PCB PATHWAY DETERMINATION FOR THE LOWER FOX RIVER/GREEN BAY NATURAL RESOURCE DAMAGE ASSESSMENT

Final Report

Prepared for:

U.S. Fish and Wildlife Service
U.S. Department of the Interior
U.S. Department of Justice

Prepared by:

Stratus Consulting Inc.
P.O. Box 4059
Boulder, CO 80306-4059
(303) 381-8000

Contacts:

Doug Beltman
Dave Cacela

August 30, 1999

William F. Hartwig
Regional Director and Authorized Official

CONTENTS

FIGURES

TABLES

ACRONYMS

CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DO	dissolved oxygen
GBMBS	Green Bay Mass Balance Study
NCR	National Cash Register Company
NOAA	National Oceanic and Atmospheric Administration
NRDA	natural resource damage assessment
PC1	principal component one
PC2	principal component two
PCA	principle components analysis
PCBs	polychlorinated biphenyls
PRPs	potentially responsible parties
TSS	total suspended solids
USFWS	U.S. Fish and Wildlife Service
WDNR	Wisconsin Department of Natural Resources
WSLH	Wisconsin State Laboratory of Hygiene

CHAPTER 1
INTRODUCTION

This document presents a pathway determination for polychlorinated biphenyls (PCBs) released from paper company facilities along the Lower Fox River, Wisconsin. This determination is part of the natural resource damage assessment (NRDA) being performed for the Lower Fox River/Green Bay environment by the U.S. Department of the Interior (the Department) through the U.S. Fish and Wildlife Service (USFWS, or the Service), the National Oceanic and Atmospheric Administration (NOAA), the Oneida Tribe of Indians of Wisconsin, and the Menominee Indian Tribe of Wisconsin. This report was prepared by Stratus Consulting Inc., with assistance from Amendola Engineering, Inc. (Chapter 2).

The purpose of this report is to evaluate and describe the pathways by which PCBs have been transported from the points of release to where the PCBs have come to be located and result in PCB exposure of natural resources in the Lower Fox River, Green Bay, and northern Lake Michigan environment.

Previous NRDA reports addressed PCB injuries to avian resources in the Lower Fox River/Green Bay environment (Stratus Consulting, 1999b) and injuries resulting from PCB fish consumption advisories (Stratus Consulting, 1998). The pathway determination presented in this report provides documentation of the physical and biological transport pathways by which the avian and fishery resources addressed in those previous reports become exposed to PCBs released from Lower Fox River paper company facilities.

The pathway determination presented in this report is based on existing information. No new data were collected.

1.1 DEPARTMENT NRDA REGULATIONS ON PATHWAY

The Department's regulations for conducting NRDAs address pathway determination [43 CFR §11.63]. A pathway is defined in the regulations as "the route or medium through which oil or a hazardous substance is or was transported from the source of the discharge or release to the injured resource" [43 CFR §11.14(dd)]. The pathway is determined by

> either demonstrating the presence of the oil or hazardous substance in sufficient concentrations in the pathway resource or by using a model that demonstrates that the conditions existed in the route and in the oil or hazardous substance such that the route served as the pathway. [43 CFR §11.63(a)(2)]

The determination presented in this report relies on both approaches by (1) evaluating PCB concentrations, concentration gradients, and PCB congener patterns in pathway resources, and (2) presenting information from the Green Bay Mass Balance Study (GBMBS) relevant to pathway determination of PCBs. This overall approach to determining pathway is based on the Service's Assessment Plan for the Lower Fox River/Green Bay (U.S. FWS, 1996).

The NRDA regulations also specify factors that should be considered in the pathway determination, including the chemical and physical characteristics of the hazardous substance in natural media and the rate or mechanism of transport [43 CFR §11.63(a)(1)(I)-(ii)]. In addition, when the surface water resource [defined to include suspended, bed, bank, and shoreline sediments, 43 CFR §11.14(pp)] is a component of the pathway, the following characteristics should be determined [43 CFR §11.63(b)(3)(ii)]:

- hydraulic parameters and streamflow characteristics
- sediment characteristics
- volume, inflow-outflow rates, degree of stratification, and bathymetry of surface water bodies
- suspended sediment loads
- water current direction and current rate.

These factors are addressed in this report and summarized in Chapter 7.

1.2 REPORT SUMMARY

The individual chapters in this report address different aspects of the pathway determination for PCBs in the Lower Fox River/Green Bay system.

Chapter 2 summarizes information on the release of PCBs from paper company facilities into the Lower Fox River, and demonstrates the following:

- Paper companies released PCBs into the Lower Fox River as a result of several paper-making processes involving carbonless copy paper, which contained PCBs as a carrier solvent.
- PCB releases into the river began in the early 1950s, increased dramatically through the 1960s, and dropped sharply after 1971.

- An estimated 300,000 kg of PCBs were released from paper company facilities into the Lower Fox River.

Chapter 3 discusses the application of models developed as part of the GBMBS to pathway determination, and documents that PCB transport models confirm PCB pathways in the Lower Fox River and Green Bay. Specifically, the models show the following:

- The Fox River is the dominant source of PCBs to Green Bay.
- Water circulation patterns in Green Bay transport the Fox River PCBs throughout the bay.
- Aquatic biota in the system are exposed to PCBs in their diet and in surface water, with food chain exposure the dominant PCB pathway for predatory fish such as walleye and brown trout.
- PCBs are transported out of the Lower Fox River/Green Bay system via water currents into Lake Michigan and air currents.

Chapter 4 uses available PCB sediment and water data to demonstrate that PCBs are carried downstream in the Lower Fox River into Green Bay. Green Bay water circulation and sediment deposition patterns are also described, with the following conclusions:

- Contaminated Lower Fox River water entering the bay tends to move up the bay along the eastern shore. Most Lower Fox River sediments are deposited in the inner bay, along the eastern shore.
- Some of the Lower Fox River water and sediment moves through the inner bay into the outer bay. One study estimated that 10% to 33% of the Lower Fox River sediment entering the bay was transported to the outer bay.
- A large exchange of water between outer Green Bay and Lake Michigan allows PCBs that enter the outer bay to be transported into the northern portion of Lake Michigan.

Chapter 5 describes the spatial and temporal patterns of PCB contamination in Green Bay. In addition to documenting PCB concentrations in pathway resources (surface water, sediment, aquatic biota) throughout the bay, the analysis presented in this chapter demonstrates the following:

- Spatial patterns of PCB concentrations in Green Bay sediment, surface water, and fish are consistent with the Lower Fox River being the primary source of PCBs to the bay. In general, concentrations are highest along the eastern shore of the inner bay and decline with distance from the Lower Fox River mouth.

- PCB concentrations have generally declined since the 1970s, corresponding with reductions in PCB releases from Fox River paper company facilities. However, Green Bay PCB concentrations are decreasing at a much slower rate than the rate of decline of original PCB releases from paper company facilities, indicating that PCBs are environmentally persistent and continue to be transported within the system. Some species of fish show no decline in PCB concentrations over the last 10 to 15 years.

Chapter 6 presents a statistical analysis of PCB congener patterns in the sediment of the Lower Fox River, inner Green Bay, outer Green Bay, and Lake Michigan, and demonstrates that:

- The PCB congener profiles in Green Bay sediments are consistent with inner Green Bay and outer Green Bay being contaminated by the transport and weathering of PCBs from the Lower Fox River.

- The PCB congener pattern in outer Green Bay sediment is more similar to that in inner Green Bay than in Lake Michigan. Furthermore, the pattern observed in outer Green Bay samples is unlikely to have been derived from the transport and weathering of Lake Michigan sediment. Therefore, outer Green Bay PCBs most likely came from inner Green Bay (and hence Lower Fox River paper companies). The congener patterns are consistent with the transport and weathering of outer Green Bay PCBs to Lake Michigan.

Chapter 7 presents a summary of the pathway determination in accordance with the Department NRDA regulations. The summary constitutes a pathway determination for PCB transport from the points of release from Lower Fox River paper companies to the Lower Fox River, Green Bay, and Lake Michigan.

Chapter 8 presents references cited in the report.

CHAPTER 2
PCB RELEASES TO THE LOWER FOX RIVER

This chapter presents a summary of information related to releases of PCBs from paper companies into the Lower Fox River. The summary is based on published reports on PCB use in the paper industry and on information obtained by the Service and the Wisconsin Department of Natural Resources (WDNR).

Information is presented on the manufacturing processes associated with PCB releases, temporal patterns of PCB releases into the Lower Fox River, and specific facilities that have released PCBs into the Lower Fox River. Information for this chapter was obtained primarily from responses to requests for information issued by the Department under the authority of Section 104(e) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and supplemental information and data obtained by the WDNR. Information requests were issued to pulp and paper mills located in the Fox River valley; publicly owned treatment works located in the Fox River valley; several trade associations; and selected wastepaper brokers. Requests were issued by the Department from 1996 through 1999. Some of the information supplied in responses to the requests is considered confidential business information, and such information is not presented here.

2.1 BACKGROUND

During the post-World War II period from 1946 to 1953, The National Cash Register Company (NCR) in Dayton, Ohio, conducted research and development of carbonless copy paper using a micro-encapsulation technique for imprinting images (Appleton Papers, 1987). Commercial sales of carbonless copy paper, which became known as "NCR paper," began in March 1954 (Appleton Papers, 1987). Images were formed on the second sheet of paper by applying mechanical pressure (e.g., handwriting, typing) to the top sheet, which was coated on the back with microcapsules containing ink and a solvent. The pressure caused the microcapsules on the back of the top sheet to break, forming an image on the second sheet, which was coated with a receiver material. PCB emulsions were used as the solvent for the ink contained in the NCR paper until 1971, when a substitute for PCBs was used (U.S. EPA, 1977). Aroclor 1242 was the only commercial mixture of PCBs used to produce the emulsions (U.S. EPA, 1977; Appleton Papers, year unknown).

The Monsanto Company was the largest commercial producer of PCBs in the United States and was the source of PCBs used in the NCR paper. Emulsion for the NCR paper was produced at plants in Dayton, Ohio, and Portage, Wisconsin, and shipped to the Appleton Coated Paper Company in Appleton, Wisconsin, and to a Mead Paper plant in Ohio. At these plants, the emulsion was applied as a coating solution to selected grades of paper stock using paper coating machines adapted for that purpose. Appleton Coated Paper produced approximately 50-60% of the NCR paper produced annually in the United States during the period when PCB emulsions were used (W.E. Spearin, personal communication, 1976).[1] The majority of the coating solution containing PCBs in microcapsules was applied to the paper stock and left the Appleton Papers coating mill as part of the semi-finished NCR paper. Coated papers were sold to paper converters who manufactured the carbonless copy forms used in commerce.

During preparation of the coated papers, losses of coating solution as well as coated side trimmings, off-grade paper, and waste paper generated during paper machine breaks occurred. Collectively, these paper losses are called "broke." Much of the broke contained about the same concentration of PCBs as did the product grade NCR paper (approximately 3.4% PCBs by weight) (W.E. Spearin, personal communication, 1976). NCR paper broke was sold to waste paper brokers and directly or subsequently to secondary fiber pulp and paper mills, where it was processed with other waste papers to make secondary fiber pulp and paper products. In addition, trimmings from NCR paper converter operations were also used by secondary fiber mills as a fiber source. Secondary fiber mills also processed post-consumer waste papers that contained NCR paper. Consequently, secondary fiber mills took in PCBs with their fiber supply. A portion of those PCBs was partitioned to secondary fiber pulp and became part of the secondary fiber products, a portion was partitioned to the wastewater sludge generated at the secondary fiber mills, and the remainder was discharged with partially treated or fully treated wastewaters. Figure 2-1 is a schematic diagram that illustrates the mass flow of PCBs associated with NCR paper production.

