279 to 0.181	0.0548	75
27M	16	0.0630	0.0104 to 0.115	0.0434	71
31	5	0.0619	0.0103 to 0.152	0.0354	69
36	4	0.150	0.0776 to 0.744	0.183	80
38	6	0.0575	0.0127 to 0.365	0.0385	79
40M	11	0.0271	0.0211 to 0.122	0.0132	67
41	9	0.0307	0.0151 to 0.181	0.0198	53
43	5	0.0549	0.0144 to 0.0541	0.0443	49
45	5	0.0527	0.0115 to 0.0734	0.0269	64
47M	13	0.0312	0.0165 to 0.123	0.0239	81
52	8	0.0416	0.00637 to 0.0894	0.0333	77
57	5	0.0558	0.0157 to 0.112	0.0512	80
63	5	0.0654	0.0203 to 0.159	0.055	84
72M	8	0.0275	0.00 to 0.0663	0.0205	75
110	6	0.0424	0.0141 to 0.234	0.0236	104
140	10	0.0547	0.0129 to 0.109	0.0297	79
180	11	0.0500	0.0110 to 0.420	0.0261	120
240	11	0.0590	0.0306 to 0.200	0.0418	53
280	14	0.0581	0.0199 to 0.0681	0.0358	39
310	7	0.297	0.00 to 0.101	0.237	62
340	11	0.134	0.0232 to 0.108	0.106	57
380	13	0.103	0.0253 to 0.421	0.0549	122
GB17	8	1.02	0.468 to 2.30	0.553	54
GB24M	9	0.0810	0.0402 to 0.137	0.0341	42
GB100M	10	0.0459	0.0105 to 0.109	0.0312	68
LH54M	13	0.0379	0.00976 to 0.103	0.0268	71

Table 5-11. Concentrations of Dissolved *trans*-Nonachlor Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
1	5	0.00507	0.00227 to 0.00863	0.00303	60	0
3	5	0.00545	0.00 to 0.0119	0.00296	59	10
5	10	0.0111	0.000359 to 0.0124	0.0118	76	11
6	6	0.00870	0.00 to 0.0102	0.00656	77	23
6A	5	0.00429	0.00 to 0.00594	0.00302	115	40
9	6	0.00430	0.00 to 0.00590	0.00405	63	25
13	5	0.00548	0.00160 to 0.0392	0.00338	106	0
17	8	0.0236	0.000807 to 0.00786	0.0494	70	20
18M	16	0.00659	0.00124 to 0.0165	0.00393	71	17
19M	11	0.00773	0.000917 to 0.00888	0.00613	62	20
20	5	0.00450	0.00 to 0.0463	0.00423	156	30
21	9	0.00366	0.00 to 0.145	0.00467	209	13
23M	17	0.00368	0.00 to 0.0102	0.00367	68	18
24	5	0.00579	0.00 to 0.0131	0.00258	60	19
25	5	0.00478	0.00 to 0.00984	0.00361	94	40
26	3	0.00440	0.00 to 0.0150	0.00467	127	44
27M	16	0.00524	0.00 to 0.0108	0.00432	100	41
31	5	0.00402	0.00118 to 0.0101	0.00366	76	20
36	4	0.00228	0.00 to 0.0145	0.00457	66	8
38	6	0.00432	0.00 to 0.00962	0.00467	91	20
40M	11	0.00433	0.00 to 0.0138	0.00376	88	27
41	9	0.00475	0.00 to 0.00913	0.00361	200	75
43	5	0.00289	0.00 to 0.0127	0.00251	108	33
45	5	0.00397	0.000786 to 0.0129	0.000926	63	8
47M	13	0.00388	0.00 to 0.00998	0.00300	87	27
52	8	0.00375	0.000239 to 0.00650	0.00261	87	40
57	5	0.00232	0.00296 to 0.00542	0.00266	23	0
63	5	0.00296	0.00152 to 0.00494	0.00135	46	20
72M	8	0.00330	0.00152 to 0.176	0.00207	238	0
110	6	0.00728	0.00108 to 0.00832	0.00516	54	20
140	10	0.00869	0.00 to 0.0193	0.0136	75	17
180	11	0.00481	0.00 to 0.00932	0.00328	94	33
240	10	0.00627	0.00 to 0.0169	0.00368	79	18
280	12	0.00637	0.00146 to 0.00789	0.00422	45	0
310	7	0.00530	0.00 to 0.00930	0.00184	106	33
340	11	0.00551	0.00 to 0.0139	0.00483	82	19
380	13	0.00604	0.00253 to 0.00749	0.00383	35	0
GB17	8	0.00560	0.00145 to 0.0159	0.00497	89	0
GB24M	10	0.00348	0.00 to 0.00733	0.00213	61	10
GB100M	9	0.00531	0.00 to 0.0113	0.00347	65	22
LH54M	13	0.00876	0.00 to 0.0774	0.0210	239	46

Table 5-12. Concentrations of Particulate *trans*-Nonachlor Measured in Open-lake Samples

Sampling Station	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
1	5	0.0026	0.000509 to 0.00844	0.0033	127	0
3	5	0.0012	0.000365 to 0.00771	0.0011	96	9
5	11	0.0027	0.000109 to 0.00575	0.0029	116	22
6	6	0.0013	0.00 to 0.00644	0.0017	133	31
6A	5	0.0040	0.000396 to 0.00687	0.0023	103	0
9	6	0.0025	0.000531 to 0.00298	0.0019	60	0
13	5	0.0014	0.00 to 0.0104	0.0010	105	18
17	8	0.0015	0.00121 to 0.00621	0.0008	57	0
18M	17	0.0018	0.000571 to 0.00636	0.0024	98	0
19M	11	0.0012	0.00 to 0.00245	0.0011	72	20
20	6	0.0021	0.000552 to 0.00652	0.0013	79	0
21	9	0.0027	0.000912 to 0.00342	0.0022	52	0
23M	17	0.0021	0.00 to 0.00475	0.0016	82	18
24	5	0.0027	0.00 to 0.00844	0.0021	138	29
25	5	0.0014	0.000773 to 0.00403	0.0007	64	0
26	4	0.0024	0.00 to 0.00665	0.0027	80	11
27M	16	0.0022	0.000391 to 0.00622	0.0021	76	0
31	5	0.0016	0.000468 to 0.00217	0.0008	51	0
36	4	0.0031	0.000180 to 0.00657	0.0024	84	14
38	6	0.0025	0.000423 to 0.00228	0.0024	46	20
40M	11	0.0011	0.00 to 0.00889	0.0010	95	9
41	9	0.0015	0.00102 to 0.00639	0.0018	79	0
43	5	0.0023	0.000604 to 0.00683	0.0020	96	0
45	5	0.0026	0.000452 to 0.00679	0.0023	84	0
47M	13	0.0014	0.00 to 0.00344	0.0018	88	27
52	8	0.0017	0.000887 to 0.00583	0.0016	90	0
57	5	0.0025	0.000264 to 0.00596	0.0026	90	20
63	5	0.00226	0.00 to 0.00542	0.0022	97	20
72M	7	0.0016	0.00 to 0.00542	0.0009	109	14
110	6	0.0023	0.00 to 0.00261	0.0022	91	20
140	10	0.0029	0.00 to 0.00474	0.0023	132	33
180	11	0.0017	0.000508 to 0.00583	0.0014	75	0
240	11	0.0023	0.00 to 0.00409	0.0022	93	18
280	14	0.0025	0.000501 to 0.00570	0.0021	77	0
310	7	0.0030	0.000918 to 0.00643	0.0022	112	0
340	11	0.0031	0.00 to 0.00791	0.0029	96	13
380	13	0.0025	0.000887 to 0.00761	0.0021	75	0
GB17	8	0.0037	0.00119 to 0.00893	0.0025	66	0
GB24M	9	0.0020	0.000253 to 0.00355	0.0011	56	11
GB100M	10	0.0019	0.00 to 0.00580	0.0020	102	20
LH54M	13	0.0011	0.00 to 0.00307	0.0009	87	38

Figures 5-4 to 5-13 illustrate the concentrations of PCBs 33, 118, 180, total PCBs, and *trans*-nonachlor in the dissolved and particulate samples collected over the course of the LMMB Study.

Note: The color scales used in these contour plots vary with each plot. Therefore, although the red end of the visible spectrum always represents higher concentrations than the violet end of the spectrum, the absolute magnitude represented by each color differs with the contaminant and the phase (dissolved versus particulate). Each plot includes a concentration scale and readers are advised to consult those scales carefully when comparing the plots.

The plots of the dissolved PCB congeners (Figures 5-4 to 5-6) indicate that the concentrations of these contaminants are generally lowest in the far northern areas of the lake that are removed from urban influences. The highest dissolved concentrations generally are found in the southwest area of the lake, centered around Station 9, which lies between the urban areas of Chicago and Milwaukee. The dissolved PCB concentrations suggest that there may be a point source at Waukegan Harbor, Illinois. The concentrations of these dissolved contaminants show some increase in Green Bay, with dissolved PCB 118 concentrations highest overall at Station GB 17, near the discharge of the Fox River. (The apparent decrease in concentrations of these contaminants from Station GB 17 to the head of Green Bay likely is a function of the lack of a sampling station further up Green Bay).

The plots of the particulate PCB congeners (Figures 5-7 to 5-9) illustrate the importance of contaminant sources in Green Bay. The particulate PCB concentrations are highest in Green Bay, at Station GB 17, with much lower particulate PCB concentrations in the remainder of the lake. The particulate concentrations of PCBs 118 and 180 show a slight increase in the southeast portion of the lake, in the area between the mouths of the St. Joseph and Kalamazoo Rivers. However, the concentrations of particulate PCBs 118 and 180 in that area are still 2 to 5 times lower than in the upper reaches of Green Bay.

The patterns of dissolved concentrations of *trans*-nonachlor (Figure 5-10) are similar to those of the dissolved PCB congeners, with an apparent increase in concentration in the southwest portion of the lake, near Chicago. The increase in concentration on the western shore of the lake seen in Figure 5-10 suggests that the Sturgeon Bay ship canal, which connects lower Green Bay with this portion of Lake Michigan, results in the transfer of water containing dissolved *trans*-nonachlor from Green Bay into Lake Michigan.

The particulate concentrations of *trans*-nonachlor (Figure 5-11) are similar to those of the particulate PCB congeners, with the highest concentrations in Green Bay, near Station GB 17. However, particulate *trans*-nonachlor concentrations appear to be increased in areas of the lake adjacent to most of the major urban areas around the lake. However, similar increases occur near the discharges of the Manistique and Pere Marquette Rivers, which are not associated with urban areas, suggesting that the increases near the urban area may be a function of river-borne sources of particulate *trans*-nonachlor, including resuspension of contaminated sediments. The particulate *trans*-nonachlor results also suggest the transfer of contaminants from lower Green Bay to Lake Michigan via the Sturgeon Bay ship canal.

The plots of dissolved and particulate total PCBs (Figures 5-12 and 5-13) illustrate the importance of the sources of these contaminants in Green Bay. The dissolved total PCB concentrations are highest in Green Bay. However, the dissolved total PCB concentrations in the lower portion of Lake Michigan are higher than in the northern portion of the lake, with an apparent hot spot near Chicago. The particulate total PCB concentrations are also highest in Green Bay and lower throughout the main portion of the lake, with a slight increase in the southeast portion of the lake, similar to the particulate PCB 118 and 180 results. The dissolved and particulate PCB results show less indication of the transfer of contaminants from lower Green Bay to Lake Michigan via the Sturgeon Bay ship canal than the results for *trans*-nonachlor, with increases for the congeners reported here evident only for dissolved PCB 118 and dissolved total PCBs.

Figure 5-4. Concentrations of Dissolved PCB Congener 33 Measured in Open-lake Samples

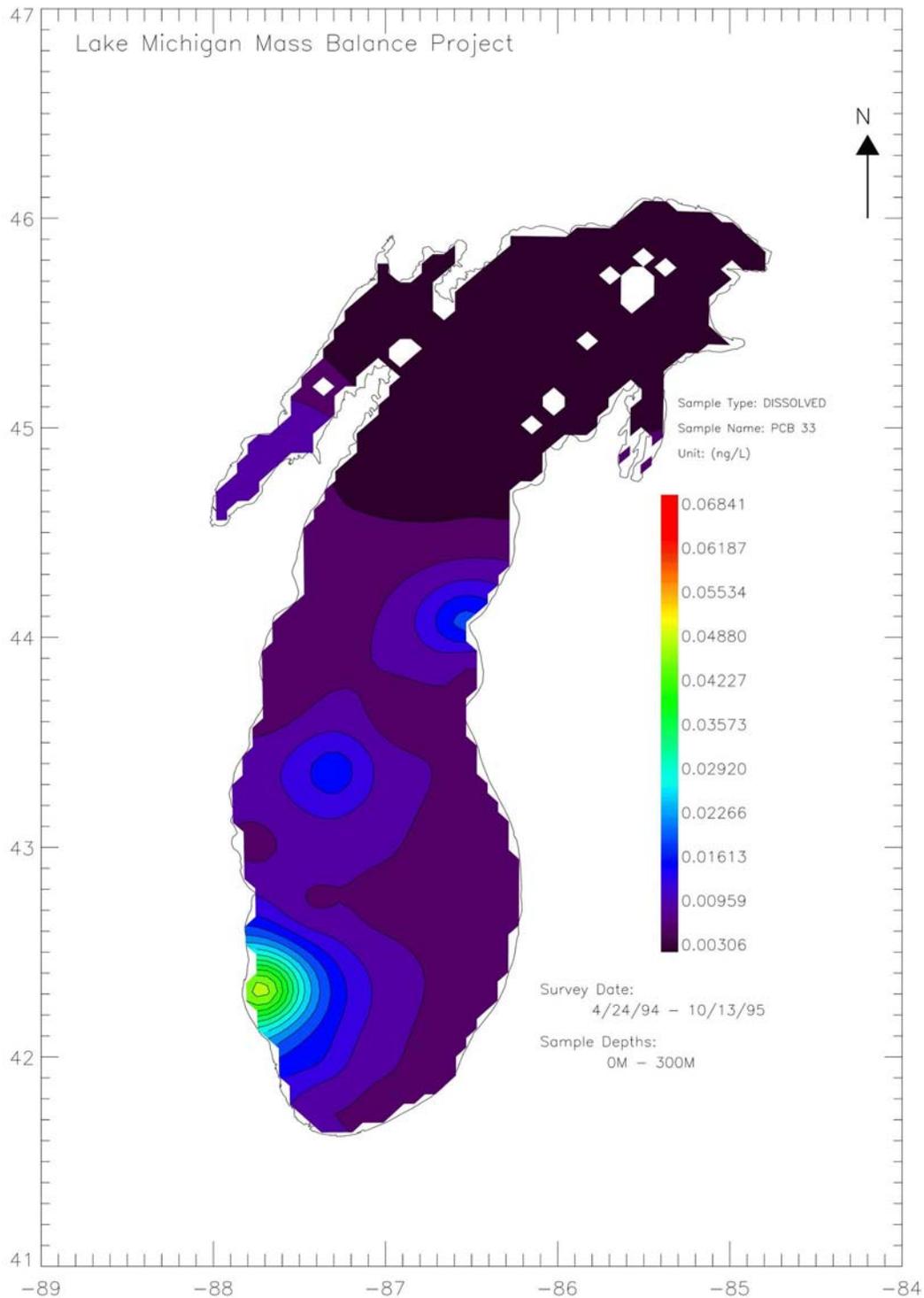


Figure 5-5. Concentrations of Dissolved PCB Congener 118 Measured in Open-lake Samples

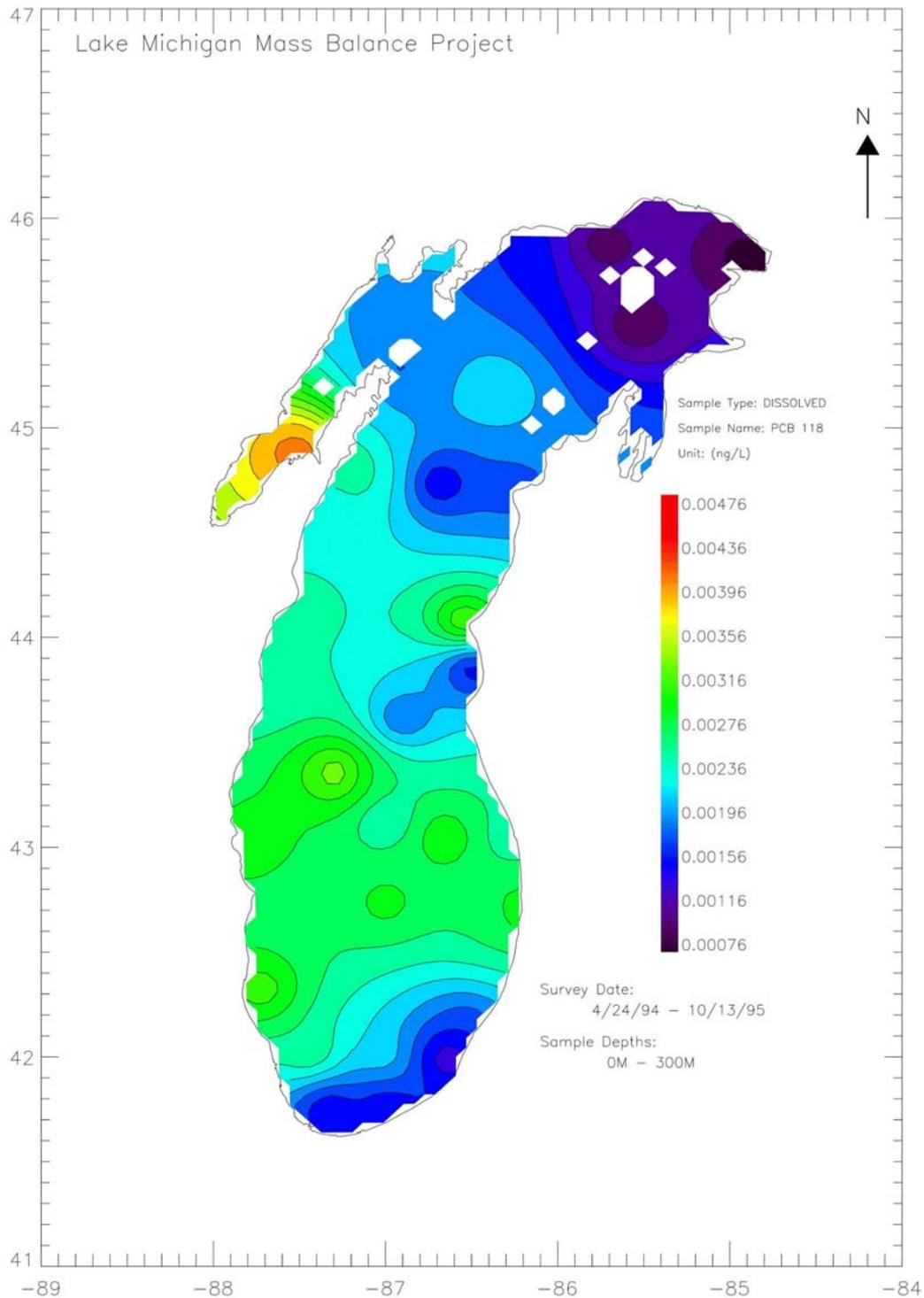


Figure 5-6. Concentrations of Dissolved PCB Congener 180 Measured in Open-lake Samples

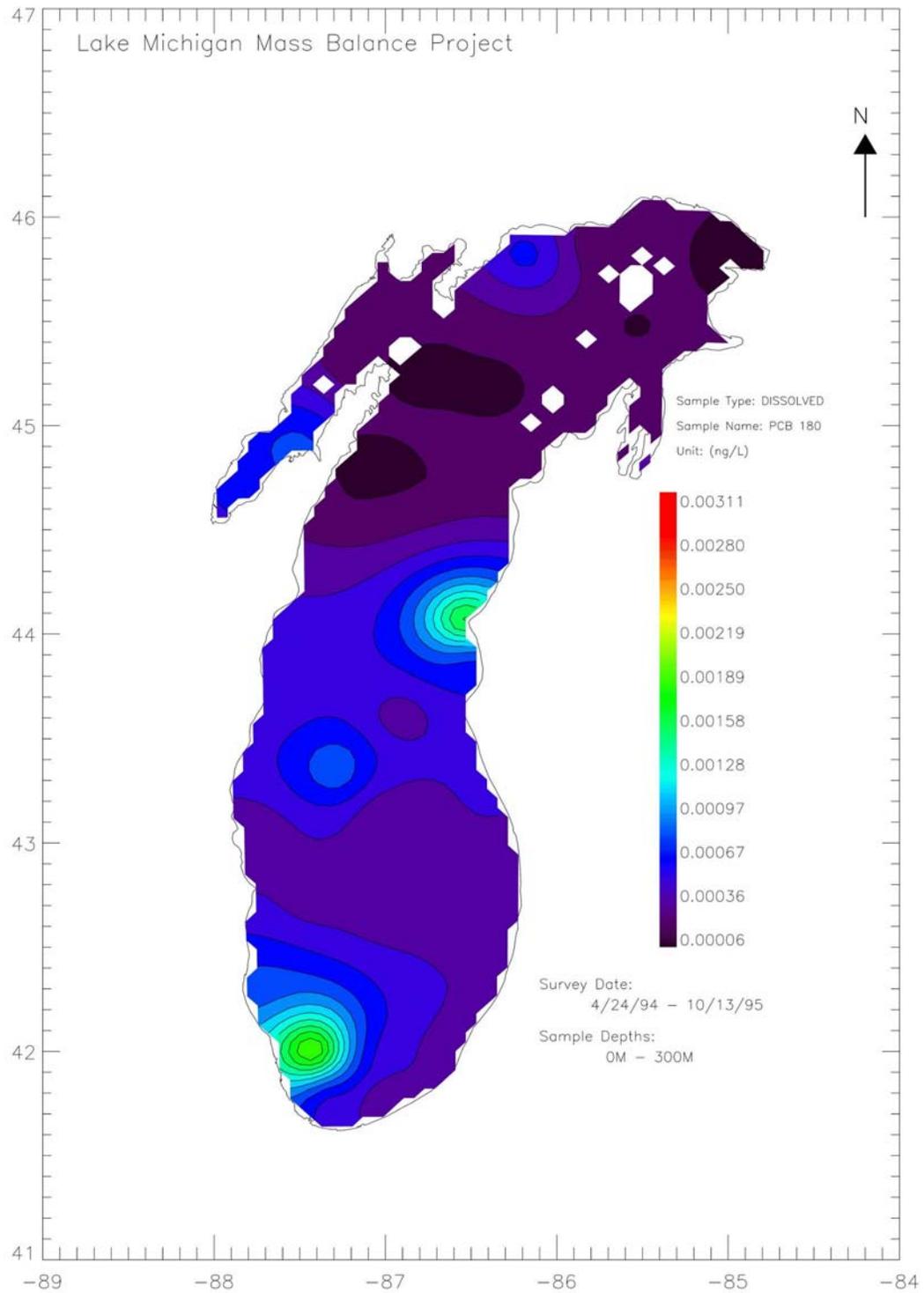


Figure 5-7. Concentrations of Particulate PCB Congener 33 Measured in Open-lake Samples

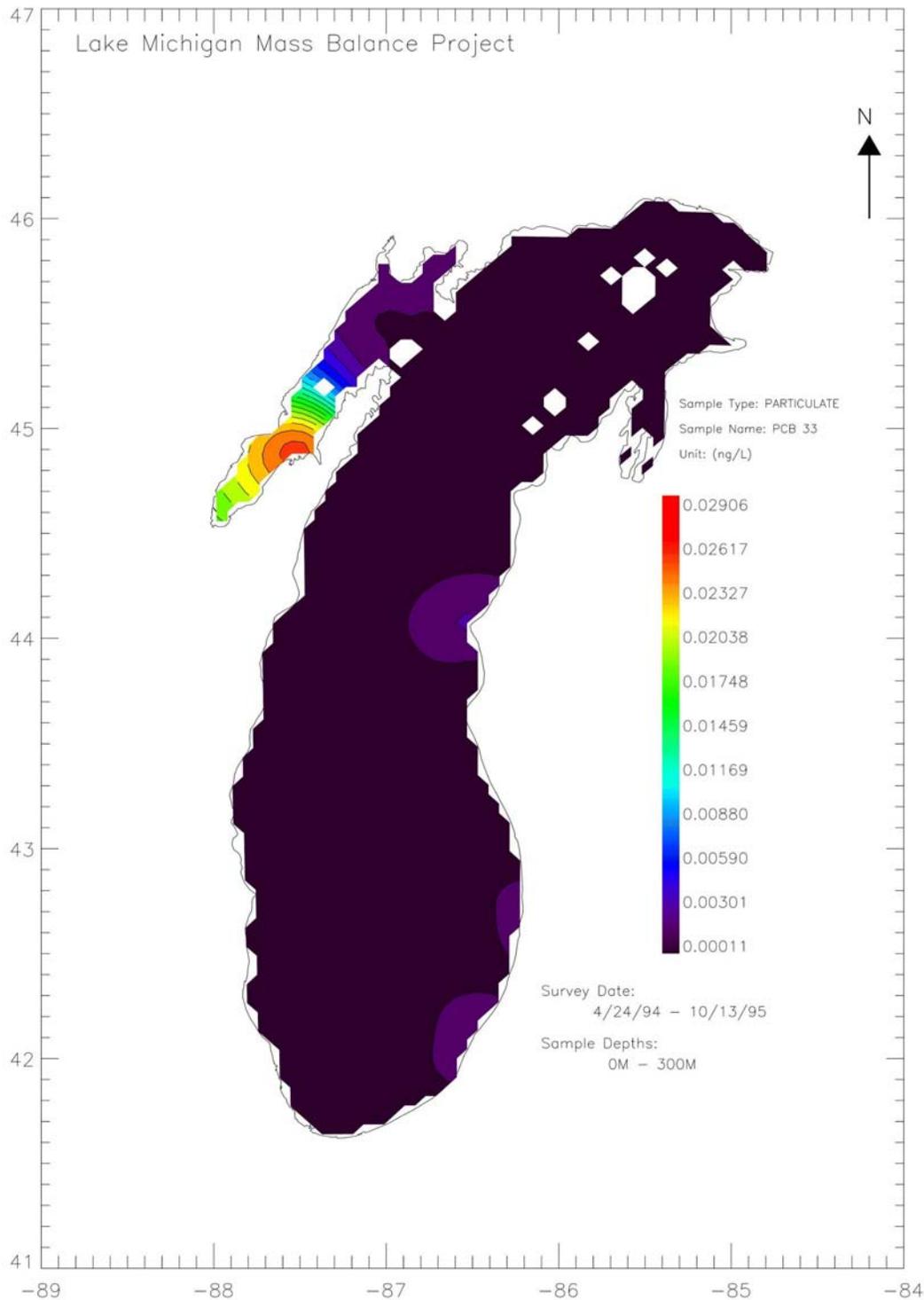


Figure 5-8. Concentrations of Particulate PCB Congener 118 Measured in Open-lake Samples

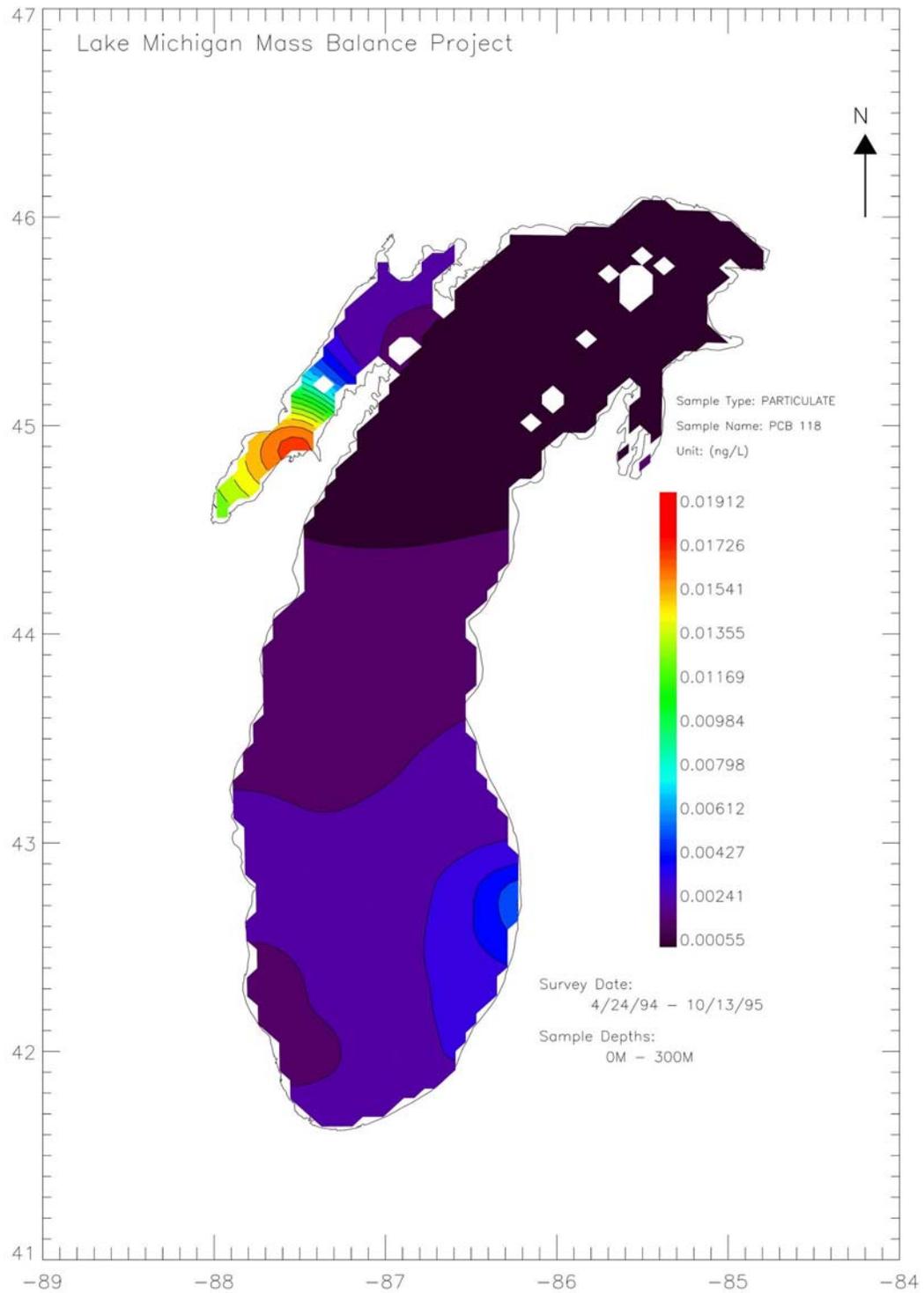


Figure 5-9. Concentrations of Particulate PCB Congener 180 Measured in Open-lake Samples

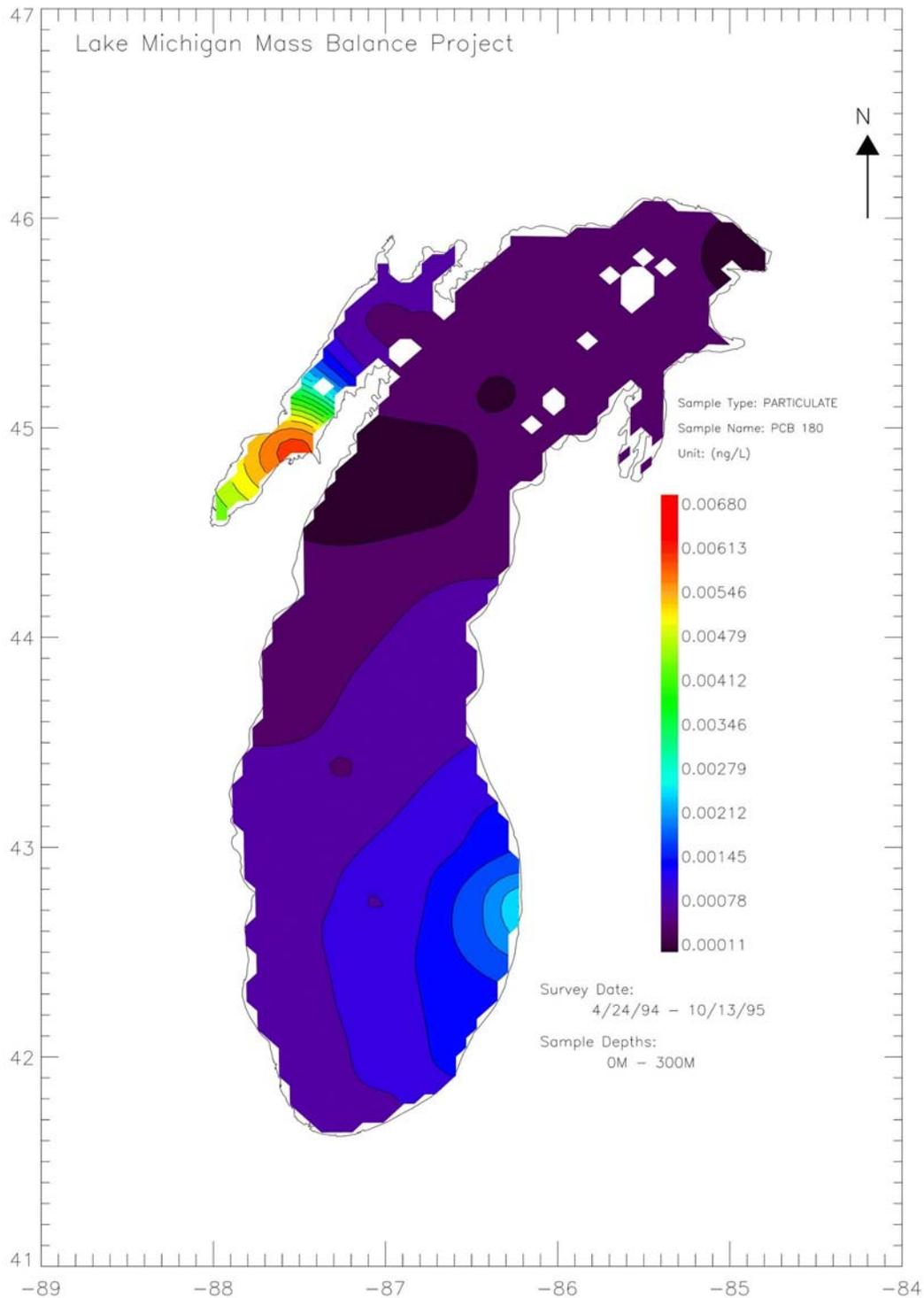


Figure 5-10. Concentrations of Dissolved *trans*-Nonachlor Measured in Open-lake Samples

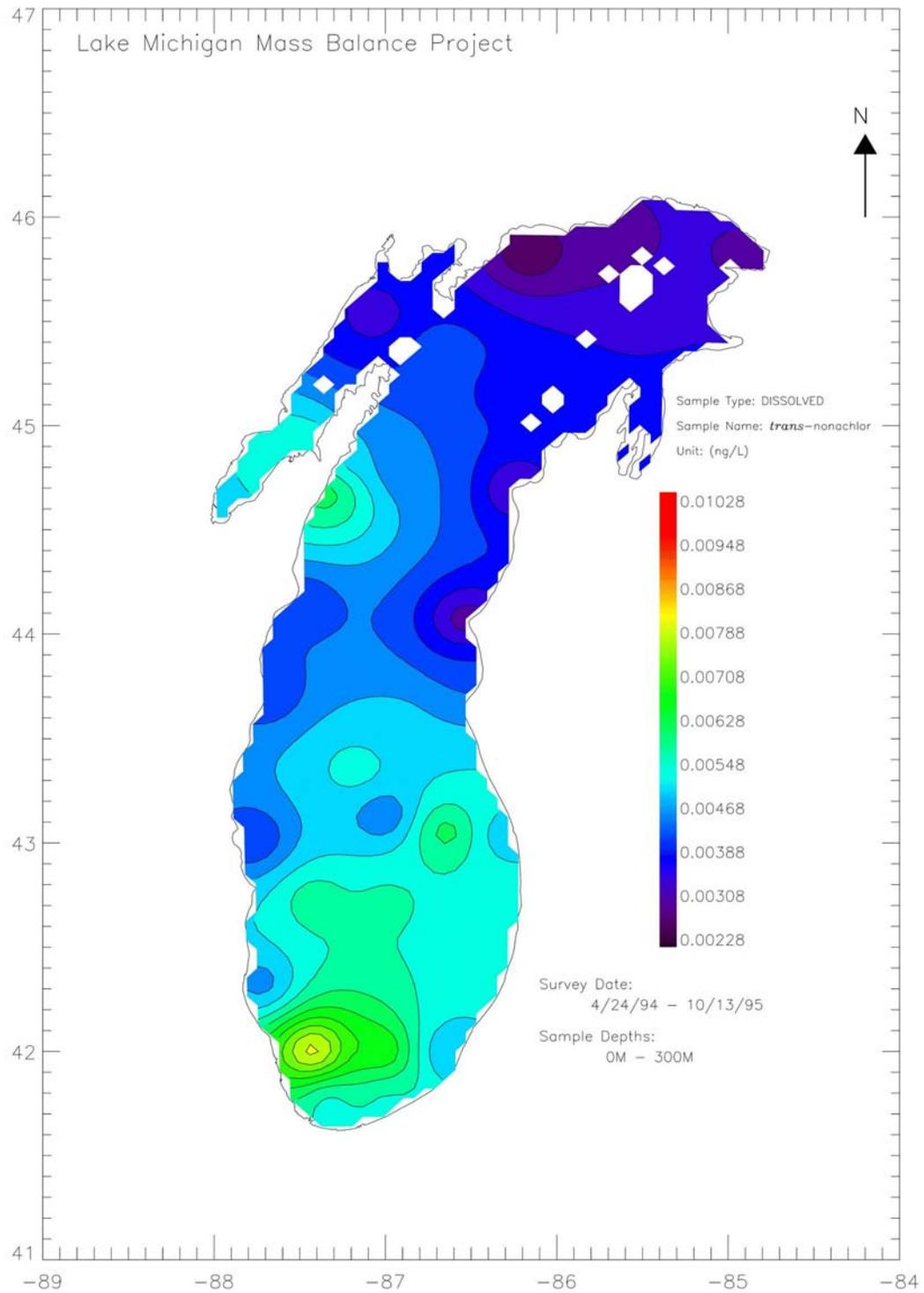


Figure 5-11. Concentrations of Particulate *trans*-Nonachlor Measured in Open-lake Samples

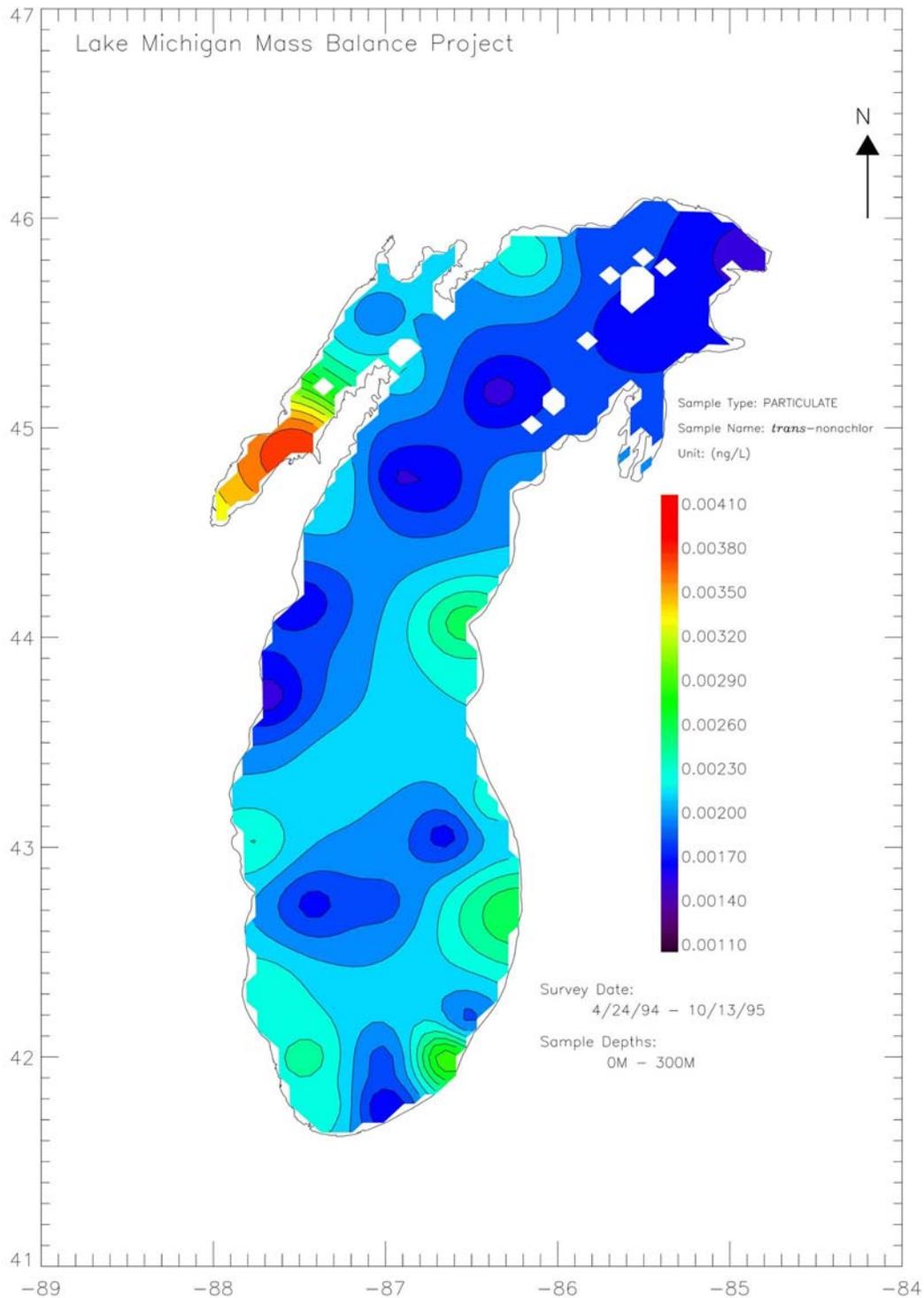


Figure 5-12. Concentrations of Dissolved Total PCBs Measured in Open-lake Samples

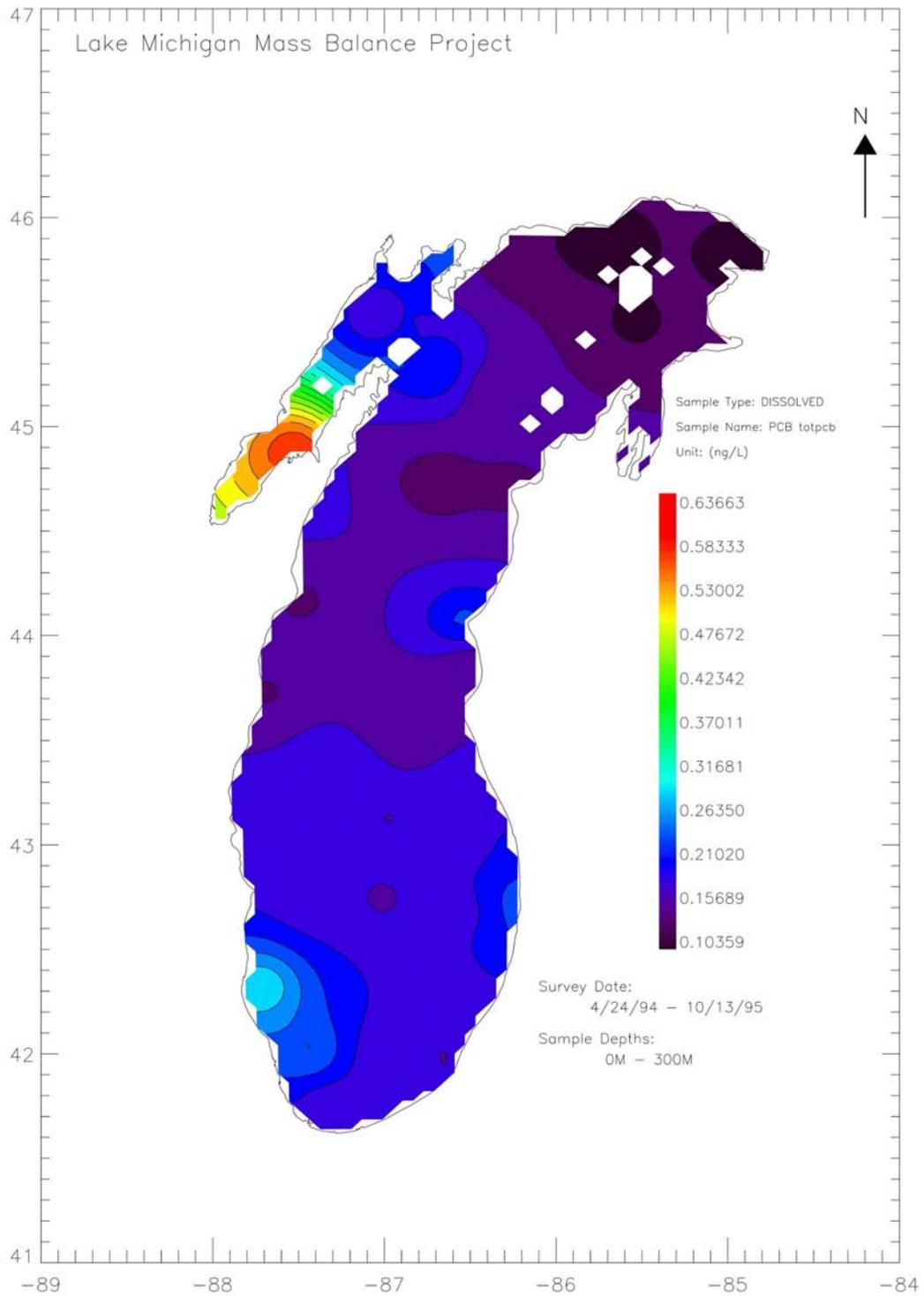
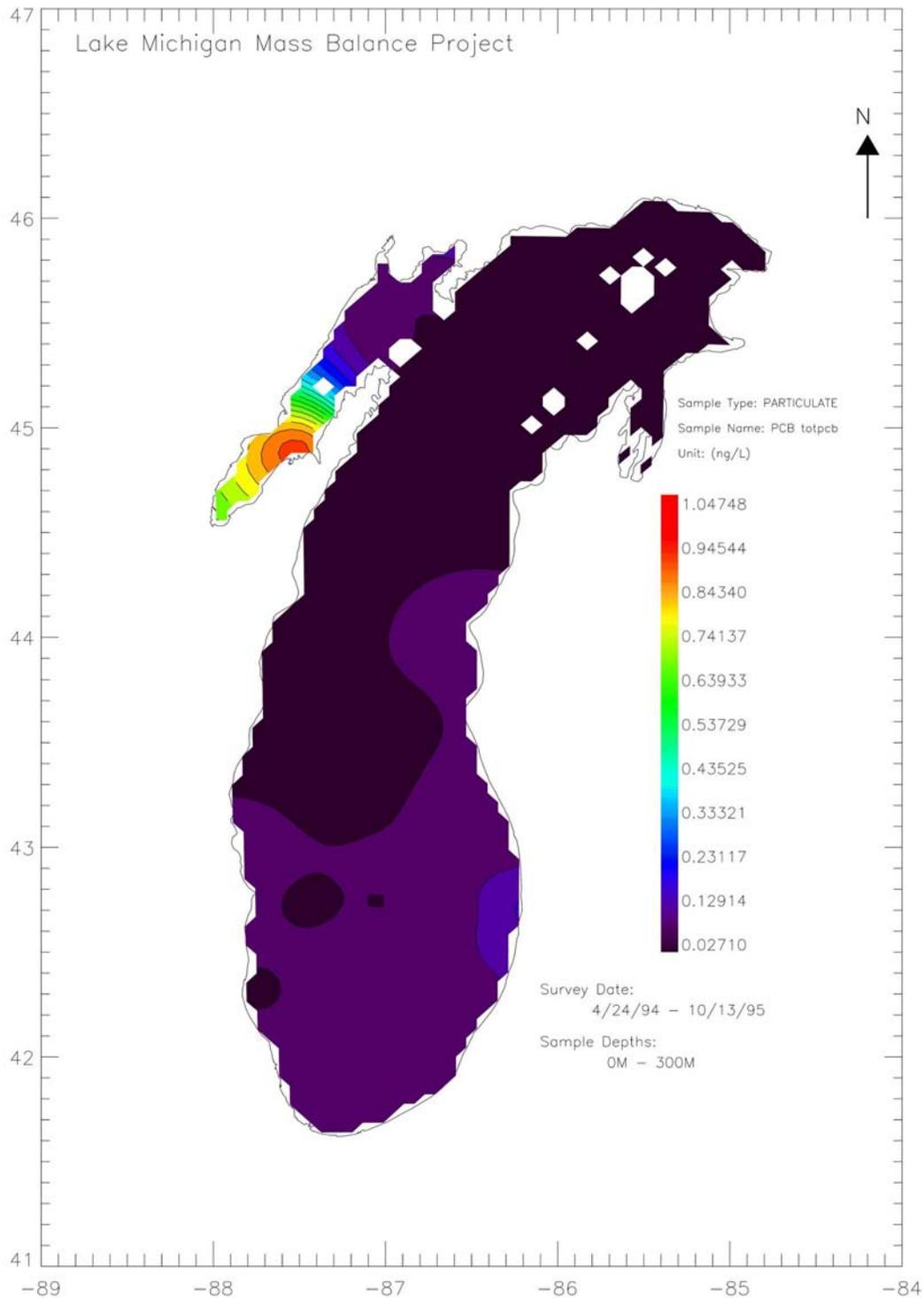


Figure 5-13. Concentrations of Particulate Total PCBs Measured in Open-lake Samples



5.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the PCBs and *trans*-nonachlor monitoring portion of the study are further described in Section 2.7 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in the *Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of data quality issues for the open lake PCBs and *trans*-nonachlor data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.5, because data comparability was important to the successful development of the mass balance model, the PIs used similar sample collection, extraction, and analysis methods for the PCB and *trans*-nonachlor monitoring in this study.

5.2.1 Sample Collection

During examination of the field collection records for field duplicates, it was discovered that some field duplicates were not actually collected at the same time as the field sample due to equipment mobilization. Samples collected within five minutes of each other were considered field duplicates (FD1), and if more than five minutes elapsed, the samples were considered sequential field duplicates (SFD1). Separate labeling of these data points as FD1 and SFD1 was done in order to assess if precision differed based on the elapsed time.

5.2.2 Data Assessments

As discussed in Section 2.7, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 5-13 provides a summary of flags applied to the open lake PCB and *trans*-nonachlor data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.7.

PIs used surrogate spikes to monitor the bias of the analytical procedure. The PCB results were corrected for the recoveries of the surrogates. The *trans*-nonachlor results were *not* surrogate-corrected. Only 1% of each of the open-lake particulate results for PCBs 33, 118, and 180, and *trans*-nonachlor were qualified because of surrogate recovery problems (Table 5-13). For the dissolved PCB samples from the open lake, 3 to 5% of the results for PCBs 33, 118, and 180 were qualified for surrogate recovery problems (Tables 5-13), while 19% of the dissolved *trans*-nonachlor results were qualified.

Laboratory matrix spike samples also were used to monitor the bias of the analytical procedure. The results for the matrix spike samples were compared to the MQO for spike recoveries (50 - 125%). Analytical results associated with matrix spike samples with recoveries below the MQO limits were flagged with failed matrix spike and low bias flags, and results associated with matrix spike samples that had recoveries higher than the MQO limits were flagged with failed matrix spike and high bias flags. Analytical results were considered invalid and flagged as such when the analyte was undetected and recoveries for associated matrix spike samples were less than 10%. None of the open-lake particulate *trans*-nonachlor results or PCB 33, 118, or 180 results failed the matrix spike MQOs. However, 8% of the open-lake dissolved PCB 33 results, 14% of the open-lake dissolved PCB 118 results, and 71% of the open-lake dissolved *trans*-nonachlor results were flagged as failing the matrix spike MQOs. A maximum of 1% of the samples were flagged as invalid.

Field blanks were collected for PCBs and *trans*-nonachlor. Field blanks were to be collected at a frequency of 5%. Due to the limited availability of samplers and resin, the actual frequency was only 3.5%. When field blank contamination was greater than 3.3 times the method detection limit, all of the associated results were flagged with the failed field blank sample code (FFR). Field blanks were not collected at all stations, so potential station-specific contamination associated with these sites cannot be evaluated. However, contamination associated with sampling equipment, collection, processing, shipping, storing, and analysis can be evaluated based on the field blanks collected throughout the study. Large percentages of samples were associated with field blanks in which PCBs 33, 118, or 180, or *trans*-nonachlor were reported above the sample-specific detection limit (Table 5-13). This issue is discussed in greater detail in Section 5.2.3.

Trip blanks were collected for PCBs and *trans*-nonachlor. Trip blanks were to be collected at a frequency of 5%. Due to the limited availability of samplers and resin, the actual frequency was only 2.2%. As with the field blanks, large percentages of samples were associated with a trip blank in which PCBs 33, 118, or 180, or *trans*-nonachlor were reported above the sample-specific detection limit (Table 5-13). This issue is discussed in greater detail in Section 5.2.3.

Field duplicates were to be collected at a frequency of 5%. Duplicate samples collected within 5 minutes of each other were considered field duplicates. However, an examination of the field collection records indicated that some of the planned field duplicates were not collected within that 5-minute time frame as a result of problems with equipment mobilization or the time required to pump the sample through the filter and resin cartridge. Those “duplicates” that were collected more than 5 minutes apart were considered “sequential field duplicates” and the data were labeled accordingly (e.g., SDF1 vs. FD1). Combining the field duplicates and sequential field duplicates, the actual rate of collection of duplicates was 7.6%.

The results from the original field sample and the associated duplicate were compared on the basis of the relative percent difference (RPD). The RPD value for each PCB congener and *trans*-nonachlor was compared to the MQO for field duplicate precision. None of the particulate PCB results were qualified because of the field duplicate precision (FFD) concerns (Table 5-13). Only 2% of the particulate *trans*-nonachlor results were so qualified. The percentage of dissolved PCB and *trans*-nonachlor results that were qualified because of field duplicate precision concerns ranged from 0.3% to 2%.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean relative percent difference (RPD) between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean relative percent difference (RPD) between the results for laboratory duplicate pairs. Table 5-14 provides a summary of data quality assessments for several of these attributes for the open-lake PCB and *trans*-nonachlor data.

Because the relative variability of most measurement techniques increases as one approaches the detection limit of the technique, the assessment of the field duplicate results were divided into two concentration regimes. One measure of system precision was calculated for those field duplicate results that were less than 5 times the sample-specific detection limit (SSDL) of the analyte, and a separate measure was calculated for those field duplicate results that were greater than 5 times the SSDL. None of the open lake particulate sample field duplicate pairs contained *trans*-nonachlor concentrations above 5 times the SSDL.

The precision of the particulate field duplicate results above 5 times the SSDL ranged from approximately 5 to 11% for the PCB congeners (Table 5-14), while the precision of the particulate field duplicate results below 5 times the SSDL ranged from approximately 23% to 55%.

None of the field duplicate pairs for dissolved samples contained PCB 180 above 5 times the SSDL, and the precision of the dissolved field duplicate results for PCBs 33 and 118, and *trans*-nonachlor above the SSDL ranged from approximately 17% to 36% (Table 5-14).

Analytical bias was assessed using the results from matrix spike samples. The mean recoveries were very good for the particulate-phase PCBs and *trans*-nonachlor, ranging from 88.8% to 105% for the analytes in Table 5-14. These results demonstrate that the analytical techniques applied to the field samples introduced little or no bias into most of the results, and only a slight low bias was introduced into the particulate PCB 118 results.

The matrix spike recoveries of the dissolved analytes were considerably more varied than the particulate results. The recoveries of dissolved PCBs 33 and 180 were very good to excellent, at 80.9% and 109%, respectively. However, the dissolved PCB 118 results indicate a significant high bias, with a mean recovery of 157%, while the dissolved *trans*-nonachlor recoveries average only 33.7%, indicating a significant low bias.

Analytical sensitivity was assessed on the basis of the percentage of study samples that were reported with concentrations below the sample-specific detection limit (SSDL). The sensitivity varied by congener for the PCBs, partly as a function of the analytical instrumentation and its response to the individual congeners.

The three PCB congeners and *trans*-nonachlor were not detected in substantial portions (1 - 55%) of the dissolved and particulate samples from the open lake ("UND" flag in Table 5-13). These analytes were detected below the sample-specific detection limits in substantial portions (1 - 23%) of the samples as well ("MDL" flag in Table 5-13). For the three congeners listed in Table 5-13, the percentage of the dissolved samples with results reported below the sample-specific detection limits increases (i.e., 10, 18, and 23%) with the congener number (e.g., with molecular weight), suggesting that solubility may play a role in the distribution.

The percentages of *trans*-nonachlor results that were not detected or detected below the sample-specific detection limits (Table 5-13) generally fell between the same percentages for the three PCB congeners, and were most similar to the percentages for PCB 118 (e.g., 6 - 12% for *trans*-nonachlor and 5 - 18% for PCB 118).

Table 5-13. Summary of Routine Field Sample Flags Applied to Select PCB Congeners and *trans*-Nonachlor in Open-lake Samples

Analyte	Fraction	Flags									
		Sensitivity		Contamination		Precision	Bias				
		MDL	UND	FFR	FFT	FFD	FSS	FMS	LOB	HIB	INV
PCB 33 - 348 Dissolved 349 Particulate	Dissolved	0	1% (2)	85% (297)	59% (206)	1% (2)	5% (16)	8% (29)	0	68% (238)	1% (4)
	Particulate	1% (5)	24% (85)	29% (101)	41% (142)	0	1% (4)	0	0	19% (65)	0.3% (1)
PCB 118 - 348 Dissolved 349 Particulate	Dissolved	18% (63)	5% (19)	57% (200)	77% (269)	0.3% (1)	3% (10)	14% (48)	0	57% (197)	1% (4)
	Particulate	8% (28)	5% (18)	30% (104)	48% (169)	0	1% (4)	0	0	25% (86)	0.3% (1)
PCB 180 - 348 Dissolved 349 Particulate	Dissolved	23% (79)	55% (190)	53% (183)	38% (131)	1% (3)	3% (10)	0	0	33% (115)	1% (4)
	Particulate	3% (12)	39% (135)	20% (71)	14% (48)	0	1% (4)	0	0	9% (33)	0.3% (1)
<i>trans</i> -Nonachlor - 343 Dissolved 349 Particulate	Dissolved	8% (29)	12% (42)	35% (119)	56% (193)	2% (6)	19% (66)	71% (244)	5% (16)	11% (37)	0
	Particulate	6% (22)	6% (20)	21% (73)	48% (169)	2% (6)	1% (2)	0	0	7% (26)	0

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

- MDL = Less than method detection limit (Analyte produced an instrument response but reported value is below the calculated method detection limit. Validity of reported value may be compromised.)
- UND = Analyte not detected (Analyte produced no instrument response above noise.)
- FFR = Failed field blank (A field blank sample, type unknown, associated with this analysis failed the acceptance criteria. It is unknown whether the blank that failed was a field blank or a lab blank. Validity of reported value may be compromised.)
- FFT = A trip blank associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.
- FFD = Failed field duplicate (A field duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- FSS = Failed surrogate (Surrogate recoveries associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- FMS = Failed matrix spike (A matrix spike associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- LOB = Likely biased low (Reported value is probably biased low as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery or other internal lab QC data. Reported value is not considered invalid.)
- HIB = Likely biased high (Reported value is probably biased high as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery, blank contamination, or other internal lab QC data. Reported value is not considered invalid.)
- INV = Invalid

Table 5-14. Data Quality Assessment for Select PCB Congeners and *trans*-Nonachlor in Open-lake Water Samples

Analyte/Number Field Samples	Parameter	Number of QC samples		Assessment	
		Dissolved	Particulate	Dissolved	Particulate
PCB 33 - 344 Dissolved 348 Particulate	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	8 field duplicate pairs	7 field duplicate pairs	55.9%	23.6%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	19 field duplicate pairs	11 field duplicate pairs	17.1%	11.3%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	24 matrix spikes	22 matrix spikes	80.9%	97.6%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	-	0.3%	25.9%
PCB 118 - 344 Dissolved 348 Particulate	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	21 field duplicate pairs	8 field duplicate pairs	30.4%	18.2%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	4 field duplicate pairs	13 field duplicate pairs	35.6%	4.96%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	24 matrix spikes	22 matrix spikes	157%	88.8%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	-	23.0%	13.2%
PCB 180 - 344 Dissolved 348 Particulate	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	10 field duplicate pairs	6 field duplicate pairs	77.4%	54.9%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	0 field duplicate pairs	12 field duplicate pairs	--	8.98%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	24 matrix spikes	22 matrix spikes	109%	105%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	-	77.3%	42.2%
<i>trans</i> -Nonachlor - 343 Dissolved 349 Particulate	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	23 field duplicate pairs	22 field duplicate pairs	41.0%	36.7%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	1 field duplicate pair	0 field duplicate pairs	17.8%	--
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	24 matrix spikes	22 matrix spikes	33.7%	95.1%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	-	20.7%	12.0%

As noted in Section 2.6.4, the laboratory did not obtain separate cleanup fractions containing the PCBs and *trans*-nonachlor, but analyzed the sample extracts on two dissimilar GC columns (DB-5 and DB-1701). While the DB-1701 column provided clear chromatographic separation of any *trans*-nonachlor in the sample, this analyte coeluted with PCB 99 on the DB-5 column. As a result of the potential coelution, the reported concentrations of PCB 99 in open-lake samples are probably biased by any *trans*-nonachlor present in the samples.

5.2.3 Evaluation of Blanks

Because PCBs are a ubiquitous contaminant, both in the environment and in environmental testing laboratories, the LMMB Study design included a wide range of types of blanks that were designed to identify many of the potential sources of PCB contamination that might be encountered during the study. Contamination of the samples from other sources was a particular concern because the study attempted to investigate the very low concentrations present in the open lake. When the data were examined, a large number of open-lake PCB sample results (20 - 90%) in the LMMB Study were flagged as being associated with one or more blanks that exhibited signs of contamination.

The data presented in this report thus far include all of the sample results except those flagged as invalid. Samples that were flagged with blank contamination were included in the analyses, and as a result, the estimates of mean concentrations may be biased due to contributions from the various blanks. An evaluation of the blank contaminants was conducted to examine the impacts of these contaminants on the results and conclusions by comparing several alternative approach to flagging and treating sample results.

The reported concentrations of PCBs in the open lake were evaluated with regard to the results of the three types of routine blanks that were prepared for the study. Blanks are important to consider when estimating concentrations of PCB congeners in this study for several reasons including:

- Blank contamination is typical for PCB sampling and analysis, especially for low concentrations of PCB congeners that are close to the detection limit of the analytical method,
- Blank contamination affected a significant number of field samples results collected in the LMMB Study, and
- The analytical laboratory changed its resin cleaning procedures in the middle of the study to comply with a revised criteria for “clean” resin set by GLNPO.

Mean concentrations of open lake PCB congeners were calculated in two ways: using all the LMMB data, and using only those data that were not affected by contamination of the field reagent blank, the laboratory dry blank, or the laboratory reagent blank. For the purposes of this evaluation, a field sample result was considered unaffected by blank contamination if the results of all of the associated blank samples were less than 1/3 of the concentration reported in the field sample.

The criteria for the evaluation were based on the measurement quality objectives (MQOs) established by the principal investigators for open lake PCBs, when possible, because the PIs are most knowledgeable about the performance of their sampling and analytical method.

Table 5-15 provides criteria used to evaluate whether to include a sample result in the estimation of the mean concentrations in the open lake. The approach taken in this evaluation was conservative, in that it was designed to leave as many samples as possible in the estimation of the mean. This evaluation did not consider the effects of the field trip blanks on the sample results for several reasons. First, there were fewer field trip blanks than the other types of blanks. Therefore, there is concern that the results for a given field trip blank may not be as representative of the actual sample collection procedures as other types of blanks. Secondly, the potential contamination illustrated by the field trip blank also could be

evaluated using the field reagent blank results, because the field reagent blank should theoretically capture most of the same sources of contamination.

In addition to the blank considerations listed in Table 5-15, data also were excluded if they were flagged “Invalid” in the database. The invalid flag indicates that the PI and the QC coordinator deemed the data to be unusable for any purpose.

All sample results were included as reported by the PI in the estimate of the mean. If the PI reported a result as zero, then the zero was included in the estimate. A zero result should be interpreted as a concentration that is below the sample-specific detection limit for that sample. In addition, the results that were reported as a value below the sample-specific detection limit also were included in the estimate. These results were flagged in the database with the “MDL” flag and should be interpreted as a concentration that is below the sample-specific detection limit.

Table 5-15. Criteria Used to Evaluate Data to be Included in the Estimation of the Mean Concentrations of PCB Congeners

Quality Control Consideration	Criteria	Rationale
Blanks, including: <ul style="list-style-type: none"> • field reagent blanks, • lab dry blanks¹, and • lab reagent blanks.¹ 	Exclude the sample result when any of the three associated blanks has a result that is greater than 1/3 of the concentration in the sample	When a sample is associated with a blank that has greater than 1/3 of the concentration in the sample result, the result is likely to be biased high and contamination may be a significant portion of the concentration reported in the sample. The multiplier of 1/3 is based on the MOOs established by the PI for several blank types.

¹Lab dry blanks and lab reagent blanks were reported in mass units because there is no actual volume of “sample” pumped through the filter and resin column. The sample results were compared to the results for these two types of blanks by converting the sample results to mass units as well.

The estimation of the mean concentration of each PCB in the open lake was complicated by the use of detection limits that are specific to each sample, rather than using one detection limit for each congener across all lake samples. The sample-specific detection limits take into account the actual volume of lake water pumped through the filter and resin column, which may differ between samples.

There are several approaches that may be used to estimate the mean concentration of each PCB congener in the open-lake samples. One common approach is to substitute the sample-specific detection limit for any result below that limit and use the result as reported for any result above the sample-specific detection limit. However, that approach introduces a high bias into the mean concentration because no result used in the mean will ever be less than the detection limit for that sample. Another common approach is to use the concentrations as reported by the investigator. This approach recognizes that the actual concentrations in the samples may range from zero to the sample-specific detection limit. The modelers using the LMMB data are using the results as reported, including the values reported by the PIs as zero or below the sample-specific detection limit. Therefore, this same approach was used to estimate the mean concentrations for this evaluation.

The mean concentrations for the three PCB congeners are presented in Table 5-16 in four ways, using:

1. All data except those flagged invalid in the database,
2. Only data without associated blank failures as described in Table 5-15,
3. Only data without associated blank failures as described in Table 5-15 for 1994, and
4. Only data without associated blank failures as described in Table 5-15 for 1995.

The differentiation between the 1994 and 1995 data was made because GLNPO lowered the acceptable level of PCBs that could be in the XAD-2[®] resin and particulate collection filters at the beginning of 1995 and the PIs responded by changing their cleaning procedures. The standard deviation, the concentration range, and the mean sample-specific detection limit are presented in Table 5-16 for the three congeners.

Table 5-16. Comparison of Summary Statistics for LMMB Open-lake PCB Congener Results after Removal of Sample Results associated with Contaminated Blanks

Analyte	Fraction	Data Included in Mean ¹	N	Mean (pg/L)	SD (pg/L)	Range (pg/L)	Mean SSDL (pg/L)
PCB 33	Dissolved	All data	303	9.15	23.16	0.00 - 205.62	0.578
		Data Without Blank Failures	128	8.70	22.27	0.00 - 193.50	0.591
		1994 Data Without Blank Failures	64	5.92	1.60	0.00 - 11.78	0.637
		1995 Data Without Blank Failures	64	11.47	31.33	2.37 - 193.50	0.545
	Particulate	All data	306	0.77	1.54	0.00 - 18.01	0.108
		Data Without Blank Failures	216	0.78	1.79	0.00 - 18.01	0.106
		1994 Data Without Blank Failures	112	1.13	2.36	0.00 - 18.01	0.127
		1995 Data Without Blank Failures	104	0.41	0.63	0.00 - 3.89	0.084
PCB 118	Dissolved	All data	303	2.46	3.01	0.00 - 18.33	0.788
		Data Without Blank Failures	213	3.04	3.30	0.00 - 18.33	0.778
		1994 Data Without Blank Failures	132	3.76	3.32	0.00 - 15.53	0.798
		1995 Data Without Blank Failures	81	1.87	2.94	0.00 - 18.33	0.746
	Particulate	All data	306	2.24	2.88	0.00 - 26.26	0.252
		Data Without Blank Failures	277	2.44	2.96	0.00 - 26.26	0.253
		1994 Data Without Blank Failures	161	2.49	3.26	0.00 - 26.26	0.295
		1995 Data Without Blank Failures	116	2.36	2.48	0.00 - 15.23	0.196
PCB 180	Dissolved	All data	303	0.49	2.03	0.00 - 29.53	0.388
		Data Without Blank Failures	189	0.32	2.45	0.00 - 29.53	0.385
		1994 Data Without Blank Failures	104	0.02	0.06	0.00 - 0.31	0.392
		1995 Data Without Blank Failures	85	0.70	3.62	0.00 - 29.53	0.376
	Particulate	All data	306	0.94	1.40	0.00 - 11.72	0.155
		Data Without Blank Failures	289	0.97	1.44	0.00 - 11.72	0.157
		1994 Data Without Blank Failures	172	1.08	1.61	0.00 - 11.72	0.181
		1995 Data Without Blank Failures	117	0.81	1.13	0.00 - 6.15	0.122

Figures 5-14 to 5-16 provide a graphical display of the means presented in Table 5-16, along with the standard error of each mean (i.e., the standard deviation divided by the square root of the number of observations in each mean), and the mean sample-specific detection limit (SSDL) for the congener.

The four bars in each graph above represent the mean concentrations of the analyte derived from: all data, all data without the samples associated with contaminated blanks, all data from 1994 without samples associated with contaminated blanks, and all data from 1995 without samples associated with contaminated blanks. The y-axis units are the mean concentration of the PCB congener in ng/L. The narrow vertical lines represent ± 1 standard error around the mean concentration. The horizontal line across each graph is the approximate position of the mean sample-specific detection limit (SSDL) for the results from all of the samples for that congener and phase. Note that the vertical scale used for the y-axis differs from congener to congener, based on the observed range of mean concentrations.

The results for dissolved PCB 33 and PCB 180 illustrate the potential for high bias in the mean concentrations derived from all of the data. For both of these congeners, the mean dissolved concentration decreases slightly when the data associated with the contaminated blanks are removed (e.g., the second bar in each graph labeled “data without QC failures”). In contrast, the results for dissolved PCB 118 and the particulate fraction for all three congeners show an *increase* in the mean concentration when the data associated with the contaminated blanks are removed.

The effect of the change in the acceptance criteria for the XAD-2[®] resin between 1994 and 1995 is not consistent across the dissolved congeners. For PCB 118, the 1995 mean concentration of samples without QC failures is about half of the 1994 mean concentration. However, for dissolved PCB 33, the trend is exactly opposite, with the 1995 mean concentration approximately twice the 1994 mean concentration. For dissolved PCB 180, the 1995 mean is actually 35 times higher than the 1994 mean.

For the particulate sample results, the mean concentrations were lower in 1995 for PCBs 33, 118, and 180. This suggests that the contribution of the blanks to the particulate results may have been less in the 1995 data than in the 1994 data.

The data for the mean SSDL for each congener and fraction also illustrate a significant aspect of the situation. For dissolved PCB 33, the mean sample results, regardless of QC failures, are 7 to 10 times higher than the mean SSDL value. For dissolved PCB 118, the ratio drops to 2 to 4 times the SSDL, and the error bars for the mean dissolved PCB 180 encompass the mean SSDL for three of the four bar graphs. For the particulate PCB results, the mean concentrations of all three congeners are at least five times higher than the mean SSDL values. These results illustrate the congener-specific difficulties in measuring open-lake concentrations that are near or below the capabilities of the analytical techniques.

Figure 5-14. Summary Statistics for LMMB Open-lake PCB 33 Results after Removal of Sample Results associated with Contaminated Blanks

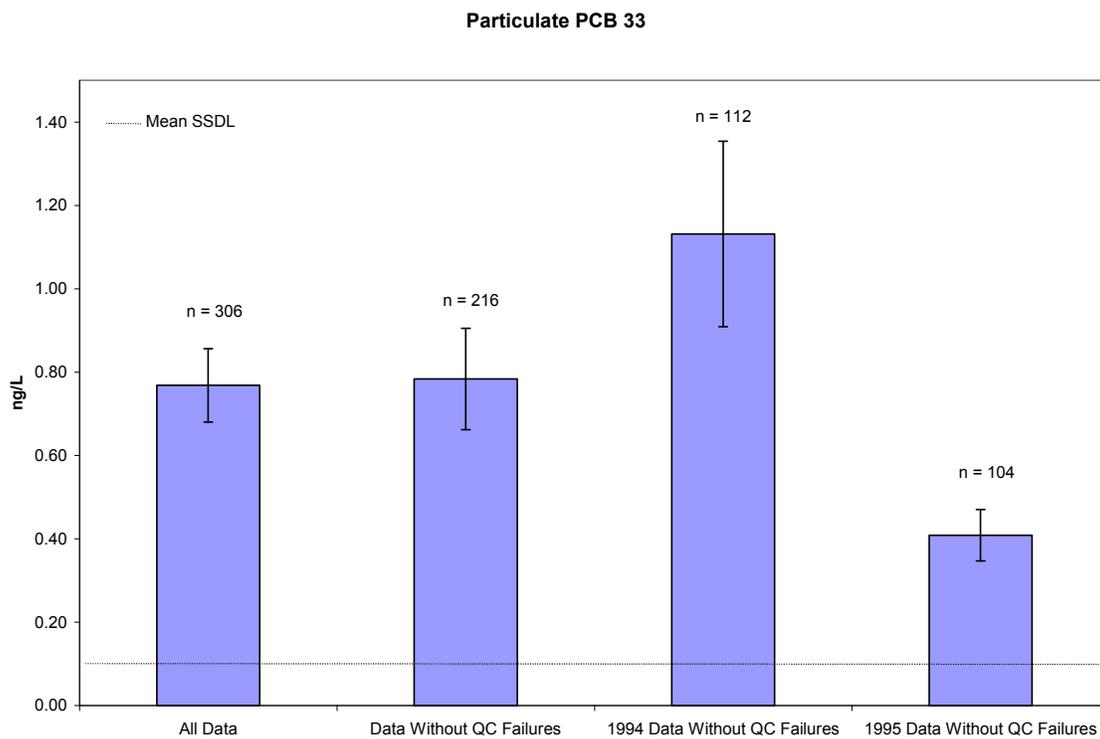
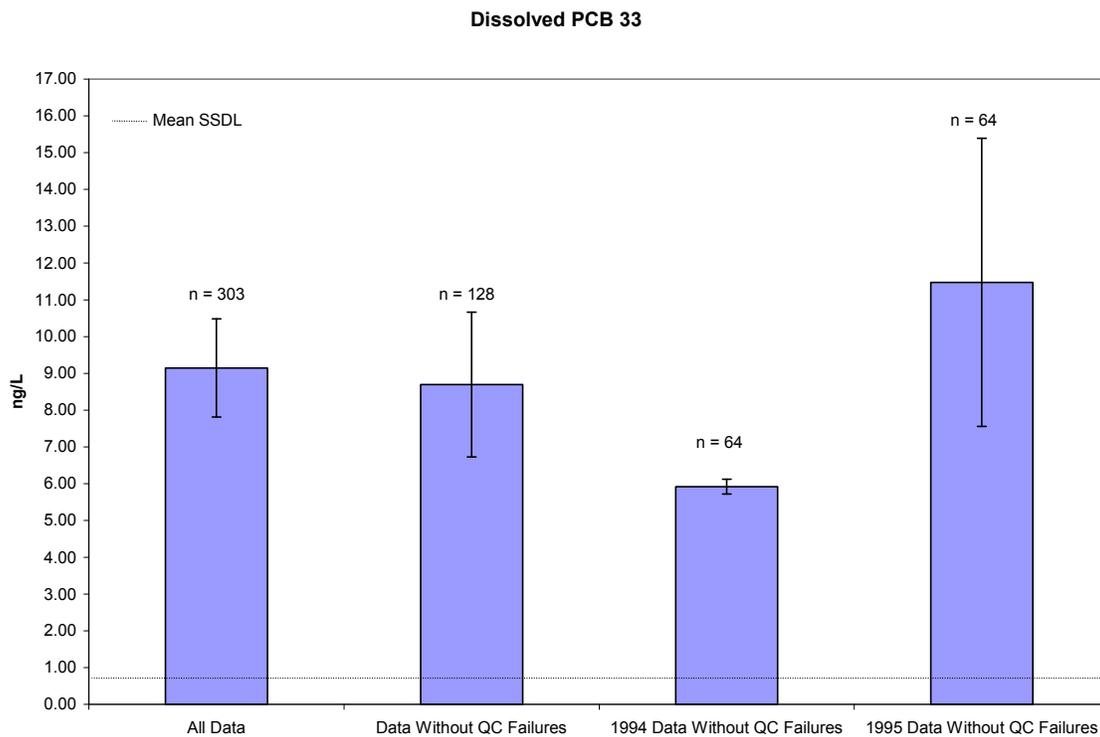


Figure 5-15. Summary Statistics for LMMB Open-lake PCB 118 Results after Removal of Sample Results associated with Contaminated Blanks

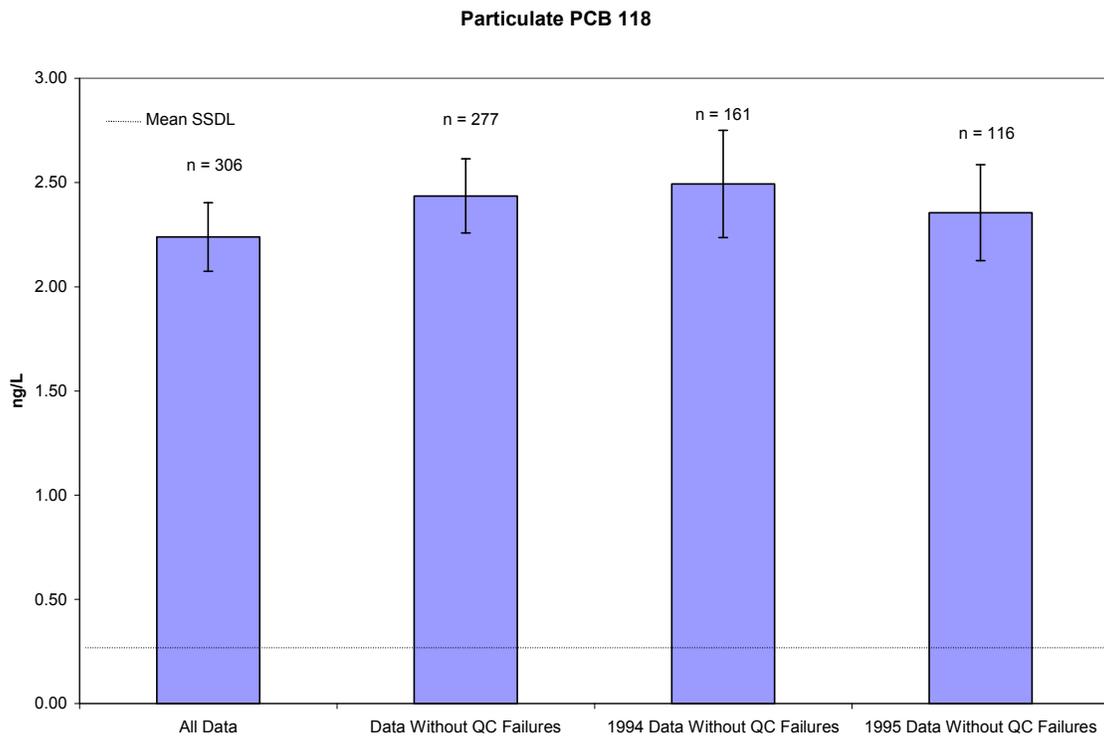
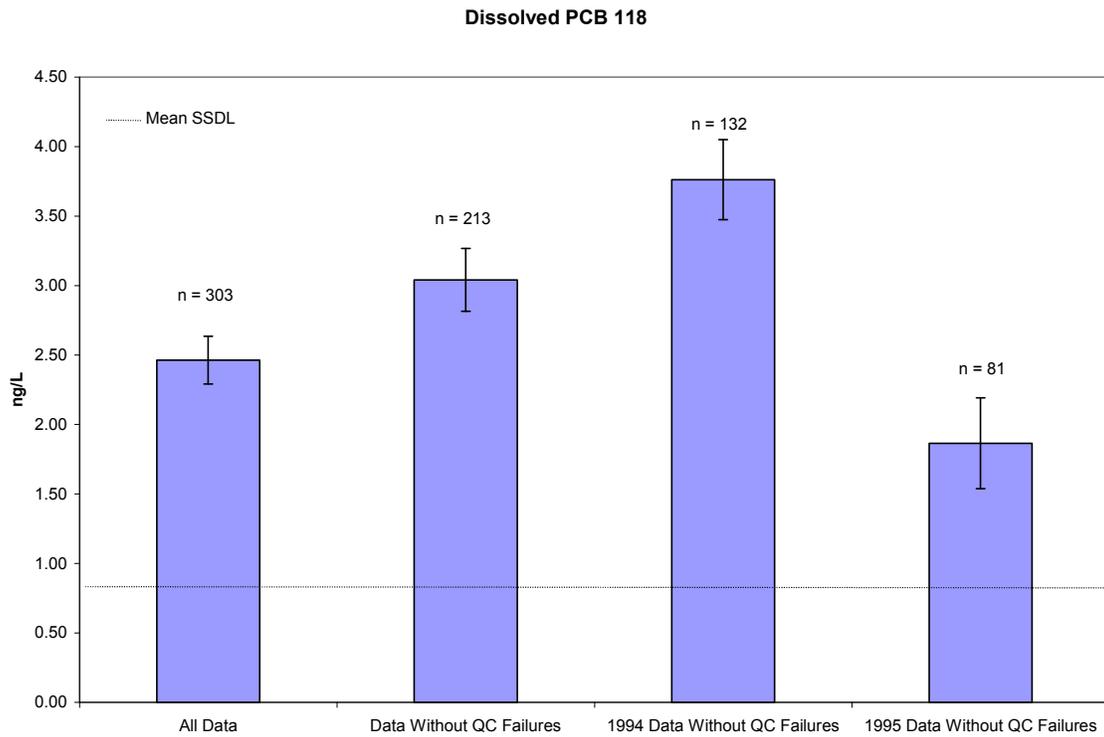
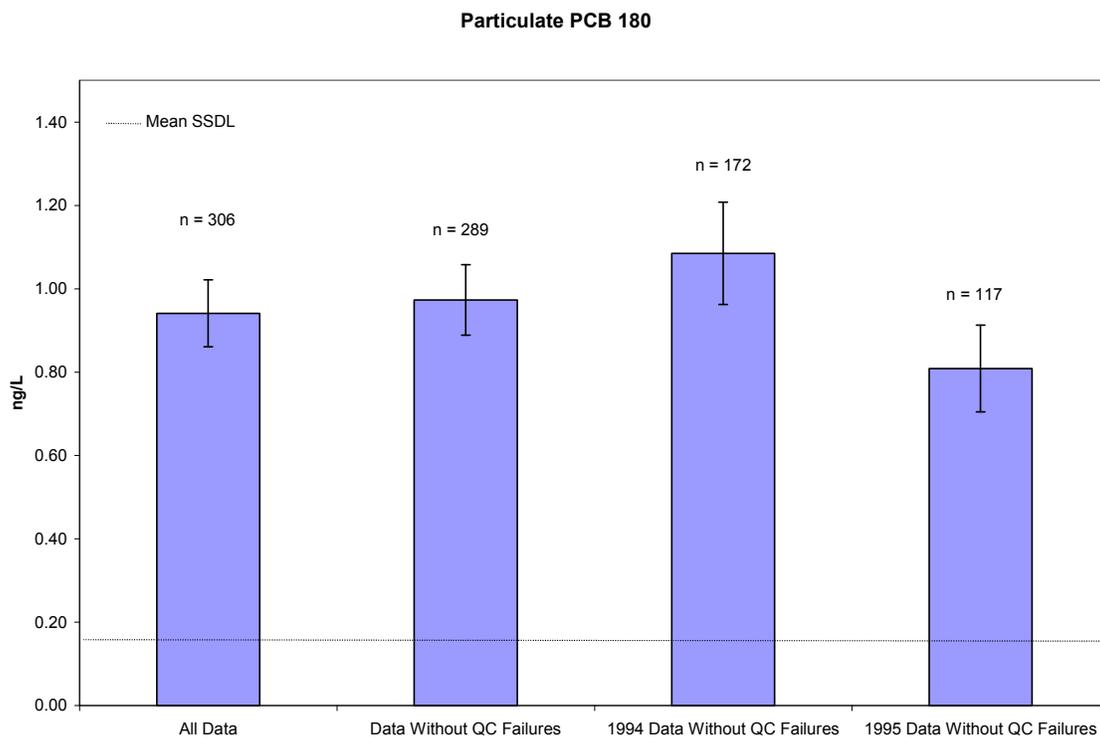
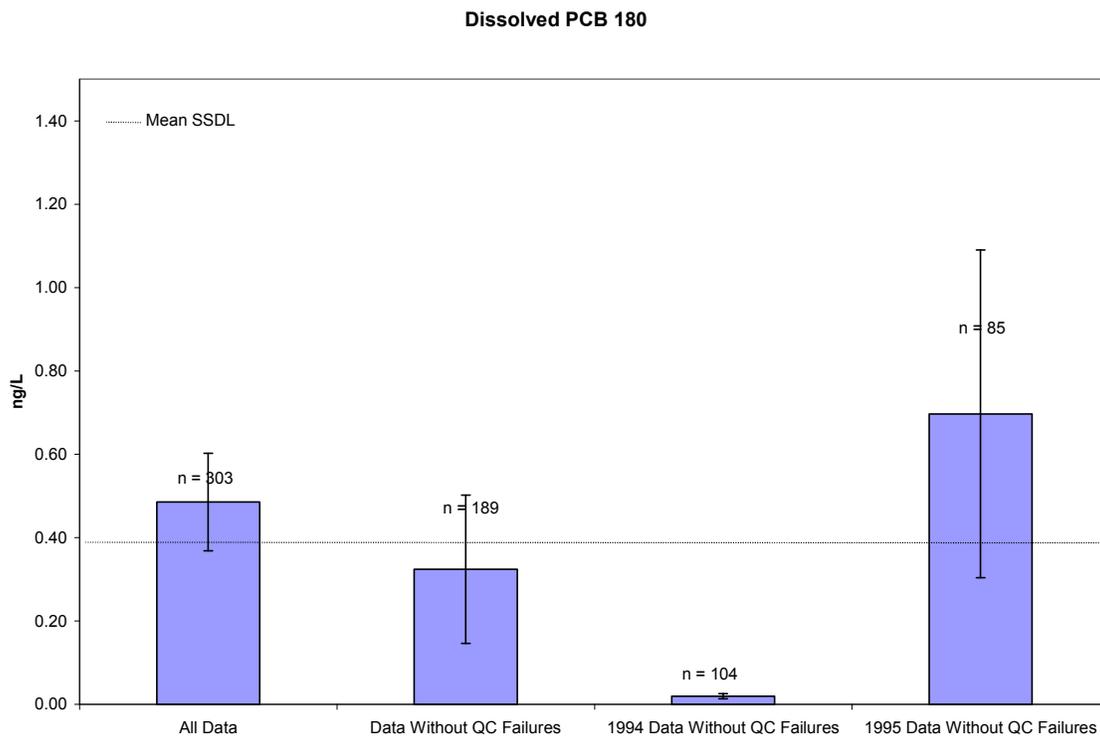


Figure 5-16. Summary Statistics for LMMB Open-lake PCB 180 Results after Removal of Sample Results associated with Contaminated Blanks



5.3 Data Interpretation

The LMMB Study resulted in one of the largest collections of PCB and *trans*-nonachlor data ever produced for any of the Great Lakes. The data for PCBs and *trans*-nonachlor from the LMMB Study indicate that the concentrations of individual PCB congeners and *trans*-nonachlor vary among the stations in the open lake. In addition, the concentrations of the congeners differ, both within a station, as well as across the stations.

5.3.1 Comparison to Historical Studies

The magnitude of the LMMB data set makes it difficult to find comparable historical results that are useful for comparisons. Even where data are available from other investigators for the same analytes, the potential differences in spatial and temporal coverage present concerns that are further complicated by the likely differences in the sampling and analytical procedures.

Three historical data sets have been identified by EPA's Large Lakes Research Station as relevant to such comparisons. Swackhamer and Armstrong (1987) collected PCB data during September 1980 under a project partially supported by USEPA Cooperative Agreement CR807836. Filkins *et al.* (1983), at the Cranbrook Institute, collected PCB data during September 1981 under a project supported by USEPA Cooperative Agreement CR810232. Pearson *et al.* (1996) collected PCB data during September 1991 under a project supported by GLNPO Grant No. GL995233.

These historical data represent the "total PCB" concentration in each sample, without regard for the dissolved or particulate fraction, and without distinguishing among the PCB congeners. Therefore, the historical results can only be compared to the sum of the dissolved and particulate PCB results from the LMMB Study. Figures 5-17 to 5-20 present the results from the three historical studies and the LMMB results for samples collected in September 1995. Figure 5-20 presents the summary plot for total PCBs for the entire LMMB data set. As with the earlier contour plots, note that the concentrations scales differ among the four plots. The data from the three historical studies represent samples collected in the top 30 meters of the lake, while the LMMB data include samples collected at greater depths as well. Additional comparisons could be made using only the LMMB results for samples collected in the top 30 meters of the lake. However, such plots were not available at the time of this report.

Swackhamer and Armstrong (1987) collected 45-L water samples from 19 stations in the open lake. The water samples were filtered through glass-fiber filters on board the *R/V Roger R. Simons*. The filtrates were passed through glass columns containing XAD-2[®] resin. The filter and the XAD-2[®] resin were extracted separately, and the extracts were analyzed by GC/ECD. Total PCB concentrations were determined by comparison to standards of Aroclor mixtures, as well as through the use of standards for some individual PCB congeners.

The data from September 1980 (Swackhamer and Armstrong, 1987, Figure 5-17) ranged from 0.4 to 7.9 ng/L, with a mean concentration in the open lake of 1.8 ng/L. The total PCB concentration in central portion of Lake Michigan is between 1.2 and 1.6 ng/L, with lower concentrations (< 0.8 ng/L) in the extreme northern portion of the lake, and with concentrations as high as 6 to 8 ng/L near the shore in the lower portion, close to major urban areas.

Filkins *et al.*, (1983) collected approximately 120 L of water from a depth of 4 m at four stations in Lake Michigan, as part of a larger study involving 21 stations in all five Great Lakes. The water samples were collected as 3-L aliquots placed in multiple 1-gallon glass bottles. Methylene chloride was added to each bottle, and the bottles were shaken for 3 minutes. After standing for two hours to allow the solvent and water sample to separate, the methylene chloride was removed from each bottle and stored. The extracts

from the individual bottles were concentrated and combined into a single final extract that was analyzed by GC/ECD. Total PCB concentrations were determined by comparison to specific PCB congeners identified in a mixed Aroclor standard. Filkins *et al.* (1983) provide data on the percentage of the sample result represented by the method blanks associated with each sample. For the four Lake Michigan samples, the associated blanks represent 14 to 122% of the associated sample result.

The data from September 1981 (Filkins, *et al.*, 1983, Figure 5-18) represent the results from only four samples in all of Lake Michigan. The total PCB concentrations in this study ranged from about 0.25 ng/L in the extreme northern portion and the central portion of the lake, to about 0.31 ng/L at a station near Chicago, with a similar concentration found at the mouth of Green Bay.

Pearson *et al.* (1996) collected approximately 100 L of water at each of 11 stations in Lake Michigan aboard the *R/V Lake Guardian*. Samples were filtered through glass fiber filters on board the ship. The filtrate was collected in 70-L stainless steel tanks and returned to the laboratory where it was extracted using a continuous flow liquid-liquid Goulden large-volume extraction device. Particulate and dissolved extracts were analyzed separately, using GC/ECD. The total PCB concentrations were calculated by summing the results determined for individual congeners using an internal standard method and surrogate correction.

The data from September 1991 (Pearson, *et al.*, 1996, Figure 5-19) includes significantly more stations than in 1981. Total PCB concentrations range from 0.34 to 1.7 ng/L, with a lake-wide mean concentration of 0.64 ng/L. Because the congener distribution patterns at two of the stations differed from those at the other nine stations, Pearson *et al.* also calculated a mean concentration of 0.47 ng/L for the nine stations alone. The northern portions of the lake contain approximately 0.5 ng/L of total PCBs, with concentrations of about 1 ng/L in the southern portion of the lake. The hot spot apparent in the southern portion of the lake has a maximum concentration of 1.7 ng/L. Overall, the total PCB concentrations are lower than in 1980 throughout the lake.

The LMMB data from September 1995 (Figure 5-20) suggest further decreases in the total PCB concentrations lake-wide since 1991. These data suggest that the concentrations in the northern portion of the lake are less than 0.15 ng/L. A hot spot appears in the southern portion of the lake with a maximum concentration of about 0.7 ng/L, roughly half the concentration is a similar hotspot found in 1991. Thus, the September 1995 total PCB data suggest a drop in concentration of about 50% from the 1991 results, and a drop of almost an order of magnitude from the 1980 results. In addition, the data in Figure 5-21 for the entire LMMB Study suggest that the results from September 1995 (Figure 5-20) are not unusual for the period of the LMMB Study itself.

Historical data for *trans*-nonachlor were not available, so no inferences can be made regarding changes in the concentrations of this contaminant in Lake Michigan.