2.2 PCB RELEASES FROM PAPER COMPANY FACILITIES

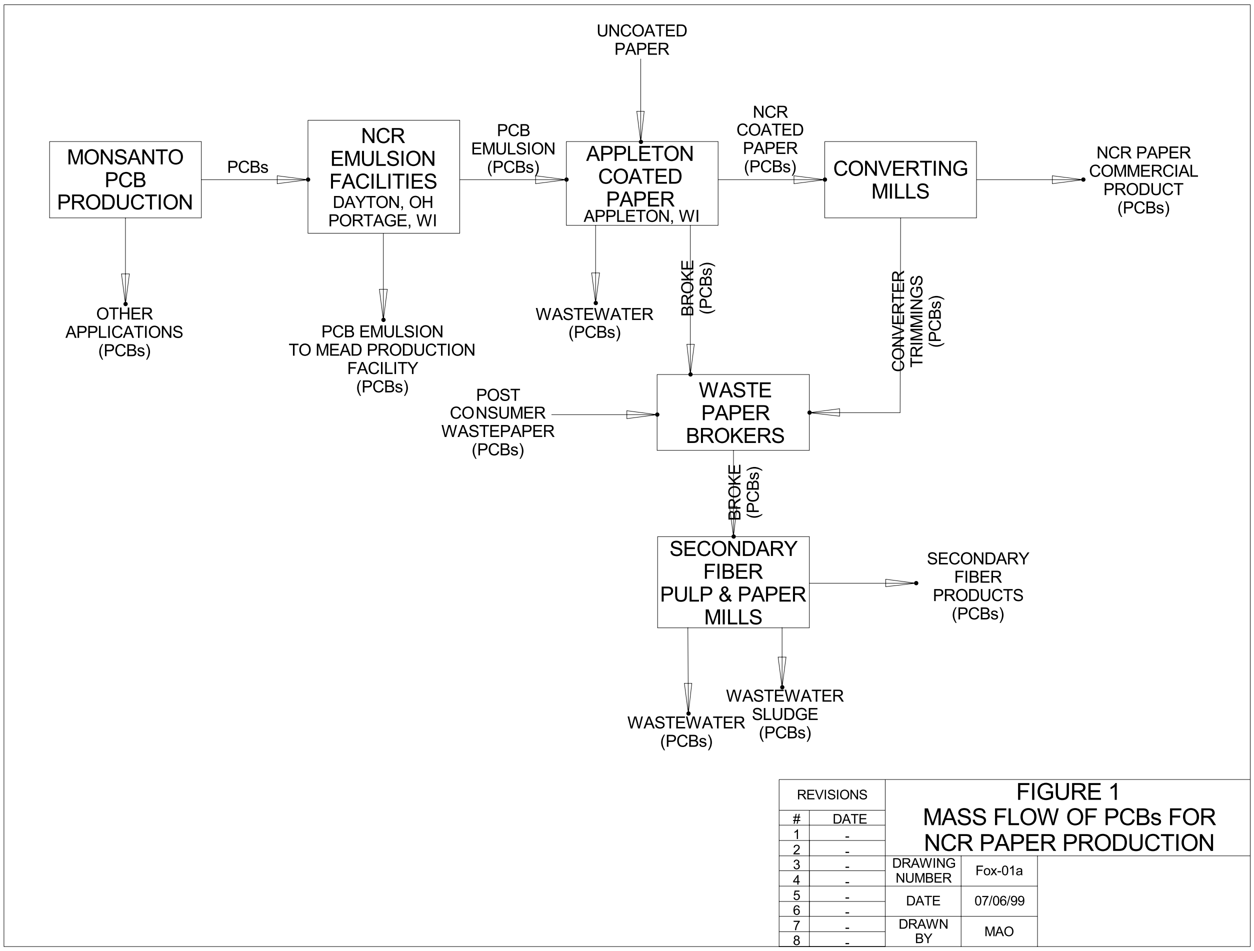
Carbonless copy paper using PCB emulsions was manufactured at Appleton Coated Paper from 1954 to about April 1971 (NCR Corporation, 1996). During and after that period, Appleton Coated Paper discharged process wastewaters to the City of Appleton sewerage system for disposal. There were also trial runs of NCR paper production at the Appleton Papers Combined Locks Mill starting in 1969 (Appleton Papers, year unknown).

Information and data obtained by the Service and the WDNR show that PCB releases to the Lower Fox River occurred principally through the following routes (Figure 2-2):

- Loss of PCB emulsions during the paper coating process at Appleton Coated Paper and, to a lesser extent, during mill trials at the Appleton Papers Combined Locks Mill.

1. Personal Communication: From Spearin of NCR Appleton Papers Division, Appleton, Wisconsin to J.S. Haney, Public Affairs Director, Bergstrom Paper Company, Neenah, Wisconsin. January 19.

Figure 2-1
Mass Flow of PCBs for NCR Paper Production

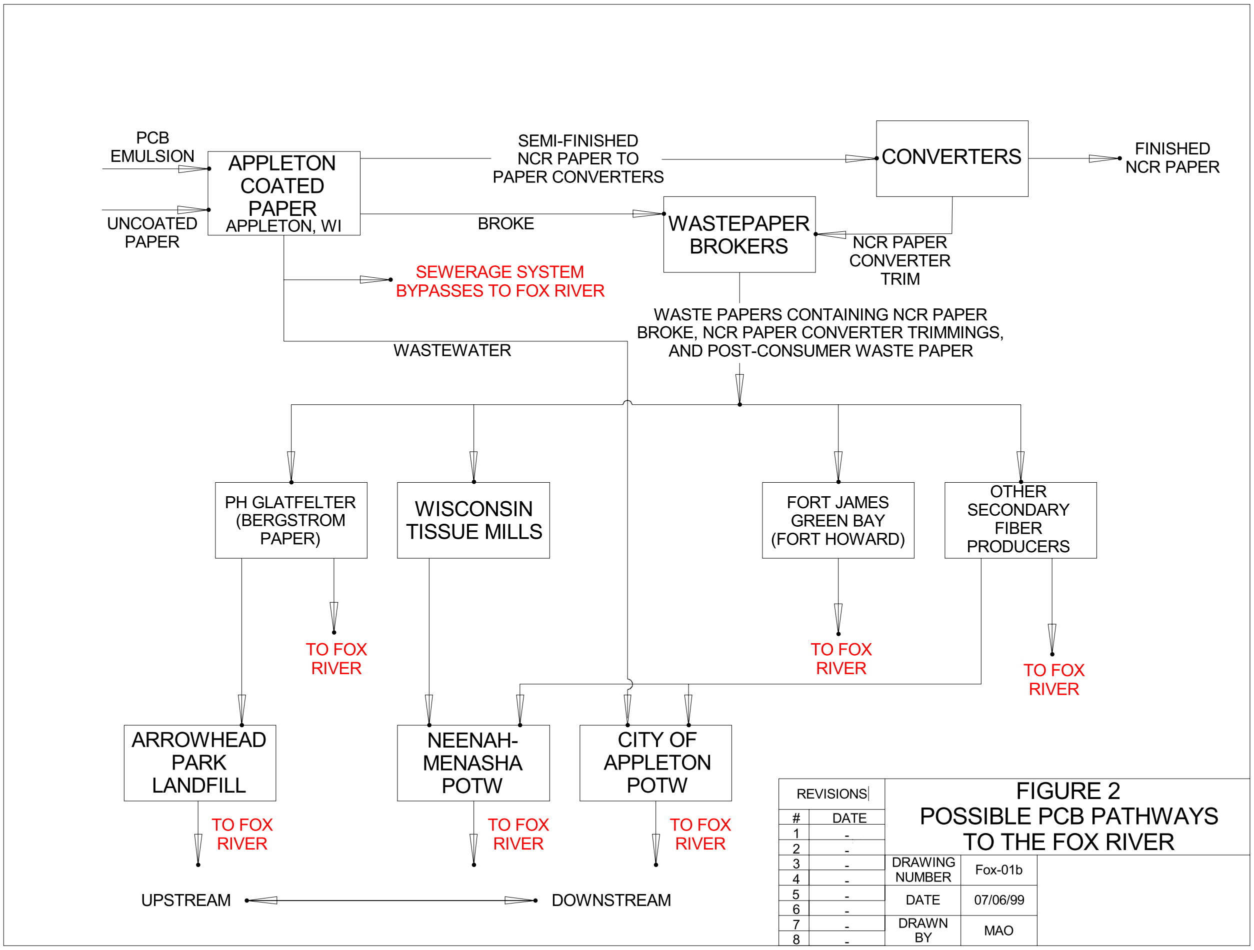


Source: Provided by Amendola Engineering.

- Releases of PCBs from secondary fiber mills that processed NCR paper broke, NCR paper converter trimmings, and post-consumer papers that contained NCR paper. The following secondary fiber mills had the largest PCB releases: Fort James Green Bay West Mill (formerly Fort Howard), Green Bay, Wisconsin; PH Glatfelter — Bergstrom Division (formerly Bergstrom Paper), Neenah, Wisconsin; and, Wisconsin Tissue Mills, Neenah, Wisconsin (WDNR, 1999b).

- Overflows, bypasses, and treated effluent discharges to the Lower Fox River from the City of Appleton sewerage system and wastewater treatment plant that received wastewater from Appleton Coated Paper.

Figure 2-2
PCB Releases to the Lower Fox River



Source: Provided by Amendola Engineering.

- Releases of PCBs from the Neenah-Menasha POTW that received wastewater discharges from Wisconsin Tissue and other secondary fiber mills.