Figure 5-17. Concentrations of Total PCBs Measured in Open-lake Samples in September 1980

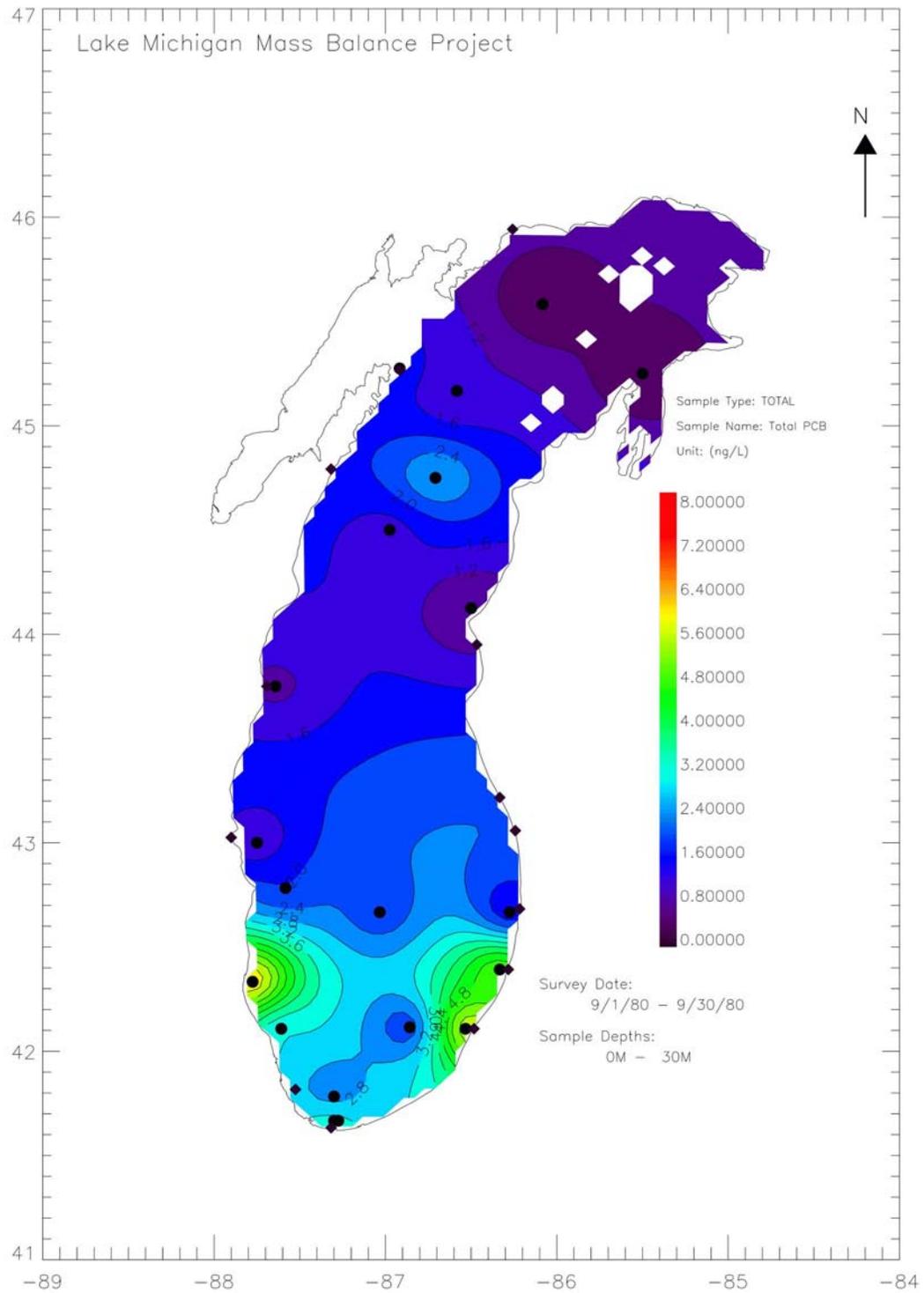


Figure 5-18. Concentrations of Total PCBs Measured in Open-lake Samples in September 1981

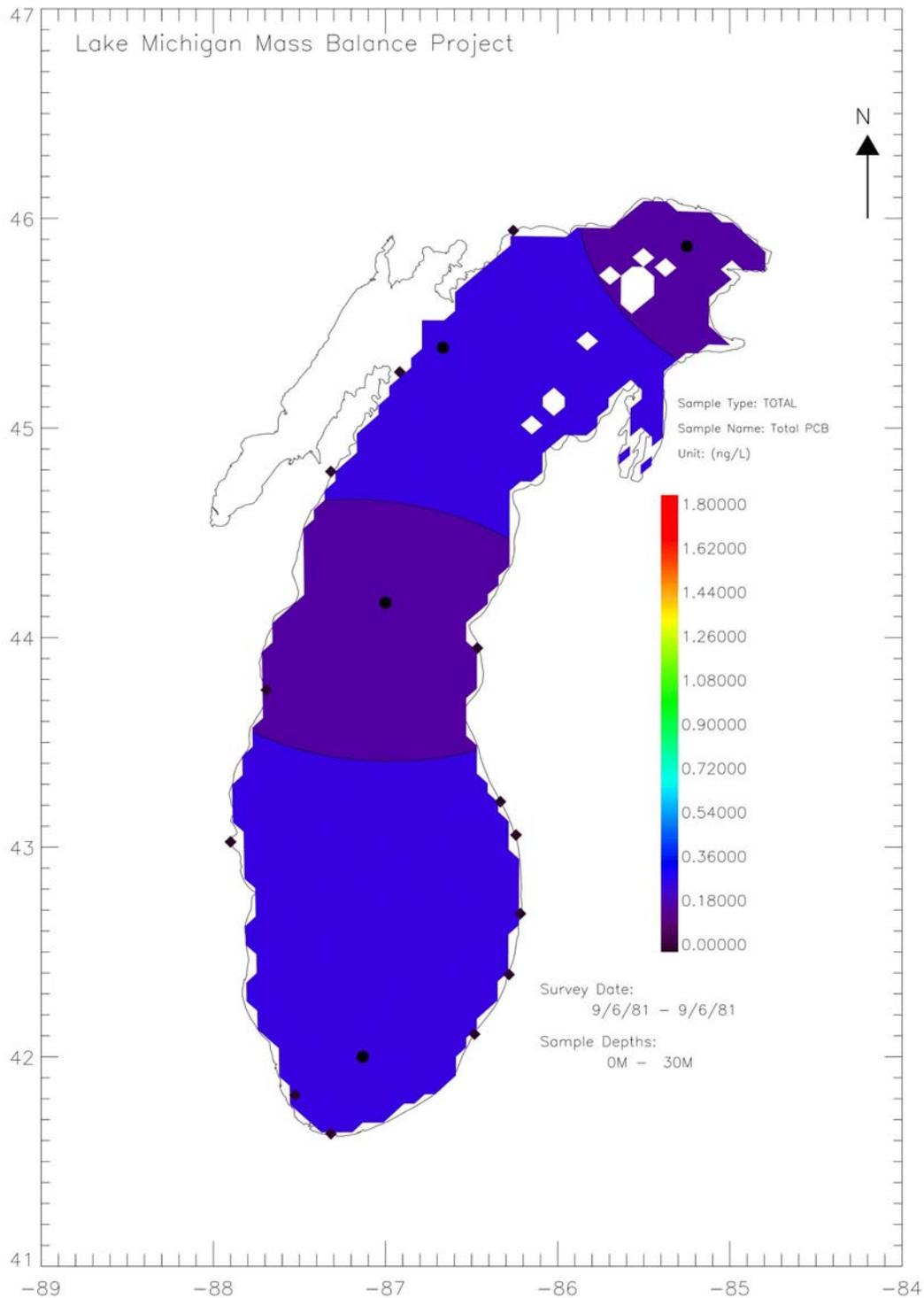


Figure 5-19. Concentrations of Total PCBs Measured in Open-lake Samples in September 1991

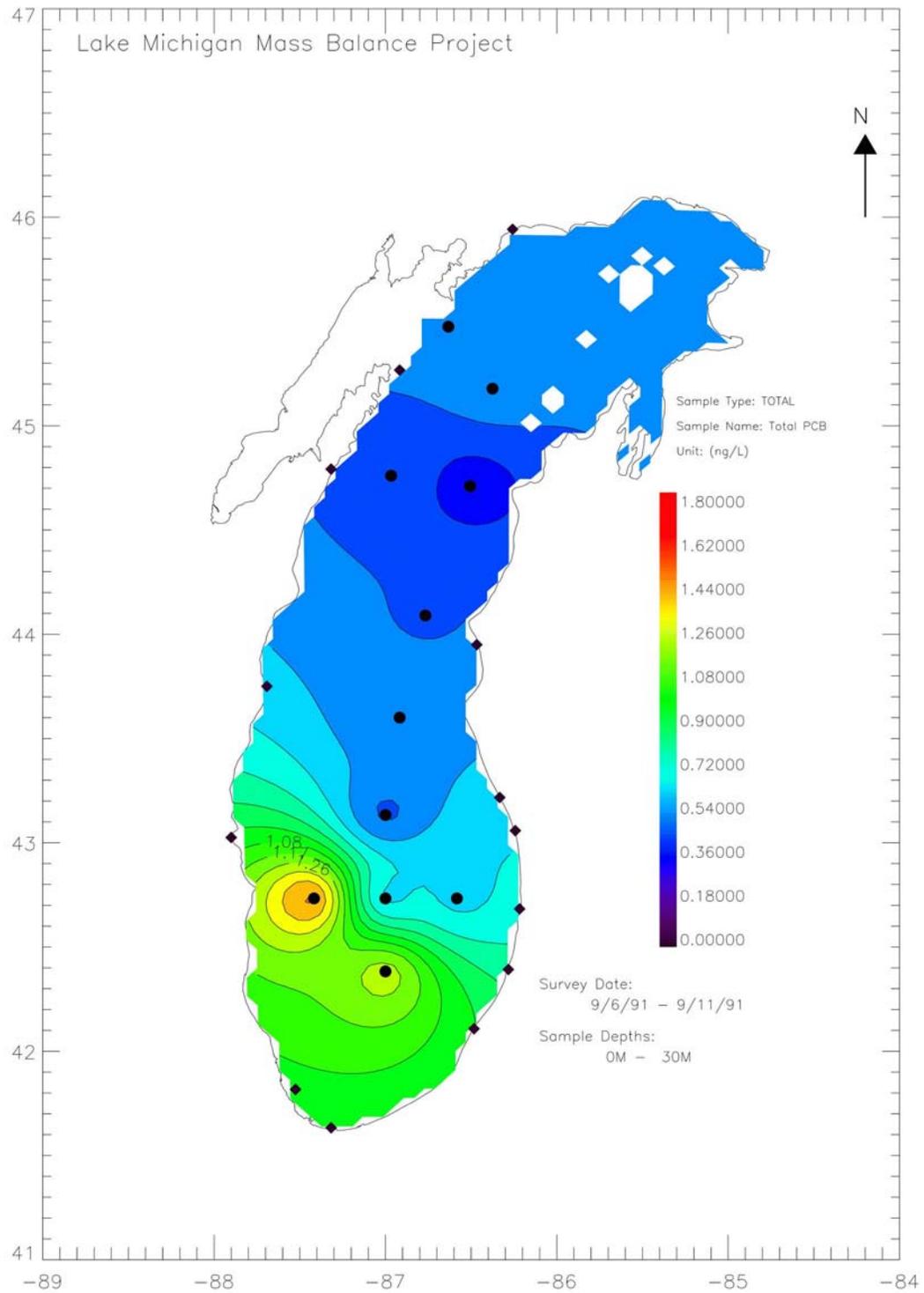


Figure 5-20 Concentrations of Total PCBs Measured in LMMB Open-lake Samples in September 1995

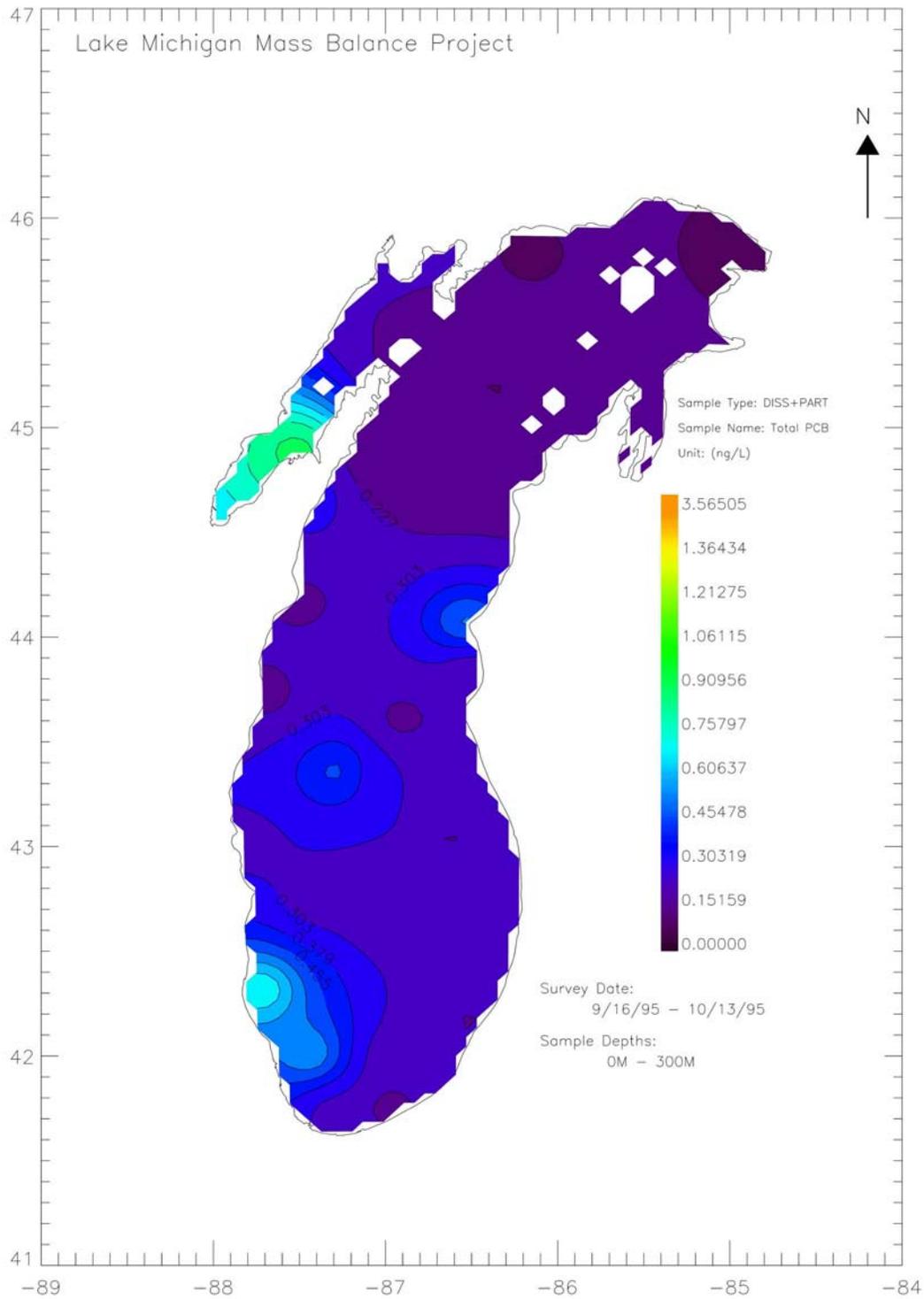
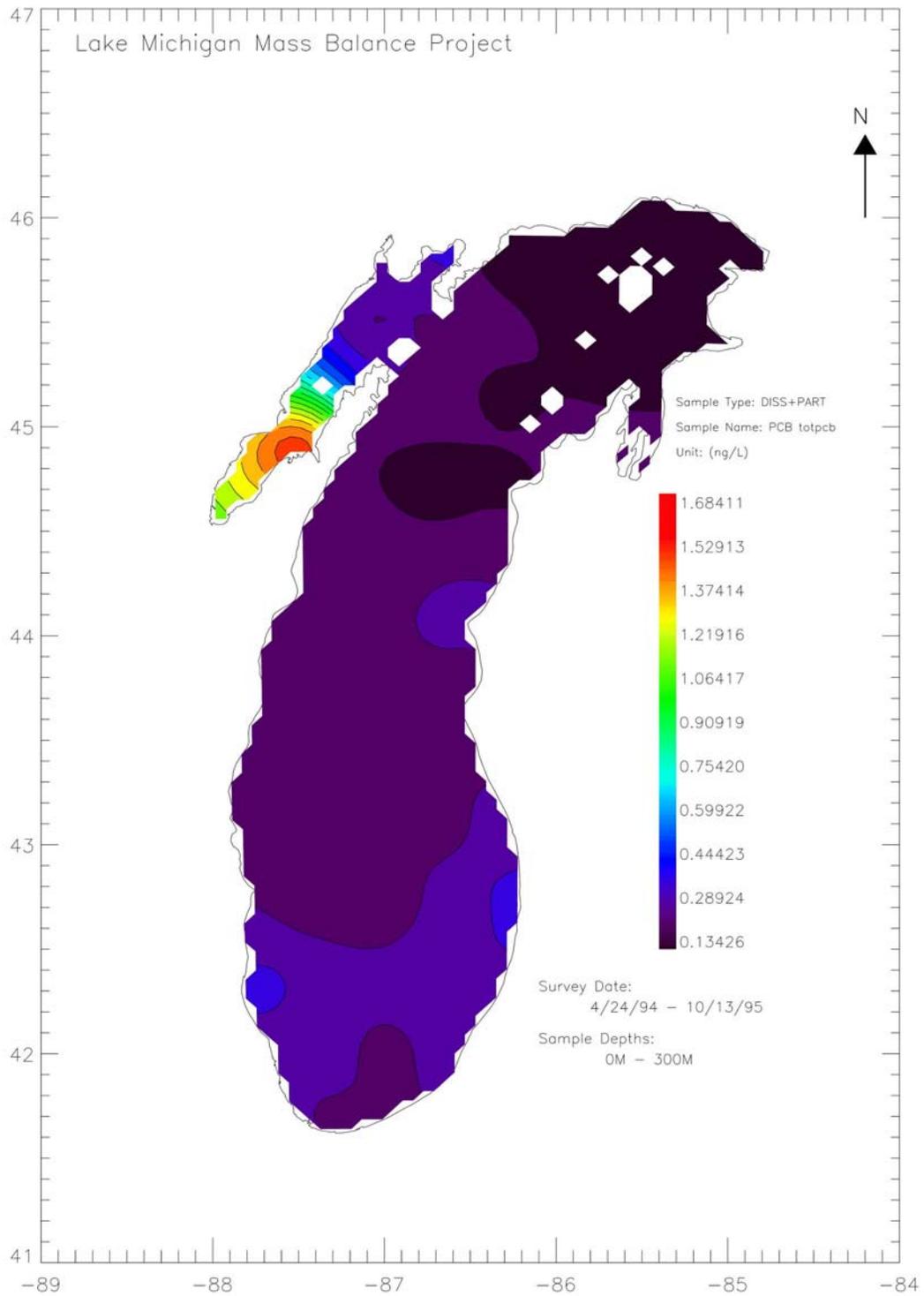


Figure 5-21. Concentrations of Total PCBs Measured in All LMMB Open-lake Samples



5.3.2 Regional Considerations

Among the general trends evident in the contour plots for the particulate-phase results for PCBs 33, 118, and 180 (Figures 5-7 to 5-9, shown earlier) are the presence of “hot spots” in the upper reaches of Green Bay (on the western side of Lake Michigan). The apparent decrease in concentrations to the southwest of the hot spot, e.g., towards the head of Green Bay, is an artifact of the lack of a sampling station further up Green Bay (see Figure 5-1 for the locations of the two sampling stations in Green Bay). The lower reaches of the Fox River are a known source of sediments containing high levels of PCBs (see Chapter 4), and these hot spots in particulate PCB concentrations may be the result of resuspended sediments from the Fox River that are carried into Green Bay.

The PCB and *trans*-nonachlor results were examined to determine if there were any statistically significant differences between the northern and southern portions of Lake Michigan. For these comparisons, the data from the LMMB Study were divided at approximately 44° north latitude (see Figure 5-17 for the latitude). The dividing line at 44° N is not intended as a formal differentiation between hydrographic basins in the lake, and other means of differentiating the results from north to south could be considered. Rather, the line at 44° N yields approximately equal numbers of stations in each portion of the lake. The results from the two stations in Green Bay and the one station in Lake Huron were excluded from these comparisons. The stations in the lower portion of the lake include Stations 1 through 29, plus 310, 340, and 380. Stations 31 through 180 were in the northern portion of the lake.

The results of these comparisons for PCB congeners 33, 118, and 180, total PCBs and *trans*-nonachlor are shown in Table 5-17 for both the dissolved and particulate samples. There are statistical interactions between the effects of the cruise and the north/south division for some analytes, in which case, a comparison between the northern and southern stations cannot be made.

Table 5-17. Results of North/South Comparisons of Open-lake Concentrations of PCBs and *trans*-Nonachlor

Fraction/Analyte	Significant Difference Between North and South?	Probability	Direction
<i>Dissolved</i>			
PCB 33	Yes	< 0.0001	South > North
PCB 118	Interaction with cruise		
PCB 180	No	0.2326	NA
Total PCBs	Yes	< 0.0001	South > North
<i>trans</i> -Nonachlor	Yes	0.0043	South > North
<i>Particulate</i>			
PCB 33	Interaction with cruise		
PCB 118	Yes	< 0.0001	South > North
PCB 180	Yes	< 0.0001	South > North
Total PCBs	Interaction with cruise		
<i>trans</i> -Nonachlor	Interaction with cruise		

NA = Not applicable

Of the 10 possible comparisons shown in Table 5-17, there were four interactions between the cruise and location. In five of the other six possible comparisons, there was a statistically significant difference, with concentrations in the southern portion of the lake greater than those in the northern portion of the lake.

Samples were collected from more than one depth at many of the stations during the periods when the lake was stratified. The choice of the depths of the samples was based on the position of the thermocline and other factors, but not a clear cutoff at a specific depth. As a result, it was possible to compare the concentrations of PCBs and *trans*-nonachlor between the samples collected near the surface and those collected below the thermocline. The results of these comparisons for PCB congeners 33, 118, and 180, total PCBs and *trans*-nonachlor are shown in Table 5-18 for both the dissolved and particulate samples, and for the results from the lake overall, those in the northern portion, and those in the southern portion of the lake. Generally speaking, most of the “shallow” samples were collected above 30 m, and all of the deep samples were collected below 30 m.

For the dissolved PCB results, the samples from the greater of the two depths at a station (e.g., the deeper samples) were significantly higher than the samples from the lesser of the two depths (e.g., the shallower samples) for all of the analytes except dissolved PCB 33. The differences between depths were consistent across the northern and southern stations, and for the lake overall.

For the particulate samples, the samples from the greater of the two depths at a station (e.g., the deeper samples) were significantly higher than the samples from the lesser of the two depths (e.g., the shallower samples) for all of the analytes except for particulate PCB 33 and *trans*-nonachlor in the northern portion of the lake. In both of those cases, the differences apparent in the results from the samples in the southern portion of the lake were sufficient to make the results different at depth in the lake overall.

These differences in concentrations with depth are consistent with the expected behavior of these hydrophobic contaminants. PCBs and *trans*-nonachlor are likely to be introduced into the open lake in a particulate form, either from atmospheric deposition or associated with particulate matter in tributary flows, or become associated with particulate matter in the lake through biological processes. As that particulate matter settles under the influence of gravity, the contaminants will settle too. In addition, based on the bathymetry of the Mackinac Channel between Lake Michigan and Lake Huron, the sill between the two lakes is at a depth of approximately 50 m. Therefore, even during winter months when the lakes are not thermally stratified, water below 50 m cannot flow out of Lake Michigan into Lake Huron. Although mixing of deeper water and surface water does occur and the mixed water may flow out of the lake, the deeper waters may retain their pollutant loads from historical sources long after the surface waters of the lake.

Table 5-18. Results of Depth Comparisons of Open-lake Concentrations of PCBs and *trans*-Nonachlor

Fraction/Analyte/Location	Significant Difference between Shallow and Deep Results?	Probability	Direction
<i>Dissolved</i>			
PCB 33 - Overall	No	0.3615	NA
PCB 33 - South	No	0.1570	NA
PCB 33 - North	No	0.5513	NA
PCB 118 - Overall	Yes	<0.0001	Deep > Shallow
PCB 118 - South	Yes	<0.0001	Deep > Shallow
PCB 118 - North	Yes	<0.0001	Deep > Shallow
PCB 180 - Overall	Yes	0.0006	Deep > Shallow
PCB 180 - South	Yes	0.0245	Deep > Shallow
PCB 180 - North	Yes	0.0093	Deep > Shallow
Total PCB - Overall	Yes	< 0.0001	Deep > Shallow
Total PCB - South	Yes	< 0.0001	Deep > Shallow
Total PCB - North	Yes	0.0091	Deep > Shallow
<i>trans</i> -Nonachlor - Overall	Yes	< 0.0001	Deep > Shallow
<i>trans</i> -Nonachlor - South	Yes	< 0.0001	Deep > Shallow
<i>trans</i> -Nonachlor - North	Yes	< 0.0001	Deep > Shallow
<i>Particulate</i>			
PCB 33 - Overall	Yes	<0.0001	Deep > Shallow
PCB 33 - South	Yes	<0.0001	Deep > Shallow
PCB 33 - North	No	0.3049	NA
PCB 118 - Overall	Yes	<0.0001	Deep > Shallow
PCB 118 - South	Yes	<0.0001	Deep > Shallow
PCB 118 - North	Yes	<0.0001	Deep > Shallow
PCB 180 - Overall	Yes	<0.0001	Deep > Shallow
PCB 180 - South	Yes	<0.0001	Deep > Shallow
PCB 180 - North	Yes	0.0013	Deep > Shallow
Total PCB - Overall	Yes	< 0.0001	Deep > Shallow
Total PCB - South	Yes	< 0.0001	Deep > Shallow
Total PCB - North	Yes	< 0.0001	Deep > Shallow
<i>trans</i> -Nonachlor - Overall	Yes	0.0003	Deep > Shallow
<i>trans</i> -Nonachlor - South	Yes	< 0.0001	Deep > Shallow
<i>trans</i> -Nonachlor - North	No	0.3507	NA

NA = Not applicable

5.3.3 Other Interpretations and Perspectives

As noted in various earlier sections of this report, there are limitations to the interpretations of the LMMB Study data presented here. Among the most basic considerations is the fact that this report has focused on providing the results for only three of the PCB congeners. The rationale for the choice of congeners is presented in Chapter 2. The interpretations suggested from the data for these three congeners may not apply to all other PCB congeners studied in the LMMB, and it would be advisable to examine the actual results for other congeners of interest before accepting the interpretations presented in this report.

The issues surrounding the evaluation of the blanks results in Section 5.2.3, and the impacts of the blanks on the interpretation of the field sample results cannot be overemphasized. As implemented in the LMMB Study, the sample collection and analysis procedures applied to PCBs and *trans*-nonachlor in open-lake waters represent a carefully crafted balance among practicality, affordability, and the size of the data set. Since the time that this study was conducted, more powerful analytical techniques such as high resolution GC/MS have been routinely applied to PCB congener analyses. However, the cost of such analyses would *severely* limit the number of samples that could be collected and analyzed the LMMB Study. While high resolution GC/MS may be able to better resolve some of the congeners, it would not necessarily better address the presence of PCBs in the blanks, except in instances where the contaminants are not actually PCBs, but had similar GC retention times.

Assessing temporal variation within the LMMB Study is hampered by the fact that not all stations were sampled on all cruises and that there are relatively few data from winter cruises. Comparisons between shallow and deep water samples suffer from similar problems, in that not all stations had samples at more than one depth. Therefore, the results for stations at different depths must be interpreted carefully.

Comparisons to historical data must consider not only the differences in the sizes of the various data sets (with the LMMB data set generally far larger than any other), but must also take into account significant differences in the sample collection and analysis procedures.

The concern about blanks for the LMMB data set is readily apparent in the data from Filkins *et al.* (1983) and although the investigators in the other two studies do not present similar blank results, it would be reasonable to assume that blanks would also have been a problem for those studies.

Finally, this report has used “contour” plots of PCB concentrations as a means of visually presenting parts of a large and complex data set. However, as noted earlier, there are limitations to those plots, particularly with regard to the identification of “hot spots” in Green Bay, as well as with the demarcation of PCB concentrations in the open lake when relatively few samples were collected.

Chapter 6

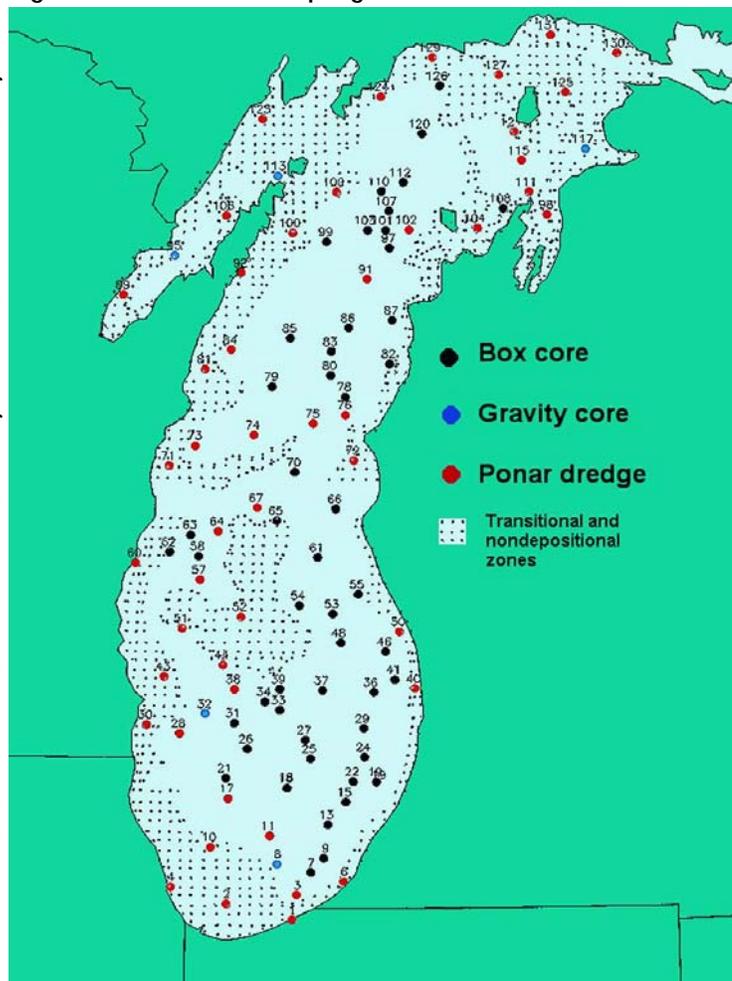
PCBs/trans-Nonachlor in Sediment

6.1 Results

A total of 133 sediment samples were collected from 117 stations in Lake Michigan and 6 stations in Green Bay and analyzed for PCBs and *trans*-nonachlor. The samples were collected as described in Sections 2.2.4 and 2.5.4. Selection of sampling sites was based on prior information of the spatial distribution of sediment grain size, composition (e.g., organic carbon), sediment layer thickness, mixed layer depth, and ¹³⁷Cs and ²¹⁰Pb inventories. Emphasis was placed on sampling the more permanent accumulations of recent sediment in the depositional basins of the lake. Sediment samples were collected using three types of equipment: a box core, a Ponar dredge, and a gravity core.

The locations of the LMMB stations sampled by each of the three sampling methodologies are shown in Figure 6-1, along with the depositional classifications of Cahill (1981). Cahill developed the classifications of depositional, transitional and nondepositional zones in Lake Michigan from an examination of the physical description of sediment from 286 stations, grain size information, and echo-sounding tracks.

Recently deposited sediments were obtained from depositional basins through the use of a specially designed box corer. A modified Soutar box corer was used to retrieve cores approximately 60 cm in length, with extremely well preserved sediment-water interfaces. The 25- x 25- x 60-cm core was subsequently subcored with four 10-cm diameter butyrate tubes. Care was taken to preserve the interface and reduce distortion of the core upon insertion of the tube and during subsequent extrusion of the subcore. Two of the subcores were used for analysis of PCBs and *trans*-nonachlor, as well as to determine the organic carbon (OC) content of the sediment. A third subcore was used for analysis of radionuclides, trace elements, and biogenic components. The fourth subcore was archived. The sections of two cores from 0-1 cm were combined to allow for enough material for analysis of the PCBs and *trans*-nonachlor.



In transitional regions where recent deposits thinly overlie older glaciolacustrine clays, modern sediment is difficult to collect with a box corer. Therefore, a Ponar dredge was used at most transitional and nondepositional stations. However, this device does not collect modern sediment very efficiently, due to the bow wave's impact on the uppermost flocculent material. A gravity corer was used instead of a box corer at a few of the depositional stations, due to the lack of box coring capability of the vessel.

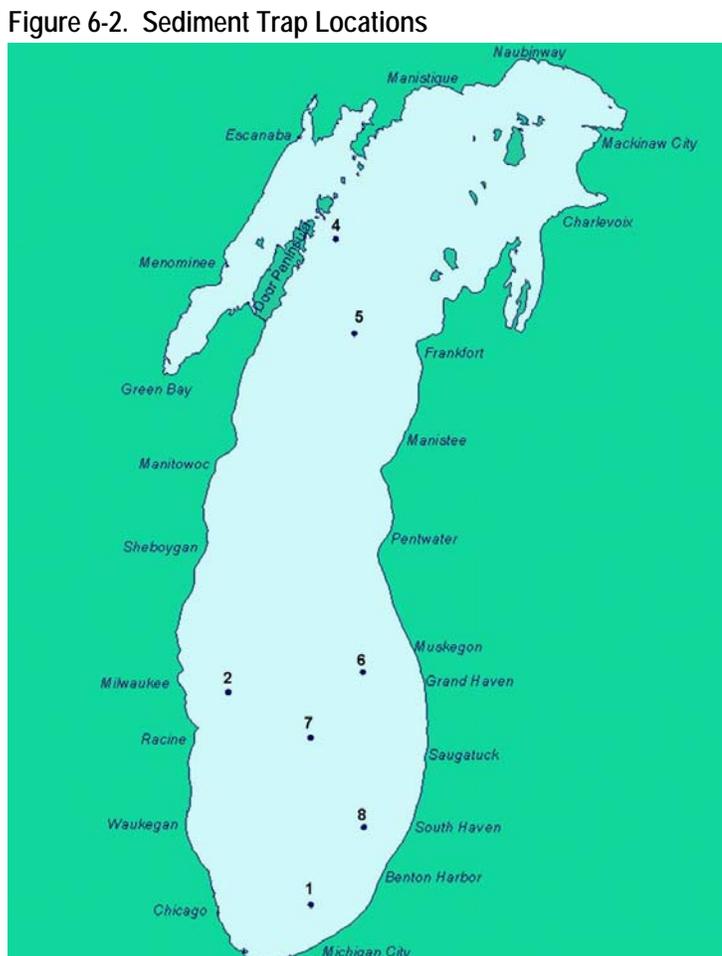
In addition to the core samples, sediment traps were deployed at eight locations (Figure 6-2), but the traps at two stations could not be recovered. Sample retrieval was successful at trap locations 1, 2, 5, 6, 7, and 8.

As noted in Chapter 2, there are 209 possible PCB congeners and the investigators in this study reported results for 65 to 110 of these congeners, depending on the capabilities of each laboratory. The investigators for the sediment portion of the study determined results for 105 congeners or co-eluting congeners.

For the purposes of this report, we are presenting summaries of the results for the following subset of the analytes:

- The coeluting pair of PCB congeners 28 + 31 (2,4,4'-trichlorobiphenyl and 2,4',5-trichlorobiphenyl)
- PCB congener 118
- PCB congener 180
- Total PCBs
- *trans*-nonachlor

The PI for the sediment sample analyses focused on the coeluting pair 28 + 31 because of concerns that PCB congener 33 coeluted with the pesticide heptachlor. Based on matrix spike results for heptachlor and given the possibility that heptachlor was present in the sediments as a result of its historical use in the area around Lake Michigan, the PI flagged all of the PCB 33 results and presented data for PCB 28 + 31.

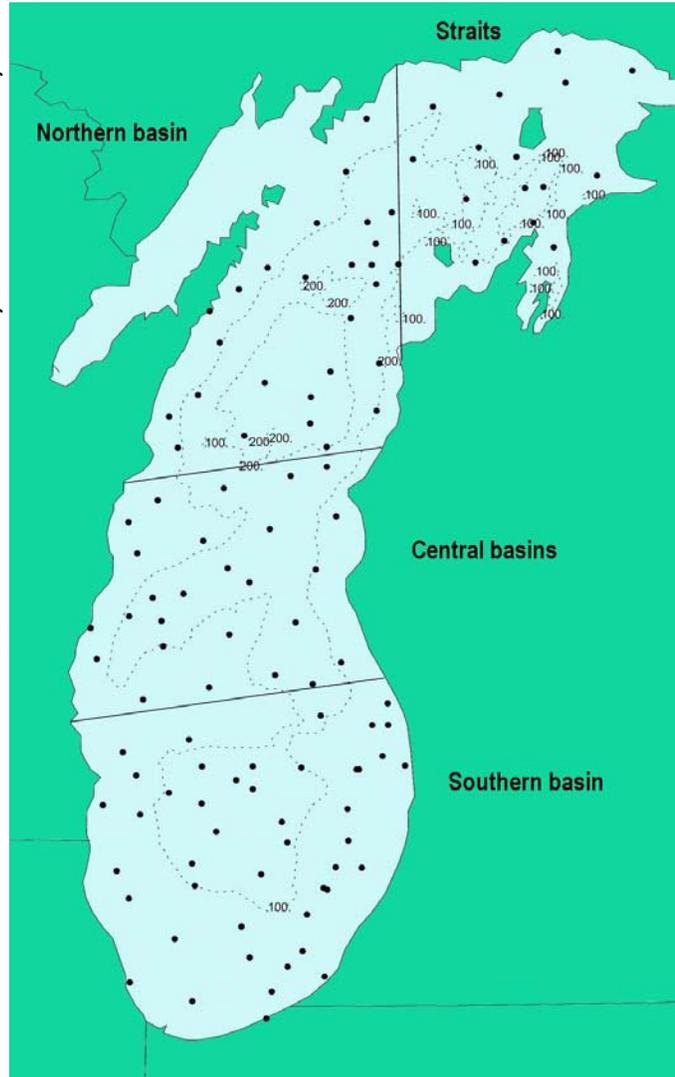


6.1.1 Geographical Variation

In addition to Cahill's three depositional zones, Lake Michigan can be divided into four geographical regions, based on characterizations of bottom morphology by the U.S. Department of the Interior (1967) (Figure 6-3):

- The southern basin lies south of a line between Milwaukee and Muskegon. In this basin the bottom has a gentle relief and maximum depth of 180 m. The southern basin receives urban and industrial inputs of PCBs from Waukegan Harbor, IL, and the metropolitan areas of Chicago, IL, Gary, IN, and Milwaukee, WI.
- The divide area, located between the northern and southern basins, is bounded by two approximately east-west ridges. Two small depositional basins reside within the divide, the Grand Haven basin on the east side and the Milwaukee basin on the west side. For this study, the two basins' stations will be lumped together and referred to as the "Central basins."
- The northern basin is bounded by a line between Manitowoc and Manistee and another line from Frankfort to Manistique. Bottom topography of the northern basin is much more complex than the southern basin. A steep grade defines this basin resulting in a maximum depth of 282 m. The northern basin receives lower inputs from industrial and urban centers relative to the southern basin. However, the extent to which PCB-laden Green Bay sediments contribute to the northern basin's inventory is unknown.
- The straits area, including Grand Traverse Bay, has a very irregular bottom with isolated depressions where sediments accumulate. Its morphology is more similar to that of northern Lake Huron than northern Lake Michigan.

Figure 6-3. Lake Michigan Basins



Green Bay samples were not included in this analysis, because only six stations were visited, and these stations were not the focus of the LMMB Study.

The summary statistics for the four basins are provided in Table 6-1.

Table 6-1. Summary Statistics for Surficial Sediments

Analyte	Basin	N	Mean (ng/g)	Range (ng/g)	Std. Dev. (ng/g)
Organic Carbon*	Southern	50	22.634	0.440 - 42.620	14.346
	Central	22	22.755	0.930 - 49.920	17.280
	Northern	32	21.479	0.430 - 41.490	15.999
	Straits region	16	12.172	1.560 - 46.070	16.042
PCB 28+31	Southern	50	4.593	0.0490 - 16.486	3.841
	Central	22	2.563	0.110 - 11.558	2.855
	Northern	31	1.879	0.0111 - 4.010	1.466
	Straits region	16	0.405	0.0625 - 1.640	0.493
PCB 118	Southern	50	3.271	0.0130 - 9.840	2.608
	Central	22	2.668	0.0404 - 7.190	2.478
	Northern	31	2.176	0.00653 - 4.940	1.709
	Straits region	16	0.404	0.0655 - 1.660	0.493
PCB 180	Southern	50	1.562	0.00740 - 4.783	1.318
	Central	22	1.223	0.00570 - 3.512	1.179
	Northern	31	1.070	0.00299 - 2.400	0.873
	Straits region	16	0.175	0.0264 - 0.745	0.238
Total PCBs	Southern	50	69.724	0.545 - 219.288	53.114
	Central	22	50.541	1.240 - 149.390	49.406
	Northern	31	41.599	0.138 - 91.220	33.102
	Straits region	16	7.271	1.056 - 28.600	9.187
<i>trans</i> -Nonachlor	Southern	49	0.599	0.00250 - 2.830	0.522
	Central	21	0.638	0.00576 - 2.243	0.644
	Northern	32	0.560	0.00661 - 1.200	0.456
	Straits region	16	0.168	0.0296 - 0.681	0.217

* Units for organic carbon content are mg/g.

The mean concentrations of the PCB congeners and total PCBs in Table 6-1 exhibit a general trend of decreasing concentrations from south to north, with the lowest concentrations in the Straits region. In contrast, the mean concentrations of *trans*-nonachlor, while lowest in the Straits region, exhibit no south to north trend. The organic carbon content data exhibit a pattern similar to that for *trans*-nonachlor.

6.1.2 Frequency Distributions

Frequency distributions of total PCBs, *trans*-nonachlor and organic carbon (OC) content for surficial sediment samples from Lake Michigan are shown in Figure 6-4. These data are not normally distributed. It should also be noted that these distributions are biased as a result of our emphasis on sampling the depositional regions of the lake, especially in the southern basin.

Total PCBs exhibit a wide range in concentration. Although not a true bimodal distribution, two distinct groups are evident within the total PCB distribution. The first group of samples, from nondepositional and transitional stations, has very low concentrations that exponentially decline in number with increasing concentration (0 - 30 ng/g). The second group of samples taken mainly from depositional sites (35 - 225 ng/g) is more normally distributed, though tailing toward higher levels is evident.

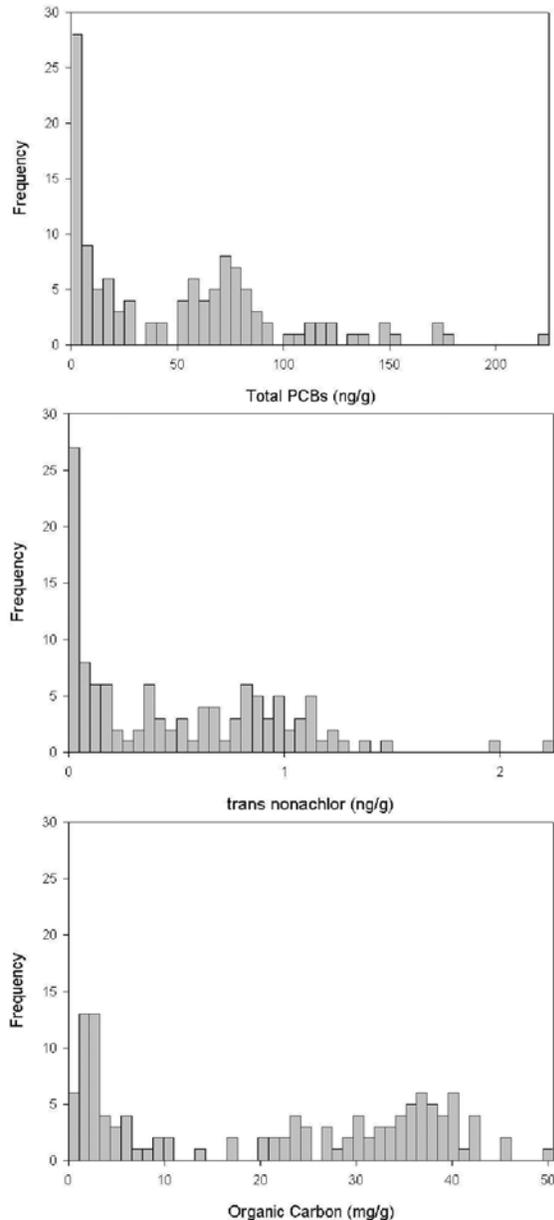
While the distribution of *trans*-nonachlor also is skewed toward lower concentrations in nondepositional and transitional regions (0 - 0.2 ng/g), this compound's distribution in the depositional region (0.25 - 2.25 ng/g) differs from PCBs by being more evenly distributed. The distribution of OC more closely resembles a bimodal distribution with the first peak representing nondepositional and transitional stations (0 - 11 mg/g), and the second peak representing depositional stations (20 - 51 mg/g).

The frequency distribution of total PCBs in each of the regions are shown in Figure 6-5. Even when divided by basin, the total PCB data are not normally distributed. It should also be noted that these distributions are biased as a result of our emphasis on sampling the depositional regions of the lake, especially in the southern basin. Because of this sampling bias, less discussion is devoted to a statistical comparison of basins.

Instead, more emphasis is placed on descriptions of their lake-wide distribution (contour maps), and examining relationships of these chlorinated organic contaminants (COCs) with OC in later sections.

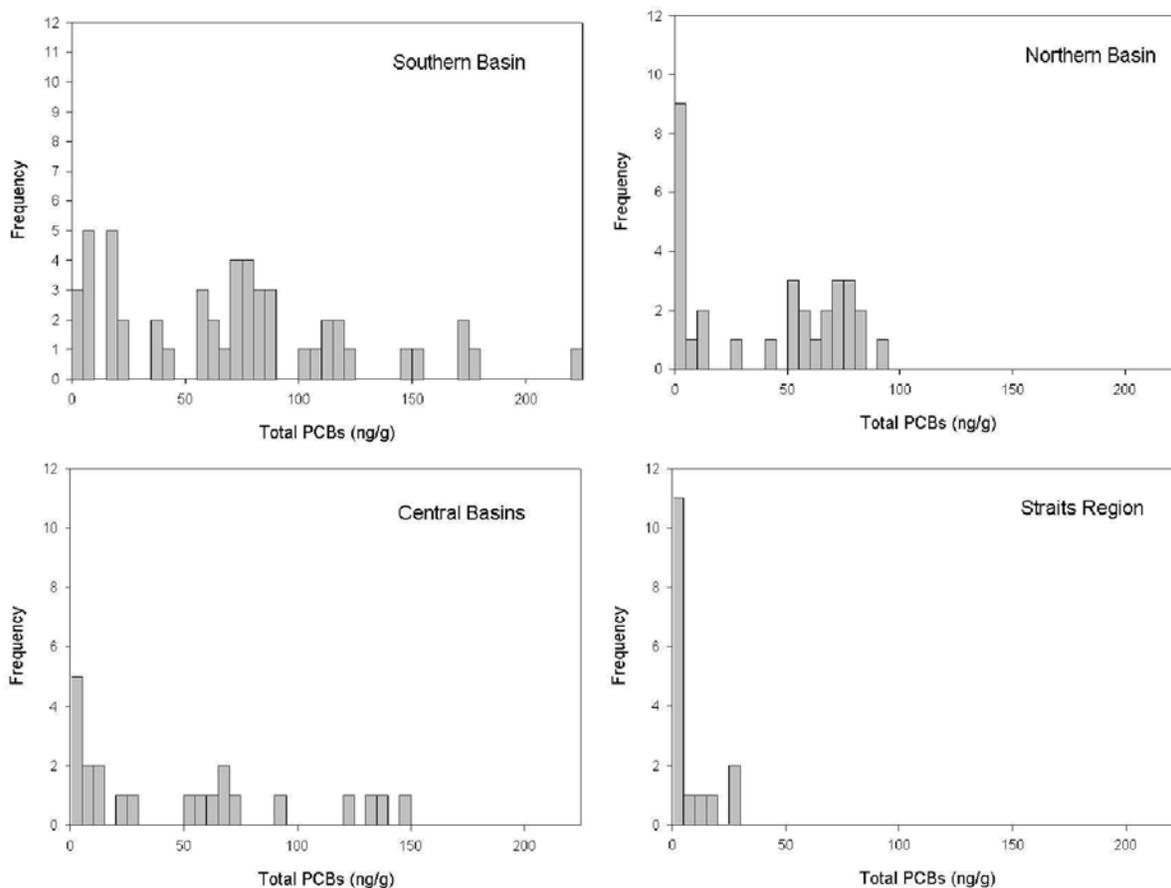
The total PCB data from all four basins are skewed toward lower concentrations. The large number of low PCB concentrations in these sediments is not unexpected, given the relatively large area of the nondepositional and transitional regions in Lake Michigan, which tend to have lower silt and clay content, and thus lower particle-associated contamination. The range in concentration is wider in the

Figure 6-4. Frequency Distributions of Total PCBs, *trans*-Nonachlor, and Organic Carbon

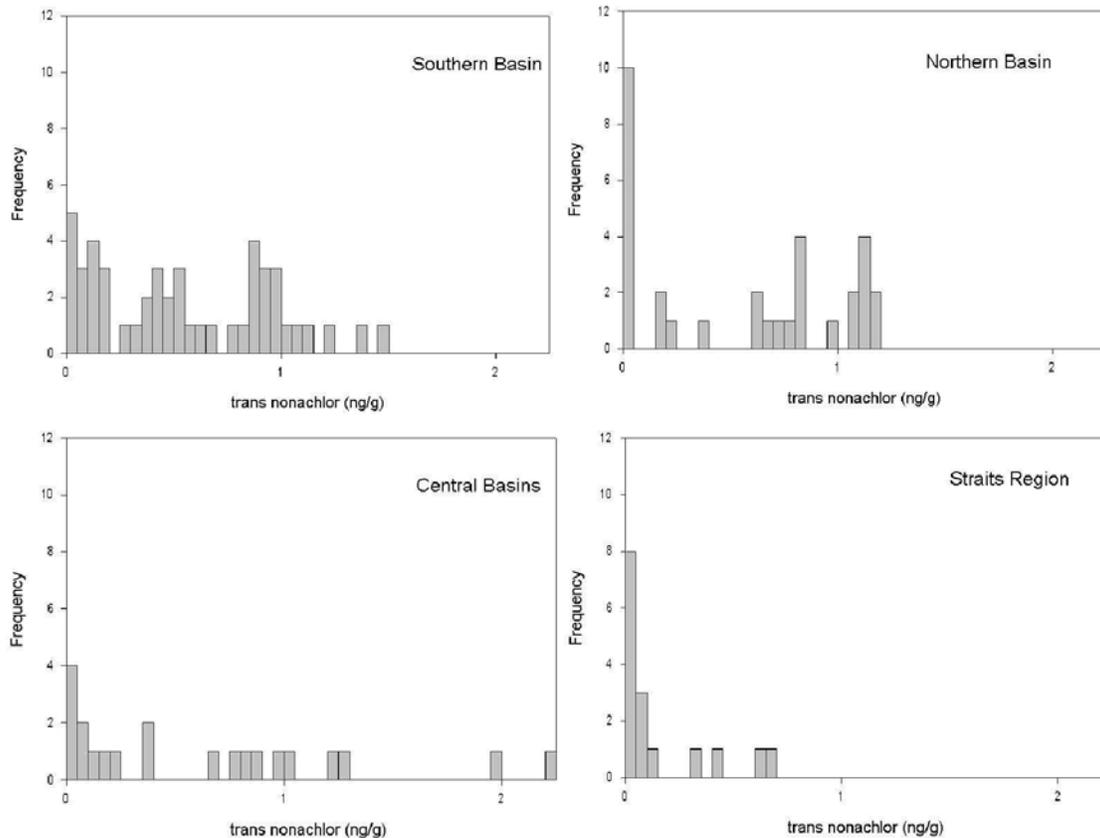


northern basin than straits region, while the southern and central basins have an even wider range due to a few stations with very high concentrations. Only in the southern and central basins did total PCBs exceed 100 ng/g, and only in the southern basin did total PCBs exceed 150 ng/g. The distribution of PCB would indicate that the accumulation of this contaminant is not evenly distributed throughout the lake but rather is preferentially collecting in depositional areas.

Figure 6-5. Frequency Distributions of Total PCBs by Basin



The distribution of *trans*-nonachlor for all basins is generally similar to that of total PCBs (Figure 6-6). One notable exception is the relative similarity of ranges between basins for *trans*-nonachlor.

Figure 6-6. Frequency Distributions of *trans*-Nonachlor by Basin

6.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the PCBs and *trans*-nonachlor monitoring portion of the study are further described in Section 2.7 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in the *Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of data quality issues for the sediment PCBs and *trans*-nonachlor data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.5, because data comparability was important to the successful development of the mass balance model, the PIs used similar sample collection, extraction, and analysis methods for the PCB and *trans*-nonachlor monitoring in this study.

6.2.1 Sample Collection

The LMMB work plan indicated that 131 sediment sampling sites were to be visited. Field records indicated that only 117 stations were actually sampled. Of the eight sediment trap locations to be sampled, sample retrieval occurred at trap locations 1, 2, 5, 6, 7, and 8. Numerous attempts were made to retrieve samples from trap locations 3 and 4, but they were not successful.

The LMMB work plan specified that the sediment depth intervals to be sampled was from 0 to 1 cm. Actual intervals sampled and analyzed ranged from 0-0.5 to 0-1.5 cm, due to sporadic slanting at the top surface of the core after retrieval.

During examination of the field collection records for field duplicates, it was discovered that some field duplicates were not actually collected at the same time as the field sample due to equipment mobilization. Samples collected within five minutes of each other were considered field duplicates (FD1), and if more than five minutes elapsed, the samples were considered sequential field duplicates (SFD1). Separate labeling of these data points as FD1 and SFD1 was done in order to assess if precision differed based on the elapsed time.

6.2.2 Data Assessments

As discussed in Section 2.7, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 6-2 provides a summary of flags applied to the sediment PCB and *trans*-nonachlor data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.7. Compared to other matrices, the percentage of results that were qualified for these criteria is relatively small.

PIs used surrogate spikes to monitor the bias of the analytical procedure. The PCB results were corrected for the recoveries of the surrogates. The *trans*-nonachlor results were *not* surrogate-corrected. Only 0.5% of the PCB 28 +31 results, 2% of PCB 118 results, and 1% of the PCB 180 results were qualified for surrogate recovery problems (Table 6-2).

Laboratory matrix spike samples also were used to monitor the bias of the analytical procedure. The results for the matrix spike samples were compared to the MQO for spike recoveries (50 - 125%). Analytical results associated with matrix spike samples with recoveries below the MQO limits were flagged with failed matrix spike and low bias flags and results associated with matrix spike samples that had recoveries higher than the MQO limits were flagged with failed matrix spike and high bias flags. Analytical results were considered invalid and flagged as such when the analyte was undetected and recoveries for associated matrix spike samples were less than 10%. No sediment *trans*-nonachlor samples failed the matrix spike MQOs. None of the results for PCBs 28+31 or 180 were flagged as failing the matrix spike MQOs. For PCB 118, 5% of the results were flagged as failing the matrix spike MQOs.

Field blanks were collected for PCBs and *trans*-nonachlor. When field blank contamination was greater than 3.3 times the method detection limit, all of the associated results were flagged with the failed field blank sample code (FRB). Field blanks were not collected at all stations, so potential station-specific contamination associated with these sites cannot be evaluated. However, contamination associated with sampling equipment, collection, processing, shipping, storing, and analysis can be evaluated based on the field blanks collected throughout the study. For PCB 28+31, 11% of the field samples were associated with a field blank in which this congener was reported above the sample-specific detection limit (Table 6-2). None of the field sample results for *trans*-nonachlor were qualified because of field blank results.

Field duplicates were to be collected at a frequency of 5%. Duplicate samples collected within 5 minutes of each other were considered field duplicates. However, an examination of the field collection records indicated that some of the planned field duplicates were not collected within that 5-minute time frame as a result of problems with equipment mobilization or the time required to pump the sample through the filter and resin cartridge. Those “duplicates” that were collected more than 5 minutes apart were considered “sequential field duplicates” and the data were labeled accordingly (e.g., SFD1 vs. FD1). Combining the field duplicates and sequential field duplicates, the actual rate of collection of duplicates was 5.5%.

The results from the original field sample and the associated duplicate were compared on the basis of the relative percent difference (RPD). The RPD value for each PCB congener and *trans*-nonachlor was compared to the MQO for field duplicate precision. None of the field samples results for PCBs or *trans*-nonachlor were qualified because of the field duplicate precision (FFD) concerns (Table 6-2).

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean RPD between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between the results for laboratory duplicate pairs. Table 6-3 provides a summary of data quality assessments for several of these attributes for the sediment PCB and *trans*-nonachlor data.

Because the relative variability of most measurement techniques increases as one approaches the detection limit of the technique, the assessment of the field duplicate results were divided into two concentration regimes. One measure of system precision was calculated for those results that were less than 5 times the sample-specific detection limit (SSDL) of the analyte and a separate measure was calculated for those results that were greater than 5 times the SSDL. However, none of the sediment sample results with corresponding field duplicates contained PCB 28+31, 118, or 180 at concentrations below the SSDL. The precision of the field duplicate results above the SSDL ranged from 19 to 24% for the PCB congeners in Table 6-3.

Three of the four field duplicate pairs contained *trans*-nonachlor below the SSDL and the mean precision of those pairs was 37%, compared to one field duplicate pair containing *trans*-nonachlor above the SSDL, with an RPD of 26%.

The variability of the laboratory measurement technique was assessed through the preparation and analysis of laboratory duplicate pairs. Eleven laboratory duplicate pairs were analyzed for the PCB congeners, and ten pairs were analyzed for *trans*-nonachlor. The laboratory duplicate precision ranged from 9 to 13% for the PCB congeners and *trans*-nonachlor (Table 6-3). As expected, the laboratory duplicate results are more precise than the field duplicate results.

Table 6-2. Summary of Routine Field Sample Flags Applied to Select PCB Congeners and *trans*-Nonachlor in Sediment Samples

Analyte	Flags										
	Sensitivity		Contamination	Precision	Bias						
	MDL	UND	FFR	FFD	FSS	FMS	LOB	HIB	INV	FBK	FDL
PCB 28 + 31	5% (11)	0	11% (23)	0	0.5% (1)	0	0	0	0	0	0
PCB 118	3% (6)	0	0	0	2% (3)	5% (10)	0	0	0	0	0
PCB 180	6% (13)	0	0	0	1% (3)	0	0	0	0	0	0
<i>trans</i> -Nonachlor	28% (54)	0	0	0	0	0	0	0	0	0	0

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

- MDL = Less than method detection limit (Analyte produced an instrument response but reported value is below the calculated method detection limit. Validity of reported value may be compromised.)
- UND = Analyte not detected (Analyte produced no instrument response above noise.)
- FFR = Failed field blank (A field blank sample, type unknown, associated with this analysis failed the acceptance criteria. It is unknown whether the blank that failed was a field blank or a lab blank. Validity of reported value may be compromised.)
- FFD = Failed field duplicate (A field duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- FSS = Failed surrogate (Surrogate recoveries associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- FMS = Failed matrix spike (A matrix spike associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- LOB = Likely biased low (Reported value is probably biased low as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery or other internal lab QC data. Reported value is not considered invalid.)
- HIB = Likely biased high (Reported value is probably biased high as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery, blank contamination, or other internal lab QC data. Reported value is not considered invalid.)
- INV = Invalid.
- FBK = Failed laboratory blank (Laboratory reagent blank result greater than the SSDL).
- FDL = Failed laboratory duplicate

Table 6-3. Data Quality Assessment for Select PCB Congeners and *trans*-Nonachlor in Sediment Samples

Analyte/Number Field Samples	Parameter	Number of QC samples	Assessment
PCB 28 + 31 197 samples	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	0 field duplicate pairs	—
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	9 field duplicate pairs	16 %
	Analytical Precision - Mean Laboratory Duplicate RPD (%), > 5 * SSDL	11 lab duplicate pairs	10%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	24 matrix spikes	102%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	6%
PCB 118 189 samples	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	0 field duplicate pairs	—
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	9 field duplicate pairs	17%
	Analytical Precision - Mean Laboratory Duplicate RPD (%), > 5 * SSDL	11 lab duplicate pairs	9%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	24 matrix spikes	112%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	—	3%
PCB 180 196 samples	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	0 field duplicate pairs	—
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	9 field duplicate pairs	18%
	Analytical Precision - Mean Laboratory Duplicate RPD (%), > 5 * SSDL	11 lab duplicate pairs	13%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	24 matrix spikes	108%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	—	7%
<i>trans</i> -Nonachlor 185 samples	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	8 field duplicate pairs	25%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	0 field duplicate pairs	—
	Analytical Precision - Mean Laboratory Duplicate RPD (%), > 5 * SSDL	10 lab duplicate pairs	12%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	22 matrix spikes	88%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	—	28%

RPD = Relative percent difference
SSDL = Sample-specific detection limit

Analytical bias was assessed using the results from matrix spike samples. The mean recoveries of the analytes were excellent for the PCBs, ranging from 102% to 112% for the PCB congeners in Table 6-3. The mean recovery for *trans*-nonachlor was very good, at 88%. Thus, these results demonstrate that the analytical techniques applied to the field samples introduce little or no bias into the PCB results, and a slight low bias into the *trans*-nonachlor results.

6.3 Data Interpretation

6.3.1 Comparison to Historical Studies

LMMB surficial sediment concentrations of total PCBs were compared to measurements made by Swackhamer and Armstrong (1988), Hermanson *et al.* (1991), and Golden (1994). Swackhamer and Armstrong (1988) collected 20 box cores from the southern and Grand Haven depositional basins in 1978-1980. Hermanson *et al.* (1991) collected five box cores from the northern, southern and Grand Haven basins in 1984. More recently, Golden (1994) collected four box cores from the northern and southern basins in 1991 and 1992. Only box cores taken from depositional regions were used for this comparison because of the lack of permanent sediment accumulation in the transitional and nondepositional regions.

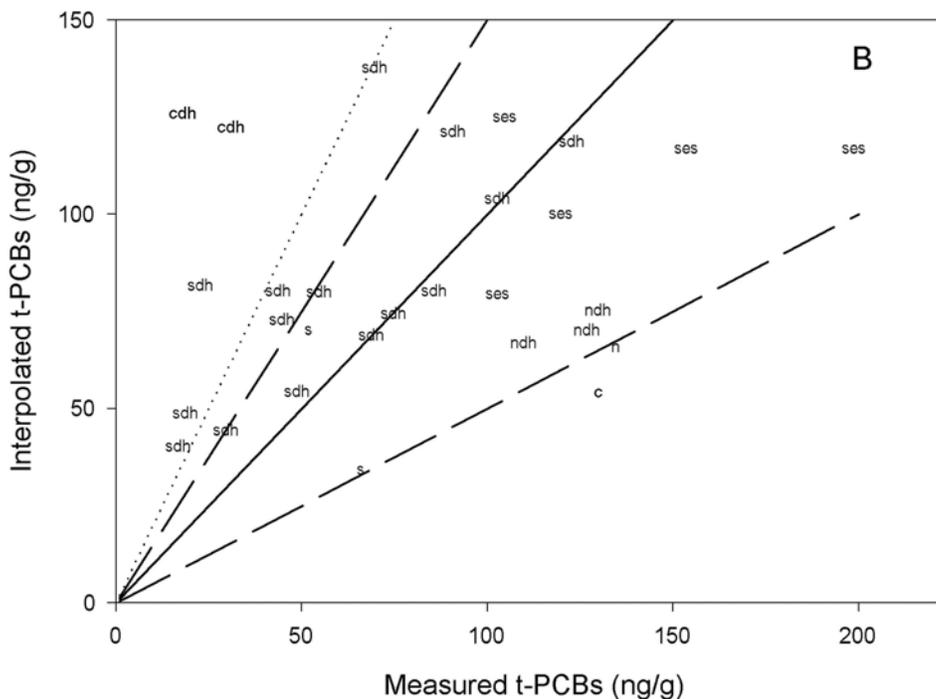
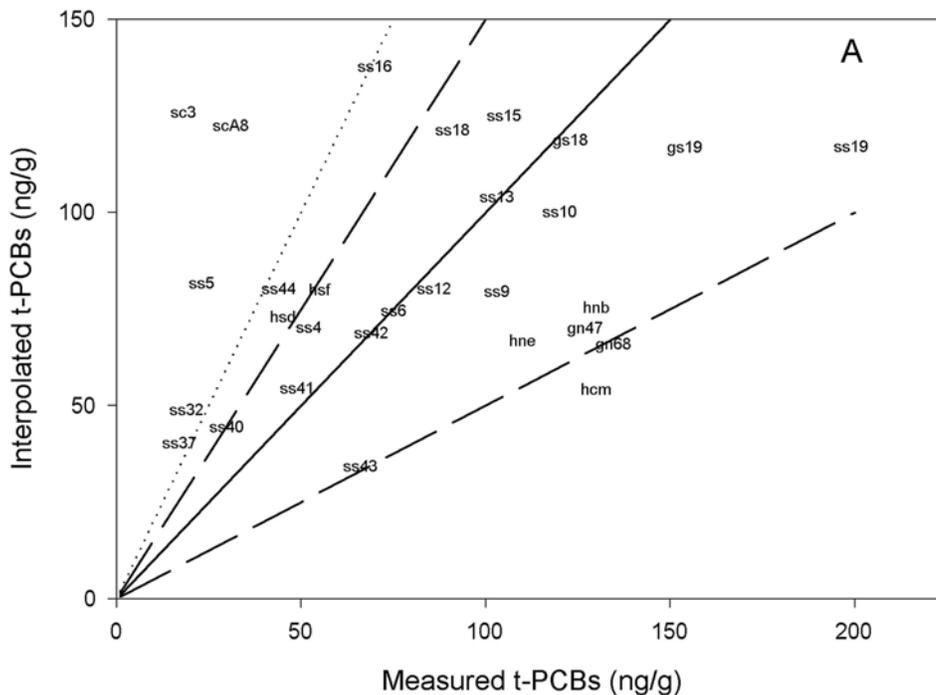
Swackhamer and Armstrong (1988) and Hermanson *et al.* (1991) used Aroclor analysis to quantify total PCBs. Aroclor analysis using COMSTAR, a multiple linear regression analysis program that provides the best fit to Aroclor composition, has been shown to compare favorably (90-95%) with total PCBs measurements using congener analysis (Burkhard and Weininger, 1987). Interpolated values from the contour map of LMMB surficial PCBs (1994-1995) were compared to the measured historical values. Plots of the interpolated versus measured total PCB values are shown in Figure 6-7.

Differences between LMMB values and historical measurements are compared to gains/loss lines (solid line, 0% change; dashed lines, 50% gain or loss; dotted line, 100% gain). In Figure 6-7A, the author, basin, and station are designated for each data point (s=Swackhamer and Armstrong [1988]; h=Hermanson *et al.* [1991]; g=Golden [1994]). In Figure 6-7B, the stations are divided into basins (n=north, c=central, s=south) followed by areas within basins (dh=deep hole, es=eastern side).

It appears that in the southern deep hole (sdh) and central deep hole (cdh) regions, total PCB levels have either increased (35 - 100%) or remained un-changed since they were measured in 1978-1984. In contrast, 4 of 5 stations on the eastern side of the southern basin (ses) exhibited reductions in PCB concentrations.

In the northern basin, surficial sediment total PCBs appear to have declined significantly (~40%) since Hermanson's 1984 collection, and even over the 3-year period since Golden's 1992 collection. It is possible that the northern basin's complex topography results in a very heterogenous distribution of total PCB sediment concentrations. Thus, comparisons of historical data with recent interpolated values could be misleading. There is other evidence, however, that a significant decline in total PCB levels is occurring in the northern basin. A core profile of total PCBs at LMMB station 103 indicates that a 33% decline in PCB concentrations has occurred since the early 1980s. Looking at Golden's sediment core profiles, a loss of only 1-9% was noted for two northern cores between about 1984 and 1992. However, a 30% loss was noted between about 1980 and 1992.

Figure 6-7. Comparison of Measured Historical Total PCB Results in Surficial Sediment and Interpolated Total PCB Results from Contours of the 1994-1995 LMMB Collections



— 0% change - - - 50% gain or loss 100% gain
 See text for the key to the letter designations of each data point.

Since PCBs were banned from use in North America in 1979 and loadings to the Great Lakes have decreased (Eisenreich *et al.*, 1989; Rapaport and Eisenreich, 1988), reductions in surficial sediment PCB content are expected. Decreasing sediment PCB concentrations have been observed in Lakes Ontario and Superior (Golden *et al.*, 1993). The lack of a decline in sediment PCB content in the southern basin of Lake Michigan may result from sediment focusing processes that redistribute the PCB inventory, and/or continued external source inputs.

6.3.2 Other Interpretations and Perspectives

6.3.2.1 Relationship of PCB Congeners and trans-Nonachlor with Sediment Organic Carbon

Concentrations of PCBs and *trans*-nonachlor in surficial sediments increase with increasing organic carbon (OC) content. The correlations of these two variables, however, were not very strong on a linear scale ($r^2 = 0.25 - 0.67$). The spread in the data suggest that the southern basin stations were significantly higher in contamination. Dividing the stations into groups, based on basin morphology and regional inputs, may explain some of the variability and improve OC correlation.

Generally, the concentrations of PCB congeners and *trans*-nonachlor increased with sediment organic carbon content according to a power equation,

$$[PCB] = a \times [OC]^b$$

This power equation best described the relationship of PCB congeners and *trans*-nonachlor with sediment organic carbon in all four regions of Lake Michigan. Coefficients of the power relationship were obtained by log transformation of the data and fitting the linear relationship,

$$\log[PCB] = A + (B \times \log[OC])$$

Linear regressions for the four compounds in each of the four regions are shown in Figures 6-8 - 6-11. Coefficients for the relationships are listed in Table 6-4. The r^2 values for these relationships, ranged from 0.865 - 0.977, indicating a strong correlation between the two variables. This finding was expected as hydrophobic compounds are known to partition strongly to organic matter. The southern basin PCB relationships exhibited an additional feature not seen in other basins. A peak in PCB concentration was observed at ~25 mg/g OC for PCB 28+31 and at ~35 mg/g for PCB 118 and PCB 180 (Figure 6-8). *trans*-Nonachlor did not exhibit such a peak.

A comparison of coefficient results was used to discern any differences in compound behavior between basins, as well as differences between compounds within a basin. Congener-specific behavior within a basin was examined by comparing regression slopes (i.e., extent of association with OC). A slope greater than 1 suggests that enrichment of the compound is occurring with increasing OC content. A slope of 1 also indicates a linear relationship of contaminant content with OC content, while a slope of < 1 indicates a dilution of contaminant content with increasing OC content. Non-unity slopes may result from differences in OC composition or PCB loadings between nearshore sandier stations and offshore siltier stations.

Generally, slopes were >1 for all chlorinated organic contaminants in the southern, central and northern basins. An exception occurred for PCB 28+31 in the southern and central basins where the slopes ranged from 0.88 to 1. In the straits region, all compounds exhibited slopes <1.

Significant differences in slopes between compounds for a specific basin are designated by dissimilar superscripts in Table 6-4. For the southern and central basins, a difference in PCB congener behavior was

noted. Within these basins, the slopes of the more highly chlorinated congeners, PCB 118 and PCB 180 were significantly greater than those of the trichlorobiphenyls, PCB 28+31. In the northern basin, only congeners PCB 180 and PCB 28+31 were significantly different. For the straits region, no significant difference in slopes was observed between congeners.

The relationship of *trans*-nonachlor with OC did not follow the same pattern as any particular PCB congener. No significant differences between the slopes of *trans*-nonachlor and any of the PCB congeners were noted for the central basins and straits region. However, in the southern basin, the slope for *trans*-nonachlor was lower than that of PCB 180, while in the northern basin its slope was lower than the slopes for PCB 118 and PCB 180.

Figure 6-8. Relationships of PCB/*trans*-Nonachlor Concentrations and Organic Carbon Content for the Southern Basin

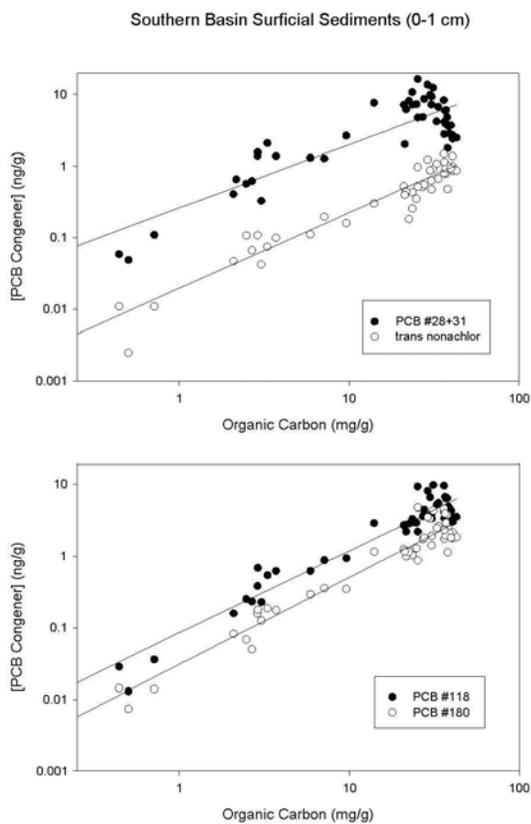


Figure 6-9. Relationships of PCB/*trans*-Nonachlor Concentrations and Organic Carbon Content for the Central Basins

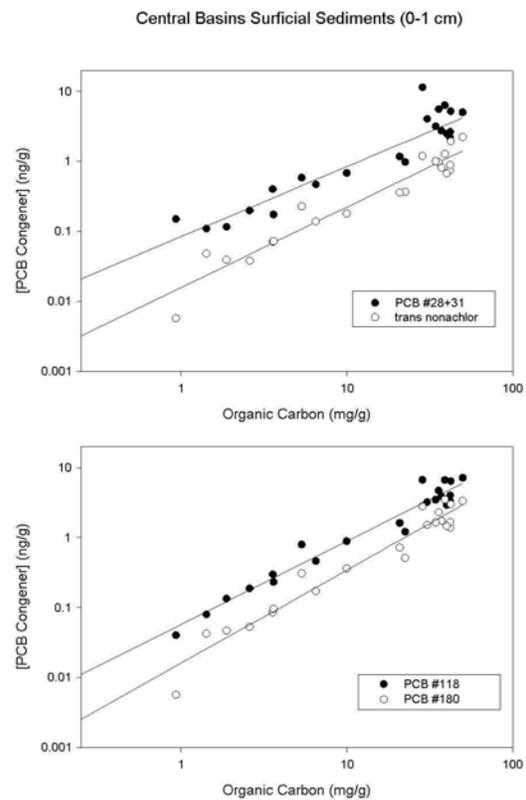


Figure 6-10. Relationships of PCB/trans-Nonachlor Concentrations and Organic Carbon Content for the Northern Basin

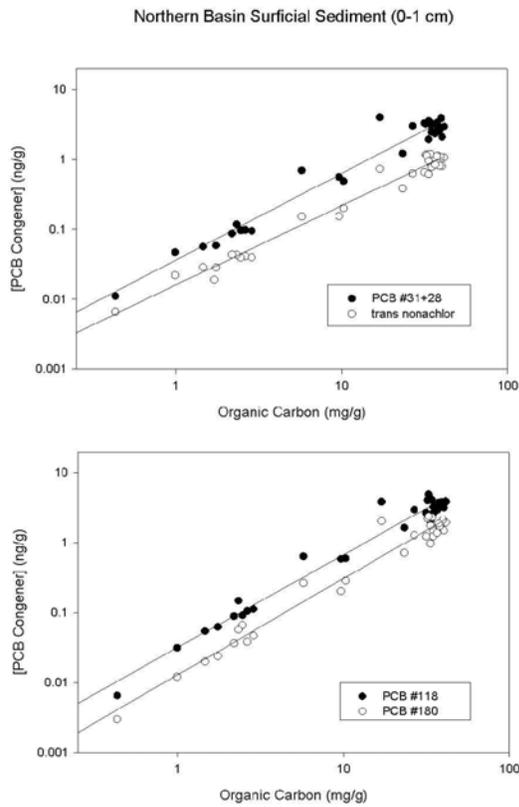


Figure 6-11. Relationships of PCB/trans-Nonachlor Concentrations and Organic Carbon Content for the Straits Region

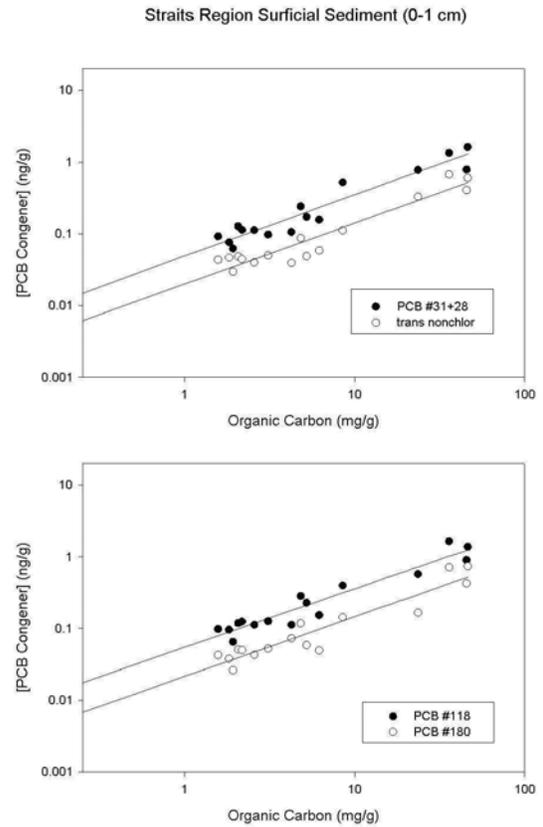


Table 6-4. Linear Regression Parameters of Log PCB and *trans*-Nonachlor versus Log OC Content in Surficial Sediments in Lake Michigan

Basin	Parameter	PCB 28+31	PCB 118	PCB 180	<i>trans</i> -Nonachlor
Southern	slope	0.8809 ^a	1.1461 ^{bc}	1.2178 ^b	1.0761 ^c
	intercept	-0.5799	-1.0717	-1.5113	-1.7336
	r^2	0.7329	0.9810	0.9370	0.9048
	n	50	50	50	48
Central	slope	1.003 ^a	1.1884 ^b	1.3326 ^b	1.1500 ^{ab}
	intercept	-1.076	-1.2402	-1.7968	-1.8006
	r^2	0.9160	0.9562	0.9457	0.9278
	n	21	22	22	21
Northern	slope	1.2393 ^{ac}	1.3269 ^{bc}	1.3763 ^b	1.1341 ^a
	intercept	-1.4384	-1.4963	-1.8870	-1.7966
	r^2	0.9611	0.9718	0.9691	0.9773
	n	31	31	31	32
Straits	slope	0.8587 ^a	0.8160 ^a	0.8307 ^a	0.8496 ^a
	intercept	-1.3100	-1.2589	-1.6658	-1.7002
	r^2	0.9138	0.9189	0.8870	0.9095
	n	16	16	16	16
Whole lake	slope	1.091	1.2215	1.2945	1.0878
	intercept	-1.0893	-1.2938	-1.7365	-1.7645
	r^2	0.7587	0.9024	0.9077	0.9300
	n	119	120	120	117

Dissimilar superscripts denote a significant difference ($p < 0.05$) in slopes between compounds for a specific basin.

Several general observations can be made based on the relationships of organic carbon content and the chlorinated organic contaminants for each of the basins (Table 6-5). For the high molecular weight (HMW) congeners, PCB 118 and PCB 180, and *trans*-nonachlor, the straits region slopes were significantly lower than the other basins, and the northern basin slopes were higher than those of the southern basin (except for *trans*-nonachlor). For the low molecular weight (LMW) congeners, PCB 28+31, the northern basin slope was significantly higher than for all other basins. No significant difference was detected between slopes for PCB 28+31 in the central, southern and straits regions. Interestingly, the southern basin stations that had high OC content and lower than expected PCB concentrations were located in the basin's deep hole at >100 m depth; *trans*-nonachlor did not exhibit reduced concentrations at the deep-hole stations. If these stations are excluded from the regressions, then the slopes of the southern basin (1.11 for PCB 28+31, 1.23 for PCB 118, 1.27 for PCB 180) are not significantly different from those of the central and northern basins for all PCB congeners tested.

The intercept parameter is an indication of the level of contamination as a net result of loading and removal rates. For *trans*-nonachlor, the intercept was similar for all four basins, suggesting that regional inputs may be similar if removal rates are not significantly different between basins (Tables 6-7 and 6-8). At the other end of the spectrum, PCB 28+31 had higher intercepts in the southern and central basins relative to the northern basin and straits region. The HMW congeners, PCB 118 and PCB 180 had higher intercepts in the southern basin than the northern basin, while the intercepts in the central basins and straits region fell in between.

In summary, while it would appear at first glance that there is not much of a relationship of either PCB or *trans*-nonachlor concentration to the OC content of surficial sediments in Lake Michigan, strong power relationships resulted when the stations were divided into basin groups. The association between *trans*-nonachlor concentration and sediment OC does not vary throughout the lake's basins, except in the straits

region. For the PCB congeners, more variability in their associations with sediment OC was noted between basins. The variability appears to result, in part, from differences in regional source input functions. Other variables that control burial, such as sedimentation rate, residence time in the sediment mixed layer, sediment focusing processes, and compound hydrophobicity, may also influence PCB associations with particles and particulate OC in Lake Michigan.

Table 6-5. Significant Differences between Linear Regression Parameters among Lake Michigan Basins for Log Analyte versus Log Organic Carbon

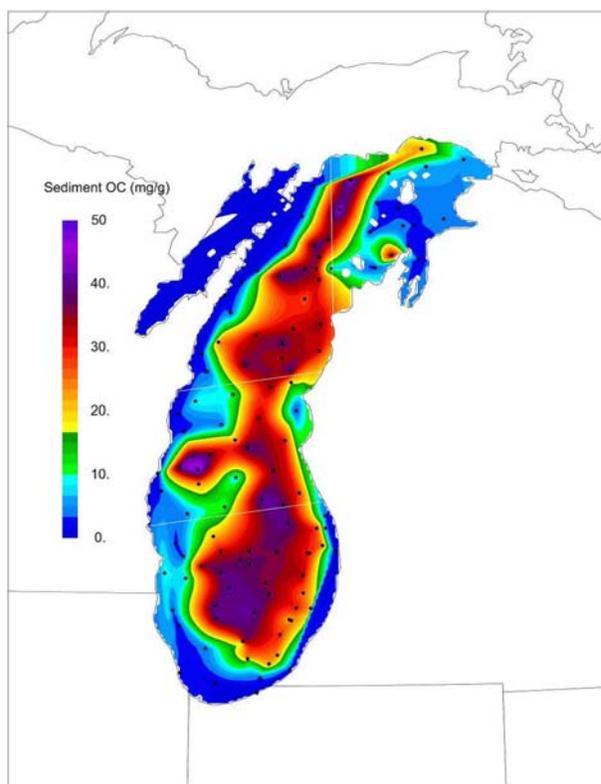
Analyte	Regression Parameter	Significant Differences at $\alpha = 0.05$			
		Southern (So)	Central (C)	Northern (N)	Straits (St)
PCB 28+31	slope	N	N	C, St, So	N
	intercept	C, N, St	So, N, St	C, So	C, So
PCB 118	slope	N, St	St	So, St	C, So, N
	intercept	N, St	N	C, So, St	N, So
PCB 180	slope	N, St	St	So, St	C, So, N
	intercept	C, N	So	So, St	N
<i>trans</i> -Nonachlor	slope	St	St	St	C, So, N
	intercept	--	--	--	--

6.3.2.2 Contour Maps

The data for the 117 LMMB stations were used to create contour maps of surficial sediment concentrations for organic carbon, total PCBs, PCB 28+31, PCB 118, and PCB 180, and *trans*-nonachlor (Figures 6-12 - 6-17). Note that the contour maps for PCB congeners are normalized to the highest concentration measured in order to facilitate comparisons.

High OC concentrations (20-50 mg/g) are associated with the accumulation of recent sediments in the depositional and transitional regions of Lake Michigan (Figure 6-12). In addition, the OC distribution in Lake Michigan generally tracks with the depth contours of the lake (Figure 6-18). Sediment OC concentrations > 30 mg/g are generally found at depths greater than 100 m. The other cluster of high OC content stations is located in the eastern portion of the southern basin. These sites are located at a depth range of 45 - 85 m and have OC contents of 20 - 33 mg/g. The cluster of low OC content stations (< 10 mg/g) includes those generally located at depths less than 100 m. Stations that do not fall within these three clusters are either located in transition areas, or located in the straits area. Stations in the straits region tend to have higher OC content than other stations located at similar depths.

Figure 6-12. Contour Plot of Organic Carbon Content in Lake Michigan Sediments



PCBs are also accumulating in the depositional and transitional regions of Lake Michigan (Figure 6-13). In particular, PCBs accumulate at relatively high concentrations (> 100 ng/g) along the eastern side of the southern basin, as well as at a few of the deeper stations in the southern and central basins. Enrichment of most PCB congeners with increasing OC content in sediments was demonstrated by the slopes of greater than 1 for the relationship of log PCB versus log OC (except the straits region, Table 6-4). Localized input sources may contribute to the depositional pattern and explain the enrichment of PCBs relative to OC. Southern basin surficial sediment concentrations have a higher maximum, and greater areal coverage for the high Total PCB concentration range (>100 ng/g) than the northern basin. Additionally, focusing processes may be responsible for concentrating PCBs into select regions of the lake.

The contour maps of PCB 118 and PCB 180 exhibit similar distribution patterns to one another throughout Lake Michigan (Figures 6-15 and 6-16). The accumulation of these PCB congeners occurs in the depositional and transitional regions with the highest concentrations located in the deepest parts of the southern and central basins, and in the upper half of the eastern side of the southern basin. The straits region has some of the lowest concentrations of these two PCBs despite having some stations with relatively high levels of OC content.

The contour map for PCB 28+31 provides evidence of accumulation in the surficial sediments of the lake's depositional and transitional regions (Figure 6-14). Relative to PCB 118 and PCB 180, however, elevated concentrations of PCB 28+31 are found on the eastern side of the southern basin and for Station 55, in the Grand Haven basin. A plot of the concentrations of PCB 28+31 versus PCB 180 for stations in the southern and central basins illustrates the enhanced levels of this low molecular weight PCB congener on the eastern side of the southern basin (Figure 6-19). In contrast, depositional/transitional stations located in the rest of the lake, including the northern basin (not shown), are about a factor of four lower in their concentrations of PCB 28+31, for a given concentration of PCB 180. PCBs 15+17 (not shown) also demonstrated enrichment in this region, while PCB 101 (not shown) and PCB 118 had a one-to-one correspondence with PCB 180 (Figure 6-19). Other stations with elevated levels of PCB 28+31 relative to PCB 180 are located in nearshore nondepositional areas (< 25 km offshore) with low concentrations of PCBs: along the northern coast, and western coast of the southern and central portion of the lake. Note that Waukegan Harbor and Green Bay also have elevated levels of PCB 28+31 relative to PCB 180, due to point-source contamination of Aroclors 1242 and 1248 (Swackhamer and Armstrong 1988, and Manchester 1993).

Figure 6-13. Contour Plot of Total PCBs in Lake Michigan Sediments

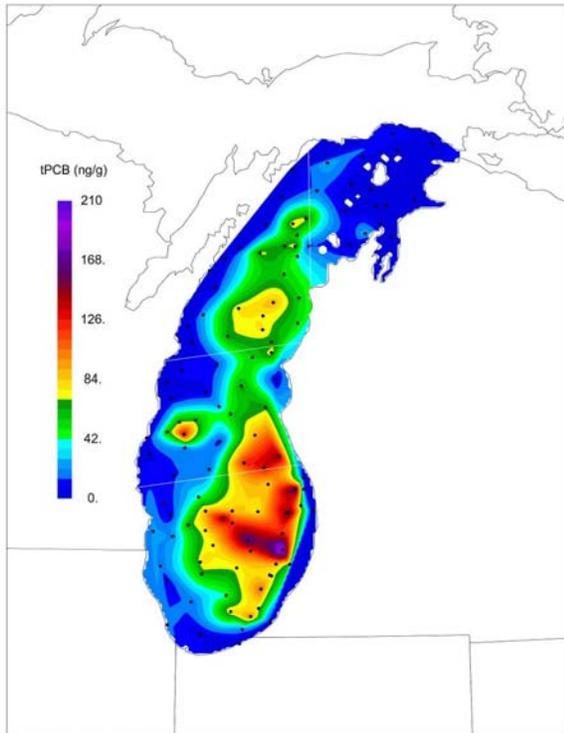


Figure 6-14. Contour Plot of PCB 28+31 in Lake Michigan Sediments

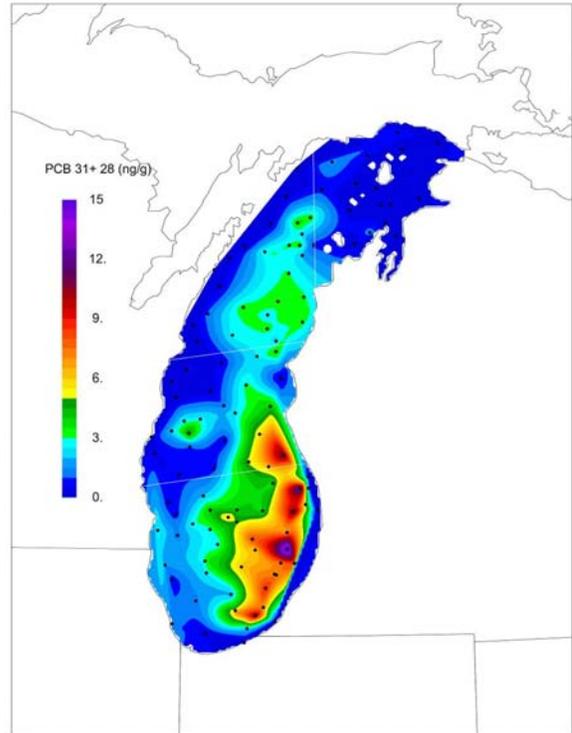


Figure 6-15. Contour Plot of PCB 118 in Lake Michigan Sediments

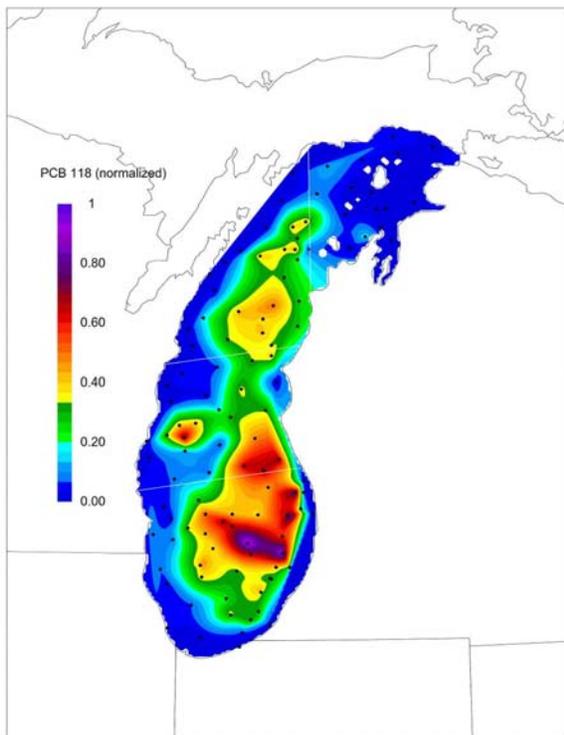
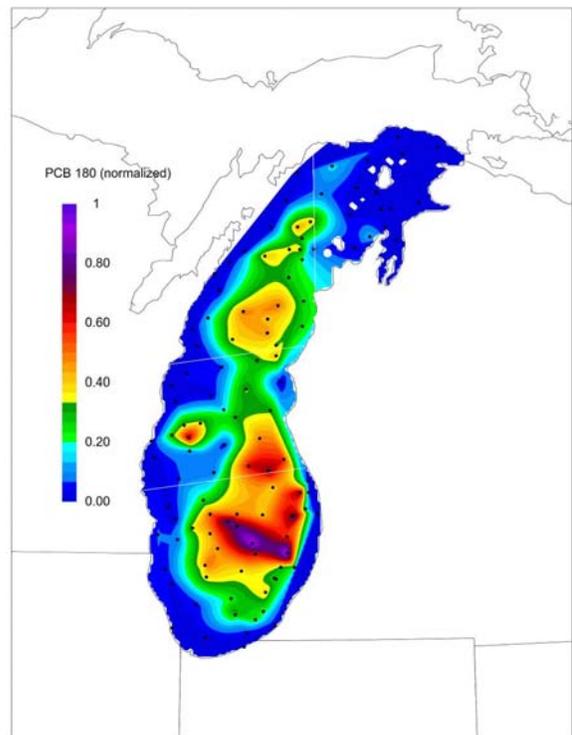


Figure 6-16. Contour Plot of PCB 180 in Lake Michigan Sediments



trans-Nonachlor is also accumulating in the depositional and transitional regions of Lake Michigan. Unlike PCBs, *trans*-nonachlor is not preferentially accumulating along the eastern side of the southern basin. Nor does *trans*-nonachlor have the elevated concentrations in the southern basin relative to the northern basin that PCBs exhibit. The log-log slope of 1.09 for *trans*-nonachlor and OC suggests more of a linear relationship and less of a power relationship with OC compared to PCBs.

Figure 6-17. Contour Plot of *trans*-Nonachlor in Lake Michigan Sediments

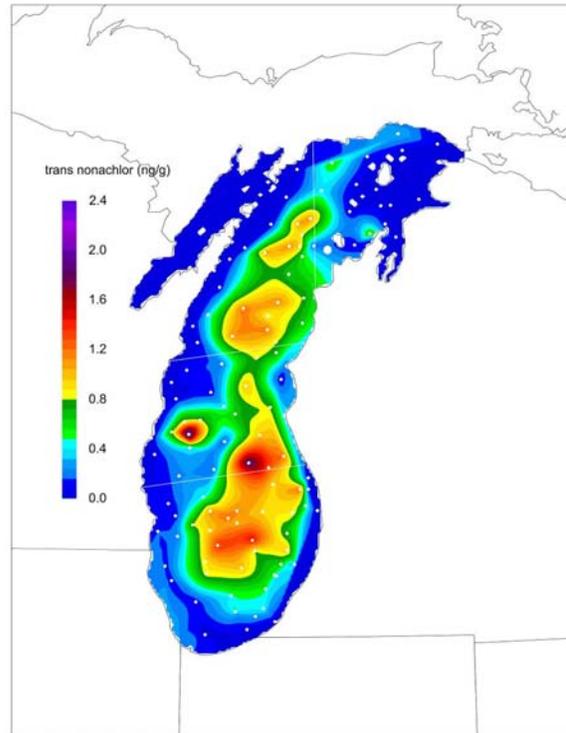


Figure 6-18. Organic Carbon Content versus Depth in Lake Michigan

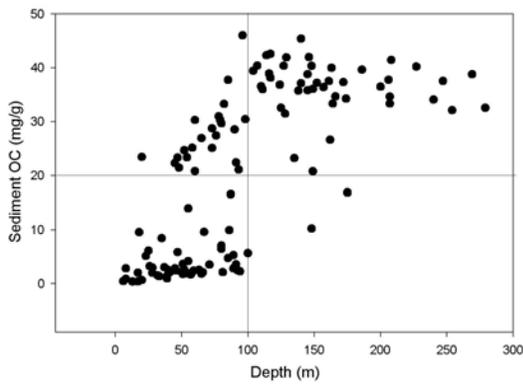
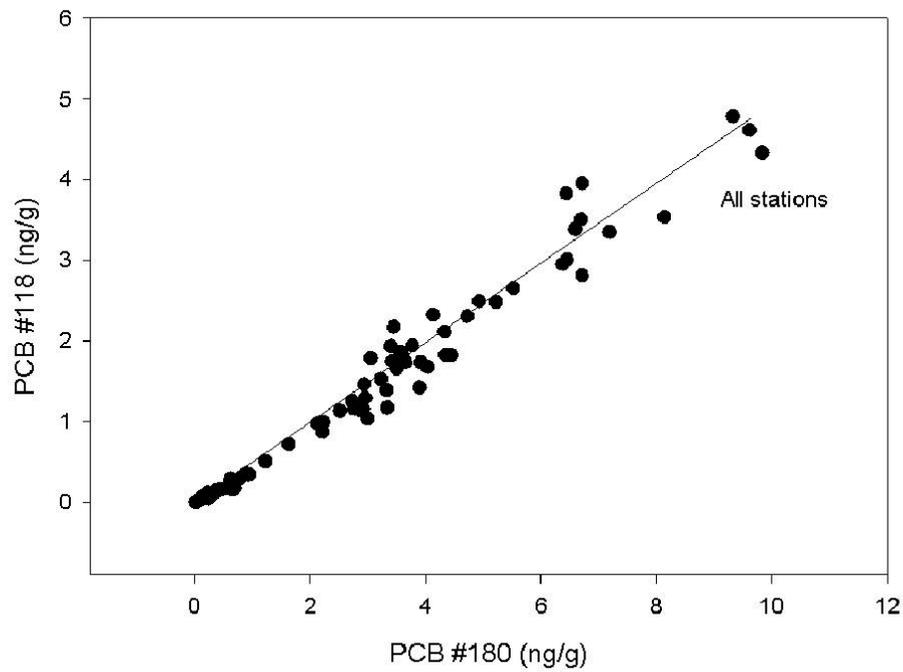
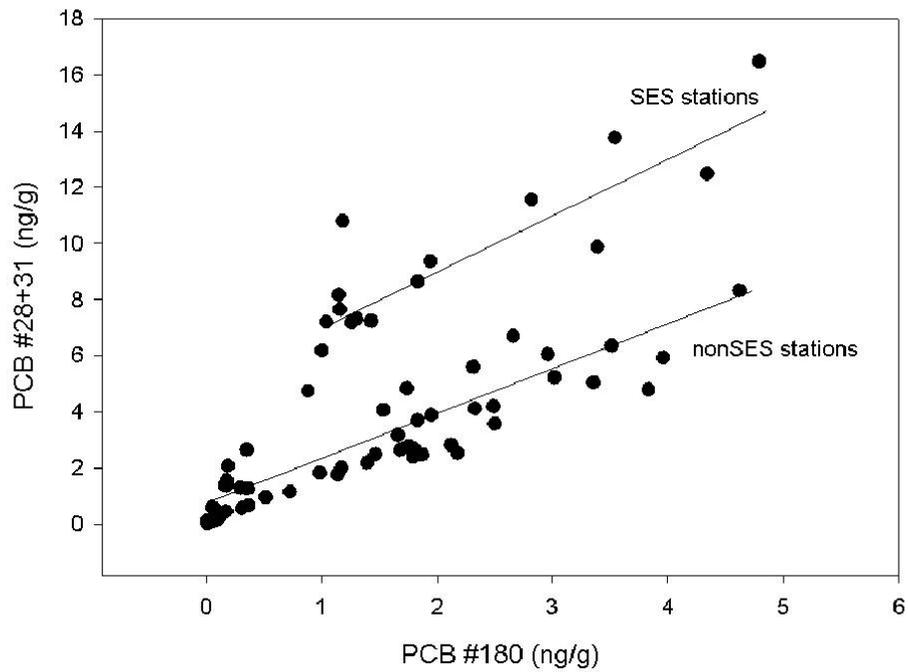


Figure 6-19. Plot of PCB 28+31 Concentrations versus PCB 180 Concentrations in Lake Michigan Sediments



Chapter 7

PCBs/trans-Nonachlor in the Lower Pelagic Food Web

7.1 Results

The lower pelagic food web was sampled from June 1994 through October 1995 for PCB and *trans*-nonachlor analysis. Individual samples of the lower pelagic food web included mixed phytoplankton, mixed zooplankton, *Diporeia* spp., and *Mysis* spp. Phytoplankton were collected by pumping water from the water column at the optimum depth for maximum phytoplankton density, zooplankton were collected in vertical tows, *Diporeia* spp. were collected in benthic tows, and *Mysis* spp. were collected in vertical and benthic tows (see Section 2.5.5 for details of the sample collection procedures). Lower pelagic food web samples were collected from 15 locations in Lake Michigan, including 9 stations within 4 designated biological sampling areas (biota boxes) and 6 additional routine monitoring stations (Table 7-1).