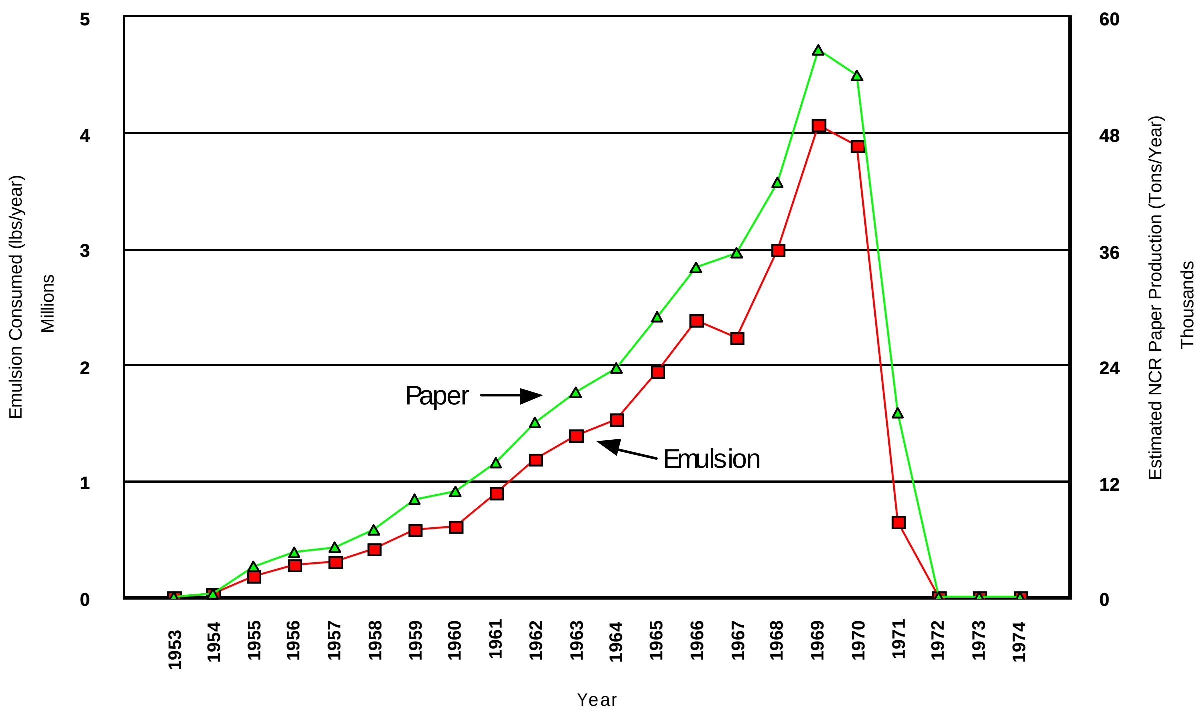
- Releases of PCBs from the PH Glatfelter Arrowhead Park landfill.

2.3 TIMING OF PCB RELEASES

Information obtained from paper company facilities shows that the majority of PCB releases to the Lower Fox River were associated with losses of PCBs from the paper coating operations and from recycling of NCR paper broke. Recycling of NCR paper converter trim was a lesser but substantial source of PCBs. Post-consumer waste paper containing NCR paper was a less important source of PCB releases to the Lower Fox River compared to these sources.

Figure 2-3 shows annual PCB emulsion use and NCR paper production at the Appleton Coated Paper Mill. PCB releases to the Fox River most likely coincided temporally with NCR paper production according to the nature of the production activity: (1) PCB releases from paper coating operations were contemporaneous with NCR paper production; (2) releases associated with the recycle of NCR paper broke most likely followed production by periods of weeks to a few months; (3) releases associated with the recycle of NCR paper converter trim most likely followed production by periods of several weeks to several months; and (4) releases associated with the recycling of post-consumer waste papers containing NCR paper followed production by indeterminable periods extending to several years.

Figure 2-3
NCR PCB Emulsion Consumed (lbs/year) and Paper Produced (tons/year) at the Appleton Coated Paper Mill



WDNR estimated the total amount of PCBs released to the Lower Fox River during the mid-1950s to 1997 as approximately 300,000 kg (660,000 lbs) (WDNR, 1999b). Alternative assumptions (but deemed by the WDNR report authors to be less likely) provided estimates of from 126,000 kg to 399,000 kg (WDNR, 1999b). The temporal pattern of releases to the Lower Fox River would have approximately followed the patterns of NCR paper production and use of PCB emulsions shown in Figure 2-3. Consequently, more than two-thirds of the releases are likely to have occurred during peak production years from 1965 to 1970. Use of PCBs in the production of NCR paper ceased in 1971, but NCR paper broke and converter trim remained in the recycled fiber stream after 1971. Releases into the 1980s and later continued to decline, reflecting both declining amounts of NCR paper containing PCBs in the post-consumer waste paper stream, and improvements in municipal and industrial wastewater treatment.

2.4 CONCLUSIONS

PCBs were released from paper company facilities that used PCBs in the production of NCR paper or that processed secondary fibers containing PCBs. The facilities released PCBs into the Lower Fox River either directly or via municipal wastewater systems. An estimated 300,000 kg (660,000 lbs) of PCBs were released from paper company facilities into the Lower Fox River.

The timeline of much of the releases is expected to track, within weeks to months, the timeline of PCB emulsion use and NCR paper production, which increased through the 1960s, peaked in 1969, and declined sharply in 1971. However, some releases are expected to have occurred for years after production of NCR paper ceased. Furthermore, as described in subsequent chapters, PCBs continue to be released into the environment through surface water and sediment transport processes.

CHAPTER 3
PCB PATHWAY MODELS IN THE GREEN BAY MASS BALANCE STUDY

The Lower Fox River/Green Bay system has been the focus of an intensive effort to study the fate and transport of PCBs. Researchers from government, academic, and private institutions worked collaboratively for over a decade as part of a government-sponsored mass balance study of PCBs in the system (the GBMBS). The results of these efforts include a suite of numerical models that describe the transport and fate of PCBs in the system.

Models can be used for pathway determination in NRDA [43 CFR §11.63(a)(2)]. The models available for the Lower Fox River/Green Bay system are comprehensive, detailed descriptions of the physical and biological routes that serve as pathways for PCBs, and have been validated with extensive field data collection. The models themselves are representations of the various processes that together serve as PCB pathways in the system, and they bring together much of the available information into a combined, coherent description of PCB pathways in the system.

This chapter describes the mass balance models developed as part of the GBMBS and uses them to describe the PCB pathways in the Lower Fox River/Green Bay system.

3.1 BACKGROUND

The overall objective of the GBMBS was to evaluate the feasibility of toxic substance mass balance modeling in Great Lakes environments (DePinto, 1994). Specific objectives included (DePinto, 1994):

- identifying the major sources of PCBs entering the Green Bay ecosystem and ranking their relative significance

- gaining an understanding of sources, transport routes, and fates of pollutants (including PCBs) in the Green Bay ecosystem.

These specific objectives have direct application to the PCB pathway evaluation for the NRDA, as discussed in more detail below.

The development of the GBMBS was conducted under the overall coordination efforts of the U.S. EPA Great Lakes National Program Office and the WDNR (DePinto, 1994). Many government, private, and academic researchers participated in the development, calibration, and application of the models, which cost approximately $12 million (Beltran, 1992; DePinto, 1994).

The study included intensive field data collection over a 1.5 year period in 1989-1990 that produced thousands of data points used to calibrate the models (DePinto, 1994).

The GBMBS includes several numerical models of PCB pathways in the Lower Fox River/Green Bay system. Preliminary reports on the development and results of some of the models were first published in 1992 (e.g., Bierman et al., 1992; Connolly et al., 1992). Subsequent reports documented updates to some of the model components, including the Green Bay PCB fate and transport portion and the Green Bay bioaccumulation portion (DePinto et al., 1994; HydroQual Inc., 1995).

GBMBS models are undergoing an evaluation as to their utility in assisting site cleanup decisions (WDNR, 1997). The work is being conducted as part of a 1997 agreement between the State of Wisconsin and seven companies identified as potentially responsible parties (PRPs) (WDNR, 1997). Metrics for quantifying model performance were established at the start of the evaluation process (Limno-Tech, Inc. and WDNR, 1998). The evaluation is intended to determine if the present models meet the performance metrics and, if not, identify areas of model refinement that would result in the metrics being met. Components being evaluated include Lower Fox River sediment bed properties (WDNR, 1999a); loadings of suspended sediment and PCBs (LTI Environmental Engineering, 1998; WDNR, 1999b); water velocity distributions and circulation models for Green Bay (HydroQual Inc., 1999); and the food web (Exponent Environmental Group, 1998).

Despite the fact that the GBMBS models are undergoing an evaluation, the models can be used in an NRDA pathway evaluation. The use of the models in a pathway evaluation is based on the models' general description of the movement of PCBs in the system and the linkage between different environmental compartments (e.g., sediment-surface water-plankton-fish). This general description is based primarily on the extensive field data collected in 1989-90 that were used to calibrate the models. Since any refined models will also be based on these same field data, the models' general description of PCB transport pathways in the system will not change. The ongoing evaluation of the models is designed to determine whether the models meet specific performance metrics, and any refinements to the models may affect the models' predictions of future PCB concentrations in specific media at specific times. However, the NRDA pathway determination is not dependent on these specific predictions,[1] and can use the GBMBS models that are currently available for pathway determination.

Section 3.2 describes the basic approaches of the models in the GBMBS, and Section 3.3 discusses the results of the models that are relevant to a pathway determination.

1. The models' predictions of future PCB concentrations will, however, be useful in determining concentrations of PCBs during and after any remedial action. This determination is a factor in restoration planning (Hagler Bailly Services, Inc., 1998).

3.2 MASS BALANCE STUDY MODELING APPROACH

The different GBMBS models address different geographic regions and/or environmental components of the Lower Fox River/Green Bay system (Figure 3-1). Separate models were developed for the Lower Fox River between Lake Winnebago and DePere, the Lower Fox River between DePere and the river mouth, and Green Bay. Individual models within these geographic areas address (Connolly et al., 1992; DePinto et al., 1994; Velleux and Endicott, 1994; Steuer et al., 1995):

- the hydrology of the Lower Fox River
- sediment transport in the Lower Fox River
- PCB movement and deposition in the Lower Fox River
- water circulation in Green Bay
- eutrophication in Green Bay
- sediment transport in Green Bay
- PCB movement and deposition in Green Bay
- bioaccumulation and food chain transfer of PCBs in Green Bay.

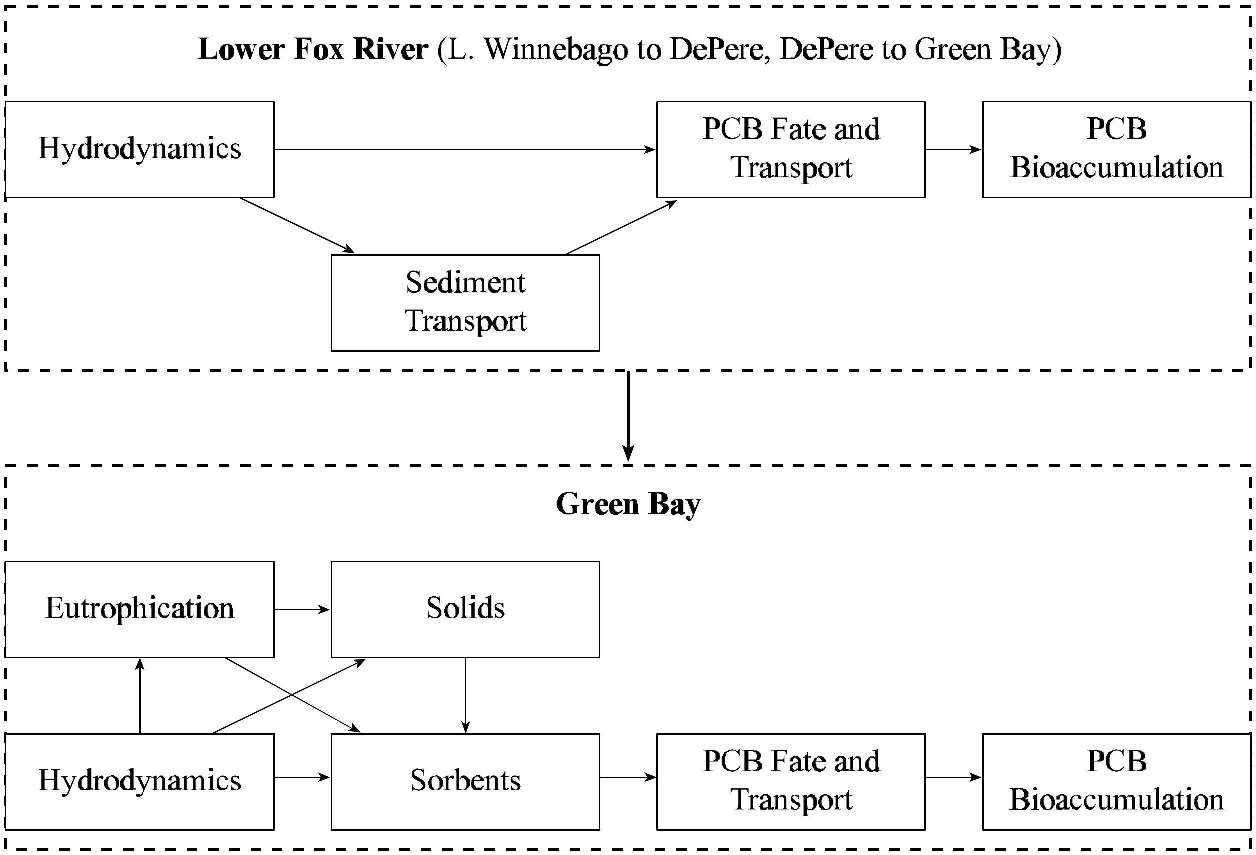
When linked together, this series of models provides an overall mass balance description of PCBs in the Lower Fox River downstream of Lake Winnebago and for Green Bay.

In essence, the models are numeric representations of the following PCB transport and fate processes (Connolly et al., 1992; DePinto et al., 1994; Velleux and Endicott, 1994; Steuer et al., 1995):

- advective and dispersive water column transport
- settling, resuspension, and burial of particulate-bound PCBs
- PCB partitioning between dissolved, particulate, and dissolved organic carbon phases
- sediment-water exchange of PCBs
- air-water exchange of PCBs
- external PCB loadings
- PCB uptake, metabolism, excretion, and accumulation by biota.

Conceptual frameworks outlining how these processes work were first developed to provide a theoretical basis for the models. These frameworks were then converted to mathematical algorithms that reflect the specific aspects of the processes. As an example, the conceptual framework developed for PCB fate and transport in Green Bay is shown in Figure 3-2. This figure shows that the model addresses multiple, interactive processes occurring between the sediment, sediment porewater, water column, and atmospheric compartments. Not shown in this figure are the frameworks for the separate models that address hydrodynamics, eutrophication, sediment transport, sorbent dynamics, and bioaccumulation in Green Bay.

Figure 3-1
Model Components Developed in the GBMBS



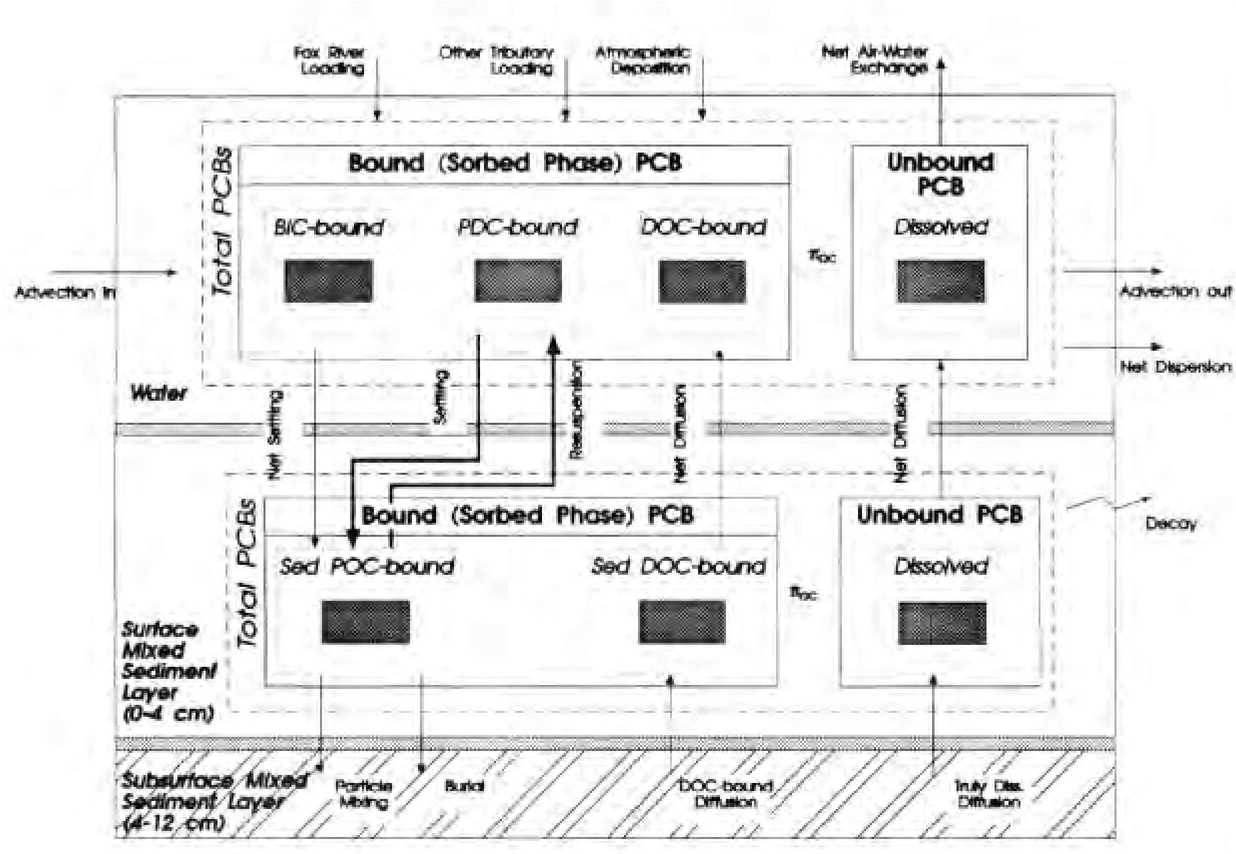
Source: Modified from DePinto, 1994.

3.3 GENERAL CONCLUSIONS OF THE GREEN BAY MASS BALANCE STUDY MODELS

3.3.1 PCB Sources and Transport Within the Fox River/Green Bay System

The models show that the surface water pathway is the primary pathway by which PCBs are transported through the Lower Fox River/Green Bay system. PCBs are carried with water currents downstream in the Lower Fox River to Green Bay and throughout Green Bay (DePinto et al., 1994; Velleux and Endicott, 1994). The largest mass of PCBs that moves through the system is adhered to particulate matter that is carried with water currents. PCBs also move through the system via the dissolved phase in surface water, via atmospheric transport, and via

Figure 3-2
Conceptual Model Framework for PCB Fate and Transport in Green Bay
See DePinto (1994) for full discussion of figure.

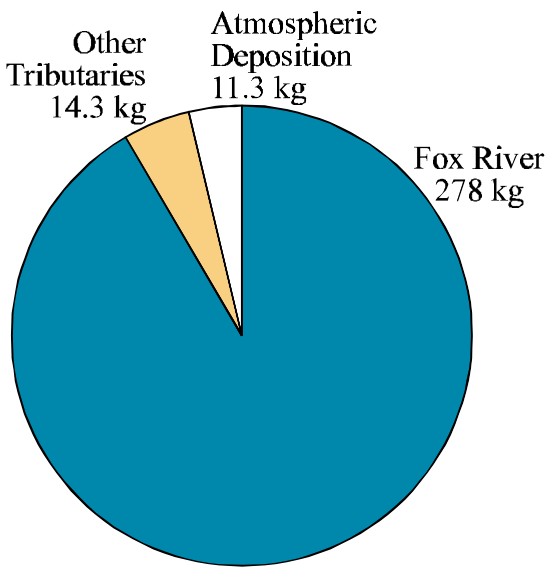


Source: DePinto, 1994.

fish migration. However, the mass of PCBs that are carried by these pathways is much less than the mass carried with particulate matter in the water column (DePinto et al., 1994).

Another conclusion of the GBMBS models relates to the sources of PCBs into the system. Based on calibration to the intensive 1989-1990 GBMBS data collection, the models estimate that the Fox River discharged 278 kg of PCBs into Green Bay in 1989, which is 92% of the PCBs that entered Green Bay from all bay tributaries and atmospheric deposition combined (Figure 3-3) (DePinto et al., 1994). Most of the PCBs transported out of the Fox River during this period are estimated to be associated with river bottom sediments that are resuspended and moved downstream (Velleux and Endicott, 1994). Thus, the GBMBS models demonstrate that the Lower Fox River was the primary source of PCBs into the bay in 1989.

Figure 3-3
Estimated PCB Loadings into Green Bay for 1989



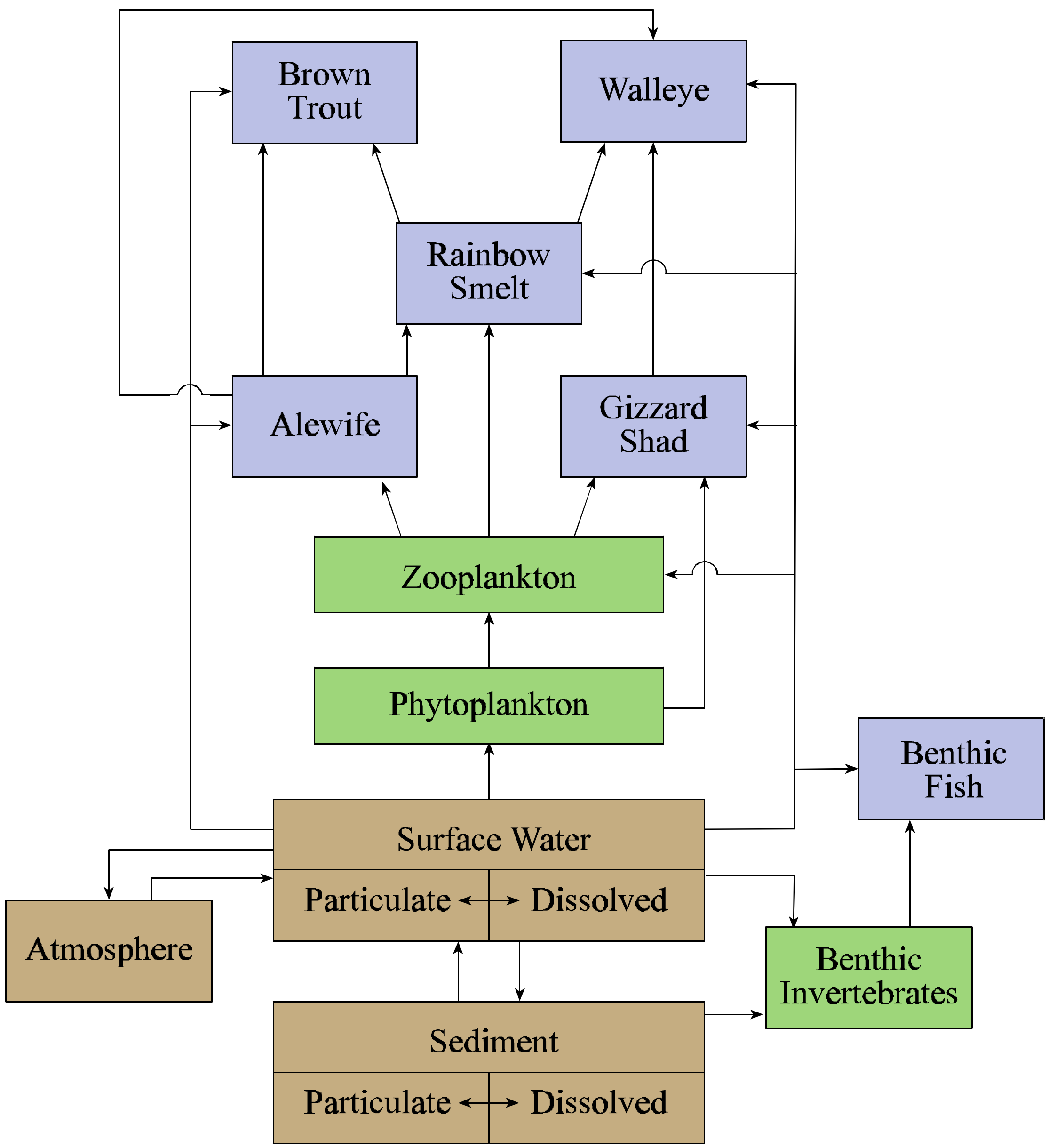
Data from DePinto et al. (1994).