- ▶ **Chicago biota box** – a station in southern Lake Michigan basin near Chicago
- ▶ **Sturgeon Bay biota box** – a combination of three stations on the western side of the northern Lake Michigan basin near Sturgeon Bay, Wisconsin
- ▶ **Port Washington biota box** – a combination of two stations in the central Lake Michigan basin near Port Washington, Wisconsin
- ▶ **Saugatuck biota box** – a series of three stations on the eastern side of the southern Lake Michigan basin near Saugatuck, Michigan.

A total of 208 lower pelagic food web samples were collected and analyzed for *trans*-nonachlor, and 233 lower pelagic food web samples were collected and analyzed for PCBs (Table 7-1).

As noted in Chapter 2, there are 209 possible PCB congeners, and the investigators in this study reported results for 65 to 110 of these congeners, depending on the capabilities of each laboratory. The University of Minnesota determined results for 110 congeners or co-eluting congeners.

For the purposes of this report, we are presenting summaries of the results for the following subset of all of the analytes:

- PCB congener 33
- PCB congener 118
- PCB congener 180
- Total PCBs
- *trans*-nonachlor

Table 7-1. Number of Lower Pelagic Food Web Samples Analyzed for PCB Congeners and *trans*-Nonachlor

Sample Type	Sampling Locations		Sampling Dates	Number of Samples Analyzed for <i>trans</i> -Nonachlor	Number of Samples Analyzed for PCB Congeners and Total PCBs
<i>Diporeia</i>	Chicago biota box	5	06/26/94 to 10/10/95	6	6
	Sturgeon Bay biota box	40	06/18/94 to 09/23/95	5	5
		180	08/10/94 to 09/22/95	4	4
	Port Washington biota box	240	06/21/94 to 10/02/95	5	5
		280	06/21/94 to 10/01/95	6	6
	Saugatuck biota box	340	06/25/94 to 10/06/95	6	6
		380	06/25/94 to 10/06/95	6	6
Other	47M	06/17/94 to 06/17/94	1	1	
Total				39	39
<i>Mysis</i>	Chicago biota box	5	06/26/94 to 10/10/95	6	6
	Sturgeon Bay biota box	140	06/18/94 to 09/23/95	6	6
		180	08/10/94 to 09/22/95	5	5
	Port Washington biota box	240	06/21/94 to 10/02/95	6	6
		280	06/21/94 to 10/01/95	6	6
	Saugatuck biota box	340	06/25/94 to 10/06/95	6	6
		380	06/24/94 to 10/06/95	6	6
	Other	18M	06/22/94 to 10/09/95	5	6
		27M	08/09/95 to 08/09/95	1	1
47M		06/17/94 to 09/19/95	5	5	
Total				52	53
Phytoplankton	Chicago biota box	5	06/26/94 to 10/10/95	7	7
	Sturgeon Bay biota box	110	06/19/94 to 09/23/95	6	6
		140	06/18/94 to 09/23/95	6	6
		180	06/18/94 to 09/22/95	6	6
	Port Washington biota box	240	06/21/94 to 10/02/95	6	6
		280	06/21/94 to 10/01/95	5	6
	Saugatuck biota box	310	06/26/94 to 10/08/95	6	6
		340	06/25/94 to 10/06/95	6	6
		380	06/24/94 to 10/06/95	7	7
	Other	18M	06/22/94 to 10/09/95	6	6
		23M	06/23/94 to 06/23/94	1	1
		27M	06/20/94 to 06/20/94	1	1
41		06/18/94 to 06/18/94	1	1	
47M		06/17/94 to 09/19/95	6	6	
Total				70	71

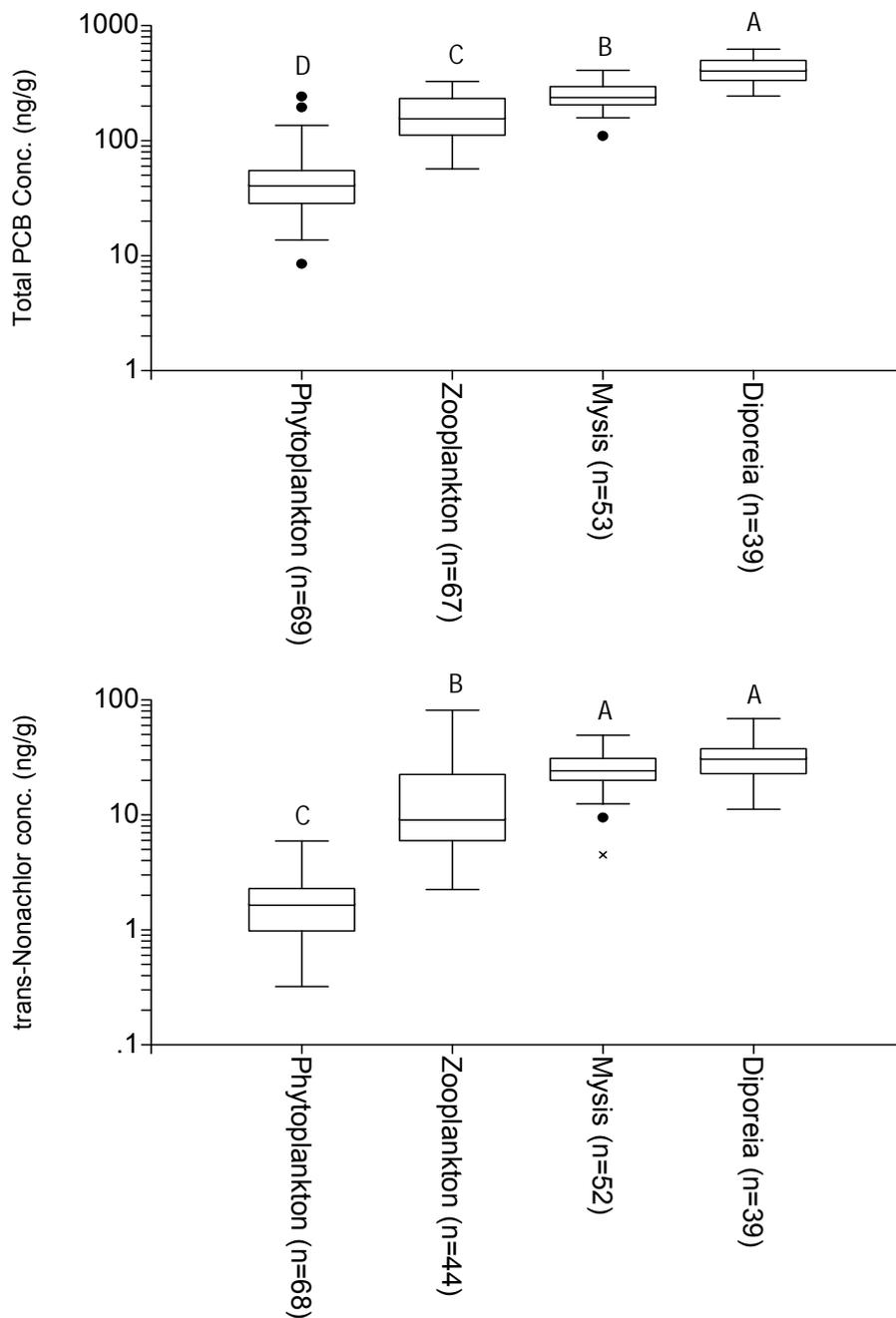
Sample Type	Sampling Locations		Sampling Dates	Number of Samples Analyzed for <i>trans</i> -Nonachlor	Number of Samples Analyzed for PCB Congeners and Total PCBs
Zooplankton	Chicago biota box	5	06/26/94 to 10/10/95	7	7
	Sturgeon Bay biota box	110	06/19/94 to 09/23/95	5	6
		140	06/18/94 to 09/23/95	5	6
		180	06/18/94 to 09/22/95	5	6
	Port Washington biota box	240	06/21/94 to 10/02/95	5	6
		280	06/21/94 to 10/01/95	2	6
	Saugatuck biota box	310	06/26/94 to 10/08/95	6	6
		340	06/25/94 to 10/06/95	5	6
		380	06/25/94 to 10/06/95	2	7
	Other	18M	06/22/94 to 10/09/95	1	6
		27M	06/20/94 to 06/20/94	1	1
		47M	06/17/94 to 09/19/95	2	6
		19M	01/24/95 to 01/24/95	1	1
	Total				47
Total				208	233

7.1.1 Sample Type and Species Variation

PCB and *trans*-nonachlor concentrations measured in the lower pelagic food web differed significantly among phytoplankton, zooplankton, *Mysis* spp., and *Diporeia* spp. samples (Figure 7-1). Concentrations of PCB 33, PCB 118, PCB 180, total PCBs, and *trans*-nonachlor were highest in samples of *Diporeia* spp., followed by *Mysis* spp., zooplankton, and phytoplankton, respectively (Table 7-2). Total PCB concentrations were 9 times higher in *Diporeia* spp. than in phytoplankton, averaging 420, 250, 170, and 49 ng/g dry weight in *Diporeia* spp., *Mysis* spp., zooplankton, and phytoplankton samples, respectively. *Trans*-Nonachlor concentrations were 19 times higher in *Diporeia* spp. than in phytoplankton, averaging 32, 25, 16, and 1.7 ng/g dry weight in *Diporeia* spp., *Mysis* spp., zooplankton, and phytoplankton samples, respectively.

A portion of the difference in PCB and *trans*-nonachlor concentrations among lower pelagic food web sample types is likely due to variations in the lipid content of the samples. Hydrophobic organic contaminants such as PCBs and *trans*-nonachlor preferentially concentrate in the fatty tissues of organisms, so those organisms with higher lipid content will likely concentrate more of these contaminants. This is evidenced by the fact that lipid content was positively correlated with total PCB and *trans*-nonachlor concentrations (r^2 of 0.25 for total PCB and 0.40 for *trans*-nonachlor), and the lipid content of phytoplankton was significantly lower than for the other sample types. The differences in lipid content among the sample types, however, explained only a quarter to less than half of the variability in total PCB and *trans*-nonachlor concentrations. Even when total PCB and *trans*-nonachlor concentrations were normalized by lipid content, the trends in PCB and *trans*-nonachlor concentrations among the sample types were almost always the same (Figure 7-2). Normalized total PCB and *trans*-nonachlor concentrations in *Diporeia* spp. and *Mysis* spp. were significantly higher than in zooplankton and phytoplankton, and normalized *trans*-nonachlor concentrations in zooplankton were significantly higher than in phytoplankton. Normalized total PCB concentrations in zooplankton, however, were not significantly different than in phytoplankton.

Figure 7-1. Total PCB and *trans*-Nonachlor Concentrations in the Lower Pelagic Food Web

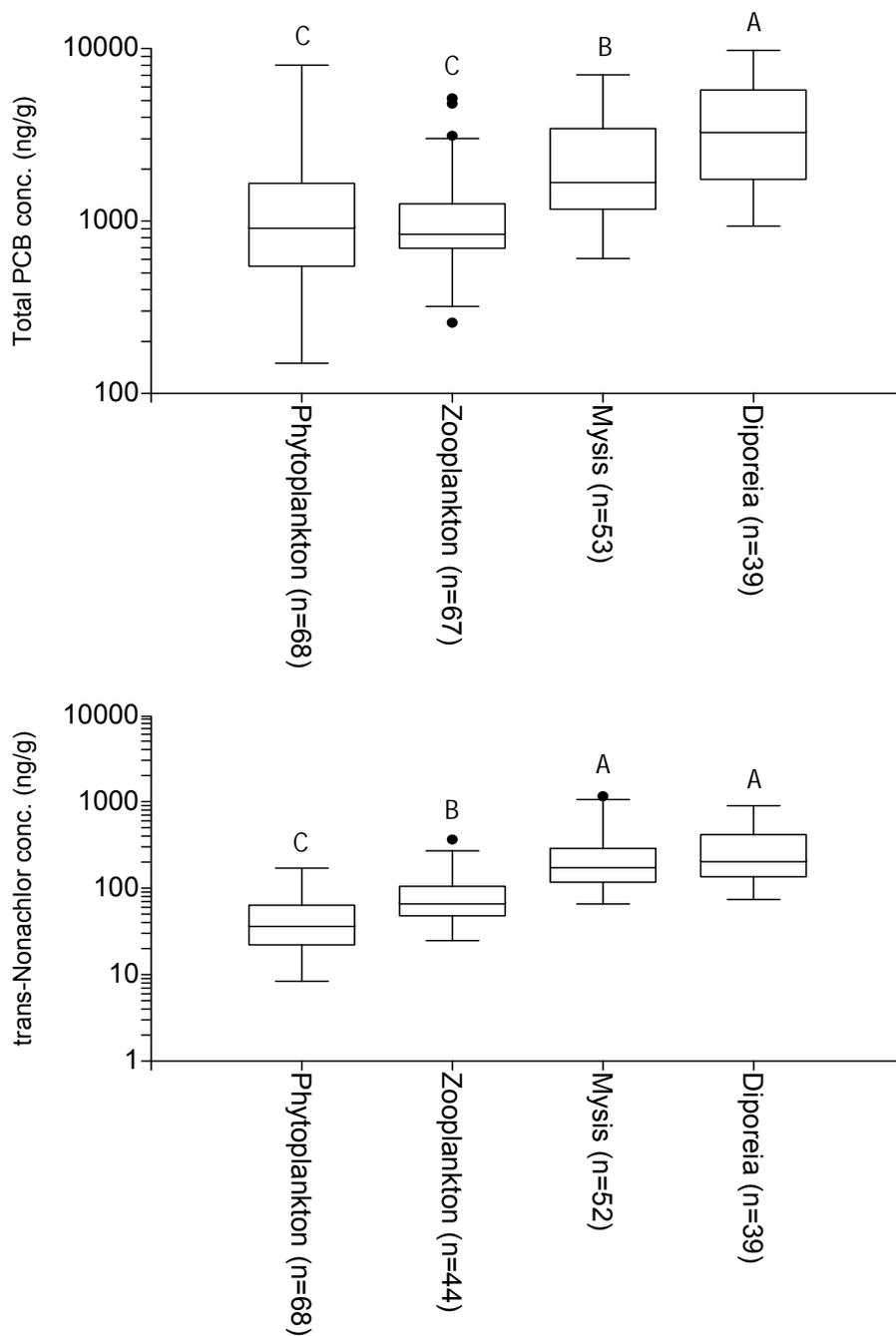


Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The Xs represent results beyond 3*IQR from the box. The letters (A - D) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Concentration is plotted on a log scale.

Table 7-2. Mean Concentrations of PCBs and *trans*-Nonachlor Measured in the Lower Pelagic Food Web

Analyte	Sample Type	N	Mean (ng/g)	Range (ng/g)	SD (ng/g)	RSD (%)	Below DL (%)
PCB 33	<i>Diporeia</i>	39	0.99	0 to 3.0	0.76	77	5.1
	<i>Mysis</i>	53	0.64	0 to 5.0	0.85	130	15
	Phytoplankton	71	0.27	0 to 2.8	0.37	130	9.9
	Zooplankton	70	0.53	0 to 2.2	0.59	110	24
PCB 118	<i>Diporeia</i>	39	15	8.6 to 36	5.2	34	0
	<i>Mysis</i>	53	13	6.3 to 28	3.6	29	0
	Phytoplankton	71	1.6	0.20 to 10	1.5	97	0
	Zooplankton	70	5.5	0.072 to 20	3.4	63	0
PCB 180	<i>Diporeia</i>	39	17	6.4 to 49	7.3	43	0
	<i>Mysis</i>	53	9.4	3.1 to 18	3.4	36	0
	Phytoplankton	71	1.4	0.11 to 7.2	1.2	87	0
	Zooplankton	70	6.3	0.35 to 18	4.0	63	0
Total PCBs	<i>Diporeia</i>	39	420	240 to 620	100	24	0
	<i>Mysis</i>	53	250	110 to 410	61	24	0
	Phytoplankton	71	49	8.5 to 240	38	76	0
	Zooplankton	70	170	57 to 330	74	44	0
<i>trans</i> -Nonachlor	<i>Diporeia</i>	39	32	11 to 69	12	38	0
	<i>Mysis</i>	52	25	4.5 to 49	9.3	37	0
	Phytoplankton	70	1.7	0 to 5.9	1.0	60	2.9
	Zooplankton	47	16	2.2 to 81	16	100	0

Figure 7-2. Normalized (by Lipid Content) Total PCB and *trans*-Nonachlor Concentrations in the Lower Pelagic Food Web



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The letters (A - D) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Concentration is plotted on a log scale.

7.1.2 Seasonal Variation

The lower pelagic food web was sampled in six separate cruises in June 1994, August 1994, October 1994, March 1995, August 1995, and September 1995. Two-way analysis of variance revealed that total PCB concentrations in *Mysis* spp., zooplankton, and phytoplankton differed significantly by station and by sampling cruise. Seasonal and geographical variations, however, were small in comparison to differences due to sample type (phytoplankton, zooplankton, *Mysis* spp., and *Diporeia* spp.). Figure 7-3 shows the seasonal variation in total PCB concentrations by sample type. While there were no absolute seasonal trends in total PCB concentrations, average concentrations across stations were often higher in the spring and early summer (June 1994 and March 1995) than in the late summer (August 1994, August 1995, and September 1995). Total PCB concentrations in *Mysis* spp. samples were significantly higher in June 1994 and March 1995 than in August 1995. In zooplankton samples, total PCB concentrations were significantly higher in March 1995 and October 1994 than in either of the August cruises (August 1994 and August 1995). In phytoplankton samples, total PCB concentrations were significantly higher in June 1994 than in August 1994. Total PCB concentrations in *Diporeia* spp. did not differ significantly among cruises.

trans-Nonachlor concentrations in all lower pelagic food web sample types differed significantly by station and by sampling cruise. Figure 7-4 shows the seasonal variation in *trans*-nonachlor concentrations by sample type. Similarly to total PCB concentrations, *trans*-nonachlor concentrations for some sample types were often higher in the spring and early summer than in the late summer. In phytoplankton samples, *trans*-nonachlor concentrations were significantly higher in March 1995 than in September 1995 and significantly higher in June 1994 than in August 1994, October 1994, August 1995 or September 1995. In zooplankton samples, *trans*-nonachlor concentrations were significantly higher in March 1995 than in all other cruises. *trans*-Nonachlor concentrations in *Mysis* spp. samples were significantly higher in June 1994, October 1994, and March 1995 than in September 1995. *Diporeia* spp. samples did not fit the general trend of higher *trans*-nonachlor concentrations in spring and early summer than in late summer. The only significant differences between *trans*-nonachlor concentrations in *Diporeia* spp. samples were between the September 1995 and the August 1994 cruises.

Figure 7-3. Seasonal Variation of Total PCB Concentrations Measured in the Lower Pelagic Food Web of Lake Michigan

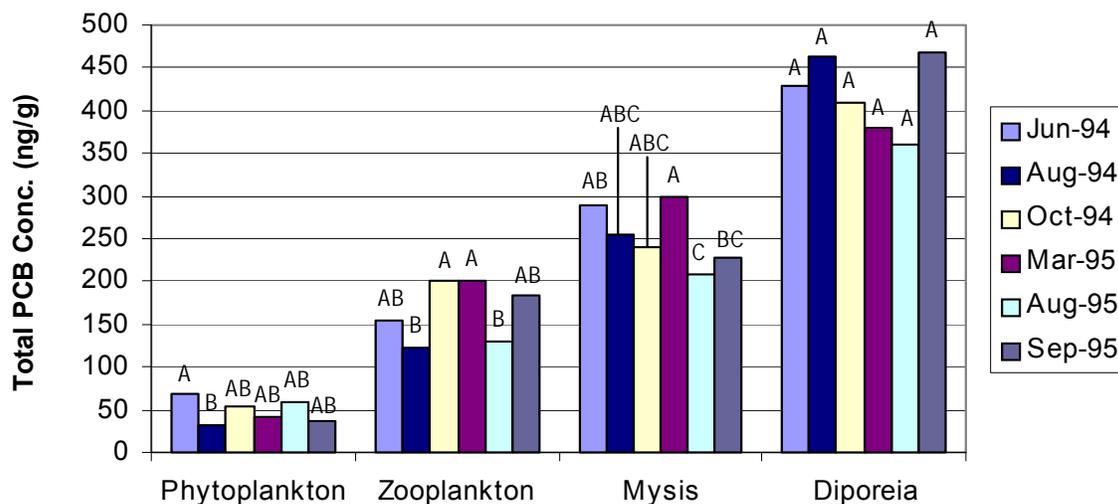
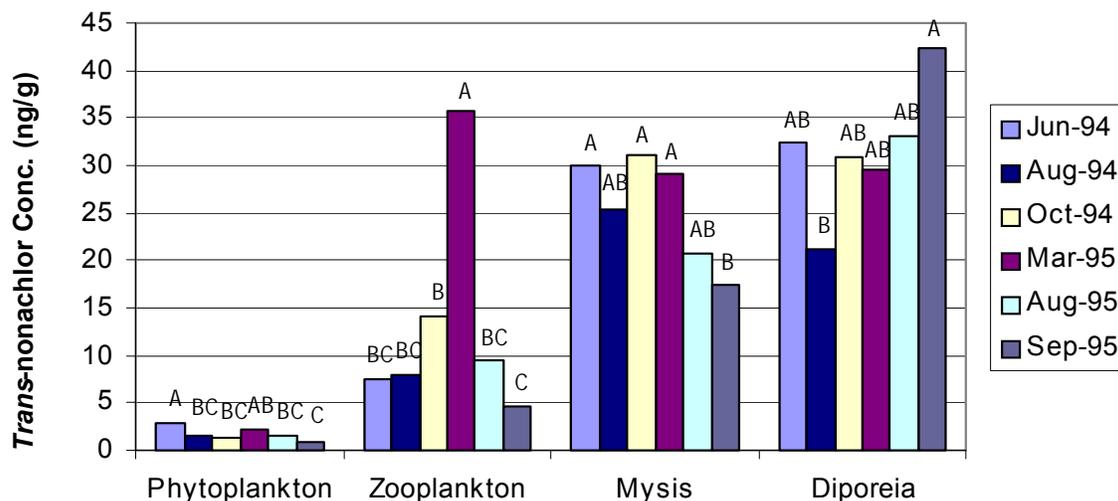


Figure 7-4. Seasonal Variation in *trans*-Nonachlor Concentrations Measured in the Lower Pelagic Food Web of Lake Michigan



7.1.3 Geographical Variation

Sampling of the lower pelagic food web was focused in the following four biological sampling areas or biota boxes:

- ▶ **Chicago biota box** – a station in southern Lake Michigan basin near Chicago
- ▶ **Sturgeon Bay biota box** – a combination of three stations on the western side of the northern Lake Michigan basin near Sturgeon Bay, Wisconsin
- ▶ **Port Washington biota box** – a combination of two stations in the central Lake Michigan basin near Port Washington, Wisconsin
- ▶ **Saugatuck biota box** – a series of three stations on the eastern side of the southern Lake Michigan basin near Saugatuck, Michigan.

In addition to focused sampling in these areas, samples also were collected from six routine monitoring sites throughout the lake (Table 7-1). Table 7-3 shows the concentrations of total PCBs measured in lower pelagic food web samples collected from the various sampling locations.

Table 7-3. Mean Concentrations of Total PCBs Measured in the Lower Pelagic Food Web at Various Sampling Locations

Sample Type	Sampling Location	N	Mean (ng/g)	Range (ng/g)	SD (ng/g)	RSD (%)	Below DL (%)
<i>Diporeia</i>	Chicago biota box	6	450	290 to 590	110	24	0
	Sturgeon Bay biota box	9	350	250 to 470	82	23	0
	Port Washington biota box	11	440	290 to 620	110	25	0
	Saugatuck biota box	12	440	240 to 560	90	21	0
	47M	1	340	NA	NA	NA	0
<i>Mysis</i>	Chicago biota box	6	200	110 to 330	82	40	0
	Sturgeon Bay biota box	11	250	180 to 320	52	21	0
	Port Washington biota box	12	230	190 to 270	24	10	0
	Saugatuck biota box	12	300	190 to 410	54	18	0
	18M	6	250	190 to 320	45	18	0
	27M	1	180	NA	NA	NA	0
	47M	5	250	160 to 410	93	37	0
Phytoplankton	Chicago biota box	7	55	35 to 100	24	43	0
	Sturgeon Bay biota box	18	40	14 to 140	27	68	0
	Port Washington biota box	12	41	22 to 63	13	32	0
	Saugatuck biota box	19	72	14 to 240	59	82	0
	18M	6	34	8.5 to 88	28	83	0
	23M	1	44	NA	NA	NA	0
	27M	1	49	NA	NA	NA	0
	41	1	52	NA	NA	NA	0
	47M	6	35	27 to 46	7.8	22	0
Zooplankton	Chicago biota box	7	180	110 to 270	62	35	0
	Sturgeon Bay biota box	18	110	57 to 270	59	56	0
	Port Washington biota box	12	180	83 to 300	59	33	0
	Saugatuck biota box	19	200	87 to 310	66	33	0
	18M	6	220	140 to 270	56	25	0
	27M	1	140	NA	NA	NA	0
	47M	6	170	110 to 330	93	53	0
	19M	1	280	NA	NA	NA	0

NA = Not applicable. Summary statistics could not be calculated for a single data point.

Among the biota boxes total PCB concentrations were generally highest at the Saugatuck biota box and lowest at the Sturgeon Bay biota box. Average total PCB concentrations in *Mysis* spp., phytoplankton, and zooplankton were higher at the Saugatuck biota box than all other biota boxes, and average total PCB concentrations in *Diporeia* spp., phytoplankton, and zooplankton were lower at the Sturgeon Bay biota box than all other biota boxes. These differences were not statistically significant for all cases, but two-

way analysis of variance (accounting for sampling station and sampling cruise) revealed that total PCB concentrations in two of the four lower pelagic food web sample types differed significantly. Total PCB concentrations in *Mysis* spp. were significantly higher at the Saugatuck biota box than at the Chicago biota box or Port Washington biota box, and total PCB concentrations in zooplankton were significantly lower at the Sturgeon Bay biota box than all other stations. This trend is consistent with the distribution of PCBs in Lake Michigan sediments (see Chapter 6). PCBs accumulated in the eastern side of the southern Lake Michigan basin, near Saugatuck, and were lower along the western shore and northern basin, near Sturgeon Bay.

The trend of increased concentrations near the Saugatuck biota box and decreased concentrations near the Sturgeon Bay biota box that was observed for total PCBs was not observed for *trans*-nonachlor accumulation in the lower pelagic food web (Table 7-4). Average *trans*-nonachlor concentrations in *Mysis* spp. were highest at the Saugatuck biota box, but concentrations in phytoplankton and zooplankton were highest at the Chicago biota box, and concentrations in *Diporeia* spp. were highest at the Port Washington biota box. Average *trans*-nonachlor concentrations were lowest at the Sturgeon Bay, Chicago, Port Washington, and Sturgeon Bay biota boxes for *Diporeia* spp., *Mysis* spp., phytoplankton, and zooplankton, respectively. Two-way analysis of variance revealed that differences in *trans*-nonachlor concentrations among sites were significant for *Mysis* spp. and zooplankton samples. *trans*-Nonachlor concentrations in *Mysis* spp. were significantly higher in Saugatuck and Sturgeon Bay biota boxes than in the Chicago biota box. *trans*-Nonachlor concentrations in zooplankton were significantly higher in the Port Washington biota box than the Sturgeon Bay biota box.

The observed trend of *trans*-nonachlor accumulation in the lower pelagic food web was also consistent with the geographical distribution of *trans*-nonachlor in sediments. *trans*-Nonachlor was not preferentially accumulated in sediments along the eastern side of the southern basin (near the Saugatuck biota box) as was the case for total PCBs (see Chapter 6). Rather, accumulation of *trans*-nonachlor in Lake Michigan sediments was concentrated towards the center of the southern and central basins. Consistent with these findings, *trans*-nonachlor was not generally higher at Saugatuck than at Sturgeon Bay. In addition, *trans*-nonachlor in two of the sample types (*Diporeia* spp. and zooplankton) was higher at the Port Washington biota box (which is in the center of the lake) than either the Saugatuck or Sturgeon Bay biota boxes.

Table 7-4. Mean Concentrations of *trans*-Nonachlor Measured in the Lower Pelagic Food Web at Various Sampling Locations

Sample Type	Sampling Location	N	Mean (ng/g)	Range (ng/g)	SD (ng/g)	RSD (%)	Below DL (%)
<i>Diporeia</i>	Chicago biota box	6	31	19 to 49	10	32	0
	Sturgeon Bay biota box	9	29	19 to 51	10	35	0
	Port Washington biota box	11	38	19 to 69	15	40	0
	Saugatuck biota box	12	30	11 to 46	11	38	0
	47M	1	27	NA	NA	NA	0
<i>Mysis</i>	Chicago biota box	6	17	4.5 to 27	7.9	47	0
	Sturgeon Bay biota box	11	27	9.5 to 49	11	40	0
	Port Washington biota box	12	22	12 to 39	7.4	33	0
	Saugatuck biota box	12	30	13 to 46	10	33	0
	18M	5	28	21 to 34	5.2	18	0
	27M	1	19	NA	NA	NA	0
	47M	5	25	20 to 33	5.4	22	0
Phytoplankton	Chicago biota box	7	2.3	1.0 to 3.6	0.97	42	0
	Sturgeon Bay biota box	18	1.6	0.60 to 3.7	0.87	54	0
	Port Washington biota box	11	1.4	0.0 to 2.5	0.89	63	18
	Saugatuck biota box	19	1.8	0.71 to 3.4	0.77	44	0
	18M	6	1.8	0.46 to 5.9	2.1	120	0
	23M	1	2.0	NA	NA	NA	0
	27M	1	3.9	NA	NA	NA	0
	41	1	2.3	NA	NA	NA	0
	47M	6	1.3	0.32 to 2.8	0.86	65	0
Zooplankton	Chicago biota box	7	24	2.2 to 81	27	108	0
	Sturgeon Bay biota box	15	8.9	2.3 to 25	6.7	75	0
	Port Washington biota box	7	21	6.3 to 59	19	89	0
	Saugatuck biota box	13	13	2.2 to 29	9.8	77	0
	18M	1	45	NA	NA	NA	0
	27M	1	9.3	NA	NA	NA	0
	47M	2	31	7.8 to 54	32	105	0
	19M	1	34	NA	NA	NA	0

NA = Not applicable. Summary statistics could not be calculated for a single data point.

7.1.4 Bioaccumulation

Persistent organic pollutants, such as PCBs and *trans*-nonachlor, typically accumulate in living organisms above concentrations found in the water. This accumulation is due to the preferred partitioning of hydrophobic organic contaminants in organic tissues (such as lipids) over water, uptake from food, and/or reduced metabolism and elimination of persistent contaminants. The degree of accumulation is often quantified by a bioaccumulation factor, which is the ratio of the concentration of pollutant in an organism to the concentration of that pollutant in the water. When pollutants are increasingly accumulated with each trophic level of a food chain (or biomagnified), a biomagnification factor can be used to quantify the degree of accumulation from one trophic level to the next. A biomagnification factor is the ratio of the concentration of pollutant in organisms at a particular trophic level to the concentration of that pollutant in the next lowest trophic level.

To evaluate the degree of accumulation of PCBs and *trans*-nonachlor in the lower pelagic food web of Lake Michigan, bioaccumulation factors were calculated for each sample type (Table 7-5). Bioaccumulation factors were calculated as the mean concentration in a lower pelagic food web sample type divided by the lake-wide mean concentration in Lake Michigan. Concentrations of total PCBs in the lower pelagic food web were generally 10^5 to 10^6 times higher than dissolved concentrations of total PCBs in Lake Michigan water, which averaged 0.18 ng/L (or 0.00018 ng/g assuming a water density of 1g/mL). Bioaccumulation factors for total PCBs from water to the lower pelagic food web were 2.3×10^6 , 1.4×10^6 , 2.7×10^5 , and 9.3×10^5 for *Diporeia* spp., *Mysis* spp., phytoplankton, and zooplankton, respectively. On a congener-specific basis, bioaccumulation factors were generally lower for the less-chlorinated PCB congeners and higher for the more-chlorinated congeners. Bioaccumulation factors for PCB 33 ranged from 3.0×10^4 to 1.1×10^5 , while bioaccumulation factors for PCB 180 ranged from 2.9×10^6 to 3.5×10^7 .

Table 7-5. Bioaccumulation Factors for PCBs and *trans*-Nonachlor in the Lower Pelagic Food Web

Analyte	<i>Diporeia</i>	<i>Mysis</i>	Phytoplankton	Zooplankton
PCB 33	1.1×10^5	7.1×10^4	3.0×10^4	5.8×10^4
PCB 118	6.2×10^6	5.1×10^6	6.5×10^5	2.2×10^6
PCB 180	3.5×10^7	1.9×10^7	2.9×10^6	1.3×10^7
Total PCBs	2.3×10^6	1.4×10^6	2.7×10^5	9.3×10^5
<i>trans</i> -Nonachlor	5.5×10^6	4.4×10^6	3.0×10^5	2.8×10^6

The accumulation of *trans*-nonachlor was slightly greater than the accumulation of total PCBs in the lower pelagic food web. Bioaccumulation factors for *trans*-nonachlor were 5.5×10^6 , 4.4×10^6 , 3.0×10^5 , and 2.8×10^6 for *Diporeia* spp., *Mysis* spp., phytoplankton, and zooplankton, respectively.

To evaluate the accumulation and transfer of PCBs and *trans*-nonachlor between trophic levels within the lower pelagic food web, biomagnification factors also were calculated. Biomagnification factors between primary producers and primary consumers were calculated as the concentration of contaminants in *Diporeia* spp., *Mysis* spp., or zooplankton divided by the concentration in phytoplankton. Total PCB biomagnification factors were 8.5, 5.1, and 3.4 for *Diporeia* spp., *Mysis* spp., and zooplankton, respectively (Table 7-6). Higher bioaccumulation and biomagnification factors for *Diporeia* spp. could be due to specific life history characteristics including this organism's close association with sediments, which contained approximately 100,000 times the concentration of PCBs in water and slightly higher concentrations of PCBs than phytoplankton. Bioaccumulation factors for *Diporeia* spp. compared to sediments were 8.3 for total PCBs and 59 for *trans*-nonachlor.

Similar to bioaccumulation factors, biomagnification factors increased with increasing chlorination of PCB congeners. Biomagnification factors ranged from 1.9 to 3.6 for PCB 33, and from 4.5 to 12 for PCB 180 (Table 7-6). For *trans*-nonachlor, biomagnification factors were 18, 15, and 9.5 in *Diporeia* spp., *Mysis* spp., and zooplankton, respectively.

Table 7-6. Biomagnification Factors for PCBs and *trans*-Nonachlor between Primary Producers and Primary Consumers

Analyte	<i>Diporeia</i> / Phytoplankton	<i>Mysis</i> / Phytoplankton	Zooplankton / Phytoplankton
PCB 33	3.6	2.4	1.9
PCB 118	9.6	7.9	3.4
PCB 180	12	6.7	4.5
Total PCBs	8.5	5.1	3.4
<i>trans</i> -Nonachlor	18	15	9.5

7.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the PCBs and *trans*-nonachlor monitoring portion of the study are further described in Section 2.7 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of the quality of lower pelagic food web PCB and *trans*-nonachlor data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.7, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 7-7 provides a summary of flags applied to the lower pelagic food web PCB and *trans*-nonachlor data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.7. No results were qualified as invalid, thus all results are represented in the analysis of lower pelagic food web PCB and *trans*-nonachlor concentrations presented in this report.

Table 7-7. Summary of Routine Field Sample Flags Applied to Select PCB Congeners and *trans*-Nonachlor in the Lower Pelagic Food Web

Analyte	Flags								
	Contamination	Precision		Bias					Invalid
	FBK	FFD	FDL	FMS	FSS	LOB	HIB	FPC	INV
PCB 33	45% (104)	7% (16)	4% (9)	0	4% (9)	0	0	0	0
PCB 118	2% (4)	2% (4)	0	0	4% (9)	0	0	0	0
PCB 180	5% (12)	3% (7)	1% (2)	0	4% (9)	0	0	0	0
<i>trans</i> -Nonachlor	0	2% (5)	2% (5)	0	31% (65)	0	0	1% (3)	0

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

FBK = Failed blank (A related blank had a measurable value above the established QC limit when the blank was analyzed using the same equipment and analytical method. Reported value may be suspect.)

FDL = Failed laboratory duplicate (A laboratory duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)

FFD = Failed field duplicate (A field duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)

FPC = Failed performance check (A laboratory performance check sample associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)

FSS = Failed surrogate (Surrogate recoveries associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)

FMS = Failed matrix spike (A matrix spike associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)

LOB = Likely biased low (Reported value is probably biased low as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery or other internal lab QC data. Reported value is not considered invalid.)

HIB = Likely biased high (Reported value is probably biased high as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery, blank contamination, or other internal lab QC data. Reported value is not considered invalid.)

INV = Invalid (Reported value is deemed invalid by the QC Coordinator.)

PIs used surrogate spikes to monitor the bias of the analytical procedure. The PCB and *trans*-nonachlor results were corrected for the recoveries of the surrogates. Only 4% of PCB results were qualified for surrogate recovery problems (Table 7-7). For *trans*-nonachlor, 31% of results were qualified for surrogate recovery problems (FSS). Surrogate recoveries were below the lower QC bound of 50% in 6% of samples and above the upper QC bound of 125% in 25% of samples. The mean surrogate recovery for *trans*-nonachlor, however, was 109%. Laboratory matrix spike samples also were used to monitor analytical bias, and no results were qualified for failed matrix spikes. Based on an analysis of matrix spikes, standard reference material recovery, blank contamination, and other internal QC data, the QC coordinator did not qualify any samples as high or low biased. The QA report (USEPA, 2001b), however, did mention that PCB 99 was prone to chromatographic interference in the plankton media, which could lead to a potentially high bias for this congener and for total PCB values that contained a significant proportion from PCB 99.

Field blanks, consisting of glass fiber filters, were collected for PCBs and *trans*-nonachlor analysis. It was later determined that these glass fiber filter blanks were not representative of the plankton matrix, so results were not flagged based on the results of field blanks. Laboratory blanks, consisting of a volume of solvent processed through an empty Soxhlet apparatus in the same fashion used to extract the field samples, also were prepared and analyzed for PCBs and *trans*-nonachlor. PCB congeners were detected in all laboratory blanks analyzed. In accordance with the researcher's data qualifying rules, samples were flagged for a failed blank (FBK) if the mass of the detected congener in the blank was greater than 10% of the field sample mass or if the blank result was greater than the method detection limit. The level of contamination varied by PCB congener, with only 2% of PCB 118 results flagged for failed blanks, and with 45% of PCB 33 results flagged for failed blanks. Congeners 4+10, 31, 33, 44, 81, 87, 114+131, 123+149, 153, 158, and 170+190 were commonly detected in laboratory blanks. None of the field sample results for *trans*-nonachlor were qualified because of laboratory blank results.

Field duplicates were collected at frequencies of 8%, 17%, 21%, and 11% for *Diporeia* spp., *Mysis* spp., phytoplankton, and zooplankton, respectively. Laboratory duplicates were prepared and analyzed at a frequency of 8.1%. In accordance with the researcher's data qualifying rules for field and laboratory duplicates, samples were flagged for a failed duplicate (FFD or FDL) if the relative percent difference between duplicate results was greater than 30%. Only a small percentage of results (0 to 7% for *trans*-nonachlor and the PCB congeners evaluated) were qualified for failed field or laboratory duplicates.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean relative percent difference (RPD) between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between the results for laboratory duplicate pairs. Table 7-8 provides a summary of data quality assessments for several of these attributes for the lower pelagic food web data.

Because the relative variability of most measurement techniques increases as one approaches the detection limit of the technique, the assessments of the system and analytical precision were divided into two concentration regimes. One measure of precision was calculated for those field and laboratory duplicate results that were less than five times the method detection limit (MDL) of the analyte, and a separate measure was calculated for those field and laboratory duplicate results that were greater than five times the MDL.

Table 7-8. Data Quality Assessment for Select PCB Congeners and *trans*-Nonachlor in Lower Pelagic Food Web Samples

Analyte/Number Field Samples	Parameter	Number of QC samples	Assessment
PCB 33 (233 samples)	System Precision - Mean Field Duplicate RPD (%), > 5 * MDL	24 field duplicate pairs	28%
	System Precision - Mean Field Duplicate RPD (%), < 5 * MDL	7 field duplicate pairs	87%
	Analytical Precision - Mean Lab Duplicate RPD (%), > 5 * MDL	12 lab duplicate pairs	39%
	Analytical Precision - Mean Lab Duplicate RPD (%), < 5 * MDL	5 lab duplicate pairs	90%
	Analytical Bias - Mean Lab Matrix Spike Recovery (%)	20 lab matrix spike samples	87%
	Analytical Sensitivity - Samples Reported as < MDL (%)	-	15%
PCB 118 (233 samples)	System Precision - Mean Field Duplicate RPD (%), > 5 * MDL	34 field duplicate pairs	16%
	Analytical Precision - Mean Lab Duplicate RPD (%), > 5 * MDL	19 lab duplicate pairs	12%
	Analytical Bias - Mean Lab Matrix Spike Recovery (%)	20 lab matrix spike samples	68%
	Analytical Sensitivity - Samples Reported as < MDL (%)	-	0%
PCB 180 (233 samples)	System Precision - Mean Field Duplicate RPD (%), > 5 * MDL	33 field duplicate pairs	23%
	Analytical Precision - Mean Lab Duplicate RPD (%), > 5 * MDL	19 lab duplicate pairs	13%
	Analytical Bias - Mean Lab Matrix Spike Recovery (%)	20 lab matrix spike samples	93%
	Analytical Sensitivity - Samples Reported as < MDL (%)	-	0%
<i>trans</i> -Nonachlor (208 samples)	System Precision - Mean Field Duplicate RPD (%), > 5 * MDL	29 field duplicate pairs	15%
	Analytical Precision - Mean Lab Duplicate RPD (%), > 5 * MDL	17 lab duplicate pairs	21%
	Analytical Bias - Mean Lab Matrix Spike Recovery (%)	14 lab matrix spike samples	77%
	Analytical Sensitivity - Samples Reported as < MDL (%)	-	0.5%

RPD = Relative percent difference

MDL = Method detection limit

System precision was relatively consistent among the PCB congeners evaluated. In samples with concentrations greater than five times the MDL, mean field duplicate RPDs were 28%, 16%, and 23% for PCB congeners 33, 118, and 180, respectively, indicating good precision. Similarly, the mean field duplicate RPD for *trans*-nonachlor was 15%. For samples with concentrations less than five times the MDL, precision was reduced, and the mean field duplicate RPD was 87% for PCB 33. For the remaining congeners presented, all duplicate sample results were greater than five times the MDL. Analytical precision was similar to system precision, and for two analytes, mean laboratory duplicate RPDs were higher than mean field duplicate RPDs. This could suggest that the majority of the variability associated with the measurement system for these analytes is due to the analytical component.

Analytical bias was evaluated by calculating the mean recovery of laboratory matrix spike samples (LMS). Results indicated a slight low bias overall for all analytes. Mean LMS recoveries were 87%, 68%, 93%, and 77% for PCB 33, PCB 118, PCB 180, and *trans*-nonachlor, respectively. The PI and QC coordinator determined, however, that the bias was not strong enough to warrant flagging the data as low biased (LOB).

Analytical sensitivity was evaluated by calculating the percentage of samples reported below the MDL. No PCB 118 or PCB 180 results were below the MDL, and only 0.5% of *trans*-nonachlor results were below the MDL. For PCB 33, 15% of sample results were reported below the MDL. Results from these samples were not censored and were used as reported in the analysis of lower pelagic food web contamination presented in this report.

7.3 Data Interpretation

7.3.1 Comparison to Historical Studies

In this study, total PCB concentrations in the lower pelagic food web averaged 420, 250, 170, and 49 ng/g for *Diporeia* spp., *Mysis* spp., zooplankton, and phytoplankton, respectively. Jackson *et al.* (1998) measured similar PCB concentrations in Lake Michigan biota in 1995 and found the same relative degree of contamination (plankton < *Mysis relicta* < *Diporeia* spp.). Jackson *et al.* (1998) measured an average total PCB concentration of 127 ng/g dry weight in the 63-243 μm size fraction of plankton and 118 ng/g in the 243+ μm size fraction, slightly less than measured for zooplankton in the LMMB Study, but Jackson *et al.* (1998) explained that the plankton samples contained both phytoplankton and zooplankton. Total PCB concentrations measured by Jackson *et al.* (1998) in *Mysis relicta* and *Diporeia* spp. averaged 354 and 1107 ng/g, respectively, and were higher than concentrations measured in the LMMB Study. Oliver and Niimi (1988) measured similar concentrations of PCBs in the lower pelagic food web of Lake Ontario. Total PCB concentrations averaged 50 ng/g in plankton, 330 ng/g in mysids, and 790 ng/g in amphipods.