3.3.2 PCB Exposure Pathways to Aquatic Biota

Figure 3-4 summarizes the pathways by which aquatic biota in the Lower Fox River/Green Bay system are exposed to PCBs, according to the GBMBS models. The largest mass of PCBs is present in the bed sediment. Sediment PCBs enter the surface water through resuspension of particulates into the water column or through diffusion of PCBs that are dissolved in pore water. PCBs in the surface water column can be redeposited on to bed sediment, volatilized to the atmosphere, or accumulated in the food chain. PCBs enter the food chain primarily via phytoplankton and benthic invertebrates. PCBs that accumulate in phytoplankton are passed on to zooplankton which consume phytoplankton. Forage fish (e.g., rainbow smelt, gizzard shad, and alewife) are exposed to PCBs in zooplankton, and in turn serve as a PCB pathway to predator fish such as walleye and brown trout.[2] PCBs that enter the food chain via benthic invertebrates are transferred to benthic-feeding fish.

2. The food web relationships in the GBMBS are dependent on fish age, since the diet of many fish species changes as the fish grow. Connolly et al. (1992) describe the age-specific food web relationships in the GBMBS in more detail.

Figure 3-4
GBMBS PCB Pathways in Lower Fox River/Green Bay System
Abiotic media are in brown, primary producers and invertebrates are in green, and fish species are in blue.



Sources: Connolly et al., 1992; DePinto et al., 1994.

Fish also accumulate PCBs directly from the water column via transfer across the gill surface. However, GBMBS models estimate that approximately 95% of the PCBs accumulated in brown trout and walleye are from food chain exposure, while direct water column exposure accounts for approximately 5% (Connolly et al., 1992). Therefore, the food chain pathway is the dominant PCB pathway for top-level predators in the Lower Fox River/Green Bay system.

3.3.3 PCB Transport Out of Green Bay

The GBMBS models document two mechanisms by which PCBs are removed from Lower Fox River/Green Bay: transport into Lake Michigan and volatilization.

Model calibration to the 1989 data shows exchange of PCBs between Green Bay and Lake Michigan, with net PCB transport from the bay to the lake. Water flow from Lake Michigan is estimated to have transported 145 kg PCBs into the bay in 1989, compared with 267 kg PCBs carried out of the bay into the lake, providing an estimated net flux from the bay to the lake of 122 kg in 1989 (DePinto et al., 1994).[3] However, these estimates are sensitive to the Green Bay/Lake Michigan boundary conditions used in the model, and the results of the ongoing Lake Michigan Mass Balance Study (being coordinated by the U.S. EPA Great Lakes National Program Office) may provide a more refined estimate of PCB transfer between the bay and the lake. Nevertheless, the available models demonstrate movement of PCBs out of Green Bay into Lake Michigan via the surface water pathway.

Volatilization of PCBs into the air column and subsequent downwind movement also transports PCBs out of the system. PCBs exchange across the air-water interface because of dissolved concentration gradients, and also are deposited from the air to the water via wet or dry deposition (DePinto et al., 1994). The models estimate that net PCB transfer was from the water to the air in 1989, with net movement of 158 kg from the water column to the air because of dissolved concentration gradients and 1.1 kg being deposited via wet/dry deposition (DePinto et al., 1994). This magnitude of net transfer into the air column, which exceeds the estimated net water column transfer of 122 kg of PCBs from the bay to Lake Michigan in 1989, demonstrates that PCBs are carried out of the Green Bay system via air currents. The prevailing southwesterly winds would carry the PCBs toward northern Lake Michigan. Therefore, the GBMBS models document the transport of PCBs out of the Green Bay system via the air pathway.

3. It should also be noted that at least some of the PCBs that move from Lake Michigan into the bay may have originated from the Lower Fox River/Green Bay system initially and were transported into the lake via water column or aerial transport pathways.

3.4 CONCLUSIONS

The GBMBS included the development of numerical models of PCB pathways in the Lower Fox River/Green Bay system that have been calibrated using extensive field data collections. The GBMBS models demonstrate that the Fox River is the dominant source of PCBs to Green Bay and that the surface water pathway is the primary pathway by which PCBs are transported downstream in the Lower Fox River and throughout Green Bay. Aquatic biota in the system are exposed to PCBs in their diet and in surface water, with food chain exposure the dominant PCB pathway for predatory fish such as walleye and brown trout. Finally, the GBMBS documents the movement of PCBs out of the Lower Fox River/Green Bay system via water currents into Lake Michigan and air currents that also tend to transport PCBs toward Lake Michigan.

CHAPTER 4
PCB TRANSPORT PROCESSES
IN THE LOWER FOX RIVER AND GREEN BAY

PCBs that enter aquatic systems such as the Lower Fox River and Green Bay can be transported via both advection (i.e., horizontal currents) and dispersion (i.e., random diffusion within the water column). Of the two processes, advection is more important for transporting PCBs in the Lower Fox River and across long distances within the bay (DePinto et al., 1994). This chapter describes the advection pathway by which PCBs are transported downstream in the Lower Fox River and throughout Green Bay. Transport of PCBs via movement of contaminated biota (fish and birds) is also discussed.

Section 4.1 summarizes data documenting the downstream transport of PCBs within the Lower Fox River and describes the distribution of PCBs in river sediments. Section 4.2 discusses available information on Green Bay water circulation patterns. Section 4.3 describes the sediment depositional patterns within the bay, which, together with the water circulation patterns, in large part determine the distribution of PCBs in bay sediments. Transport of PCBs via movement of contaminated biota is discussed in Section 4.4.

4.1 PCB TRANSPORT IN THE LOWER FOX RIVER

PCBs released from paper company facilities into the Lower Fox River are carried downstream dissolved in the water column and adsorbed to suspended sediment particles. This downstream transport pathway is documented in concentrations measured in surface water downstream of paper company facilities and in the observed distribution of PCBs in Lower Fox River sediment.

Table 4-1 summarizes data on surface water PCB concentrations and PCB transport (expressed as PCB load, or the mass of PCBs carried downstream by the river at a specific point) in the Lower Fox River. These data demonstrate that PCBs are being transported downstream in the water column of the Lower Fox River. Upstream of Lower Fox River paper companies, at the outlet of Lake Winnebago, total PCB concentrations averaged 1.77 ng/L in 1989-1990, and an estimated 5.1 kg PCBs/year were carried by the river. In contrast, total PCB concentrations and loads are much higher downstream of paper companies. At Appleton, total PCB concentrations averaged 31.13 ng/L and PCB loads were estimated at 73.0 kg/year in 1989-1990. PCB concentrations and loads then increase with distance downstream as the river mobilizes more and more PCBs from the sediment. At the river mouth, total PCB concentrations averaged 54.61 ng/L in 1994-1995, with an estimated 210 kg/year of PCBs being transported into Green Bay. These data demonstrate

Table 4-1
PCB Concentrations and Loads in the Lower Fox River

Sampling Point	Sampling Period	Average Total PCB Concentration (ng/L)	PCB Load (kg/year)
Neenah (upstream of paper companies)[a]	1989-1990	1.77	5.1
Appleton[a]	1989-1990	31.13	73.0
Kaukana[a]	1989-1990	37.65	102.2
DePere[a]	1989-1990	44.33	121.5
River Mouth[b]	1994-1995	54.61	210.1

a. From Steuer et al. (1995).
b. From WDNR (1995), as cited in (ThermoRetec Consulting Corporation and N.R.T. Inc., 1999).

the downstream transport of PCBs in the Lower Fox River and into Green Bay, and the increase in both PCB concentration and load with distance downstream.

There are consistent seasonal variations in Lower Fox River water PCB concentrations (ThermoRetec Consulting Corporation and N.R.T. Inc., 1999). Total PCB concentrations tend to be highest when flow is high in the spring and when temperatures are warmest during the summer. For example, a large increase in total PCB concentration was observed during March and April of 1994 that corresponded to increases in river flow. The increased river flow during this time of year mobilized particulate matter from the river bottom, resulting in an increase in concentrations of total suspended solids and total PCBs (which are adhered to the solids) (ThermoRetec Consulting Corporation and N.R.T. Inc., 1999).

During winter months when water temperatures fall below 40° F, total PCB concentrations in the Lower Fox River are low (ThermoRetec Consulting Corporation and N.R.T. Inc., 1999). For example, from December 1994 through February 1995, total PCB concentrations were about 10% of the yearly average (ThermoRetec Consulting Corporation and N.R.T. Inc., 1999). Steuer et al. (1995) noted that this seasonal variation is likely related to the amount of algae present in the water, since algae, which are present during warmer months, appear to facilitate suspension of PCB in the water column.

Bed sediment throughout the Lower Fox River is contaminated with PCBs (WDNR, 1999a). Much of the PCB contamination occurs in sediment downstream of DePere Dam, which is downstream of many of the points of PCB releases (ThermoRetec Consulting Corporation and N.R.T. Inc., 1999). A total of approximately 39,400 to 47,300 kg of PCBs are estimated to be contained in Lower Fox River sediments (WDNR, 1999a).

4.2 GREEN BAY WATER CIRCULATION AND MIXING PATTERNS

Once PCBs enter Green Bay from the Lower Fox River, they can be carried by the water currents that circulate through the bay. Green Bay water circulation is complex and controlled by factors such as surface water elevation changes induced by wind and barometric pressure, wind speed and direction, river discharge, upwelling of the thermocline in Lake Michigan, thermal and density gradients between the bay and Lake Michigan, ice cover, and the Coriolis effect (Mortimer, 1978).