Total PCB concentrations in the lower pelagic food web of Lake Michigan were lower than measured by other researchers in Lake Huron (Anderson *et al.*, 1982) and Green Bay (Willman *et al.*, 1999). Anderson *et al.* (1982) measured total PCB concentrations of 92 and 126 ng/g in two phytoplankton species, *Cladophora* and *Ulothrix*. In mixed plankton from Lake Huron, Anderson *et al.* (1982) measured 1651 ng/g of total PCBs, which is approximately 10 times the level measured in zooplankton from the LMMB Study and 34 times the level measured in phytoplankton from the LMMB Study. In Green Bay phytoplankton, Willman *et al.* (1999) measured total PCB concentrations of 115 to 640 ng/g, which is 2 to 13 times the level measured in Lake Michigan phytoplankton. Total PCB concentrations in Green Bay zooplankton ranged from 678 to 1670 ng/g and were 4 to 10 times the levels measured in Lake Michigan zooplankton. This could be explained by the relatively higher dissolved PCB concentrations in the water column of Green Bay compared to Lake Michigan. Willman *et al.* (1999) measured total PCB

concentrations of 2.87 to 4.67 ng/L in Green Bay water, which is an order of magnitude higher than average total PCB concentrations in Lake Michigan (see Chapter 5).

Total PCB concentrations in the lower pelagic food web of Lake Michigan were higher than measured by other researchers in Swiss lakes (Berglund *et al.*, 2000) and marine pelagic food webs (Harding *et al.*, 1997; Fisk *et al.*, 2001b). In 19 Swiss lakes, Berglund *et al.* (2000) measured mean total PCB concentrations of 28 and 33 ng/g in phytoplankton and zooplankton, respectively. Harding *et al.* (1997) measured total PCB concentrations of 0.5 to 147 ng/g in plankton from the southern Gulf of St. Lawrence, which is lower than the average concentration measured for zooplankton in the LMMB Study. Fisk *et al.* (2001b) also measured lower total PCB concentrations in high Arctic marine zooplankton, which averaged 30 ng/g total PCBs.

7.3.2 Seasonal Variation

In the LMMB Study, average PCB concentrations in the lower pelagic food web were often highest in the spring and early summer (March - June) and lowest in the late summer and fall (August - September). This finding agrees with the findings of Epplett *et al.* (2000), who found that concentrations of PCBs in plankton in Lake Erie varied seasonally, with peaks in the spring or early summer (primarily June) and decreasing concentrations throughout the summer. In the arctic marine environment, Hargrave *et al.* (2000) also found seasonal variations in planktonic total PCB concentrations. Total PCBs were maximized in the spring and early summer (May/June) and decreased in the late summer and fall (August/September). Hargrave *et al.* (2000) concluded that equilibrium occurs rapidly between plankton and water PCB concentrations. If finite amounts of dissolved PCBs are available for uptake, when planktonic biomass levels change, there must be a rapid equilibrium reflected in increasing or decreasing PCB concentrations. Hargrave *et al.* (2000) observed that the minimum PCB concentrations in plankton that occurred in July and August corresponded with high particulate organic carbon concentrations indicative of high production in the planktonic community.

Swackhamer and Skoglund (1993) and Stange and Swackhamer (1994) investigated uptake of PCBs by several phytoplankton species that were exposed to these contaminants under controlled conditions. The goals of these two studies included determining if kinetics or equilibrium partitioning of PCBs controlled the bioaccumulation of hydrophobic organic contaminants such as PCBs. Cultures of phytoplankton were exposed to a mixture of 40 PCB congeners that included representatives from all 10 levels of chlorination. Exposures were carried out for 20 and 40 days, respectively, with samples of phytoplankton and water collected at intervals throughout the study. PCB concentrations were measured in both the phytoplankton and the water, in order to estimate bioaccumulation rates and bioaccumulation factors (BAFs).

Swackhamer and Skoglund (1993) held separate phytoplankton cultures at 11°C and 20°C to simulate conditions that result in minimal algal growth (11°C) and average algal growth (20°C). The experiments at 11 °C were carried out for 20 days, with duplicate samples of both algae and water collected at 0.2 days, 1 day, 3 days, and 20 days. They found that there was a relationship between the uptake of PCBs and the growth rate of the phytoplankton. Under conditions of minimal growth (11°C), Swackhamer and Skoglund found that the uptake of PCBs was consistent with equilibrium partitioning between the water and lipids within the plankton cells. The logs of the calculated BAFs for the PCB congeners exhibited a linear relationship with the logs of the octanol-water partitioning coefficients (K_{ow}) for the contaminants, with the more highly chlorinated congeners taking longer to reach equilibrium than the less chlorinated congeners. However, even at 20 days, most of the congeners did not achieve equilibrium. Swackhamer and Skoglund noted their results differed from many reports in the literature that suggest that equilibrium is reached rapidly and that many modeling efforts assume that it is instantaneous.

Under the average growth conditions (20°C), however, there was no correlation between log BAF and log K_{ow} for most of the PCB congeners studied. Under these average growth conditions, only congeners with log K_{ow} values less than 5.5 (e.g., mono- through trichlorinated congeners) exhibited a correlation between log BAF and log K_{ow} . Swackhamer and Skoglund offered two possible explanations for the result under average growth conditions:

1. The kinetics of phytoplankton growth and contaminant uptake are of the same order. Thus, an increase in biomass (organism growth) dilutes the concentration of PCBs in the organism, resulting in a constant BAF over time.
2. Cellular metabolism increased during growth, leading to increased excretion of metabolic waste products, comprised mostly of dissolved organic carbon. Hydrophobic contaminants such as PCBs may be associated with those metabolic waste products, and thus be excreted from the cells.

Stange and Swackhamer (1994) exposed phytoplankton cultures to the PCBs for 40 days at 11°C, in order to investigate PCB uptake under minimal growth conditions that favored equilibrium partitioning. The results of that study indicate that PCB uptake under these conditions is controlled by equilibrium partitioning. Stange and Swackhamer identified an additional factor that may control PCB uptake of the highly chlorinated congeners. The movement of those congeners through cell membranes (e.g., from the water into the organism) may depend on their stereochemistry, with PCBs containing three or four chlorine atoms in the *ortho* positions able to pass more easily through membranes into the cells. We note that this additional factor is consistent with the “structure-activity relationship” theory underlying the designation of 12 of the 209 PCB congeners as “toxic” (see Section 2.1.6).

The implications of the works of Swackhamer and Skoglund (1993) and Stange and Swackhamer (1994) or the LMMB Study are that the seasonal variations in PCB concentrations in the lower pelagic food web observed may be the result of the growth rates of phytoplankton species as well as patterns of dominance of different species during the course of the year. The high PCB concentrations in spring may reflect equilibrium partitioning processes that occur at colder water temperatures and low light conditions, while the low PCB concentrations in later summer and fall may reflect the increased growth of organisms in response to warmer water and increased daylight.

7.3.3 Bioaccumulation and Trophic Transfer

PCBs and *trans*-nonachlor significantly accumulated in the lower pelagic food web of Lake Michigan above concentrations in the water column. Bioaccumulation factors from water to the lower pelagic food web ranged from 10^5 to 10^6 for *trans*-nonachlor and from 10^4 to 10^7 for total PCBs depending on the PCB congener and the compartment (e.g., *Diporeia* spp., *Mysis* spp., phytoplankton, or zooplankton). This is similar to the bioaccumulation factors measured by other researchers. Willman *et al.* (1999) measured bioaccumulation factors of 10^4 to 10^6 in Green Bay plankton. Oliver and Niimi (1988) also measured bioaccumulation factors of 10^3 to 10^5 for plankton, 10^4 to 10^6 for *Mysis*, and 10^3 to 10^6 for amphipods in Lake Ontario.

Within the lower pelagic food web, PCB and *trans*-nonachlor concentrations differed significantly among the measured compartments. Concentrations were lowest in phytoplankton, at the base of the pelagic food web. At the next trophic level (Figure 7-5), zooplankton contained significantly higher levels of PCBs and *trans*-nonachlor. Total PCB concentrations increased by a factor of 3.4 in the trophic transfer from phytoplankton to zooplankton, and *trans*-nonachlor concentrations increased by a factor of 9.5 in this transfer. Other researchers have also measured significant increases in PCB concentrations from phytoplankton to zooplankton. Willman *et al.* (1999) measured biomagnification factors of 1 to 10 between phytoplankton and zooplankton for tetra-, penta-, and hexachlorobiphenyl congeners. Willman

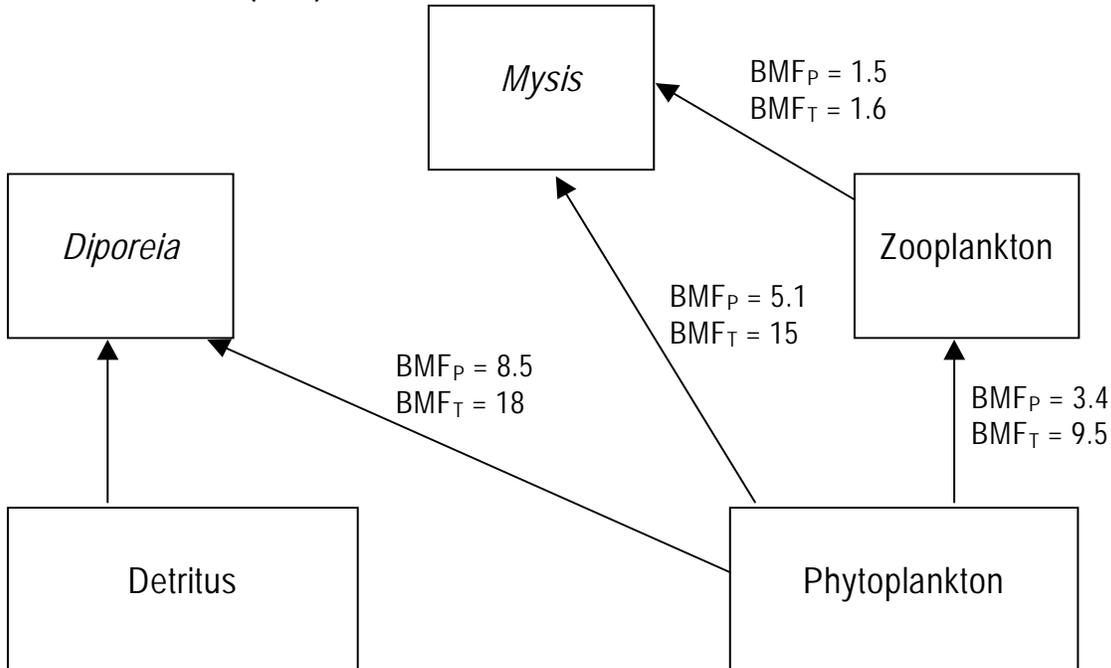
et al. (1999) found that the tri-, hepta-, and octachlorobiphenyl congeners accumulated to a lesser degree. Anderson *et al.* (1982) found approximately a 14 times increase in PCB concentrations from the phytoplankton, *Cladophora*, to zooplankton (>153- μ m size range).

Other researchers have not found evidence of biomagnification of PCBs in the lower pelagic food web and have suggested that differences in PCB concentrations are explained by factors such as lipid content, age, size, or depuration rates. Berglund *et al.* (2000) did not find significant differences in total PCB concentrations between phytoplankton and zooplankton, and Harding *et al.* (1997) did not find significant differences in total PCB concentrations as plankton size varied (presumably accounting for differences between phytoplankton and zooplankton). In fact, Berglund *et al.* (2000) noted that when concentrations were normalized to lipid content, PCB concentrations in zooplankton were lower than in phytoplankton. In the LMMB Study, the same was true when PCB concentrations were normalized based on lipid content. Because the lipid content of zooplankton (19%) was substantially higher than for phytoplankton (4.8%), lipid normalized total PCB concentrations were only 1100 ng/g lipid in zooplankton compared to 1500 ng/g lipid in phytoplankton. In the LMMB Study, however, lipid content did not explain all observed differences in PCB and *trans*-nonachlor concentrations among the lower pelagic food web compartments. Lipid-normalized total PCB concentrations were still significantly higher in *Mysis* spp. and *Diporeia* spp. than in phytoplankton, and lipid-normalized *trans*-nonachlor was significantly higher in zooplankton, *Mysis* spp., and *Diporeia* spp. than in phytoplankton (Figure 7-2).

In addition to zooplankton, *Diporeia* spp. and *Mysis* spp. also occupy the second trophic level, however, trophic transfer from phytoplankton is less direct for these species (Figure 7-5). While *Diporeia* spp. feeds on phytoplankton, it is primarily a detrital feeder. *Mysis* spp. is a non-selective filter feeder that may feed on phytoplankton or zooplankton, such that this species may functionally occupy the second or third trophic levels. PCB and *trans*-nonachlor concentrations were significantly higher in *Mysis* spp. and *Diporeia* spp. than in phytoplankton or zooplankton on either a dry-weight basis (Figure 7-1) or a lipid-normalized dry weight basis (Figure 7-2). The higher concentrations of contaminants in *Diporeia* spp. may be indicative of trophic transfer from phytoplankton, but more likely is due to this organism's close association with the more heavily contaminated sediments. Even compared to sediments, however, *Diporeia* spp. significantly accumulated organic pollutants. Biota-sediment accumulation factors for *Diporeia* spp. were 8.3 for total PCBs and 59 for *trans*-nonachlor. Jackson *et al.* (1998) also suggested that *Diporeia* spp. was more representative of sediment contamination, while plankton were more representative of water column contamination.

Mysis spp. are less associated with detrital sediments than *Diporeia* spp., and accumulation in this species may be more directly linked to transfer through phytoplankton and zooplankton. Total PCB concentrations in *Mysis* spp. exceeded phytoplankton and zooplankton by factors of 5.1 and 1.5, respectively. *trans*-Nonachlor concentrations in *Mysis* spp. exceeded phytoplankton and zooplankton by factors of 15 and 1.6, respectively. Even when normalized to lipid content, *Mysis* spp. exceeded phytoplankton and zooplankton PCB concentrations significantly, by factors of 1.8 and 2.4, and lipid-normalized *trans*-nonachlor concentrations in *Mysis* spp. exceeded phytoplankton and zooplankton significantly by factors of 5.4 and 2.7. These results are similar to the total PCB biomagnification factor of 6.6 measured between plankton and *Mysis* by Oliver and Niimi (1988) in Lake Ontario. This factor varied from approximately 1 to 12 depending upon the specific PCB congener. Fisk *et al.* (2001a) also observed biomagnification from zooplankton to predatory invertebrates. Fisk *et al.* (2001a) calculated a biomagnification factor of 7.8 for total PCB transfer from *Calanus hyperboreus* (an herbaceous copepod) to *Themisto libellula* (a predatory amphipod), however, the authors noted that differences in concentrations at this low level of the food chain may be due to differences in organism size and may be more controlled by concentrations in water than in prey. The same factors could be controlling bioaccumulation of PCBs in *Mysis* in this study, since *Mysis* were considerably larger than the zooplankton species that were collected.

Figure 7-5. Lower Pelagic Food Web Structure and Biomagnification Factors for Total PCBs (BMF_P) and *trans*-Nonachlor (BMF_T)

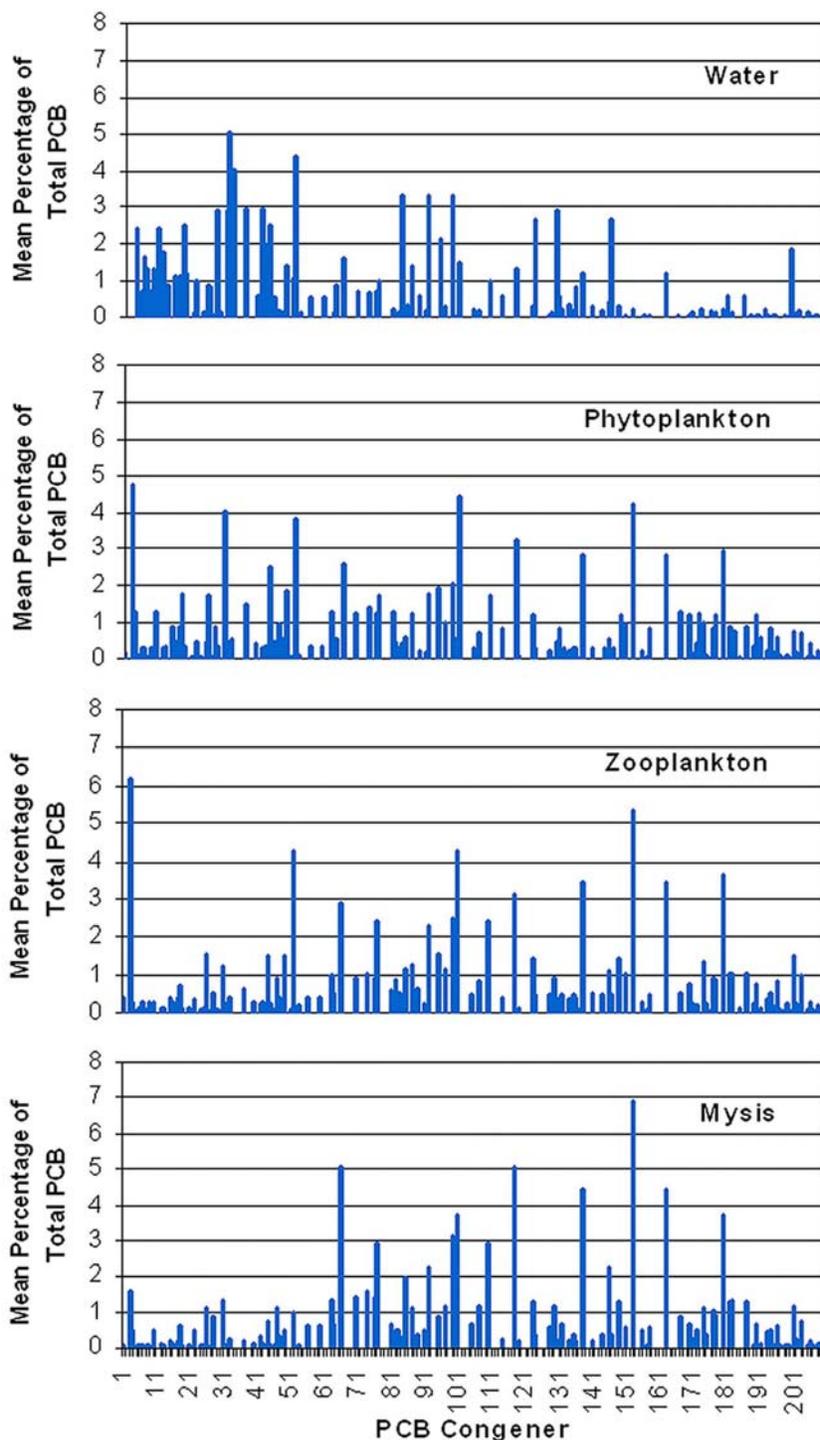


7.3.4 Fractionation

Throughout the lower pelagic food web, PCB congeners were accumulated differentially, with more highly chlorinated and more lipophilic congeners accumulated to a greater extent. For the three congeners specifically highlighted in this study (PCB 33, PCB 118, PCB 180), bioaccumulation factors generally increased by an order of magnitude from PCB 33 (a trichlorobiphenyl) to PCB 118 (a pentachlorobiphenyl) and another order of magnitude from PCB 118 to PCB 180 (a heptachlorobiphenyl) (Table 7-5). This differential accumulation of PCB congeners from water is expected based on the increasing octanol-water partition coefficients with increasing PCB chlorination. Researchers have described this relationship with linear regressions of log bioaccumulation factors versus log octanol-water partition coefficients (Mackay, 1982; Oliver and Niimi, 1988).

Not only did bioaccumulation factors increase with increasing chlorination of PCB congeners, but biomagnification factors also increased with increasing PCB chlorination. For example, biomagnification factors from phytoplankton to zooplankton increased from 1.9 to 3.4 to 4.5, for PCB congeners 33, 118, and 180, respectively (Table 7-6). While trends of increasing bioaccumulation factors and increasing biomagnification factors were observed for the three congeners specifically highlighted in this study, these trends were also generally true for all PCB congeners. Figure 7-6 shows the relative percentages of individual PCB congeners in water, phytoplankton, zooplankton, and *Mysis* spp. In water, there is a predominance of the less-chlorinated PCB congeners, and this predominance shifts progressively to more-chlorinated congeners with increasing trophic levels.

Figure 7-6. Mean Percentage of Individual PCB Congener Contribution to Total PCB Concentrations

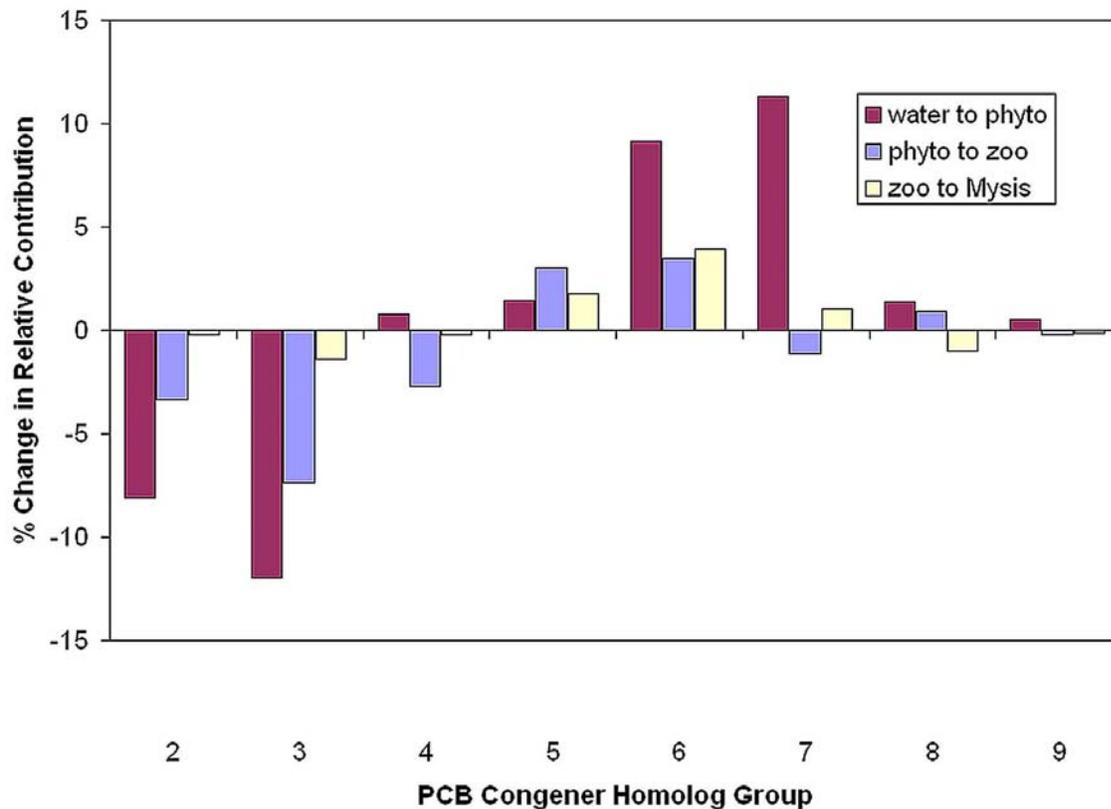


The shift from less to more-chlorinated PCB congeners with increasing trophic level can be more easily observed when PCB congeners are grouped by chlorination level homologs (e.g., di-, tri-, tetra-, penta-, hexa-, hepta-, and octachlorobiphenyls). Figure 7-7 shows the percent change in the relative contribution (to total PCB concentration) of PCB congener homologs between compartments. Positive percent

changes indicate the relative enrichment of that homolog group between compartments, and negative percent changes indicate the relative depletion of that homolog group between compartments. In transfers from water to phytoplankton, the di- and trichlorobiphenyls are reduced in relative proportion to total PCBs, while the penta-, hexa-, and heptachlorobiphenyls are enriched. The same general trend is seen in the transfer from phytoplankton to zooplankton and the transfer from zooplankton to *Mysis*.

Other researchers have observed this same trend. Jackson *et al.* (1998) found a relative shift from less-chlorinated PCB congeners in the plankton to more-chlorinated PCB congeners in *Mysis relicta* and *Diporeia* spp. Oliver and Niimi (1988) also observed differential PCB fractionation from water to plankton to mysids. Less-chlorinated PCB congeners comprised a higher fraction of total PCBs in water than in higher trophic levels. Similar to the LMMB Study, Willman *et al.* (1997) found that the penta-, hexa-, and heptachlorobiphenyl congeners were enriched relative to other congeners as PCBs moved to higher trophic levels from sediments to plankton to fish.

Figure 7-7. Relative Enrichment or Depletion of PCB Congener Homolog Groups between Compartments



Chapter 8

PCBs/trans-Nonachlor in Fish

8.1 Results

Lake Michigan fish were collected from April 1994 through November 1995 for PCB and *trans*-nonachlor analysis. Forage fish species (alewife, bloater chub, deepwater sculpin, slimy sculpin, and rainbow smelt) and piscivorous fish species (lake trout and coho salmon) were collected and analyzed. Alewife and bloater chub were collected in two distinct size classes, and coho salmon were collected in three distinct age classes. Overall, a total of 796 fish samples were collected for the analysis of PCBs and *trans*-nonachlor (Table 8-1). Each sample was a composite of up to five fish of the same species and size or age category. With the exception of coho salmon, fish were collected from the following three biological sampling areas or biota boxes:

- ▶ **Sturgeon Bay biota box** – a series of three nearshore stations on the western side of the northern Lake Michigan basin near Sturgeon Bay, Wisconsin
- ▶ **Port Washington biota box** – a series of two mid-lake reef stations in the central Lake Michigan basin near Port Washington, Wisconsin
- ▶ **Saugatuck biota box** – a series of three nearshore stations on the eastern side of the southern Lake Michigan basin near Saugatuck, Michigan.

Coho salmon were collected from various sites selected to follow the seasonal migration of coho, which travel up Lake Michigan tributaries in the fall to spawn. During the summer, coho salmon were collected from the east central and west central regions of the lake. During the fall, coho salmon were collected from the northeastern side of the lake near the Platte River and on the western side of the lake near the Kewaunee River.

As noted in Chapter 2, there are 209 possible PCB congeners, and the investigators in this study reported results for 65 to 110 of these congeners, depending on the capabilities of each laboratory. The USGS laboratory determined results for 80 congeners or co-eluting congeners.

For the purposes of this report, we are presenting summaries of the results for the following subset of all of the analytes:

- PCB congener 33
- PCB congener 118
- PCB congener 180
- Total PCBs
- *trans*-nonachlor

Table 8-1. Number of Fish Samples Analyzed for PCB Congeners and *trans*-Nonachlor

Species/Size Category	Sampling Dates	Number of Samples Analyzed for PCBs and <i>trans</i> -Nonachlor
Alewife<120mm	05/18/94 to 10/12/95	60
Alewife>120mm	05/18/94 to 10/12/95	70
Bloater<160mm	05/18/94 to 10/13/95	70
Bloater>160mm	05/18/94 to 10/13/95	67
Coho-Adult	05/10/94 to 11/06/95	54
Coho-Hatchery	04/21/94 to 04/27/94	5
Coho-Yearling	10/18/94 to 11/16/94	8
Deepwater Sculpin	05/18/94 to 10/13/95	74
Lake Trout	05/12/94 to 10/26/95	246
Smelt	05/18/94 to 10/12/95	73
Slimy Sculpin	05/18/94 to 10/26/95	69
Total		796

8.1.1 Species Variation

Tables 8-2 and 8-3 show the mean concentrations (on a wet-weight basis) of PCB 33, PCB 118, PCB 180, total PCBs, and *trans*-nonachlor in various Lake Michigan fish species. PCB and *trans*-nonachlor concentrations differed significantly among species (Figure 8-1). Significantly higher levels of total PCBs and *trans*-nonachlor were observed in Lake trout, a top predator in the Lake Michigan pelagic food web, than in any other fish species. Mean concentrations of PCB 33, PCB 118, PCB 180, total PCBs, and *trans*-nonachlor in lake trout were 1.4, 3.3, 3.4, 3.6, and 2.9 times higher than for any other species. This trend was similar for dry-weight basis PCB and *trans*-nonachlor concentrations (Table 8-4). Mean dry-weight basis total PCB concentrations in lake trout were from 1.2 to 16 times higher than in other species, and mean dry-weight basis *trans*-nonachlor concentrations were 2.4 to 34 times higher in lake trout than in other species.

When PCB and *trans*-nonachlor concentrations were compared among fish species on a lipid-normalized basis, lake trout still contained higher levels of contamination than all other species with the exception of adult coho salmon. Mean lipid-normalized total PCB and *trans*-nonachlor concentrations were highest in adult coho salmon and second highest in lake trout. Lipid-normalized total PCB and *trans*-nonachlor concentrations in these two top predator fish species were significantly higher than in any of the forage fish species (Figure 8-2 and Table 8-5). The higher mean concentrations of lipid-normalized contaminants in adult coho salmon were due to the relatively low lipid content in this species. Lipid content in adult coho salmon averaged only 4% compared to 16% in lake trout. Of the species analyzed in this study, only smelt contained lower lipid content (3.6%) than adult coho salmon.

The lowest total PCB and *trans*-nonachlor concentrations on a wet-weight, dry-weight, or lipid-weight basis were consistently found in hatchery and yearling coho salmon. This species is raised in hatcheries and annually stocked in Lake Michigan. Hatchery samples consisted of immature coho collected directly from the Platte River hatchery, and yearling samples consisted of immature coho collected in Lake Michigan. The reduced contamination in these sample types most likely reflects both the young age of the fish and reduced contaminant exposure from hatchery food and water sources.

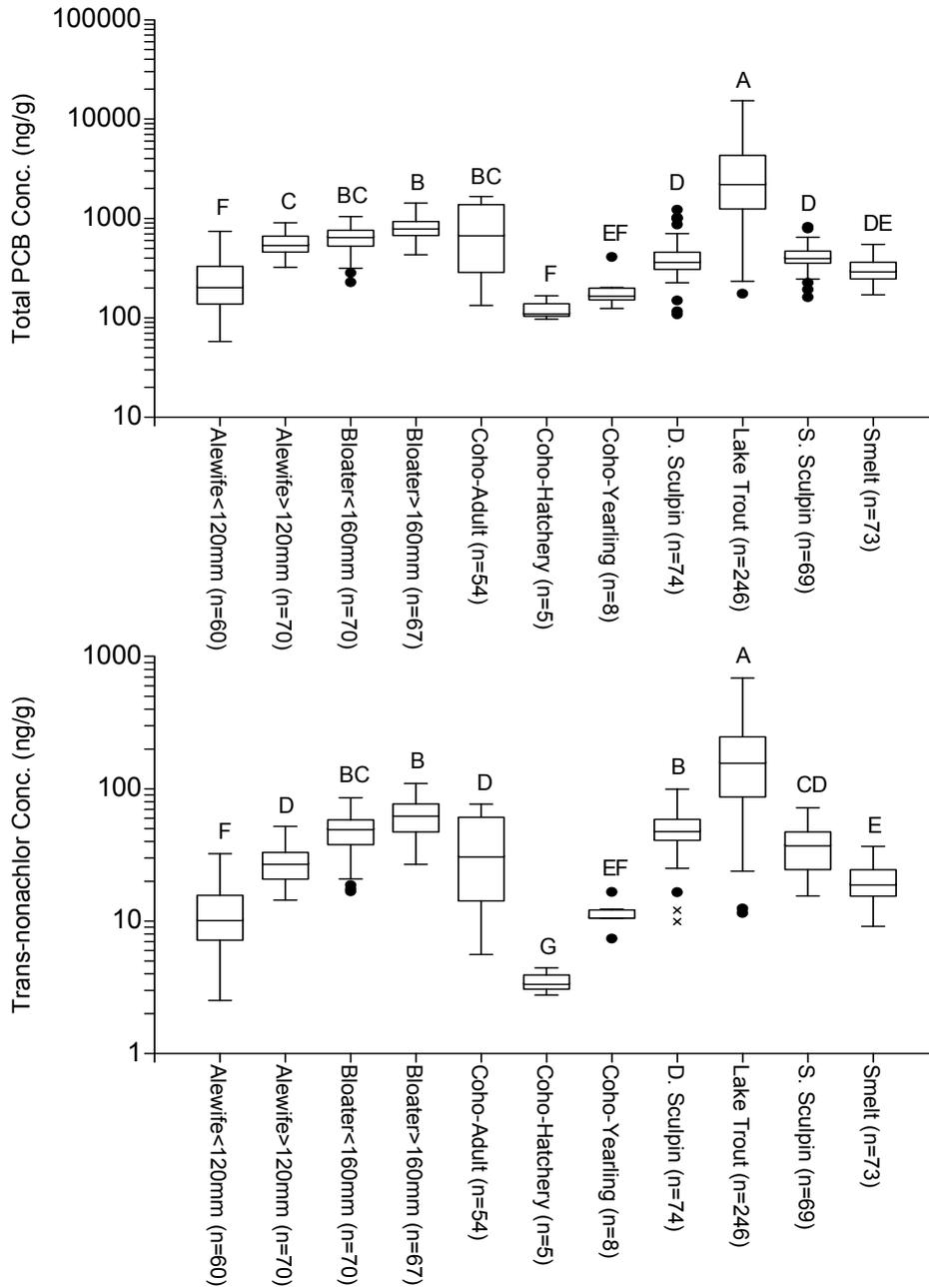
Table 8-2. Mean Concentrations of Specific PCB Congeners in Lake Michigan Fish (Wet-weight Basis)

Congener	Species/Size Category	N	Mean (ng/g)	Range (ng/g)	SD (ng/g)	RSD (%)	Below DL (%)
PCB 33	Alewife<120mm	60	8.3	0.0 to 49	9.6	120	45
	Alewife>120mm	70	23	0.0 to 83	17	75	13
	Bloater<160mm	69	3.9	0.0 to 36	9.5	240	84
	Bloater>160mm	67	4.0	0.0 to 36	9.5	240	82
	Coho-Adult	54	19	0.0 to 65	20	110	37
	Coho-Hatchery	5	0.0	0.0 to 0.0	0.0	-	100
	Coho-Yearling	8	0.0	0.0 to 0.0	0.0	-	100
	Deepwater Sculpin	74	0.16	0.0 to 7.4	1.0	620	97
	Lake Trout	246	33	0.0 to 230	50	150	50
	Smelt	72	1.7	0.0 to 18	4.1	240	83
	Slimy Sculpin	68	2.0	0.0 to 19	4.5	230	82
PCB 118	Alewife<120mm	60	8.3	1.4 to 23	4.9	59	0
	Alewife>120mm	70	23	12 to 34	5.2	22	0
	Bloater<160mm	70	28	8.2 to 56	9.9	35	0
	Bloater>160mm	67	39	16 to 76	12	32	0
	Coho-Adult	54	36	5.7 to 82	24	68	0
	Coho-Hatchery	5	6.5	5.4 to 8.7	1.3	21	0
	Coho-Yearling	8	7.7	4.5 to 19	4.8	62	0
	Deepwater Sculpin	74	34	4.1 to 110	21	61	0
	Lake Trout	246	130	4.2 to 790	100	77	0
	Smelt	73	16	7.9 to 28	4.8	31	0
	Slimy Sculpin	69	22	0 to 42	8.7	40	1.4
PCB180	Alewife<120mm	59	5.6	1.1 to 12	2.9	53	0
	Alewife>120mm	70	15	7.7 to 25	3.4	23	0
	Bloater<160mm	70	25	7.8 to 45	8.6	35	0
	Bloater>160mm	67	29	15 to 63	9.1	32	0
	Coho-Adult	54	25	4.2 to 50	16	65	0
	Coho-Hatchery	5	2.4	2.0 to 3.5	0.62	26	0
	Coho-Yearling	8	7.7	5.4 to 16	3.5	45	0
	Deepwater Sculpin	74	29	5.9 to 83	15	51	0
	Lake Trout	246	100	8.2 to 490	80	78	0
	Smelt	73	9.0	4.3 to 14	2.8	31	0
	Slimy Sculpin	69	19	7.2 to 52	7.2	39	0

Table 8-3. Mean Concentrations of Total PCBs and *trans*-Nonachlor in Lake Michigan Fish (Wet-weight Basis)

Analyte	Species/Size Category	N	Mean (ng/g)	Range (ng/g)	SD (ng/g)	RSD (%)	Below DL (%)
Total PCBs	Alewife<120mm	60	250	58 to 750	150	60	0
	Alewife>120mm	70	580	320 to 910	140	24	0
	Bloater<160mm	70	650	230 to 1000	180	28	0
	Bloater>160mm	67	830	430 to 1400	210	25	0
	Coho-Adult	54	810	130 to 1700	520	64	0
	Coho-Hatchery	5	120	97 to 170	27	22	0
	Coho-Yearling	8	200	120 to 400	90	46	0
	Deepwater Sculpin	74	420	110 to 1200	200	48	0
	Lake Trout	246	3000	180 to 15000	2300	76	0
	Smelt	73	310	170 to 550	83	27	0
	Slimy Sculpin	69	430	160 to 820	130	30	0
<i>trans</i> -Nonachlor	Alewife<120mm	60	12	2.5 to 32	7.3	59	0
	Alewife>120mm	70	28	14 to 52	9.0	32	0
	Bloater<160mm	70	48	17 to 85	15	31	0
	Bloater>160mm	67	63	27 to 110	19	30	0
	Coho-Adult	54	38	5.6 to 76	25	65	0
	Coho-Hatchery	5	3.5	2.8 to 4.4	0.60	17	0
	Coho-Yearling	8	11	7.4 to 17	2.6	23	0
	Deepwater Sculpin	74	50	9.9 to 99	17	34	0
	Lake Trout	246	180	12 to 680	120	65	0
	Smelt	73	20	9.1 to 37	6.0	30	0
	Slimy Sculpin	69	38	15 to 72	14	37	0

Figure 8-1. Total PCB and *trans*-Nonachlor Concentrations in Lake Michigan Fish (Wet-weight Basis)

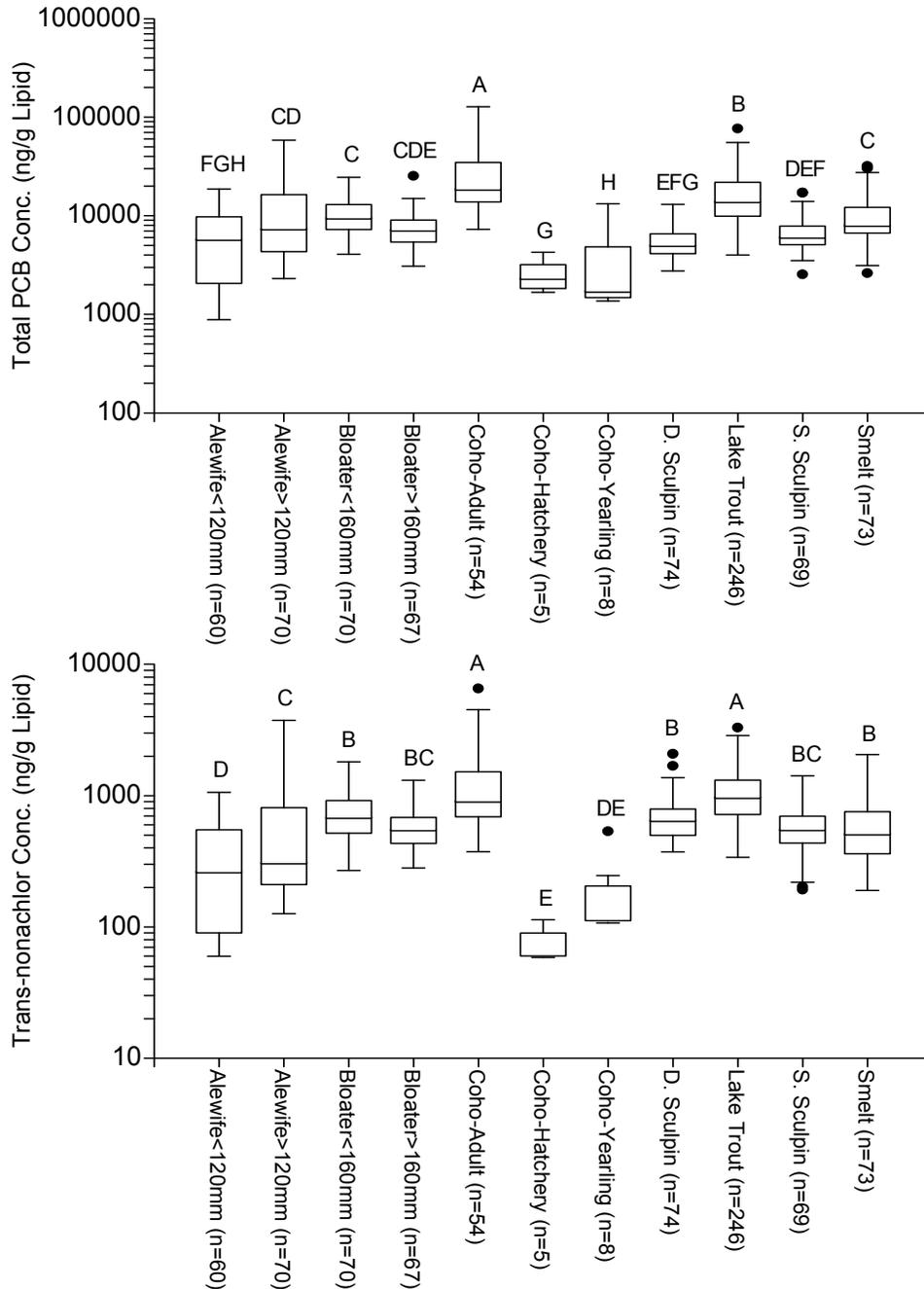


Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The Xs represent results beyond 3*IQR from the box. The letters (A - G) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Concentration is plotted on a log scale.

Table 8-4. Mean Concentrations of Total PCBs and *trans*-Nonachlor in Lake Michigan Fish (Dry-weight Basis)

Analyte	Species/Size Category	N	Mean (ng/g)	Range (ng/g)	SD (ng/g)	RSD (%)	Below DL (%)
Total PCBs	Alewife<120mm	60	990	230 to 3000	580	58	0
	Alewife>120mm	70	2100	1100 to 3500	580	27	0
	Bloater<160mm	70	2500	930 to 4000	750	30	0
	Bloater>160mm	67	6700	1300 to 5000	760	28	0
	Coho-Adult	54	2900	570 to 6000	1700	59	0
	Coho-Hatchery	5	480	370 to 710	130	27	0
	Coho-Yearling	8	690	400 to 1700	410	60	0
	Deepwater Sculpin	74	1700	440 to 4100	650	40	0
	Lake Trout	246	7800	770 to 37000	5400	70	0
	Smelt	73	1400	660 to 2400	390	28	0
	Slimy Sculpin	69	1700	620 to 3600	530	32	0
<i>trans</i> -Nonachlor	Alewife<120mm	60	50	9.8 to 130	31	62	0
	Alewife>120mm	70	110	52 to 230	38	36	0
	Bloater<160mm	70	190	69 to 310	59	32	0
	Bloater>160mm	67	200	110 to 390	61	30	0
	Coho-Adult	54	140	24 to 300	82	60	0
	Coho-Hatchery	5	14	11 to 19	2.9	21	0
	Coho-Yearling	8	38	29 to 67	12	31	0
	Deepwater Sculpin	74	200	40 to 380	69	34	0
	Lake Trout	246	480	48 to 1700	280	58	0
	Smelt	73	87	40 to 170	28	32	0
	Slimy Sculpin	69	150	60 to 290	55	38	0

Figure 8-2. Total PCB and *trans*-Nonachlor Concentrations in Lake Michigan Fish (Lipid-weight Basis)



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The letters (A - H) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Concentration is plotted on a log scale.

Table 8-5. Mean Concentrations of Total PCBs and *trans*-Nonachlor in Lake Michigan Fish (Lipid-weight Basis)

Analyte	Species/Size Category	N	Mean (ng/g)	Range (ng/g)	SD (ng/g)	RSD (%)	Below DL (%)
Total PCBs	Alewife<120mm	60	6800	880 to 19000	5200	76	0
	Alewife>120mm	70	12000	2300 to 59000	12000	98	0
	Bloater<160mm	70	10000	4100 to 25000	4100	40	0
	Bloater>160mm	67	7900	3100 to 25000	3700	46	0
	Coho-Adult	54	27000	7300 to 130000	22000	82	0
	Coho-Hatchery	5	2500	1700 to 4300	1000	40	0
	Coho-Yearling	8	3700	1400 to 13000	4300	120	0
	Deepwater Sculpin	74	5700	2800 to 13000	2300	40	0
	Lake Trout	246	17000	4000 to 77000	9800	57	0
	Smelt	73	11000	2600 to 32000	6700	64	0
	Slimy Sculpin	69	6800	3000 to 17000	2700	39	0
<i>trans</i> -Nonachlor	Alewife<120mm	60	350	60 to 1100	290	82	0
	Alewife>120mm	70	630	130 to 3700	680	110	0
	Bloater<160mm	70	760	270 to 1800	320	42	0
	Bloater>160mm	67	580	280 to 1300	200	35	0
	Coho-Adult	54	1200	370 to 6500	1000	84	0
	Coho-Hatchery	5	73	59 to 110	23	32	0
	Coho-Yearling	8	180	110 to 530	150	83	0
	Deepwater Sculpin	74	710	370 to 2100	290	41	0
	Lake Trout	246	1100	340 to 3300	490	45	0
	Smelt	73	670	190 to 2000	440	65	0
	Slimy Sculpin	69	600	190 to 1400	240	41	0

8.1.2 Factors Affecting Contaminant Concentrations

In general, log-transformed total PCB and *trans*-nonachlor concentrations were highly correlated with both lipid content and fish length (Table 8-6). For smelt and slimy sculpin, these correlations were not significant (at the 95% confidence level) or were weak, and correlations with lipid content were weak in alewife. For all other species, however, correlations were highly significant ($p < 0.0001$) and r^2 values ranged from 0.27 to 0.89 for correlations between fish contaminant concentration and length and from 0.10 to 0.69 for correlations between fish contaminant concentration and lipid content. It should be noted that analyzed fish samples were composites of up to five individual fish. Correlations with fish length reflect the midpoint of the range of fish lengths that were incorporated into the composite sample. It is likely that correlations between contaminant concentrations and fish length would be stronger had contaminant concentrations been measured in individual fish samples to allow for direct comparison of length and contaminant concentration.

Multiple regression analysis was conducted to partition the effects of length and lipid content on fish contamination (Table 8-7). Contaminant concentrations (log-transformed total PCB and log-transformed

trans-nonachlor) in alewife and lake trout were significantly affected only by length and not by lipid content. Lipid content remained correlated with contaminant concentrations (Table 8-6) through its correlation with fish length, but in a multiple regression model, only length significantly accounted for variability in alewife and lake trout contaminant concentrations. *trans*-Nonachlor concentrations in smelt also were only affected by length, and not lipid content. In slimy sculpin, contaminant concentrations (both PCB and *trans*-nonachlor) were significantly affected only by lipid content and not by fish length (Table 8-7). For the remaining fish species, both length and lipid content or an interaction of the two parameters significantly affected fish contaminant concentrations.

Table 8-6. Correlation Between Log-transformed Total PCBs and *trans*-Nonachlor Concentrations in Lake Michigan Fish and Fish Length and Lipid Content

Analyte	Species/Size Category	Fish Length			Lipid Content		
		Correlation Coefficient	p	r^2	Correlation Coefficient	p	r^2
Total PCBs	Alewife	0.78	<0.0001	0.61	0.25	0.0042	0.062
	Bloater	0.54	<0.0001	0.29	0.31	<0.0001	0.10
	Coho-Adult	0.84	<0.0001	0.70	0.73	<0.0001	0.53
	Deepwater Sculpin	0.56	<0.0001	0.32	0.62	<0.0001	0.39
	Lake Trout	0.94	<0.0001	0.89	0.83	<0.0001	0.69
	Smelt	0.40	0.0004	0.16	-0.34	0.0035	0.11
	Slimy Sculpin	0.14	0.25	0.020	0.32	0.017	0.10
<i>trans</i> -Nonachlor	Alewife	0.80	<0.0001	0.63	0.25	0.0042	0.062
	Bloater	0.52	<0.0001	0.27	0.47	<0.0001	0.22
	Coho-Adult	0.82	<0.0001	0.66	0.74	<0.0001	0.55
	Deepwater Sculpin	0.72	<0.0001	0.52	0.57	<0.0001	0.32
	Lake Trout	0.91	<0.0001	0.82	0.82	<0.0001	0.67
	Smelt	0.27	0.021	0.07	-0.20	0.098	0.038
	Slimy Sculpin	0.055	0.65	0.0031	0.311	0.020	0.10

Contaminant concentrations generally increased with increasing lipid content and with increasing fish length. Hydrophobic organic contaminants such as PCBs and *trans*-nonachlor preferentially concentrate in the fatty tissues of organisms, so those organisms with higher lipid content are expected to contain more of these contaminants. Older fish also are likely to accumulate higher levels of contaminants because they have experienced longer exposure durations to environmental contaminants. As a surrogate of fish age, fish length is similarly correlated with fish contaminant concentrations. Contaminant concentrations generally increased exponentially with increasing fish length, producing a linear relationship between fish length and log concentration. Figure 8-3 shows the relationship between fish length and contaminant concentrations in lake trout. The length of lake trout accounted for 89% ($r^2 = 0.89$) of the variability in total PCB concentrations and 82% ($r^2 = 0.82$) of the variability in *trans*-nonachlor concentrations. Significant relationships between fish length and contaminant concentrations, such as the one depicted in Figure 8-3 for lake trout, can be useful in setting and evaluating size-based fish advisory levels.

Figure 8-3. Relationship between Fish Length and Total PCB and *trans*-Nonachlor Concentrations in Lake Michigan Lake Trout

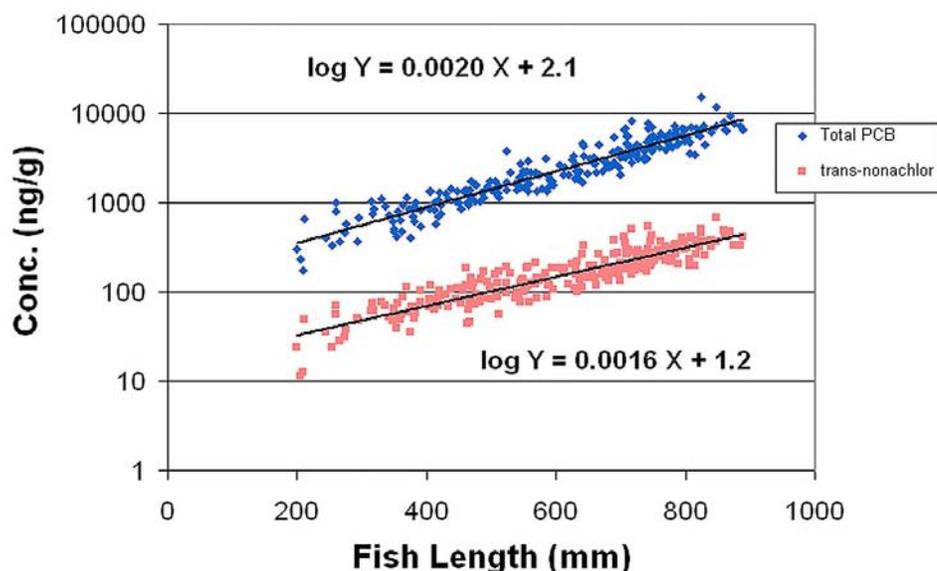


Table 8-7. Results of Multiple Regression Significance Test for Effects of Fish Length and Lipid Content on Concentrations of Total PCBs and *trans*-Nonachlor Concentrations in Lake Michigan Fish

Analyte	Species/Size Category	p-value		
		Fish Length	Lipid Content	Interaction ^a
Total PCBs ^c	Alewife	<0.0001	0.43	NS
	Bloater	<0.0001 ^b	0.014 ^b	0.0058
	Coho-Adult	<0.0001 ^b	0.0002 ^b	0.0033
	Deepwater Sculpin	0.0014	0.0001	NS
	Lake Trout	<0.0001	0.33	NS
	Smelt	0.0019	0.016	NS
	Slimy Sculpin	0.080	0.011	NS
<i>trans</i> -Nonachlor ^c	Alewife	<0.0001	0.35	NS
	Bloater	0.0004	0.036	NS
	Coho-Adult	<0.0001 ^b	<0.0001 ^b	0.0006
	Deepwater Sculpin	<0.0001 ^b	0.0043 ^b	0.015
	Lake Trout	<0.0001	0.45	NS
	Smelt	0.042	0.21	NS
	Slimy Sculpin	0.31	0.014	NS

^a NS indicates that the interaction term was not significant and was removed from the model.

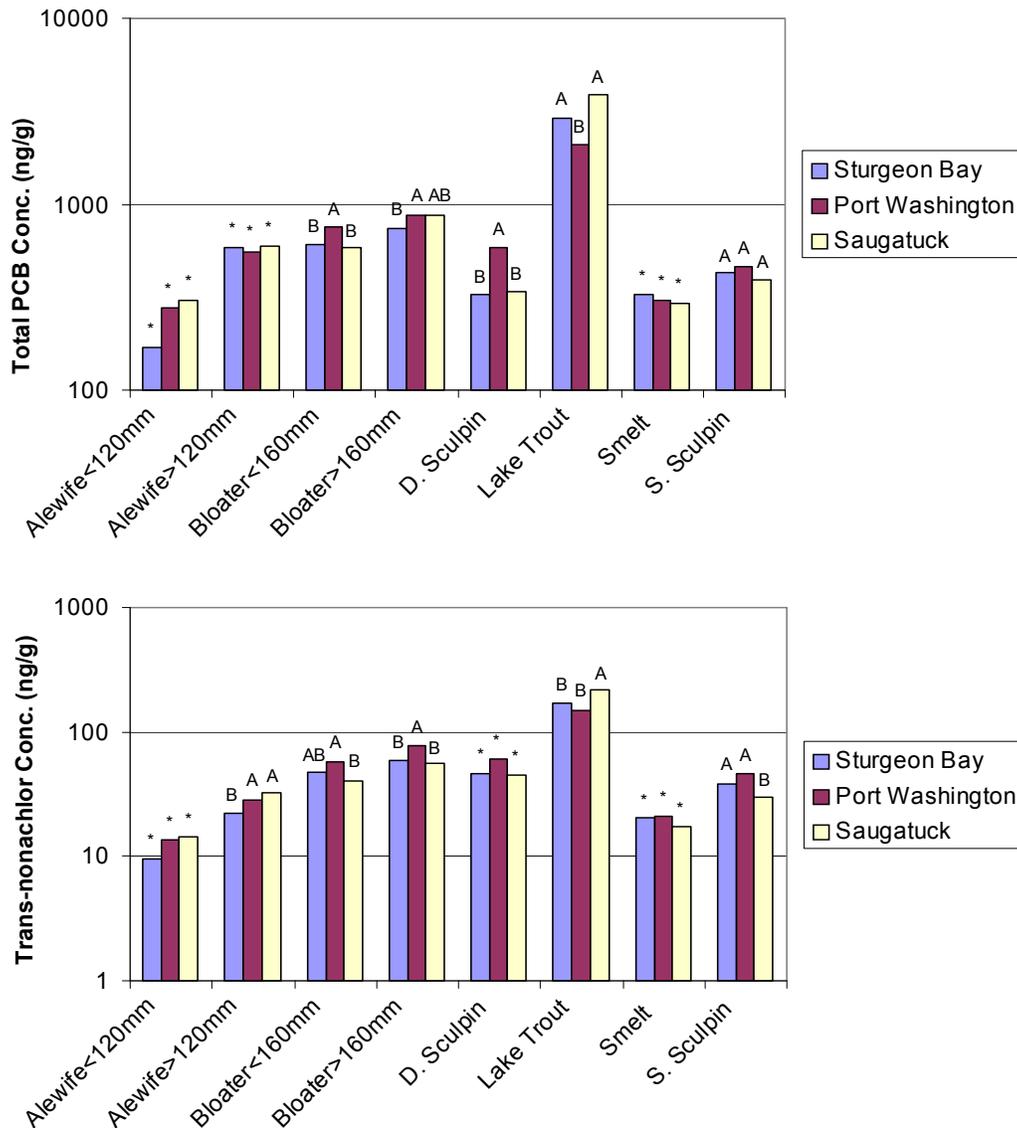
^b Due to the significant interaction term, interpretation of the effect of this variable on PCB and *trans*-nonachlor concentrations is confounded by the remaining variable.

^c Total PCB and *trans*-nonachlor concentrations were log transformed.

8.1.3 Geographical Variation

With the exception of coho salmon, fish were collected from three biological sampling areas or biota boxes (Saugatuck, Sturgeon Bay, and Port Washington) during the spring, summer, and autumn months. Mean total PCB and *trans*-nonachlor concentrations in alewife and lake trout were highest at the Saugatuck biota box, and concentrations in bloater chub, deepwater sculpin, and slimy sculpin were highest at the Port Washington biota box (Figure 8-4). Total PCB concentrations in smelt were highest at Sturgeon Bay, and *trans*-nonachlor concentrations in smelt were highest at Port Washington. For a given species, mean contaminant concentrations differed by 6 to 46% among sampling stations.

Figure 8-4. Total PCB and *trans*-Nonachlor Concentrations in Fish from Three Biological Sampling Stations in Lake Michigan



Bars with the same letter were not statistically different (at alpha = 0.05). Bars with an asterisk indicate that there was significant interaction between the effects of station and season.

Two-way analysis of variance (accounting for sampling station and season) revealed that for some species, differences in contaminant concentrations among sampling stations were statistically significant. Geographical trends in total PCB contamination, however, were species specific, with some species containing higher contamination at Port Washington and other species containing higher contamination at Saugatuck (Figure 8-4). Deepwater sculpin and small bloater chub from Port Washington contained significantly higher levels of PCBs than the same species collected at Sturgeon Bay or Saugatuck, and large bloater chub from Port Washington contained significantly higher levels of PCBs than the same species collected at Sturgeon Bay. This trend was reversed, however, in lake trout. Lake trout from Port Washington contained significantly lower levels of PCBs than lake trout from Sturgeon Bay or Saugatuck. There were no significant differences among sites in slimy sculpin contamination. For the remaining species, there was significant interaction between the effects of station and season, meaning that significant differences between stations were only observed during given seasons. In the spring, small alewife from Sturgeon Bay were significantly lower in PCBs than alewife from Port Washington or Saugatuck. In spring, smelt from Sturgeon Bay contained significantly less PCBs than smelt from Port Washington. In autumn, Port Washington smelt were significantly lower in PCBs than Sturgeon Bay or Saugatuck smelt.

Total PCBs measured in the LMMB Study were highest in lake trout from Saugatuck, and lowest in lake trout from Port Washington. This geographical pattern of PCB contamination in Lake Michigan lake trout was previously reported by Madenjian *et al.* (1999a) and also observed by Miller *et al.* (1992). Miller *et al.* (1992) found that lake trout at deep water reef locations, such as Port Washington, contained lower PCB contamination than lake trout collected from nearshore locations, such as Saugatuck and Sturgeon Bay. Using LMMB Study data, Madenjian *et al.* (1999a) identified significantly higher concentrations of PCBs in lake trout from Saugatuck than from Sturgeon Bay or Port Washington and significantly higher concentrations of PCBs in lake trout from Sturgeon Bay than from Port Washington. Madenjian *et al.* (1999a) explained that these differences in PCB fish contamination levels among various sites were likely due to differences in organism size or differences in lake trout diet at the sites. Lower concentrations in lake trout from Port Washington were explained by the fact that the fish from this site were smaller than fish from the other two sites. Lower concentrations at Sturgeon Bay than at Saugatuck were explained by a lake trout diet that consisted of a higher proportion of more contaminated prey species at Saugatuck than at Sturgeon Bay. Based on analyses of guts contents, Madenjian *et al.* (1999a) determined that at Saugatuck, lake trout diet consisted of 55% alewife, 35% bloater, and 10% sculpins and rainbow smelt. This diet contained a combined 0.64 mg/kg PCBs, compared to a 80% alewife and 20% rainbow smelt diet at Sturgeon Bay that contained a combined 0.53 mg/kg PCBs.

Similar to total PCB contamination, geographical trends in *trans*-nonachlor contamination were species specific (Figure 8-4). Large alewife, bloater chub, and slimy sculpin from Port Washington contained significantly higher *trans*-nonachlor concentrations than the same species at one or more other stations. Large alewife and lake trout from Saugatuck contained significantly higher *trans*-nonachlor concentrations than the same species at one or more other stations. Only slimy sculpin contained significantly higher *trans*-nonachlor concentrations at Sturgeon Bay than other stations. For small alewife, deepwater sculpin, and smelt, there was significant interaction between the effects of station and season. *trans*-Nonachlor contamination in small alewife was significantly higher at Port Washington and Saugatuck than at Sturgeon Bay during the spring, higher at Sturgeon Bay than Saugatuck during the summer, and higher at Port Washington than Sturgeon Bay during autumn. In deepwater sculpin, *trans*-nonachlor contamination was higher at Port Washington than Saugatuck during the summer. In smelt, *trans*-nonachlor contamination was significantly higher at Sturgeon Bay than at Port Washington during the spring and higher at Port Washington than Sturgeon Bay or Saugatuck during autumn.

In summary, differences in fish contamination levels among sites were relatively small (6% to 46%) compared to species differences, which varied by more than a factor of 12, or differences attributed to fish

size or lipid content, where contaminant levels varied over an order of magnitude (Figure 8-3). Significant differences in fish contamination levels among sites were species specific. Some species showed significantly higher contamination levels at Saugatuck, and other species showed significantly higher contamination levels at Port Washington. In general, fish contamination levels at Sturgeon Bay were lower than at the remaining sites. Differences in fish contamination levels among sites could be due to increased water, sediment, and food contamination levels at specific sites. Contours of water and sediment PCB levels did show increased concentrations (see Chapters 5 and 6) on the eastern shore of the southern basin (near Saugatuck) and in the center of the southern basin (near Port Washington biota box). PCB concentrations in the lower pelagic food web also were generally higher at Saugatuck (see Chapter 7). Differences in fish contamination levels also could be due to differences in fish size or lipid content at the various sites, or as Madenjian *et al.* (1999a) suggested, differences in fish diets among the various sites.

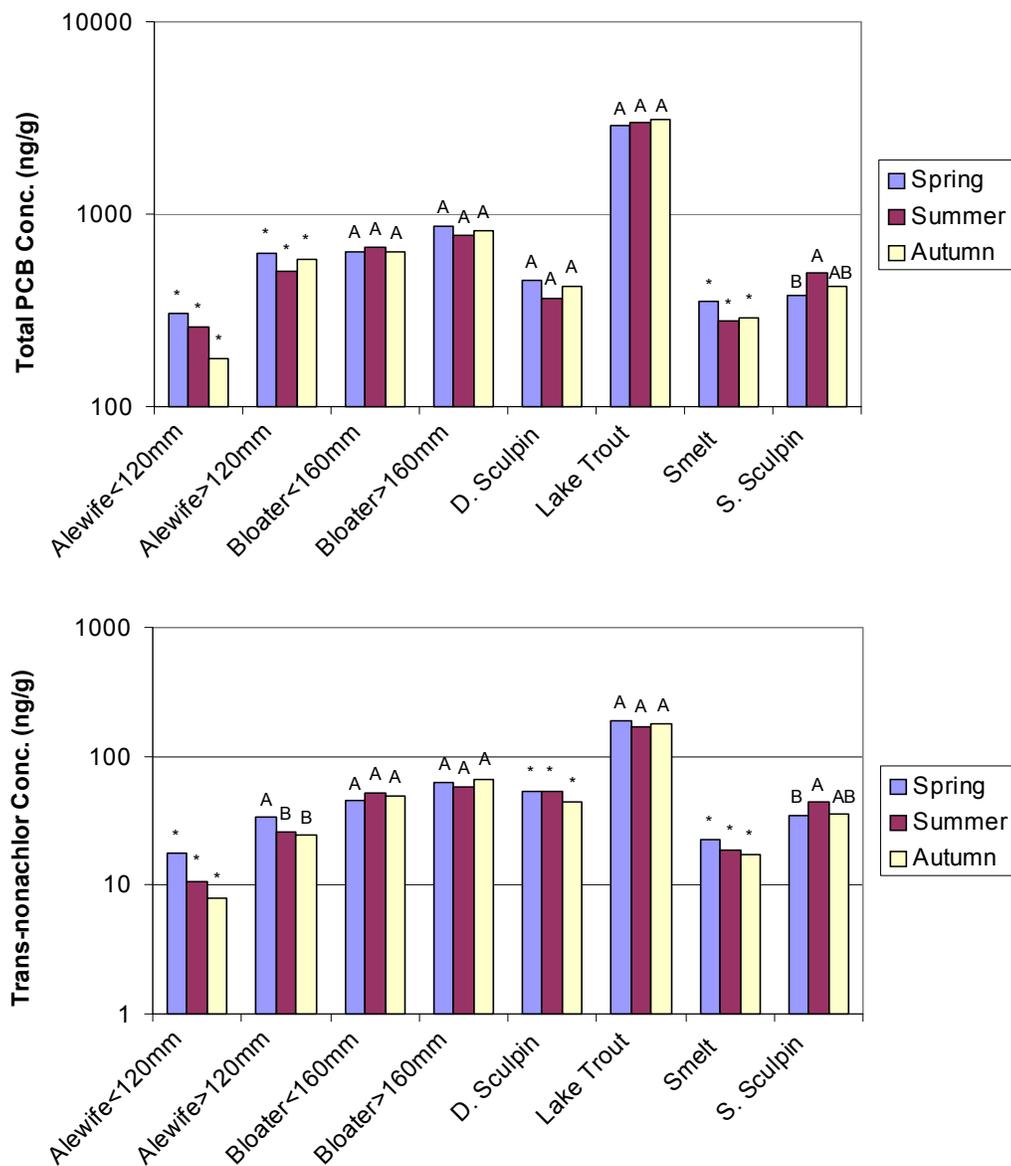
8.1.4 Seasonal Variation

Two-way analysis of variance (accounting for sampling station and season) revealed few significant differences in contaminant concentrations among the three sampling seasons (spring, summer, and autumn). No significant differences among season were observed for bloater chub, deepwater sculpin, and lake trout total PCB concentrations. Total PCB concentrations in slimy sculpin were significantly higher in summer than in spring. For alewife and smelt, there was significant interaction between the effects of season and station. At Sturgeon Bay, small alewife contained significantly higher PCB concentrations during the summer than during autumn, and smelt contained significantly higher PCB concentrations during spring and summer than during autumn. At Port Washington, large alewife contained significantly higher PCB concentrations during spring than during summer. At Saugatuck, small alewife and smelt contained significantly higher PCB concentrations during spring than in summer or autumn.

For *trans*-nonachlor, significant differences in contaminant concentrations among the three sampling seasons were observed for some species but not for others. *trans*-Nonachlor concentrations in bloater chub and lake trout did not differ significantly between seasons. Large alewife contained significantly higher *trans*-nonachlor concentrations in spring than in summer or autumn, and slimy sculpin contained significantly higher *trans*-nonachlor concentrations in summer than in spring. For small alewife, deepwater sculpin, and smelt, there was significant interaction between the effects of season and station. At Sturgeon Bay, small alewife, deepwater sculpin, and smelt contained significantly higher *trans*-nonachlor concentrations during the spring and summer than during autumn. At Port Washington, small alewife contained significantly higher *trans*-nonachlor concentrations during spring than during autumn, and deepwater sculpin contained significantly higher *trans*-nonachlor concentrations during summer than spring or autumn. At Saugatuck, small alewife contained significantly higher *trans*-nonachlor concentrations during spring than in summer or autumn, and smelt contained significantly higher *trans*-nonachlor concentrations during spring and summer than autumn.

In conclusion, most fish species did not show significant differences in fish contamination levels among seasons. Those significant differences that were observed also were relatively small in comparison to species differences and differences due to fish length or lipid content. As described for site variations, differences in fish contamination levels among seasons also could be due to differences in fish size or lipid content during the various seasons or differences in fish diet throughout the changing seasons.

Figure 8-5. Total PCB and *trans*-Nonachlor Concentrations in Lake Michigan Fish during Spring, Summer, and Autumn



Bars with the same letter were not statistically different (at alpha = 0.05). Bars with an asterisk indicate that there was significant interaction between the effects of station and season.

8.1.5 Bioaccumulation

Persistent organic pollutants, such as PCBs and *trans*-nonachlor, typically accumulate in living organisms above concentrations found in the water. This accumulation is due to the preferred partitioning of hydrophobic organic contaminants in organic tissues (such as lipids) over water, uptake from food, and/or reduced metabolism and elimination of persistent contaminants. The degree of accumulation is often quantified by a bioaccumulation factor, which is the ratio of the concentration of pollutant in an organism to the concentration of that pollutant in the water. When pollutants are increasingly accumulated with each trophic level of a food chain (or biomagnified), a biomagnification factor can be used to quantify the degree of accumulation from one trophic level to the next. A biomagnification factor is the ratio of the

concentration of pollutant in organisms at a particular trophic level to the concentration of that pollutant in the next lowest trophic level.

To evaluate the degree of accumulation of PCBs and *trans*-nonachlor in fish species of Lake Michigan, bioaccumulation factors were calculated for each species (Table 8-8). Bioaccumulation factors were calculated as the mean dry-weight concentration in fish divided by the lake-wide mean concentration in Lake Michigan. Concentrations of total PCBs in fish were generally 10^6 to 10^7 times higher than dissolved concentrations of PCBs in Lake Michigan water, which averaged 0.18 ng/L (or 0.00018 ng/g). Bioaccumulation factors for total PCBs from water to fish ranged from 5.5×10^6 for small alewife (<120mm) to 4.3×10^7 for lake trout. Bioaccumulation factors were generally lower for the less-chlorinated PCB congeners and higher for the more-chlorinated congeners. Bioaccumulation factors for PCB 33 ranged from 6.8×10^4 to 9.4×10^6 , while bioaccumulation factors for PCB 180 ranged from 4.7×10^7 to 5.6×10^8 . *trans*-Nonachlor accumulation was of the same magnitude as total PCB accumulation in fish. Bioaccumulation factors for *trans*-nonachlor ranged from 8.7×10^6 to 8.3×10^7 .

Table 8-8. Bioaccumulation Factors for PCBs and *trans*-Nonachlor in Lake Michigan Fish

Species/Size Category	Bioaccumulation Factor				
	PCB 33	PCB 118	PCB 180	Total PCBs	<i>trans</i> -Nonachlor
Alewife<120mm	3.8×10^6	1.4×10^7	4.7×10^7	5.5×10^6	8.7×10^6
Alewife>120mm	9.4×10^6	3.5×10^7	1.2×10^8	1.2×10^7	1.8×10^7
Bloater<160mm	1.8×10^6	4.4×10^7	2.0×10^8	1.4×10^7	3.2×10^7
Bloater>160mm	1.5×10^6	5.1×10^7	1.9×10^8	1.5×10^7	3.5×10^7
Coho-Adult	7.0×10^6	5.2×10^7	1.8×10^8	1.6×10^7	2.4×10^7
Deepwater Sculpin	6.8×10^4	5.5×10^7	2.4×10^8	9.1×10^6	3.5×10^7
Lake Trout	9.2×10^6	1.4×10^8	5.6×10^8	4.3×10^7	8.3×10^7
Smelt	7.9×10^5	2.8×10^7	8.2×10^7	7.5×10^6	1.5×10^7
Slimy Sculpin	8.8×10^5	3.5×10^7	1.5×10^8	9.1×10^6	2.5×10^7

To evaluate the accumulation and transfer of PCBs and *trans*-nonachlor between trophic levels within the upper pelagic food web, biomagnification factors were calculated. Biomagnification factors were calculated between forage fish species (alewife, bloater chub, sculpin, and smelt) and piscivorous fish species (lake trout and coho salmon). Total PCB biomagnification factors from forage fish to piscivorous fish were 1.6 and 4.2 for coho salmon and lake trout, respectively. *trans*-Nonachlor biomagnification factors from forage fish to piscivorous fish were 0.96 and 3.4 for coho salmon and lake trout, respectively. As evidenced by the biomagnification factor of less than one (<1) for coho salmon, *trans*-nonachlor was not biomagnified in the trophic transfer from forage fish to coho salmon.

8.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the PCBs and *trans*-nonachlor monitoring portion of the study are further described in Section 2.7 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of the quality of fish PCB and *trans*-nonachlor data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.7, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 8-9 provides a summary of flags applied to the fish PCB and *trans*-nonachlor data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.7. Compared to other matrices, the percentage of results that were qualified for these criteria is relatively small. No results were qualified as invalid, thus all results are represented in the analysis of fish PCB and *trans*-nonachlor concentrations presented in this report.

PIs used surrogate spikes to monitor the bias of the analytical procedure. The PCB and *trans*-nonachlor results were corrected for the recoveries of the surrogates. Only 8 to 9% of PCB and *trans*-nonachlor results were qualified for surrogate recovery problems (Table 8-9). Each of these samples was flagged for surrogate recoveries that exceeded the upper MQO of 130% recovery. Laboratory matrix spike samples also were used to monitor analytical bias. Only 2% of PCB 118, PCB 180, and *trans*-nonachlor samples were flagged for associated failed laboratory matrix spikes that exceeded the upper MQO of 120% recovery. Performance check samples also were used to monitor analytical bias. For PCB 180, 5% of samples were flagged for associated failed performance check samples, and 20% of *trans*-nonachlor samples were flagged for associated failed performance check samples. Based on an analysis of matrix spikes, standard reference material recovery, blank contamination, and other internal QC data, no samples were qualified by the PI and QC coordinators as high or low biased.

Laboratory blanks of sodium sulfate were used to investigate the possibility of contamination. Corn oil was added to the laboratory blanks after June 1996 to better represent the fish matrix. No total PCB results for laboratory blanks were greater than 0.10 µg, and all field sample results exceeded laboratory blank concentrations by a factor of 50, therefore no sample results were qualified for failed blanks or suspected contamination.

Duplicate samples were analyzed to evaluate the precision of analytical results. No field duplicates were collected for the fish matrix, however, laboratory duplicates were analyzed at a frequency of one per extraction batch. No results were flagged for duplicate results that exceeded the MQO of a 40% relative percent difference.

Table 8-9. Summary of Routine Field Sample Flags Applied to Select PCB Congeners and *trans*-Nonachlor in Fish

Analyte	Flags								
	Contamination	Sensitivity	Precision	Bias					Invalid
	FBK	UND	FDL	FMS	FSS	LOB	HIB	FPC	INV
PCB 33	0	62% (490)	NA	NA	9% (70)	0	0	NA	0
PCB 118	0	0.1% (1)	NA	2% (17)	8% (64)	0	0	NA	0
PCB 180	0	0	0	2% (12)	8% (64)	0	0	5% (40)	0
<i>trans</i> -Nonachlor	0	0	0	2% (19)	8% (64)	0	0	20% (158)	0

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

- FBK = Failed blank (A related blank had a measurable value above the established QC limit when the blank was analyzed using the same equipment and analytical method. Reported value may be suspect.)
- UND = Analyte not detected (Analyte produced no instrument response above noise.)
- FDL = Failed laboratory duplicate (A laboratory duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- FMS = Failed matrix spike (A matrix spike associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- FSS = Failed surrogate (Surrogate recoveries associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- LOB = Likely biased low (Reported value is probably biased low as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery or other internal lab QC data. Reported value is not considered invalid.)
- HIB = Likely biased high (Reported value is probably biased high as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery, blank contamination, or other internal lab QC data. Reported value is not considered invalid.)
- FPC = Failed performance check (A laboratory performance check sample associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
- INV = Invalid (Reported value is deemed invalid by the QC Coordinator.)
- NA = Not applicable. The relevant QC sample (e.g., duplicate, matrix spike, performance check) was not prepared or analyzed for this specific analyte.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, analytical precision was estimated as the mean relative percent difference (RPD) between the results for laboratory duplicate pairs. Table 8-10 provides a summary of data quality assessments for several of these attributes for fish data.

System precision could not be estimated for the analysis of fish tissue data because field duplicates were not collected for this matrix. While system precision was not estimated, analytical precision was estimated from the results of laboratory duplicates. Analytical precision for fish PCB and *trans*-nonachlor analysis was very good, with RPDs of only 5.3 and 6.9% for duplicate PCB 180 and *trans*-nonachlor results, respectively. Laboratory duplicates were not analyzed for PCB 33 or PCB 118.

Analytical bias was evaluated by calculating the mean recovery of laboratory matrix spike samples (LMS). Analytical bias was very low, with mean LMS recoveries of 99%, 98% and 90% for PCB 118, PCB 180, and *trans*-nonachlor, respectively. Laboratory matrix spike samples were not analyzed for PCB 33.

Analytical sensitivity was evaluated by calculating the percentage of samples reported below the MDL. No *trans*-nonachlor or PCB 180 results were below the MDL, and only 0.1% of PCB 118 results were below the MDL. For less-chlorinated PCB congeners, such as PCB 33, a majority of sample results were below the MDL. For PCB 33, 81% of 793 samples were reported below the MDL. Results from these samples were not censored and were used as reported in the analysis of fish contamination presented in this report.

Table 8-10. Data Quality Assessment for Select PCB Congeners and *trans*-Nonachlor in Fish Samples

Analyte/Number Field Samples	Parameter	Number of QC samples	Assessment
PCB 33 (793 samples)	Analytical Precision - Mean Lab Duplicate RPD (%), > 5 * MDL	-	NA
	Analytical Bias - Mean Lab Matrix Spike Recovery (%)	-	NA
	Analytical Sensitivity - Samples Reported as < MDL (%)	-	81%
PCB 118 (796 samples)	Analytical Precision - Mean Lab Duplicate RPD (%), > 5 * MDL	-	NA
	Analytical Bias - Mean Lab Matrix Spike Recovery (%)	82 lab matrix spike samples	99%
	Analytical Sensitivity - Samples Reported as < MDL (%)	-	0.1%
PCB 180 (795 samples)	Analytical Precision - Mean Lab Duplicate RPD (%), > 5 * MDL	83 lab duplicate pairs	5.3%
	Analytical Bias - Mean Lab Matrix Spike Recovery (%)	82 lab matrix spike samples	98%
	Analytical Sensitivity - Samples Reported as < MDL (%)	-	0%
<i>trans</i> -Nonachlor (796 samples)	Analytical Precision - Mean Lab Duplicate RPD (%), > 5 * MDL	83 lab duplicate pairs	6.9%
	Analytical Bias - Mean Lab Matrix Spike Recovery (%)	82 lab matrix spike samples	90%
	Analytical Sensitivity - Samples Reported as < MDL (%)	-	0%

RPD = Relative percent difference

MDL = Method detection limit

NA = Not applicable. Laboratory matrix spike samples were not analyzed for PCB 33 and laboratory duplicates were not analyzed for PCB 33 or PCB 118.

8.3 Data Interpretation

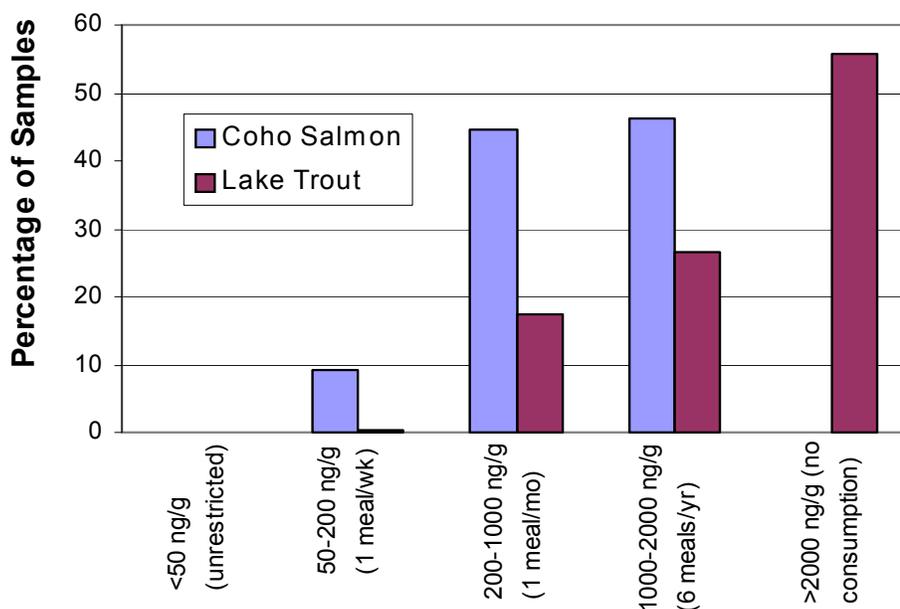
8.3.1 Comparison to Fish Advisory Levels

The Food and Drug Administration has set a tolerance level of 2000 ng/g (2 ppm) for PCBs in fish for human consumption (21 CFR 109.30). Consistent with this tolerance level, the Great Lakes Fish Consumption Advisory Task Force has set a fish advisory category of “no consumption” at PCB levels above 2000 ng/g. Of the Lake Michigan fish analyzed in the LMMB Study, only lake trout contained PCBs above the 2000 ng/g level. In fact, 56% of lake trout samples exceeded this tolerance level, and the mean total PCB concentration for Lake Michigan lake trout was 3000 ng/g (or 3 ppm), which is 50% above the 2000 ng/g tolerance level.

Figure 8-6 shows the percentages of lake trout and coho salmon samples falling into the various Great Lakes fish advisory categories. No coho salmon or lake trout samples fell into the unrestricted consumption category. Coho salmon primarily fell into the 1 meal/mo and 6 meals/yr categories. These categories contained 46% and 44% of coho salmon samples, respectively, with only 9% of coho salmon samples falling into the 1 meal/wk category. Lake trout primarily fell into the no consumption category (56%), with only 0.4%, 17%, and 26% in the 1 meal/wk, 1 meal/mo, and 6 meals/yr categories, respectively.

PCB contamination in fish is positively correlated with fish length, so fish advisories are tied to the size of the fish collected. Based on the regression equation developed from LMMB Study data (Figure 8-3), Lake Michigan lake trout above 575 mm were estimated to exceed the 2000 ng/g FDA tolerance level. Lake trout between 425 and 575 mm would fall into the 6 meals/yr advisory category, and lake trout below 425 mm would generally fall into the 1 meal/mo advisory category. Only one lake trout sample contained less than 200 ng/g (0.2 ppm) total PCBs.

Figure 8-6. Percentage of Lake Michigan Coho Salmon and Lake Trout Samples within each PCB Fish Advisory Category



8.3.2 Comparison to Historical Studies

DeVault *et al.* (1996) and others (Miller *et al.*, 1992; Huestis *et al.*, 1996; Stow *et al.*, 1995) have observed dramatic declines in PCB concentrations in Great Lakes fish since the early 1970s. In Lake Michigan lake trout, mean PCB concentrations declined from 23000 ng/g in 1974 to 2590 ng/g by 1986. Between 1986 and 1992, there was little change in concentrations, with 3490 ng/g observed in 1992. Total PCB concentrations in lake trout measured in the LMMB Study during 1994 and 1995 fit well with this trend. Total PCBs in lake trout analyzed in the LMMB Study averaged 3000 ng/g, which is consistent with the 2590 to 3490 ng/g range of mean total PCB concentrations observed from 1986 to 1992. DeVault *et al.* (1996) hypothesized that the leveling of lake trout PCB concentrations since 1986 (versus continuing decreases) could be due to significant changes in food web structure during that time that has led to increased bioaccumulation. DeVault *et al.* (1996) suggested that the introduction of the predacious cladoceran, *Bythotrephes cederstroemi*, in the early 1980s added an additional trophic level in the pelagic food chain (phytoplankton > zooplankton > *Bythotrephes* > forage fish > lake trout), thus increasing bioaccumulation at trophic levels above this insertion.

Hesselberg *et al.* (1990) measured similar decreases in PCB concentrations in Lake Michigan bloater from 1976 to 1986. Total PCB concentrations in bloater decreased from 5700 ng/g in 1972 to 1640 ng/g in 1986. By 1994 and 1995, total PCB concentrations in bloater were half of the 1986 levels. Total PCB concentrations measured in the LMMB Study averaged 650 ng/g in small bloater chub and 830 ng/g in large bloater chub.

Similar decreases in total PCB concentrations since the early 1970s have been observed for all Lake Michigan fish species (Stow *et al.*, 1995) and for fish species in other Great Lakes. DeVault *et al.* (1996) reported significant decreases in PCB concentrations in lake trout from Lakes Superior, Huron, and Ontario. In Lake Ontario, Huestis *et al.* (1996) observed declines in lake trout PCB levels of 80% between 1977 and 1993, from 9060 ng/g in 1977 to 1720 ng/g in 1993. In contrast, however, Borgmann and Whittle (1992) found no significant temporal trend from 1977 to 1988 in total PCB concentrations in Lake Ontario smelt and sculpin.

trans-Nonachlor concentrations in Lake Michigan fish species were not measured routinely prior to 1986 (DeVault *et al.*, 1996). From 1986 to 1992, *trans*-nonachlor concentrations in Lake Michigan lake trout averaged 220 to 190 ng/g (DeVault *et al.*, 1996). *trans*-Nonachlor concentrations measured in 1994 and 1995 during the LMMB Study were only slightly lower, at 180 ng/g, indicating that like total PCB concentrations, *trans*-nonachlor concentrations in Lake Michigan lake trout have remained relatively constant since the mid 1980s.

8.3.3 Regional Considerations

Among the Great Lakes, concentrations of PCBs in lake trout were highest in Lake Michigan (DeVault *et al.*, 1996). From 1986 to 1992, mean PCB concentrations in Lake Michigan lake trout ranged from 2590 to 3490 ng/g. Mean PCB concentrations ranged from 240 to 450 ng/g in Lake Superior trout, 1170 to 1570 ng/g in Lake Huron trout, 2180 to 2890 ng/g in Lake Ontario trout, and 1320 to 2200 ng/g in Lake Erie walleye (DeVault *et al.*, 1996).

In 1994, Kucklick and Baker (1998) measured PCBs and *trans*-nonachlor in the Lake Superior food web. Total PCB concentrations ranged from 130 to 180 ng/g in bloater, from 42 to 52 ng/g in deepwater sculpin, from 42 to 46 ng/g in slimy sculpin, and from 82 to 160 in lake trout. In Lake Michigan, bloater chub, deepwater sculpin, slimy sculpin, and lake trout measured in the LMMB Study contained up to 5 times, 23 times, 17 times, and 93 times the total PCB concentrations measured in Lake Superior fish species, respectively. *trans*-Nonachlor concentrations in Lake Superior ranged from 18 to 27 ng/g in

bloater, from 7.6 to 12 ng/g in deepwater sculpin, from 6.9 to 7.6 ng/g in slimy sculpin, and from 9.7 to 21 ng/g in lake trout. In Lake Michigan, *trans*-nonachlor concentrations in these same species ranged from 4 to 32 times the levels measured in Lake Superior fish.

Total PCB concentrations measured in Lake Michigan fish also were higher than reported levels in fish from numerous other lakes and water bodies. Harding *et al.* (1997) measured total PCB concentrations of 155 ng/g wet-weight in the Gulf of St. Lawrence. In 19 Swedish lakes, Berglund *et al.* (2000) measured a mean total PCB concentration of 55 ng/g dry-weight. In the relatively remote Lake Tahoe, Datta *et al.* (1998) measured 9 to 14 ng/g total PCBs in lake trout. This is up to 1000 times lower than PCB contamination of lake trout in Lake Michigan.

8.3.4 Factors Affecting Contaminant Concentrations

In the LMMB Study, fish contamination levels were primarily affected by species. Within species, contaminant levels were significantly affected by fish length, lipid content, location, and season, but the effect of these factors differed by species. In an evaluation of 20 years of data, Stow (1995) similarly observed that the variability in fish PCB concentrations were explained by year, species, location, length, and length/species effects.

For most species, fish length was strongly correlated with contaminant concentration (Table 8-6). This effect has been commonly reported by other researchers (Stow, 1995; Harding *et al.*, 1997; Huestis *et al.*, 1996), and is likely due to increased contaminant exposure with increasing fish age. Researchers, however, have differed on the importance of fish lipid content in controlling fish contaminant levels. Harding *et al.* (1997) found that the best predictors of PCB contamination in fish were lipid content, followed by size and age. Kucklick and Baker (1998) also determined that lipid content of organisms in the Lake Superior food web explained 81% of the variability in wet-weight total PCB concentrations, with trophic position exerting a smaller influence. The main influence of trophic position on total PCB concentrations was shown to be due to the concurrent increase in lipid content with trophic position.

In contrast, Jackson and Schindler (1996) and Jackson *et al.* (2001) found little evidence of a relationship between PCB concentration and lipid content within species. Stow (1995) also found that after controlling for year, species, location, length, and length/species effects, lipid content showed no relationship with PCB concentrations. In the LMMB Study, the effects of length and lipid content on fish contamination levels varied by species. For some species (lake trout and alewife), lipid content did not significantly affect fish contamination levels. For other species (slimy sculpin), lipid content did significantly affect fish contamination levels and fish length did not. For most species, however, both length and lipid content, or an interaction of the two parameters, significantly affected fish contamination levels.

8.3.5 Bioaccumulation and Trophic Transfer

In the LMMB Study, five forage fish species and two piscivorous fish species were analyzed for contaminant concentrations. Bioaccumulation and biomagnification of PCBs and *trans*-nonachlor within these fish species are discussed here, and bioaccumulation and biomagnification within the entire Lake Michigan food web are discussed in Chapter 9. PCBs and *trans*-nonachlor significantly accumulated in Lake Michigan fish species above concentrations in the water column. Bioaccumulation factors from water to fish ranged from 10^6 to 10^7 , depending upon the species and the PCB congener. This is comparable, but slightly higher than, bioaccumulation factors of 10^4 to 10^7 measured by Oliver and Niimi (1988) in Lake Ontario. Bioaccumulation factors also were higher for fish than for plankton (see Chapter 7).

Within the upper pelagic food web (fish), PCBs and *trans*-nonachlor were biomagnified in the trophic transfer from forage fish species to some piscivorous fish. Among the fish species investigated, the piscivorous lake trout accumulated significantly higher levels of PCBs and *trans*-nonachlor than any of the forage fish species. This was true regardless of whether comparisons were made on a wet-weight, dry-weight, or lipid-normalized basis. Biomagnification factors between forage fish species and lake trout were 4.2 for total PCBs and 3.4 for *trans*-nonachlor. The piscivorous coho salmon, however, accumulated significantly higher levels of PCBs and *trans*-nonachlor only when analyzed on a lipid-normalized basis. Biomagnification factors between forage fish and coho salmon (on a dry-weight basis) were below 1 for *trans*-nonachlor and near 1 for total PCBs (1.6), indicating that these contaminants were not significantly biomagnified in the trophic transfer from forage fish to coho salmon.

These findings are consistent with those of other researchers who have calculated higher PCB transfer efficiencies for lake trout than for coho salmon. Using data from 1975 to 1990, Jackson and Schindler (1996) calculated PCB transfer efficiencies of 55% for lake trout and 50% for coho salmon. Using LMMB Study data, Madenjian *et al.* (1998a) similarly estimated that coho salmon from Lake Michigan retained 50% of the PCBs that are contained within their food and lake trout retained 80% of PCBs from food (Madenjian *et al.*, 1998b). Madenjian *et al.* (1998a) suggested that higher transfer efficiencies in lake trout than coho salmon could be due to faster or more efficient gut uptake of PCBs in lake trout than coho salmon. Jackson and Schindler (1996) also suggested that the higher PCB concentrations in lake trout than other salmonids could be due to lower gross assimilation efficiencies for lake trout (~0.17) than for other salmonids (~0.23). (Gross assimilation efficiency is a measure of the rate at which an animal converts food into weight).

In conclusion, PCBs and *trans*-nonachlor were significantly accumulated in Lake Michigan fish. Accumulation was significantly greater in the predacious lake trout than in forage fish species, indicating classical biomagnification. Further evaluation of PCB and *trans*-nonachlor movement and accumulation in the Lake Michigan ecosystem will be provided through the modeling efforts that are the focus of the LMMB Study.

Chapter 9

Cross-Media Interpretations

9.1 Summary of PCB and *trans*-Nonachlor Concentrations in Lake Michigan Compartments

PCB and *trans*-nonachlor levels were measured in Lake Michigan air, water, sediment, tributaries, plankton, and fish. PCBs and *trans*-nonachlor were found throughout the Lake Michigan ecosystem. PCBs were detected above sample-specific detection limits in all samples collected from all ecosystem compartments except for tributaries (Table 9-1). Two percent of dissolved tributary samples and nine percent of particulate tributary samples did not contain detectable levels of PCBs (i.e., not even one PCB congener above its sample-specific detection limit). Within the various ecosystem compartments, an average of 30 to 92 different PCB congeners were detected above sample-specific detection limits (Table 9-1). *trans*-Nonachlor was less frequently detected than PCBs. Detection frequency of *trans*-nonachlor in environmental samples ranged from 29% in dry deposition to 100% in plankton and fish.

Table 9-1. Summary of Samples from each Ecosystem Compartment with Detectable Levels of PCBs and *trans*-Nonachlor

Ecosystem Compartment	Fraction	PCBs		<i>trans</i> -Nonachlor
		% Samples with PCBs Detected above SSDL ^a	Average Number of PCB Congeners Detected above SSDL ^a	% Samples with <i>trans</i> -Nonachlor Detected above SSDL ^a
Atmosphere	Vapor	100	59	65
	Particulate	100	35	20
	Precipitation	100	84	90
	Dry Deposition	100	30	29
Tributary	Dissolved	98	36	34
	Particulate	91	47	59
Open Lake	Dissolved	100	40	79
	Particulate	100	59	88
Sediment	–	100	74	72
Plankton	–	100	92	100
Fish	–	100	68	100

^a Sample-specific detection limit

Figure 9-1 shows the distribution of PCBs throughout the atmosphere, tributaries, water column, and sediments of Lake Michigan. Vapor-phase total PCB concentrations averaged from 21 to 2600 pg/m³ at shoreline and over-water sampling stations. Higher atmospheric total PCB concentrations were generally found above the southern Lake Michigan basin and southern shoreline, with the highest atmospheric concentration observed at the IIT Chicago site (Figure 9-1). Lower atmospheric concentrations were generally observed above the central and northern regions of the lake, however, some northern stations such as Beaver Island maintained higher concentrations. Particulate-phase total PCB concentrations were much lower than vapor-phase concentrations, averaging from 0.37 to 91 pg/m³ at shoreline and over-water sampling stations. At individual stations, average particulate-phase total PCB concentrations were

only 0.03% to 8.2% of vapor-phase concentrations. In precipitation, total PCB concentrations averaged from 360 to 16000 pg/L at shoreline and over-water sampling stations, with the highest average precipitation concentration at the IIT Chicago site. Average total PCB concentrations in precipitation at all of the stations were greater than the average dissolved total PCB concentration in Lake Michigan, and average precipitation concentrations at the IIT Chicago site were higher than dissolved total PCB concentrations in all of the tributaries except for the Grand Calumet and Sheboygan Rivers.

In Lake Michigan tributaries, total PCB concentrations averaged from 0.43 to 35 ng/L in the dissolved phase and from 0.25 to 55 ng/L in the particulate phase. Total PCB concentrations were highest in the more urban and industrialized watersheds (Fox, Sheboygan, Milwaukee, Grand Calumet, and Kalamazoo Rivers). In these tributaries, total PCB concentrations in the dissolved and particulate phases averaged more than 23 ng/L. The remaining tributaries, which are comprised of more agricultural and forested watersheds (Grand, Manistique, Menominee, Muskegon, Pere Marquette, and St. Joseph Rivers), all contained less than 2.9 ng/L of total PCBs.

Within the Lake Michigan water column, total PCB concentrations averaged 0.18 ng/L in the dissolved phase and 0.073 ng/L in the particulate phase. Dissolved total PCB concentrations were highest at the southern end of Green Bay (Figure 9-1), presumably due to the significant PCB load from the Fox River in combination with the reduced dilution available in Green Bay and limited mixing between Green Bay and Lake Michigan. Total PCB concentrations in the dissolved phase averaged as high as 0.653 ng/L at the lower end of Green Bay (Station GB17). Within Lake Michigan proper, total PCB concentrations in the dissolved phase averaged from 0.104 to 0.373 ng/L at the various sampling stations. Contour plots of dissolved phase total PCB concentrations indicate a general trend of higher concentrations in the southern Lake Michigan basin than in the northern basin. This observation is consistent with atmospheric concentrations over the lake, which also tend to be higher over the southern basin, particularly near Chicago (Figure 9-1).