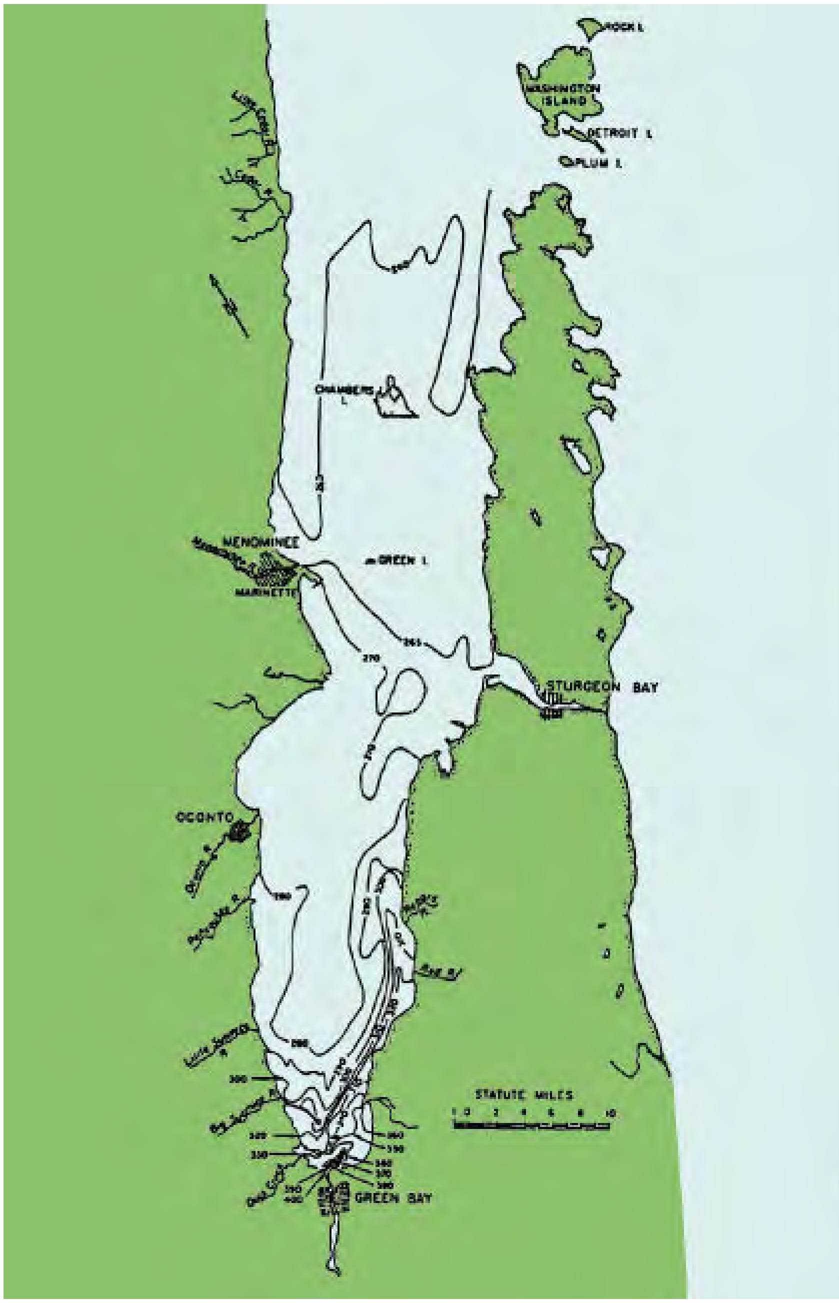
This section describes water circulation and sediment deposition patterns in Green Bay, which are important in determining PCB transport in the bay. Studies of the Fox River plume (Section 4.2.1), the circulation pattern around Chambers Island (Section 4.2.2), and mixing between Green Bay and Lake Michigan (Section 4.2.3) are summarized. The water circulation models used in the GBMBS are also briefly described (Section 4.2.4). A summary of Green Bay water circulation patterns is provided in Section 4.2.5.

4.2.1 Fox River Plume Studies

The Fox River is the dominant tributary to Green Bay, accounting for approximately 41% of the total tributary inflows (Marti and Armstrong, 1990). The water entering from the Fox River is typically warmer and more sediment-laden than the rest of the Green Bay water, allowing the Fox River plume to be tracked within the bay. Therefore, information on the movement of the Fox River plume within the bay provides one of the most direct methods of evaluating the transport of PCBs that enter the bay with the river water.

Modlin and Beeton (1970) used conductivity measurements to trace the Fox River plume in Green Bay. They found that the plume moved up the bay along the eastern shore, and were able to track the plume using conductivity measurements for 14-34 km north of the river mouth (Figure 4-1). They also tracked a plume of lower conductivity water along the western shore of the inner bay, which they concluded was outer bay water moving south along the western shore. Therefore, they concluded that the movement of the Fox River plume up the eastern side of the bay is part of an overall counterclockwise circulation pattern in the bay. The Fox River plume is deflected to the eastern side of the bay by both the prevailing southwesterly winds and the Coriolis effect (Martin et al., 1995).

Figure 4-1
Distribution of Green Bay Water Conductivity (in µmhos at 25°C) on July 23, 1968.
The contours along the southeastern shoreline indicate the Fox River plume moving up the bay along the eastern shore.



Source: Modlin and Beeton, 1970.

In a separate study, Ahrnsbrak and Ragotzie (1970) used conductivity and transmissivity measurements to observe the distribution of Fox River water in the bay, and their conclusions were similar to those of Modlin and Beeton (1970). They observed the Fox River plume up to 20 km along the eastern shore during the prevailing southerly winds. In addition, their results suggested that Long Tail Point, which is approximately 3.7 miles (6 km) north of the river mouth on the western side of the bay, limits the mixing of water in the southernmost portion of the bay.

In a more recent study, Lathrop et al. (1990) used remote sensing methods to observe the Fox River plume along the eastern shore of Green Bay. They used satellite and other remote sensing data from July 18, 1984; July 24, 1986; June 9, 1987; and July 27, 1987. As in the previous studies, the Fox River plume was observed along the eastern shoreline from 20 to 40 km away from the river mouth. The findings of Lathrop et al. (1990) also support the conclusion by Ahrnsbrak and Ragotzkie (1970) that Long Tail Point forms a mixing barrier in the southernmost portion of Green Bay, allowing Fox River water to move farther up the bay before becoming mixed.

The Fox River plume was also discernible in the water column chloride data collected in 1989 as part of the GBMBS. A plume of higher chloride concentrations extended from the mouth of the river along the eastern shore of the bay (HydroQual Inc., 1999). The plume was estimated to extend 42 km from the river mouth, consistent with other observations of the plume (HydroQual Inc., 1999).

In summary, studies of the Fox River plume in Green Bay show that Fox River water tends to move up the eastern shore of the bay as part of an overall counterclockwise circulation pattern in the inner bay. The plume can be detected using water quality measurements (temperature, conductivity) for up to 42 km from the river mouth. Therefore, based on Fox River plume studies, PCBs discharged from the river would tend to be transported initially into the bay along the eastern shore. This has important implications for evaluating the spatial distribution of PCBs in the bay, as discussed in the following chapter.

4.2.2 Inner Bay/Outer Bay Mixing Studies

Chambers Island typically is used as the boundary between inner and outer Green Bay. Several studies have examined the exchange and circulation pattern of water between the inner and outer bay by studying water movement around Chambers Island. In general, these studies have found that net flow is from the inner to outer bay, and that most of the flow from the inner to outer bay occurs along the eastern side of Chambers Island. Therefore, PCBs that travel from the Fox River along the eastern portion of the inner bay are further transported with the water currents that flow from the inner to outer bay along the eastern side of Chambers Island.

For example, Kennedy (1982) found that dissolved oxygen (DO) concentrations were greater along the west side of Chambers Island than the east side, suggesting that the higher DO water of the outer bay and/or Lake Michigan was moving along the west side and the lower DO water of the inner bay was moving along the east side. Similarly, Miller and Saylor (1985) measured current and temperature on the west and east sides of Chambers Island, and they observed that at a depth of 12 m, cold water (from the outer bay) generally flows southward along the western shore and warm water (from the inner bay) flows northward along the eastern shore. Remote sensing studies also showed a thermal difference between the surface waters on the west and east sides of Chambers Island, with colder water extending farther south on the west side, and warmer water farther north on the east side (Lathrop et al., 1990).

Miller and Saylor (1993) showed that water flow around Chambers Island is more complex than a simple counterclockwise motion. In the summer, the deeper water layer tends to flow south into the inner bay on the west of Chambers Island, and the shallow water layer flows north out of the inner bay on the west and east sides (Miller and Saylor, 1993). In the winter, water tends to flow north out of the inner bay on the east side of the island and the eastern half of the western passage. Despite the complexity of the flow, however, the movement of water from the inner to the outer bay is well documented by the Miller and Saylor (1993) study.

Miller and Saylor (1993) estimated water exchange between the inner and outer portions of Green Bay. They found that net flow for the study period (1988-1989) was from the inner to the outer bay at approximately 130 cubic meters per second ($m^3\ s^{-1}$). However, they also found that the concurrent transfer of water between inner and outer Green Bay is much larger than the net flow of water. This exchange flushes water out of the inner bay thereby transporting PCBs from the inner to outer bay (Martin et al., 1995).

4.2.3 Green Bay/Lake Michigan Mixing Studies

The water exchange between Lake Michigan and Green Bay is highly complex and variable, and difficult to measure accurately. Nevertheless, several studies have documented that large amounts of water are exchanged between the bay and the lake, providing a mechanism by which PCBs are transported from the bay into the lake.

Gottlieb (1992) estimated that the total water volume exchange between Green Bay and Lake Michigan averaged 3500 $m^3\ s^{-1}$ in 1977 and in 1989. Water exchange between the bay and the lake was complex and included some periods with inflow from the lake to the bay in the lower water layer, and some periods with inflow in the lower layer water and outflow in the upper water layer. Miller and Saylor (1985) developed a similar estimate of water exchange between Green Bay and Lake Michigan of 3300 $m^3\ s^{-1}$.

The exchange of water between Green Bay and Lake Michigan is much greater than other water inputs to and outputs from the bay. For example, Mortimer (1978) estimated precipitation input to the bay as 105 $m^3 s^{-1}$, tributary input as 336 $m^3 s^{-1}$, and evaporation loss as 87 $m^3 s^{-1}$. These values are all at least an order of magnitude less than the estimated exchange between Green Bay and Lake Michigan of 3300 to 3500 $m^3 s^{-1}$. This large volume of water exchange provides a means by which dissolved and particulate PCBs in the water column of the outer bay are transported into Lake Michigan through advection.

4.2.4 Water Circulation Models in the Green Bay Mass Balance Study

Two different mathematical models have been developed as part of the GBMBS to describe water circulation in Green Bay.

Bierman et al. (1992) developed a general Green Bay water circulation pattern for the GBMBS. They identified three major circulation patterns to describe the bay. The first pattern is a weak counterclockwise motion during the period of ice cover. The next two patterns depend on the wind direction: counterclockwise circulation during northeast or the prevailing southwest winds, and clockwise circulation during southeast or northwest winds. During 517 consecutive days in 1988 and 1989, Green Bay had counterclockwise circulation 70% of the time and clockwise circulation 30% of the time (Bierman et al., 1992). However, even during periods of clockwise circulation, the Fox River plume does not travel far up the western shore, possibly because of the barrier presented by Long Tail Point. The Bierman et al. model also includes mixing of waters within the inner bay and within the outer bay.