Total PCB concentrations in surficial sediments of Lake Michigan ranged from 0.138 to 219 ng/g. Contour plots indicate that total PCBs are accumulating in the depositional and transitional regions of Lake Michigan (Figure 9-1). In particular, PCBs accumulate at relatively high concentrations (> 100 ng/g) along the eastern side of the southern basin, as well as at a few of the deeper stations in the southern and central basins. Among the lake's depositional and transitional zones, sediment PCB concentrations generally increase from north to south. Total PCB concentrations averaged 69.7 ng/g in the southern basin, 50.5 ng/g in the central basin, 41.6 ng/g in the northern basin, and 7.27 ng/g in the straits region. Only in the southern and central basins did total PCBs exceed 100 ng/g, and only in the southern basin did total PCBs exceed 150 ng/g. Increased PCB concentrations in the sediments of the southern basin are consistent with the increased atmospheric PCB concentrations above the southern basin and the larger number of urban and industrial sources surrounding the southern portions of the lake.

Figure 9-2 shows the distribution of *trans*-nonachlor throughout the atmosphere, tributaries, water column, and sediments of Lake Michigan. Vapor-phase *trans*-nonachlor concentrations averaged from 0 to 29 pg/m³ at shoreline and over-water sampling stations. Like total PCB concentrations, higher atmospheric *trans*-nonachlor concentrations were generally found above the southern Lake Michigan basin and southern shoreline, with the highest atmospheric concentration observed at the IIT Chicago site (Figure 9-2).

Figure 9-1. Concentrations of Total PCBs in the Atmosphere, Tributaries, Water Column, and Sediments of Lake Michigan

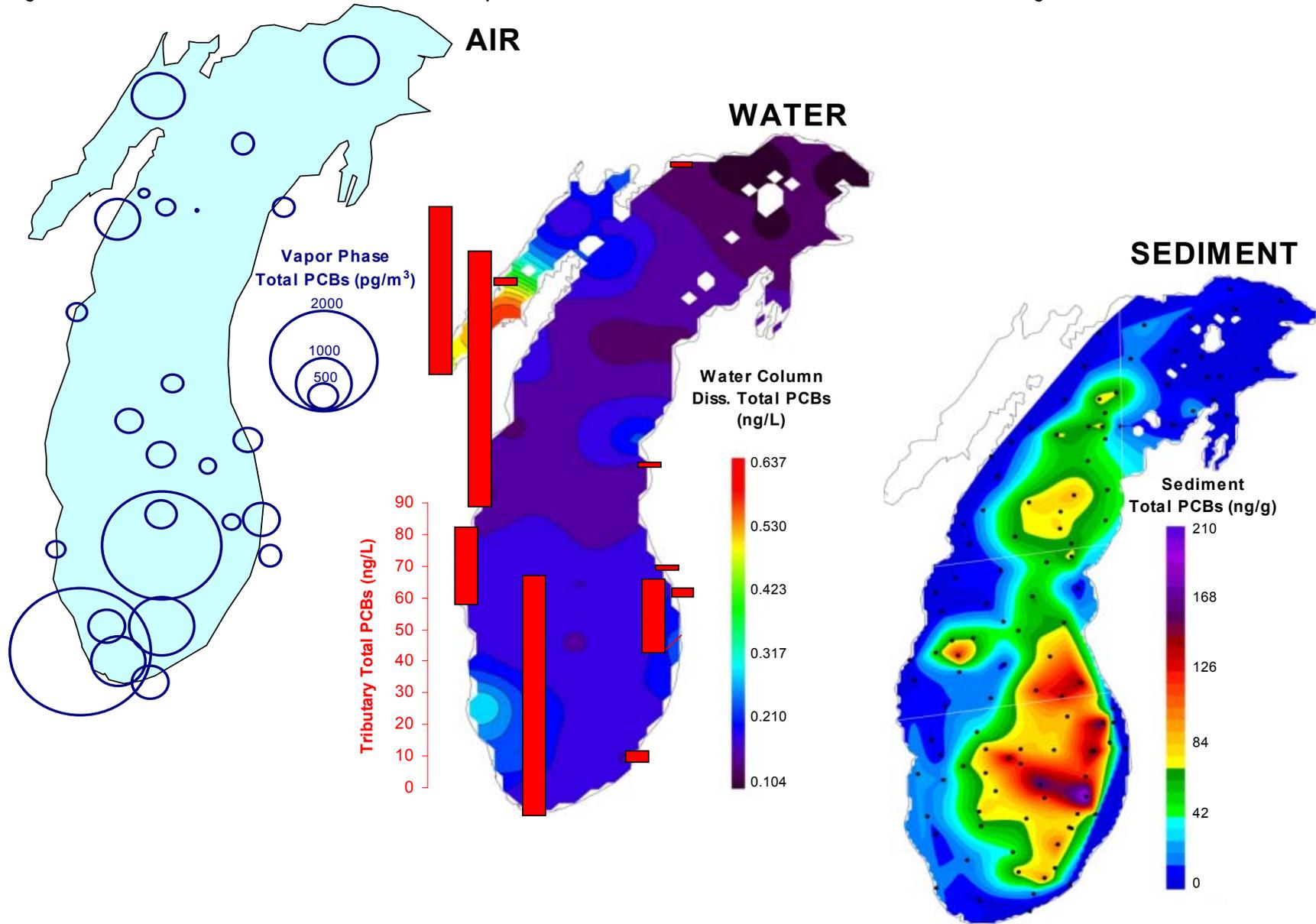
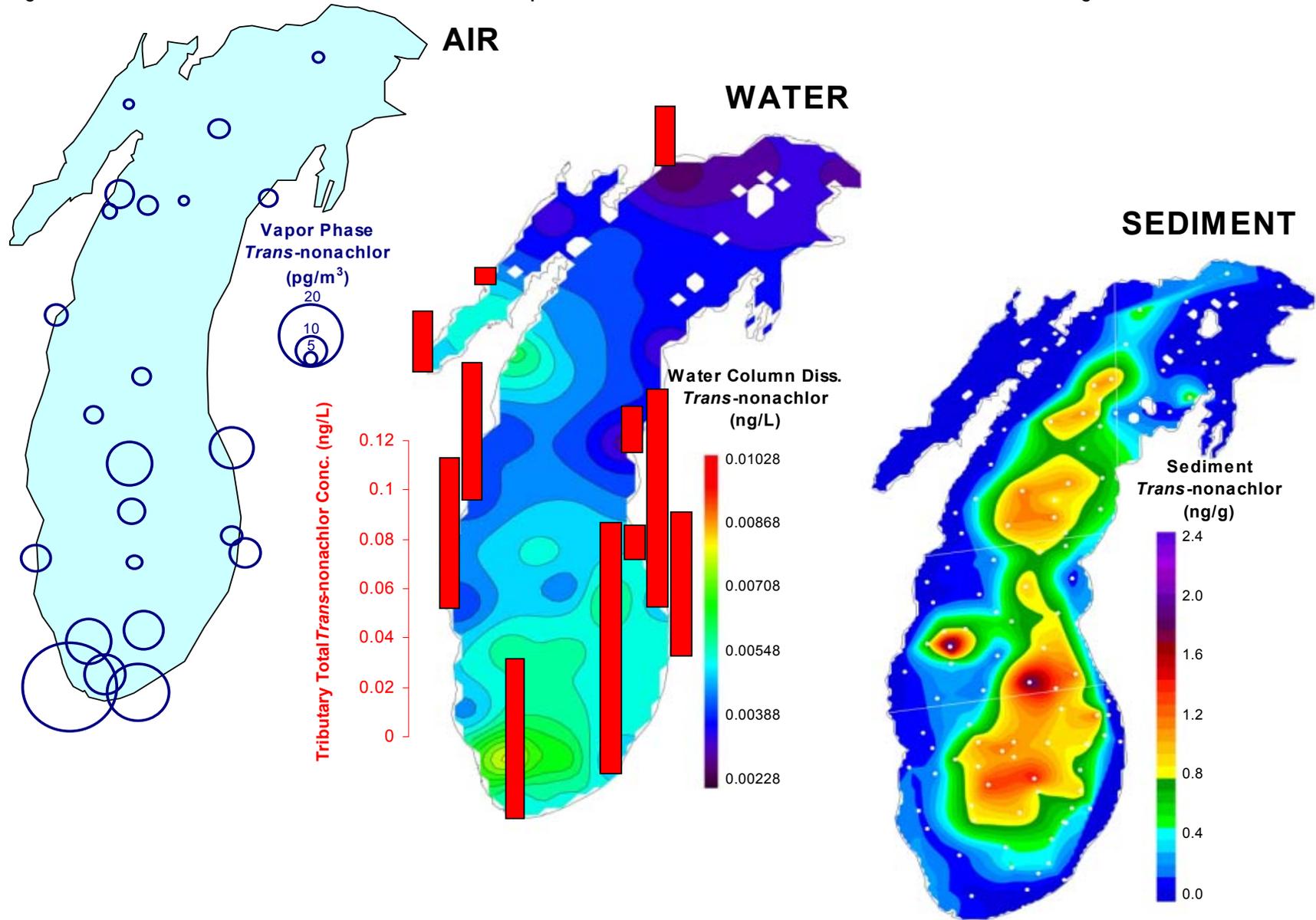


Figure 9-2. Concentrations of *trans*-Nonachlor in the Atmosphere, Tributaries, Water Column, and Sediments of Lake Michigan



Particulate-phase *trans*-nonachlor concentrations were much lower than vapor-phase concentrations, averaging from 0.16 to 1.8 pg/m³ at shoreline and over-water sampling stations. At individual stations, average particulate-phase *trans*-nonachlor concentrations were only 2.6% to 14% of vapor-phase concentrations. In precipitation, *trans*-nonachlor concentrations averaged from 0.0 to 100 pg/L at shoreline and over-water sampling stations, with the highest average precipitation concentration at the IIT Chicago site. Average *trans*-nonachlor concentrations in precipitation at all except three of the stations were greater than the average dissolved *trans*-nonachlor concentration in Lake Michigan, and average precipitation concentrations at the IIT Chicago site were higher than dissolved *trans*-nonachlor concentrations in all of the tributaries.

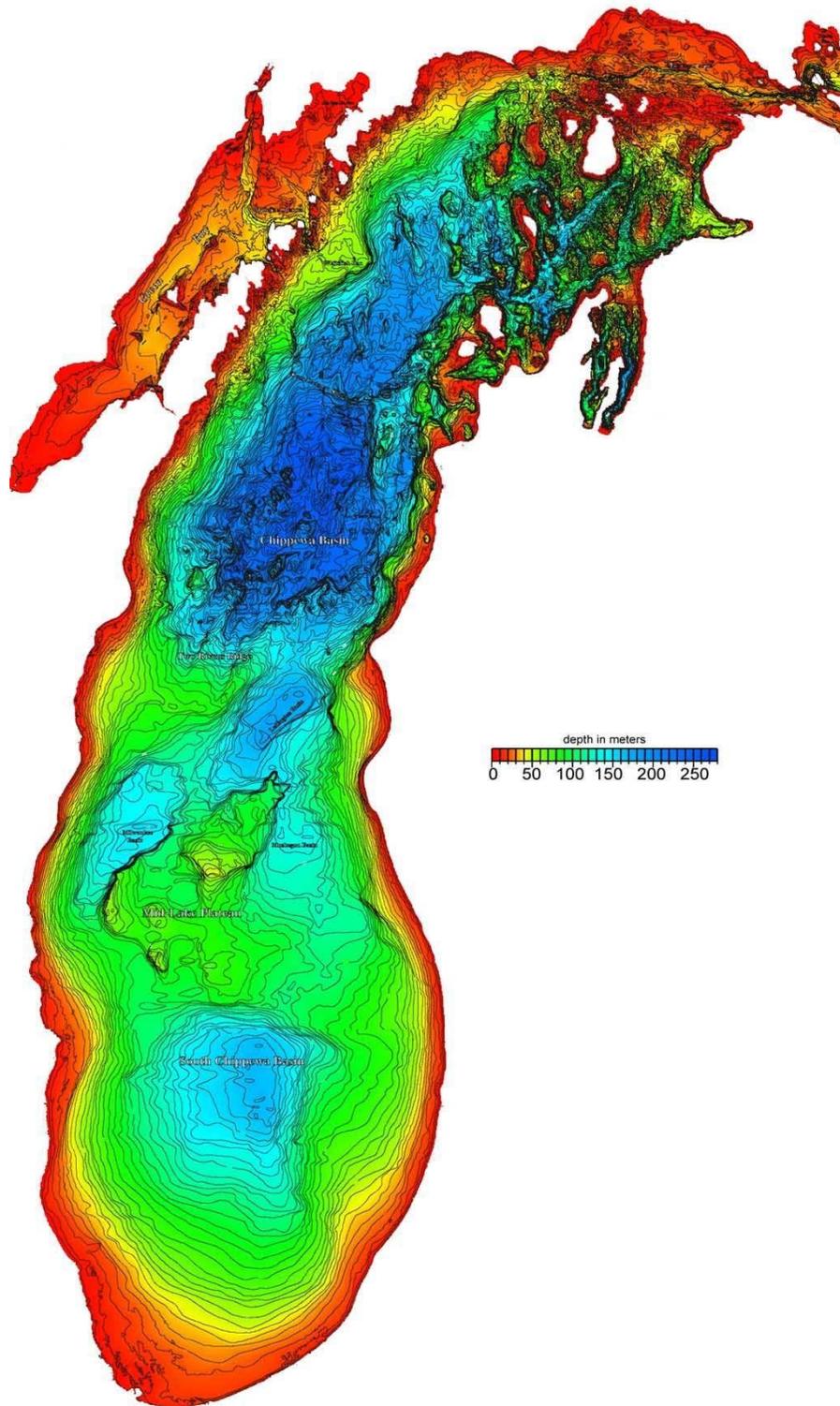
In Lake Michigan tributaries, *trans*-nonachlor concentrations averaged from 0.0033 to 0.026 ng/L in the dissolved phase and from 0.0028 to 0.074 ng/L in the particulate phase. Unlike PCBs, which were highest in urban and industrial influenced watersheds, *trans*-nonachlor concentrations were highest in the heavily agricultural watersheds of the St. Joseph and Grand Rivers. Mid-range *trans*-nonachlor concentrations were observed in the urban and industrial influenced watersheds of the Fox, Sheboygan, Milwaukee, Grand Calumet, and Kalamazoo Rivers; and the lowest *trans*-nonachlor concentrations were observed in the more forested watersheds of the Menominee, Manistique, Muskegon, and Pere Marquette Rivers.

Within the Lake Michigan water column, *trans*-nonachlor concentrations averaged 0.0058 ng/L in the dissolved fraction and 0.0021 ng/L in the particulate fraction. Among open-water sampling stations, dissolved *trans*-nonachlor concentrations averaged from 0.00228 to 0.0236 ng/L, with the highest concentration at Station 17 in the southern Lake Michigan basin (Figure 9-2). Contour plots of dissolved-phase *trans*-nonachlor concentrations indicate a general trend of higher concentrations in the southern Lake Michigan basin with isolated areas of high concentration in the northern basin. This observation is consistent with atmospheric concentrations over the lake, which also tend to be higher over the southern basin, particularly near Chicago (Figure 9-2). The apparent relationship between atmospheric and open-lake concentrations may suggest atmospheric deposition drives open-water concentrations, or it may suggest that *trans*-nonachlor may cycle between lake water and the atmosphere in manner similar to that proposed by Mackay and Patterson (1986) for PCBs (see Section 2.1.4).

trans-Nonachlor concentrations in surficial sediments of Lake Michigan ranged from 0.00250 to 2.830 ng/g. Contour plots indicate that *trans*-nonachlor is accumulating in the depositional and transitional regions of Lake Michigan (Figure 9-2). Unlike PCBs, *trans*-nonachlor does not exhibit elevated concentrations in the southern basin relative to the central and northern basins. *trans*-Nonachlor concentrations averaged 0.599 ng/g in the southern basin, 0.638 ng/g in the central basin, and 0.560 ng/g in the northern basin. Also unlike PCBs, *trans*-nonachlor is not preferentially accumulating along the eastern side of the southern basin. *trans*-Nonachlor is preferentially accumulated in the deeper regions of the lake just to the east and west of the mid-lake reef identified as the Port Washington biota box in this study (Figures 9-2 and 9-3).

Within living components of the Lake Michigan ecosystem, PCBs and *trans*-nonachlor were accumulated at concentrations higher than in any abiotic ecosystem component. PCBs and *trans*-nonachlor exhibited classical biomagnification, with concentrations increasing with increasing trophic level in the Lake Michigan food web (see Section 9.2). Accumulation of PCBs in top predator fish has reached levels of concern for human health and spawned fish consumption advisories throughout Lake Michigan and many Lake Michigan tributaries.

Figure 9-3. Lake Michigan Bathymetry

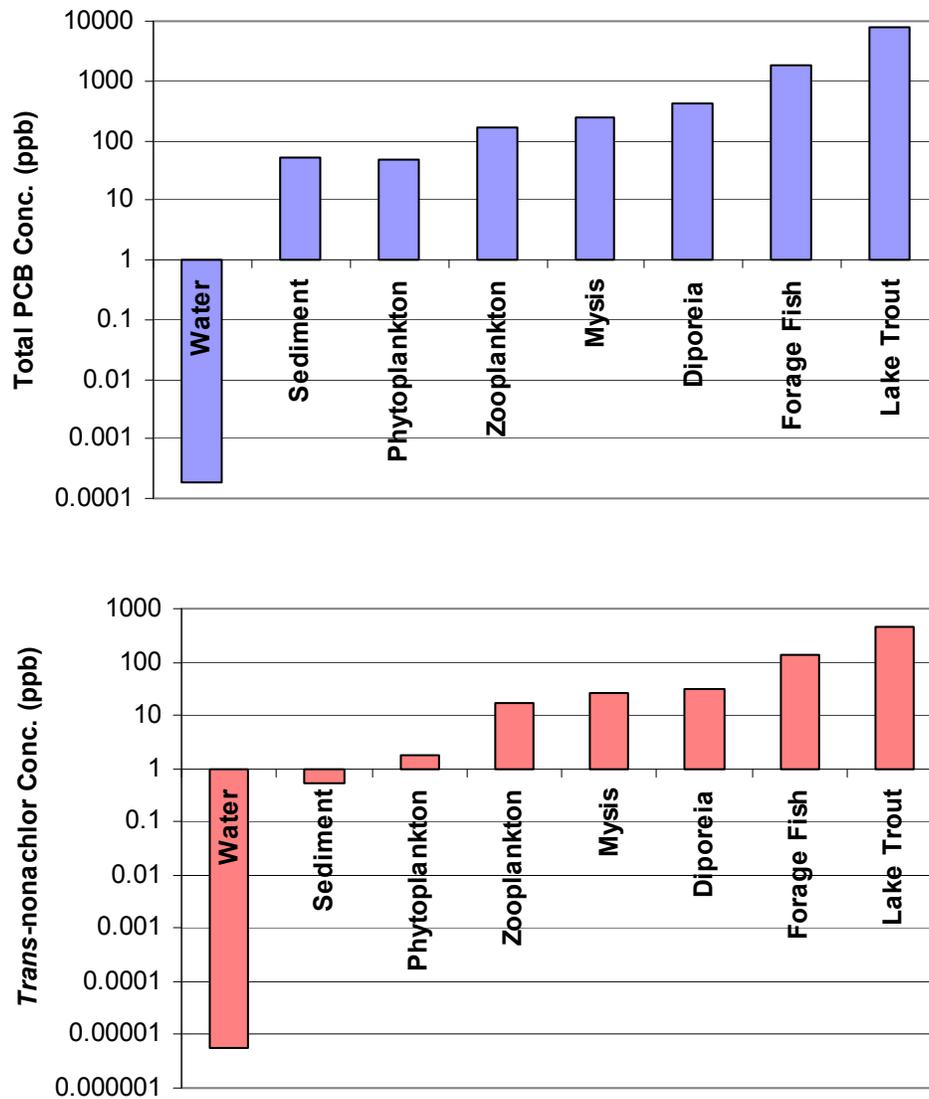


9.2 Bioaccumulation and Biomagnification

In the LMMB Study, classical bioaccumulation and biomagnification of PCBs and *trans*-nonachlor were observed. These hydrophobic and lipophilic contaminants were bioaccumulated in living tissue at levels well above water column or even sediment concentrations. Bioaccumulation factors for total PCBs ranged from 2.7×10^5 to 4.3×10^7 , and bioaccumulation factors for *trans*-nonachlor ranged from 3.0×10^5 to 8.3×10^7 .

Not only were PCBs and *trans*-nonachlor bioaccumulated in living tissue above water concentrations, but these contaminants were biomagnified within the Lake Michigan food web. PCB and *trans*-nonachlor concentrations increased with each successive trophic levels (Figure 9-4).

Figure 9-4. Total PCB and *trans*-Nonachlor Concentrations in Various Components of the Lake Michigan Ecosystem



Total PCB concentrations increased from 49 ng/g in phytoplankton to 170 ng/g in zooplankton, to 280 and 420 ng/g in *Mysis* and *Diporeia*, to 1900 ng/g in forage fish, to 7800 ng/g in the top predator, lake trout. *trans*-Nonachlor concentrations increased from 1.7 ng/g in phytoplankton, to 16 ng/g in zooplankton, to 25 and 32 ng/g in *Mysis* and *Diporeia*, to 140 ng/g in forage fish, to 480 ng/g in lake trout. From the bottom of the food web (phytoplankton) to the top of the food web (lake trout), total PCB concentrations increased by a factor of 160, and *trans*-nonachlor concentrations increased by a factor of 280.

Figure 9-5 shows the biomagnification factors between the various components of the Lake Michigan food web. The primary pelagic food web includes phytoplankton, zooplankton, forage fish, and lake trout. Biomagnification factors between each of these trophic levels varied from 3.4 to 11 for total PCBs and 3.4 to 9.5 for *trans*-nonachlor. For total PCBs, biomagnification was greatest from zooplankton to forage fish (11), with lower biomagnification from phytoplankton to zooplankton (3.4) and from forage fish to lake trout (4.2). For *trans*-nonachlor, biomagnification was high from phytoplankton to zooplankton (9.5) and from zooplankton to forage fish (8.6) and lower for forage fish to lake trout (3.4). Within this simplified pelagic food web, invertebrates such as *Mysis* may also play a role. *Mysis* may feed on herbivorous zooplankton, adding an additional trophic level to the pelagic food web, or they may be eaten directly by young top predators, effectively removing a trophic level.

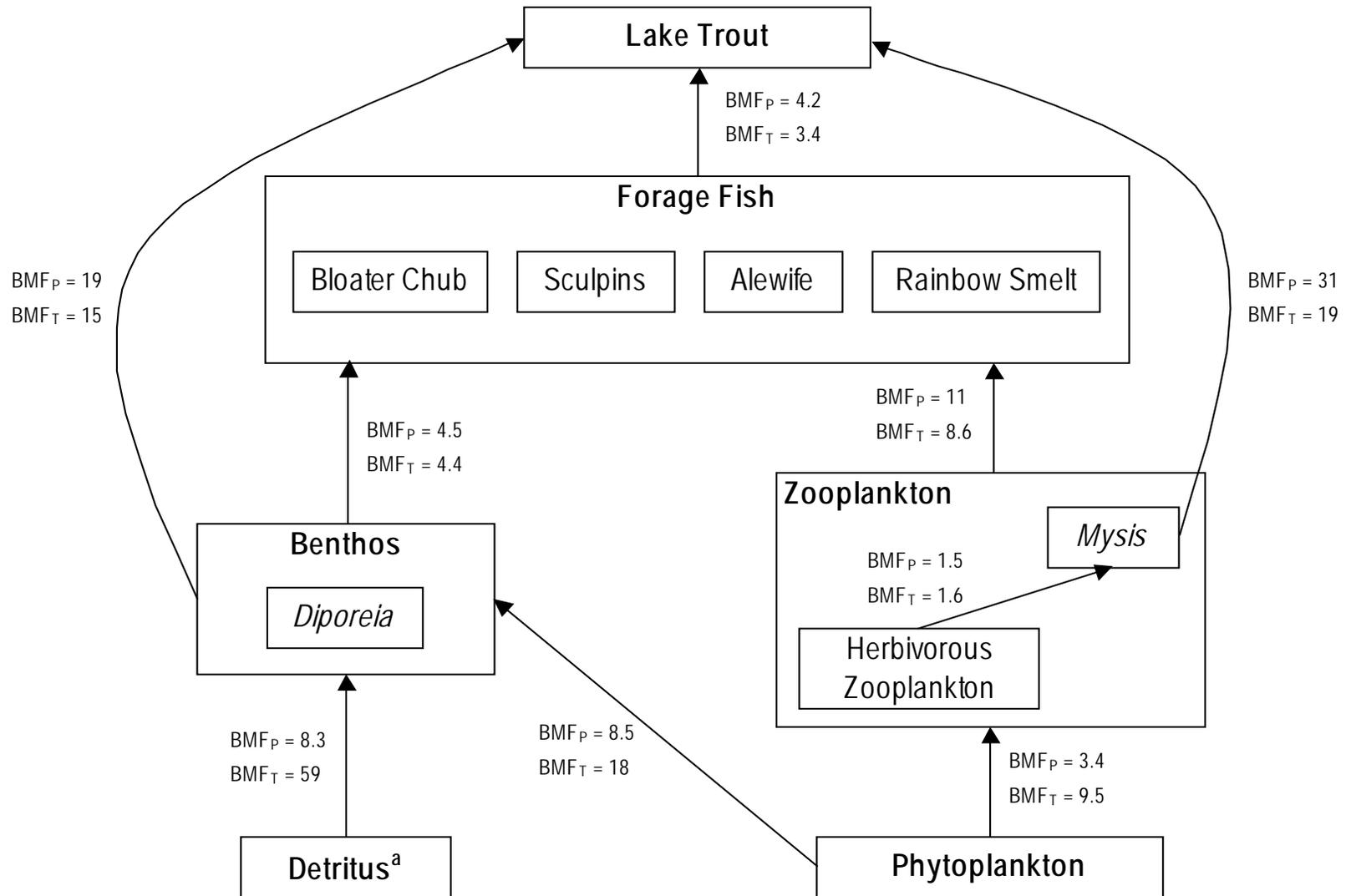
The simplified benthic food web consists of benthic invertebrates, such as *Diporeia*, that may feed on detritus or phytoplankton. The benthic invertebrates may then be preyed upon by bottom dwelling forage fish, which in turn may be preyed upon by lake trout. Within the benthic food web, biomagnification factors were greatest between phytoplankton and *Diporeia* (8.5 for PCBs and 18 for *trans*-nonachlor) and between detritus and *Diporeia* (8.3 for PCBs and 59 for *trans*-nonachlor). Biomagnification factors were lower between *Diporeia* and forage fish (4.5 for PCBs and 4.4 for *trans*-nonachlor) and between forage fish and lake trout (4.2 for PCBs and 3.4 for *trans*-nonachlor).

It should be noted that bioaccumulation and biomagnification factors for total PCBs calculated from this data are semi-quantitative. Total PCB concentrations were calculated from the sum of individual PCB congeners analyzed, and the number and the specific congeners analyzed differed among the sample matrices (water, plankton, and fish). This difference, however, should not affect conclusions concerning the biomagnification of PCBs in Lake Michigan, because water and lower trophic levels were analyzed for more PCB congeners than higher trophic levels. Total PCB concentrations in water, plankton, and fish represent 123, 126, and 93 individual or coeluting congeners analyzed for the respective matrices.

Similar to the PCB and *trans*-nonachlor biomagnification observed in the LMMB Study, Oliver and Niimi (1988) observed classical biomagnification of PCBs in the Lake Ontario food web. Oliver and Niimi (1988) observed increases in total PCB levels at each trophic level with an overall increase of 86 times from plankton to top predators. This is slightly lower than observed in Lake Michigan in the LMMB Study (factor of 160), however, Oliver and Niimi (1988) analyzed a mixture of phytoplankton and zooplankton to characterize the plankton compartment and analyzed a mixture of coho salmon, rainbow trout, and lake trout to characterize the top predator compartment. These approaches would tend to decrease the overall biomagnification measured by Oliver and Niimi (1988) in comparison to the LMMB Study data.

Koslowski *et al.* (1994) observed similar biomagnification of PCBs in the Lake Erie food web, and Kucklick and Baker (1998) observed similar biomagnification in Lake Superior. Both authors found increasing PCB concentrations with increasing trophic level. Through multiple linear regression and path analysis, Kucklick and Baker (1998) determined that the trophic level influenced PCB accumulation levels both directly and indirectly through its effect on lipid content.

Figure 9-5. Biomagnification Factors for Total PCBs (BMF_P) and *trans*-Nonachlor (BMF_T) in a Simplified Lake Michigan Food Web



^aConcentrations of PCBs and *trans*-nonachlor in the sediment were used as a surrogate for detrital concentrations.

In the marine environment, authors have observed similar biomagnification of PCBs and other persistent organic pollutants. Hop *et al.* (2002) and Fisk *et al.* (2001) investigated biomagnification through marine food webs that have included water birds and mammals as top predators. In these studies, biomagnification at the upper end of these food webs (in the homeothermic mammal and avian populations) was even greater than at the lower end of the food web (in fish and invertebrates).

In contrast to the studies that have demonstrated biomagnification of PCBs in aquatic food webs, Berglund *et al.* (2000) concluded that total PCB concentrations did not steadily increase with increasing trophic level in 19 Swedish lakes. On a dry-weight basis, total PCB concentrations in fish were not significantly different from concentrations in zooplankton, however, Berglund *et al.* (2000) only investigated young-of-the-year fish and did not investigate piscivorous fish species. On a lipid-weight basis, total PCB concentrations in fish were significantly higher than in zooplankton, but were not significantly higher than in phytoplankton. As demonstrated in the LMMB Study, age (or length as a surrogate for age) certainly affects the bioaccumulation of PCBs. In attempting to factor out this effect by only using young-of-the-year fish, however, a true comparison of trophic levels cannot be adequately made. Increases in the lifespan of organisms are a component of increasing trophic level.

9.3 Fractionation

While the discussion of bioaccumulation and biomagnification has focused primarily on total PCBs, each of the 209 PCB congeners have differing physical and chemical properties and may be accumulated and biomagnified differentially. In general, more-chlorinated PCB congeners are more hydrophobic and more lipophilic. This chemical trend can be described by the octanol-water partition coefficient (K_{OW}), which is the ratio of the concentration of a substance preferentially dissolved in an octanol phase to the concentration of that substance dissolved in the water phase. More-chlorinated PCB congeners have higher octanol-water partition coefficients (Figure 9-6).

Because more-chlorinated PCB congeners are more hydrophobic and more lipophilic, these more-chlorinated congeners more readily bioaccumulate in living tissue. Figure 9-7 shows the bioaccumulation factors for each of the trophic levels versus K_{OW} . The slope for each of the trophic levels is positive, indicating that the more-chlorinated PCB congeners with higher K_{OW} values are bioaccumulated to a greater degree. Slopes for these log-log regressions range from 0.24 to 0.46. These regressions also indicate increased bioaccumulation at each trophic level. For a given K_{OW} , PCBs are increasingly more accumulated in phytoplankton, zooplankton, forage fish, and lake trout.

Many other authors have documented this same trend of increasing PCB bioaccumulation with increasing K_{OW} or increasing chlorination. Oliver and Niimi (1988) observed that less-chlorinated PCB congeners comprised a higher fraction of total PCBs in water than in higher trophic levels in Lake Ontario. Koslowski *et al.* (1994) also observed increased bioaccumulation with increased PCB congener chlorination in the Lake Erie food web. Willman *et al.* (1997) similarly found that penta-, hexa-, and heptachloro congeners were enriched relative to other congeners as PCBs moved to higher trophic levels from sediments to plankton to fish.

Figure 9-6. Octanol-water Partition Coefficients (K_{OW}) for PCB Congeners

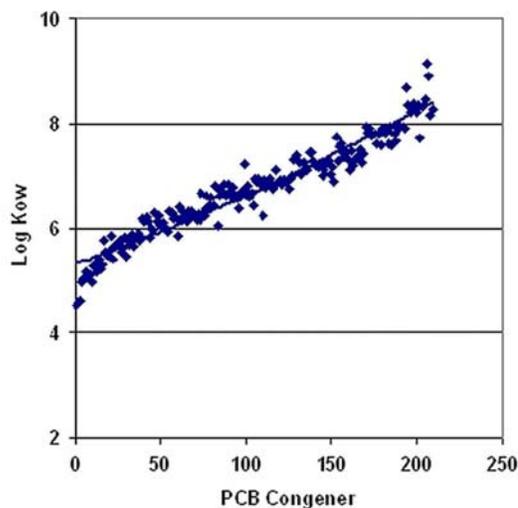
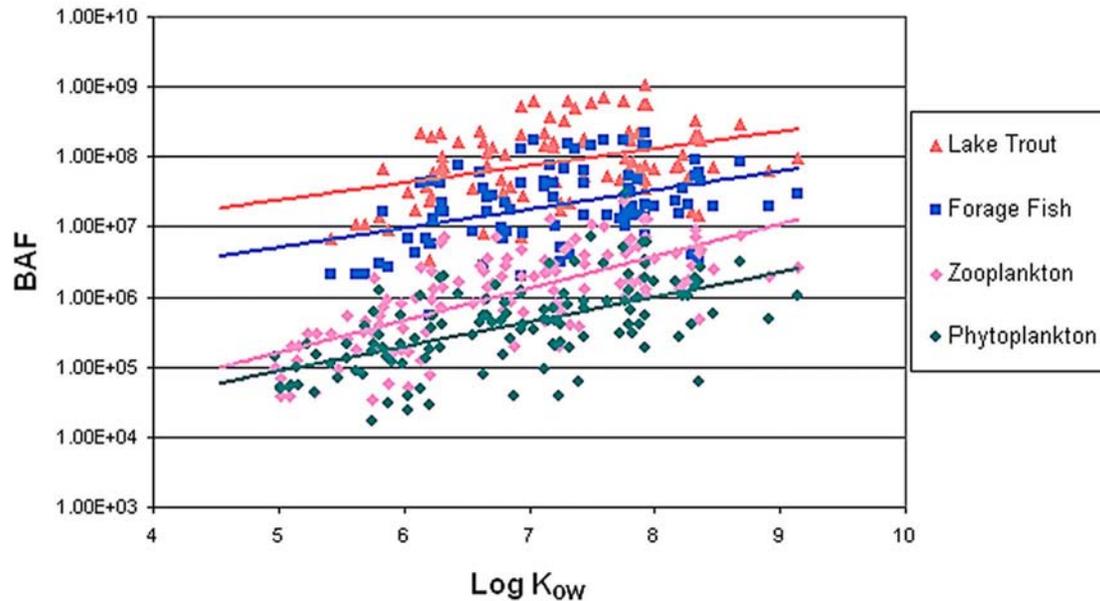
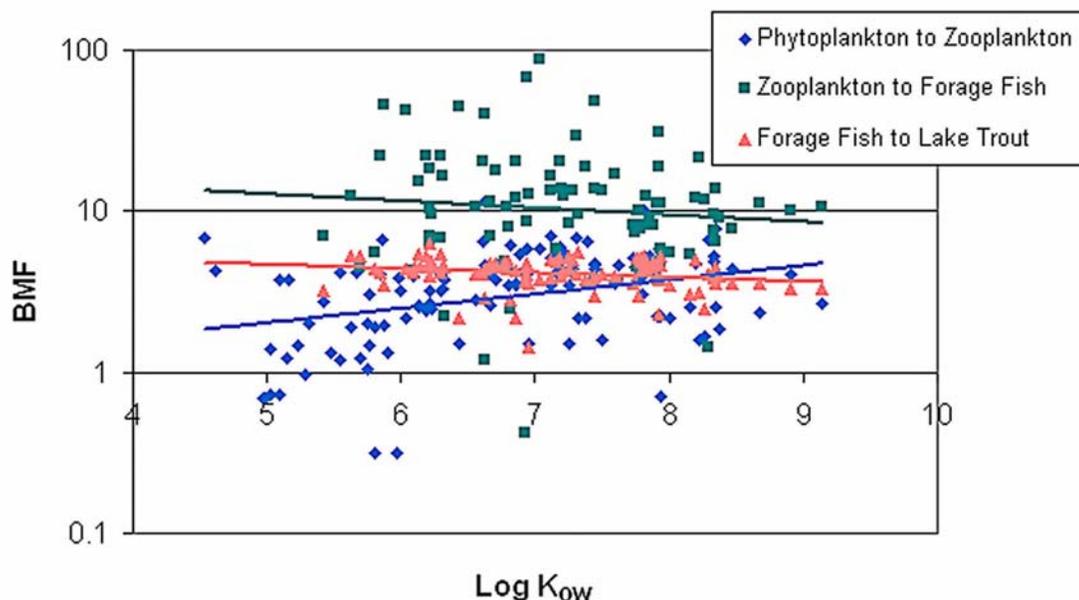


Figure 9-7. Bioaccumulation Factors in the Lake Michigan Food Web versus Log Octanol-Water Partition Coefficients for Individual PCB Congeners



In the lower pelagic food web, it was observed that more-chlorinated PCB congeners not only preferentially accumulated from water, but these more-chlorinated congeners also preferentially accumulated in the transfer from prey to predator. For example, the slope of the log BAF versus log K_{ow} curve increases from phytoplankton to zooplankton. This indicates that relative to phytoplankton, zooplankton preferentially accumulated more-chlorinated PCB congeners. This was not true of each trophic transfer, however. The slopes of the curves did not increase with each increasing trophic level. Figure 9-8 shows biomagnification factors plotted against log K_{ow} values of the PCB congeners. Only in the transfer from phytoplankton to zooplankton were more-chlorinated PCB congeners preferentially accumulated. The slopes for zooplankton to forage fish and for forage fish to lake trout were negative and close to zero. Kucklick and Baker (1998) also did not observe fractionation of PCB congeners between predator and prey. More chlorinated PCB congeners with higher K_{ow} values were not selectively accumulated in predators.

Figure 9-8. Biomagnification Factors in the Lake Michigan Food Web versus Log Octanol-Water Partition Coefficients for Individual PCB Congeners



9.4 Toxic PCB Congeners

It is important to independently consider the concentration and accumulation of individual PCB congeners, because the individual congeners bioaccumulate differentially and have varying degrees of toxicity. The World Health Organization has identified the PCB congeners listed in Table 9-2 as toxic and “dioxin-like” based on structure-activity relationships (Van den Berg *et al.*, 1998). For each of these toxic PCB congeners, the World Health Organization also has assigned toxicity equivalency factors (TEFs), which relate the toxicity of each congener to the toxicity of 2,3,7,8-tetra-chlorodibenzo-*p*-dioxin (TCDD). A compound with a TEF value of 1.0 is as potent as TCDD, and a compound with a TEF value of 0.01 is estimated to be 100 times less potent than TCDD. Based on the assumption of additivity, the product of individual PCB concentrations and TEFs can be summed to calculate the toxic equivalent concentration (TEQ) of all dioxin-like compounds in terms of TCDD.

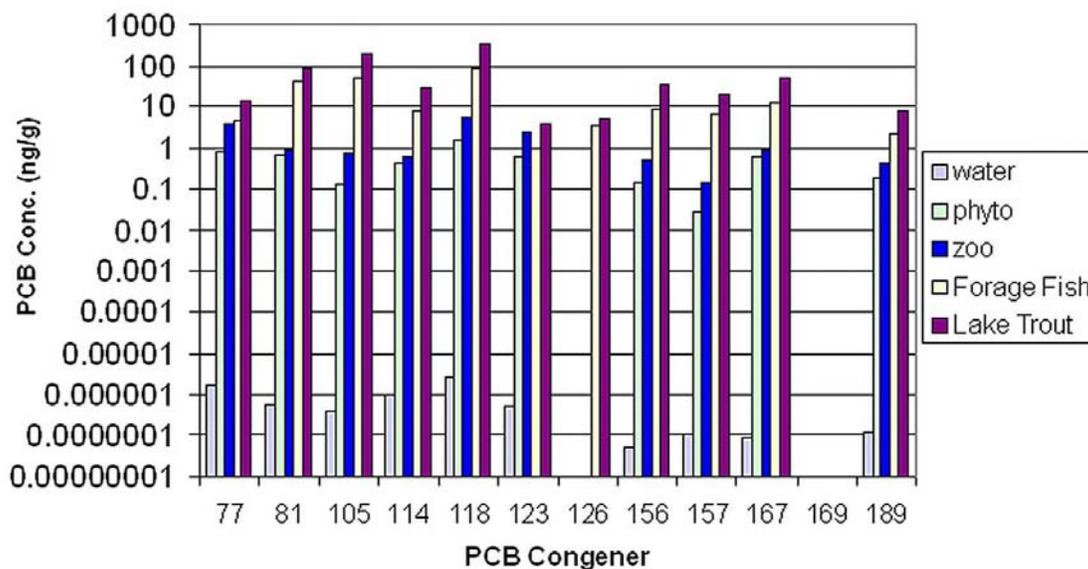
Fish samples from the LMMB Study were analyzed for 80 individual PCB congeners including all of the toxic congeners except for PCB 169. Sediment, tributary, water column, and plankton samples were not analyzed for PCB 169 or PCB 126. In the Lake Michigan food web, the toxic PCB congeners bioaccumulated and biomagnified in the same general pattern as described for total PCBs. Concentrations of these toxic PCB concentrations increased in each successive trophic level

Table 9-2. Toxic PCB Congeners and Toxicity Equivalency Factors (TEF)

PCB Congener	TEF
77	0.0001
81	0.0001
105	0.0001
114	0.0005
118	0.0001
123	0.0001
126	0.1
156	0.0005
157	0.0005
167	0.00001
169	0.01
189	0.0001

of the Lake Michigan food web (Figure 9-9). Of the toxic PCB congeners, concentrations of PCB 118 were highest. This congener has a TEF of 0.0001, meaning that the compound is one ten-thousandth as toxic as TCDD. PCB 126, which is the most toxic of the PCB congeners (TEF of 0.1), was found in fish tissue at nearly the lowest level of toxic PCB congeners.

Figure 9-9. Concentration of Toxic PCB Congeners in the Lake Michigan Ecosystem



In open-lake water, the sum of the 12 toxic PCB congeners contributed 3.9% of the total PCB concentration. In the lower pelagic food web (phytoplankton, zooplankton, *Mysis*, and *Diporeia*), the toxic PCB congeners contributed 9.5 to 12% of the total PCB concentration. In fish, the toxic PCB congeners contributed 11 to 19% of the total PCB concentration. The percentage of total PCBs attributed to the toxic congeners did not increase by trophic level. In both phytoplankton (the base of the pelagic food web) and lake trout (the top of the pelagic food web), the toxic PCB congeners contributed 11% of the total PCB concentration. The highest percentage of toxic PCB congeners (19%) was observed in the deepwater sculpin.

In relation to total PCBs, most of the toxic PCB congeners were bioaccumulated to a greater extent (Figure 9-10). The toxicity of these congeners and their potential for bioaccumulating, in part, depends upon their ability to penetrate cell membranes. In phytoplankton, bioaccumulation factors for all of the toxic PCB congeners were higher than for total PCBs. In zooplankton, bioaccumulation factors for all of the toxic PCB congeners except for PCB 114 were higher than for total PCBs. In forage fish and lake trout, bioaccumulation factors for all of the toxic PCB congeners except for PCB 77, 114, and 123 were higher than for total PCBs. This indicates that bioaccumulation based on total PCB values may underestimate the bioaccumulation of the toxic PCB congeners.

The drop in BAFs for PCBs 77 and 123 that is apparent in Figure 9-10 may be an artifact of analytical differences between the laboratories responsible for the analyses of lower pelagic food web organisms and fish. In the lower pelagic food web analyses, PCBs 77 and 123 each coeluted with another PCB congener that is not among the 12 toxic PCBs, while in the fish analyses, these two PCBs did not coelute with any other congeners. Thus, concentrations of PCBs 77 and 123 may be biased high in the phytoplankton and zooplankton samples, leading to higher BAFs for these two trophic levels, while the BAFs for forage fish and trout do not include contributions from other congeners.

Figure 9-10. Bioaccumulation Factors (BAFs) for Toxic PCB Congeners and Total PCBs in Lake Michigan Biota

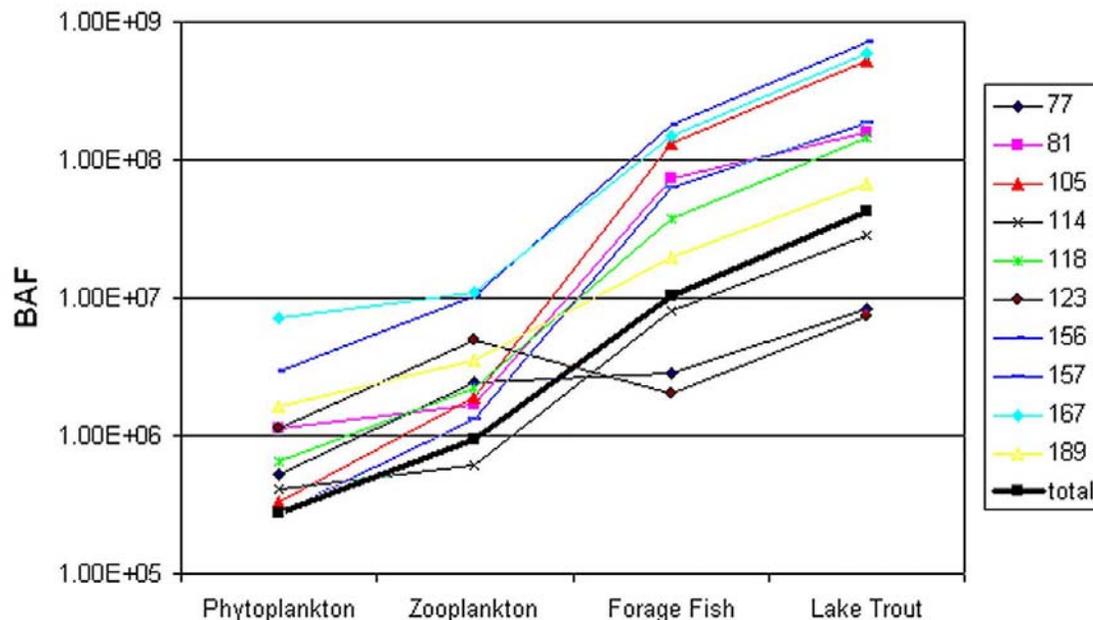


Table 9-3 shows toxic equivalent concentrations (TEQs) calculated for the toxic PCB congeners in terms of TCDD. TEQ values ranged from 0.0032 to 0.52 ng/g - TCDD equivalents. Even though these TEQs include only dioxin-like PCBs and not measured concentrations of dioxins and furans, these values exceed EPA's recommended fish consumption limits for dioxins/furans TEQs of 0.0012 ng/g. It should also be noted that these TEQ values do not include the contribution of PCB 169, because this congener was not analyzed in the LMMB Study.

PCB 126, the most toxic PCB congener, contributed 71 to 98% of the total TEQ values for each species, with the exception of coho salmon collected from the hatchery (in which PCB 126 was not detected). Surprisingly, the highest TEQ value was not calculated for lake trout but was calculated for large bloater chub. While total PCB concentrations in lake trout were 3.6 times total PCB concentrations in large bloater chub, concentrations of PCB 126 were higher in large bloater chub (5.1 ng/g) than in lake trout (2.0 ng/g). The higher concentration of this PCB congener in large bloater chub caused the higher TEQ for large bloater chub. This finding also points out the importance of measuring and evaluating individual PCB congener concentrations in addition to total PCB concentrations.

Table 9-3. Toxic Equivalent Concentrations (TEQs) for Dioxin-like PCB Congeners in Lake Michigan Fish

Species/Size Category	TEQ ^a (ng/g)
Alewife<120mm	0.015
Alewife>120mm	0.075
Bloater<160mm	0.060
Bloater>160mm	0.52
Coho-Adult	0.035
Coho-Hatchery	0.0032
Coho-Yearling	0.010
Deepwater Sculpin	0.048
Lake Trout	0.24
Smelt	0.039
Slimy Sculpin	0.029

^a TEQ based on toxicity of dioxin-like PCB congeners relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD).

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