HydroQual (1999) recently constructed a three-dimensional hydrodynamic model of Green Bay. The model, termed GBHYDRO, is based on the hydrodynamic model being used for the ongoing Lake Michigan Mass Balance Study, but has a finer spatial scale. The model simulates circulation and mixing within the bay for the period from November 1, 1988, to May 31, 1990, and is calibrated to data collected during that period (HydroQual Inc., 1999). The results of the model simulations confirm the movement of the Fox River plume along the eastern shore of the inner bay (HydroQual Inc., 1999). The model also shows that when overall water circulation in the bay is counterclockwise, small-scale variations can result in localized eddies in the opposite direction.

In summary, both the Bierman et al. (1992) and the HydroQual (1999) models indicate that:

- Fox River water moves up the eastern shore of the inner bay as part of an overall counterclockwise circulation pattern
- water exchange occurs between the inner bay and outer bay
- water mixing occurs within the inner bay and the outer bay

- water exchange occurs between the outer bay and Lake Michigan.

Therefore, these models demonstrate the transport mechanism through which advective transport of Fox River PCBs occurs throughout Green Bay and into Lake Michigan.

4.2.5 Conclusions

Based on a review of field studies and hydrodynamic models developed for Green Bay, the following conclusions can be made regarding water circulation and movement in Green Bay:

- Fox River water that enters Green Bay tends to move up the bay along the eastern shore, where it becomes mixed with bay water. PCBs being carried in the water (either in dissolved or particulate phases) would follow the same path.

- Inner bay water along the eastern shore moves into the outer bay, providing a mechanism for PCBs to be transported from the inner to outer bay.

- A large exchange of water between the outer bay and Lake Michigan provides the potential for PCBs to be transported from Green Bay into Lake Michigan.

4.3 GREEN BAY SEDIMENT TRANSPORT AND DEPOSITION

Because PCBs absorb strongly onto sediment, the transport and deposition of Fox River sediments discharged into the bay determine in large part the transport and fate of PCBs in the bay. Sediment is not deposited uniformly across the bottom of the bay, but collects within the depositional zones of the bay. The relationship of the depositional zones to the water current patterns described above determines the ultimate distribution of PCBs in Green Bay sediment.

Using data on lead and cesium isotopes (^{210}Pb and ^{137}Cs) from 63 sediment cores in Green Bay, Manchester-Neesvig et al. (1996) determined the main areas and rates of sediment accumulation in the bay. They found that the areas where most of the sediment is deposited are within the inner portion of Green Bay. One of the primary sedimentation zones is located along the eastern half of the inner bay. Because of its location, this zone is the primary depositional area for sediment discharged from the Fox River.

Most of the Fox River sediments discharged into the bay settle within the inner bay (Hawley and Niester, 1993). Lathrop et al. (1990) observed that, by the time the Fox River plume reaches Chambers Island, the water mass is still distinguishable by temperature but not by transmissivity, indicating the settling of particulate matter before the water reaches Chambers Island.

Nevertheless, sediment that has been deposited can be re-entrained and transported. Models of Green Bay sediment dynamics developed as part of the GBMBS include sediment resuspension throughout the bay as an integral component (Bierman et al., 1992; DePinto et al., 1994). Eadie et al. (1991) concluded from their measurements of high sediment settling velocities in the bay that the pool of suspended particulate matter in the Green Bay water column must be recharged at a high rate, either from sediment resuspension or horizontal movement. Hawley and Niester (1993) documented the movement of suspended sediment from the inner to the outer bay, which occurred primarily along the eastern side of Chambers Island. They also detected a pulse of suspended sediment concentrations transported from the inner bay to the outer bay during a September, 1989 storm. These studies demonstrate that some inner bay sediment is resuspended and transported to the outer bay. Rough calculations by Hawley and Neister estimated that approximately 10% to 33% of the inner bay tributary sediment load (the majority of which is from the Fox River) is transported to the outer bay.

4.4 PCB TRANSPORT IN CONTAMINATED BIOTA

PCBs can be transported via the movement of biota contaminated with PCBs. Fish and birds exposed to PCBs in the Lower Fox River/Green Bay environment that migrate to other areas serve as PCB pathways, effectively transporting PCBs to other areas. This migration of contaminated biota may serve as a particularly important transport pathway for natural resources on the Reservation of the Oneida Tribe of Indians of Wisconsin.

The Oneida Reservation is located immediately west and southwest of the city of Green Bay, near the southern end of Green Bay. The Reservation is connected to the waters of the Lower Fox River and Green Bay through several creeks that run through the Reservation. These creeks include Duck Creek, which flows through the reservation and enters Green Bay just northwest of the Fox River mouth, and Dutchman’s Creek, which flows through the Reservation and enters the Fox River a few miles upstream of its mouth.

Several studies have shown that fish migrate from Green Bay up Duck Creek and into the Reservation, thereby transporting PCBs to the Reservation. In a study conducted by the Service between 1995 and 1998, fish marked with floy tags in Green Bay were found in Duck Creek within the Reservation boundaries, and fish marked in Duck Creek were found in Green Bay (Cogswell, 1998; Cogswell and Bougie, 1998). The species documented to migrate between Duck Creek and Green Bay include northern pike, walleye, smallmouth bass and yellow perch. For example, the study found that 46% of the northern pike tagged in the Duck Creek were recaptured at several different sites in Green Bay.

PCB concentrations measured in Duck Creek walleye, white sucker and northern pike confirm that Duck Creek fish have elevated concentrations of PCBs (T. Nelson, Oneida Environmental Department, personal communication, 1999). In addition, a mink captured in March, 1999 along

Silver Creek, a tributary to Duck Creek on the Reservation, had a liver PCB concentration of 40.42 μg/g (wet weight) (T. Nelson, Oneida Environmental Department, personal communication, 1999), a concentration indicative of elevated PCB exposure (Eisler, 1986). Since fish typically comprise a large portion of mink diet (U.S. EPA, 1993), the mink exposure to PCBs most likely results from consumption of contaminated fish. Therefore, migration data document that fish move between Duck Creek and Green Bay, and PCB concentration data in fish and mink indicate that the fish migration from Green Bay up Duck Creek serves as a transport pathway for PCBs.

Waterfowl collected on the Oneida Reservation also have elevated PCB concentrations in their tissue. Several mallard ducks collected in the fall of 1998 had detectable PCB concentrations in breast tissue (T. Nelson, Oneida Environmental Department, personal communication, 1999). These data indicate that avian resources on the Reservation may be exposed to PCBs in the Lower Fox River/Green Bay environment and transport the PCBs to the Reservation.

4.5 CONCLUSIONS

The evaluation of physical transport processes in Lower Fox River/Green Bay demonstrates the following:

- PCBs are transported downstream with the river currents of the Lower Fox River. Elevated PCBs have been documented throughout the river downstream of paper company facilities, both moving with surface water and deposited in sediments.

- Fox River water that enters Green Bay tends to move up the bay along the eastern shore, where it becomes mixed with inner bay water. PCBs being carried in the water (either in dissolved or particulate phases) would follow the same path. The eastern portion of the inner bay is the primary depositional area for Fox River sediments in the bay, and thus is the primary depositional area for Fox River PCBs in the bay.

- Some of the Fox River PCBs are transported from the inner bay to the outer bay. Inner bay water along the eastern shore flows into the outer bay, providing a mechanism for PCBs to be transported from the inner to outer bay. Similarly, the extensive exchange of water between the outer bay and Lake Michigan provides a mechanism for transport of PCBs from Green Bay into Lake Michigan.

- The migration of contaminated biota is another transport process. Fish and birds that accumulate PCBs from the Lower Fox River/Green Bay system migrate to the Oneida Reservation.

These conclusions demonstrate the physical processes by which PCBs are transported within the Fox River/Green Bay system. The following chapter evaluates the resulting spatial and temporal trends of PCB contamination in the system to provide further documentation of the PCB pathways.

CHAPTER 5
SPATIAL AND TEMPORAL DISTRIBUTION OF PCBS IN GREEN BAY

This chapter presents a description of the spatial and temporal patterns of PCB contamination in Green Bay sediment, surface water, and biota. The information presented in this chapter relates to the PCB pathway determination for the bay in the following ways:

- The spatial and temporal patterns of PCB contamination in Green Bay sediment, surface water, fish, and birds are consistent with the conclusion that the Fox River is the primary source of PCBs to the bay.
- The spatial PCB data for sediment, surface water, and fish show that PCBs are transported throughout the bay.
- The evaluation of temporal patterns of PCB contamination confirm that PCB pathways to Lower Fox River/Green Bay resources are continuing.

5.1 PCB SPATIAL PATTERNS IN GREEN BAY

This section describes the spatial patterns of PCB contamination in the bed sediment, surface water, and fish of Green Bay. The spatial patterns observed in these resources are consistent with the Fox River being the primary source of PCBs into the bay and confirm the transport of PCBs from the Fox River throughout the bay.

5.1.1 Sediment

Based on the water circulation and sediment deposition patterns described in Chapter 4, PCBs that enter Green Bay from the Fox River and are deposited in bed sediment are expected to accumulate primarily in the inner bay, and within the inner bay, primarily in the depositional zone along the eastern shore. This section describes the spatial pattern of PCBs observed in Green Bay sediments and shows that the pattern is consistent with the Fox River being the primary source of PCBs in Green Bay sediment.

Although several investigators have studied the spatial distribution of PCBs in Green Bay sediment (Buser, 1985; Swackhamer, D.L and D.E. Armstrong, 1988; Hermanson et al., 1991), the most spatially complete data set is that collected as part of the GBMBS (Manchester-Neesvig et al., 1996). A 5 km x 5 km grid was established across the entire bay, resulting in 169 potential sampling locations. Sediment cores for PCB analysis were collected only from those locations with soft sediment, resulting in collection from 64 locations for PCB analysis (Manchester-Neesvig et al., 1996). Most of these locations are in the inner bay (Figure 5-1), since the outer bay sediments are primarily nondepositional.

Figure 5-1 shows the mean total PCBs measured in the upper 10 cm of Green Bay sediment at each sampling location. The figure shows that PCB concentrations are higher in the inner bay than in the outer bay, and that concentrations in the inner bay are highest along the eastern shore. The evaluation of Green Bay water circulation and sediment deposition patterns presented in Chapter 4 concluded that the sediment deposition zone along the eastern shore of the inner bay receives primarily Fox River sediments. The Fox River plume moves up the eastern half of the bay, depositing sediments in a depositional zone in the eastern half of the inner bay. Since the PCB contamination in this area is much higher than in other depositional zones in the bay, these data indicate that the Fox River sediments are much more highly contaminated with PCBs than sediment from other sources. This conclusion is consistent with direct measurements of PCBs in Green Bay tributaries, which shows that the Fox River has much higher PCB concentrations than other tributaries (DePinto et al., 1994). Therefore, the spatial pattern of PCBs in Green Bay is consistent with the Fox River being the primary source of PCBs to the bay.

The Green Bay sediment PCB data also indicate that PCBs have moved from the inner to the outer bay. Although total PCB concentrations are lower in outer bay than inner bay sediments, a gradient of PCB concentrations is still detectable within the outer bay. Locations in the southern portion of the outer bay, just northeast of Chambers Island, tend to have higher PCB concentrations than locations farther out in the outer bay (Figure 5-1). This pattern is consistent with the conclusion that the inner bay is the primary source of PCBs to the outer bay.

5.1.2 Surface Water

Swackhamer and Armstrong (1987) measured PCB concentrations in Green Bay water. A single surface water sample, collected at a depth of five meters, was taken at each of nine locations in the bay in September 1980. At some of these locations, samples were also collected at the thermocline, mid-hypolimnion, and five meters above the bottom of the bay. Each sample was analyzed for both particulate and dissolved PCBs.

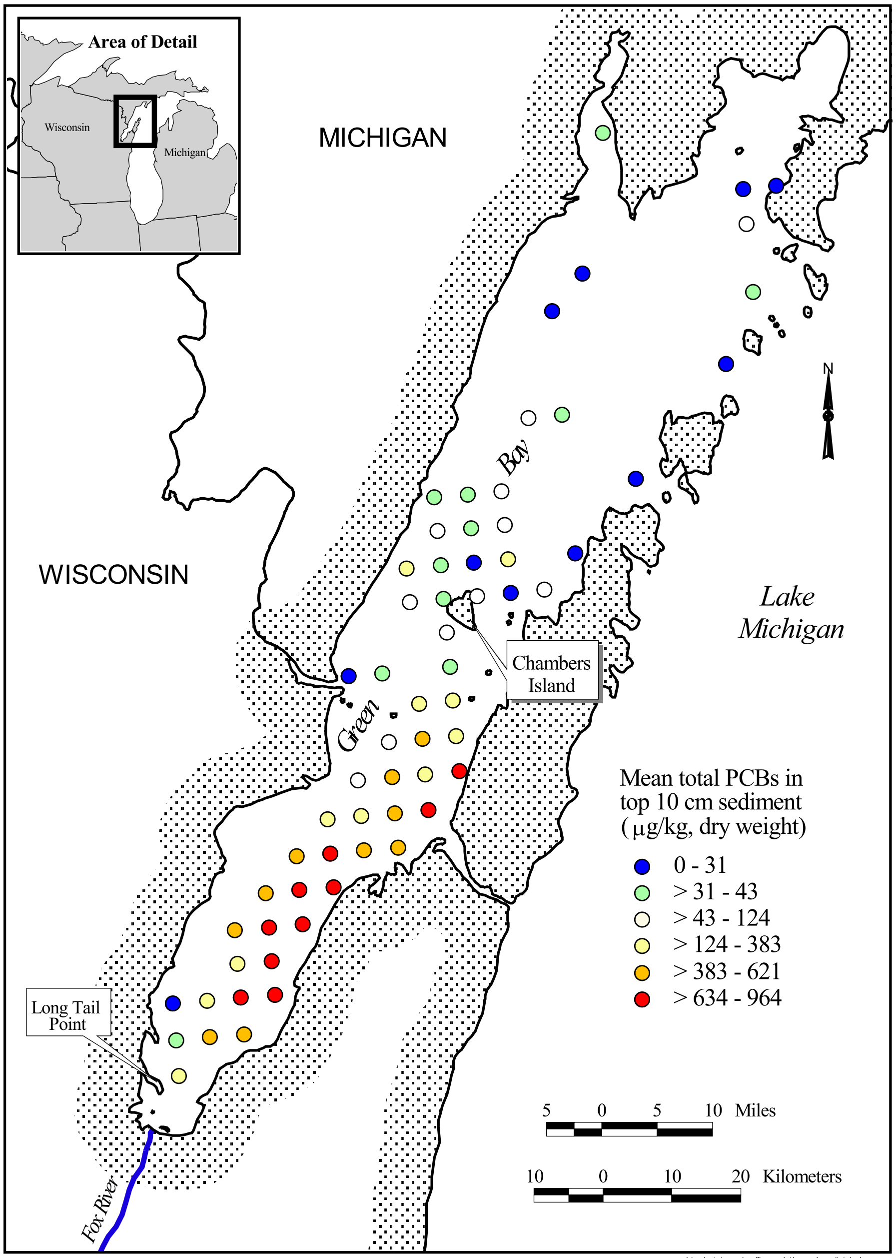
Their results show that total PCB concentration in Green Bay water decreases with increasing distance from the Fox River mouth. The station at the mouth of the Fox River had a PCB concentration of 121 ng/L. Other samples in the inner bay ranged from 2 to 20 ng/L, while outer bay samples ranged between 1.1 and 2.1 ng/L.

From May 1989 through April 1990, surface water samples were collected at 27 locations in the bay over seven sampling periods as part of the GBMBS (Figure 5-2) (DePinto et al., 1994). The

Figure 5-1

Mean Total PCB Concentrations in the Top 10 cm of Green Bay Bed Sediment, 1989

Each symbol represents a single sediment sampling location. Sediment for PCB analysis was collected only from locations with soft sediment.



Source: GBMBS data from the WDNR sponsored database at http://www.ecochem.net/FoxRiverDatabaseWeb/default.asp, downloaded July 1999.

sampling periods were May 1989, June 1989, July 1989, September 1989, October 1989, February 1990, and April 1990. Usually, one sample from each location was collected during each sampling period and analyzed for both particulate and dissolved PCBs. In some cases duplicate samples were analyzed for a single location and date. For the spatial analysis presented here, we averaged the values from the duplicate samples to obtain a single value for each sample type (dissolved or particulate) by location and date. Particulate and dissolved PCBs were then summed to obtain total PCBs in surface water by location and date. Data were then averaged across all months for each station to obtain a single value representing total PCBs in Green Bay by station. This data are presented in Table 5-1.

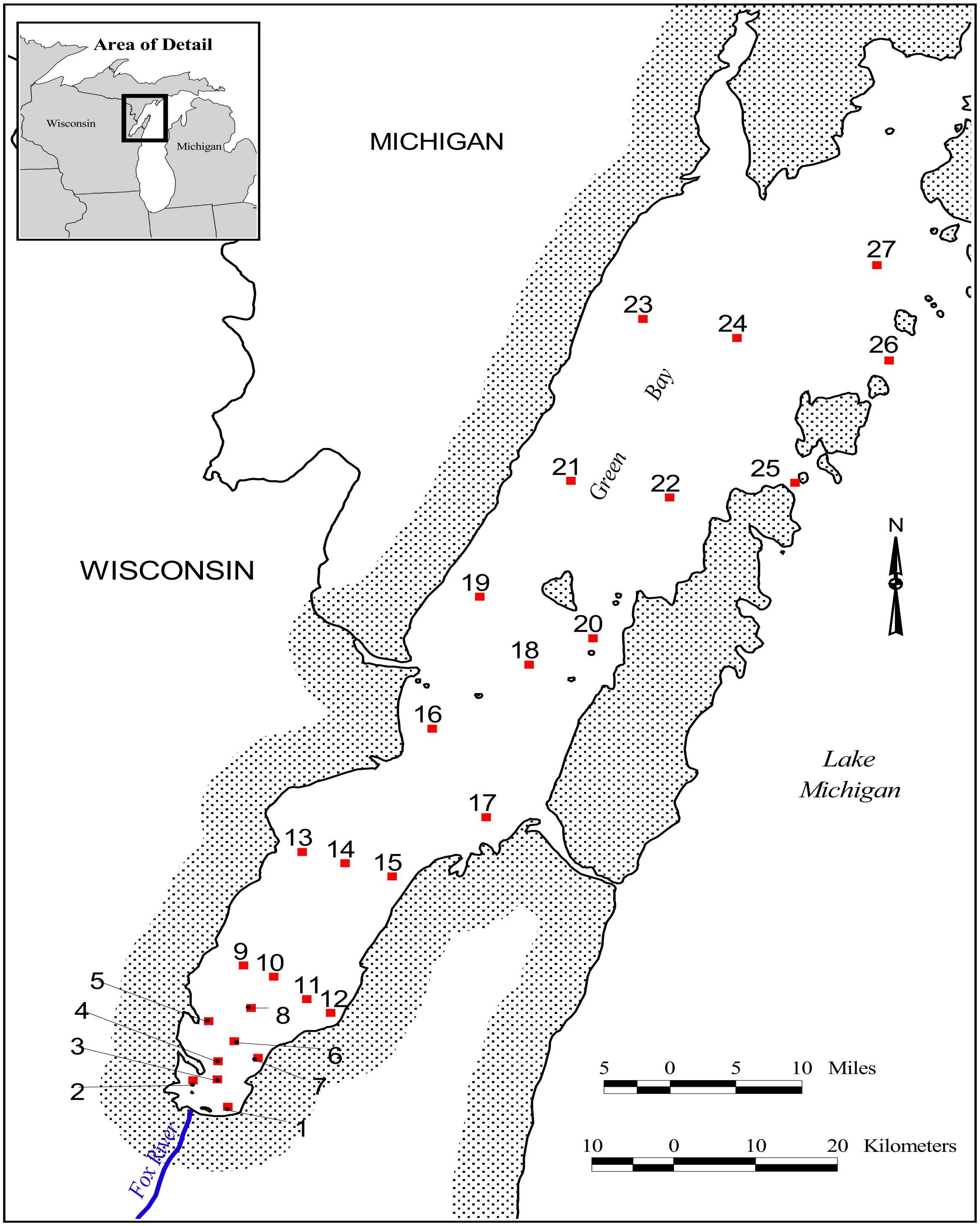
Figure 5-3 shows the spatial distribution of average total PCBs (dissolved plus particulate phases) in surface water in the bay. PCB concentrations are highest at the mouth of the Fox River, where values range between 19.7 and 42 ng/L (parts per trillion). Values in the central portion of the inner bay range from 3.6 to 10.8 ng/L, while values in the northern section of the inner bay and in the outer bay range from 0.95 to 2.0 ng/L. A trend of decreasing PCB concentrations with distance from the Fox River mouth is evident.

The strong decreasing trend of PCB concentrations with distance from the Fox River mouth is shown more clearly in Figure 5-4. In this figure, surface water PCB concentrations are plotted against distance from the Fox River mouth. The concentrations decline consistently throughout the bay with increasing distance from the Fox River. This pattern of decreasing concentrations with distance from the Fox River is consistent with the Fox River being the primary PCB source to the bay.

In addition to the PCB concentration gradient from the Fox River to the outer bay, a gradient is also present from east to west within the inner bay. Figure 5-5 shows PCB concentrations along three transects that run across the inner bay, perpendicular to the SW/NE axis of the bay. The surface water concentrations decrease from the eastern side of the bay to the western, with the decrease more evident along the transect closer to the Fox River (5,6,7; Figure 5-5). As discussed in the previous section, the highest PCB concentrations in sediment also occur along the eastern half of the inner bay. Therefore, both the sediment and the surface water of Green Bay show similar spatial patterns of PCB concentrations, consistent with both the Fox River being the primary source of PCBs to the bay and the link between surface water PCB transport and sediment PCB concentrations.

Studies that compared PCB concentrations in Green Bay with those in Lake Michigan indicate a gradient from higher concentrations in Green Bay to lower concentrations in Lake Michigan. Swackhamer and Armstrong (1987) collected water samples in September 1980 and found that PCB concentrations were higher in outer Green Bay than in Lake Michigan. Total PCBs at a location near the middle of the outer bay were 1.1 and 1.4 ng/L at two different depths. In contrast, concentrations in northern Lake Michigan were 0.36 and 1.0 ng/L, indicating a PCB

Figure 5-2
Surface Water Sampling Locations in the GBMBS, 1989 to 1990



j:/projects/greenbay/fingerprint/newpcb.apr/totalpcbs

Table 5-1
1989-1990 GBMBS Total PCBs in Surface Water (ng/L)

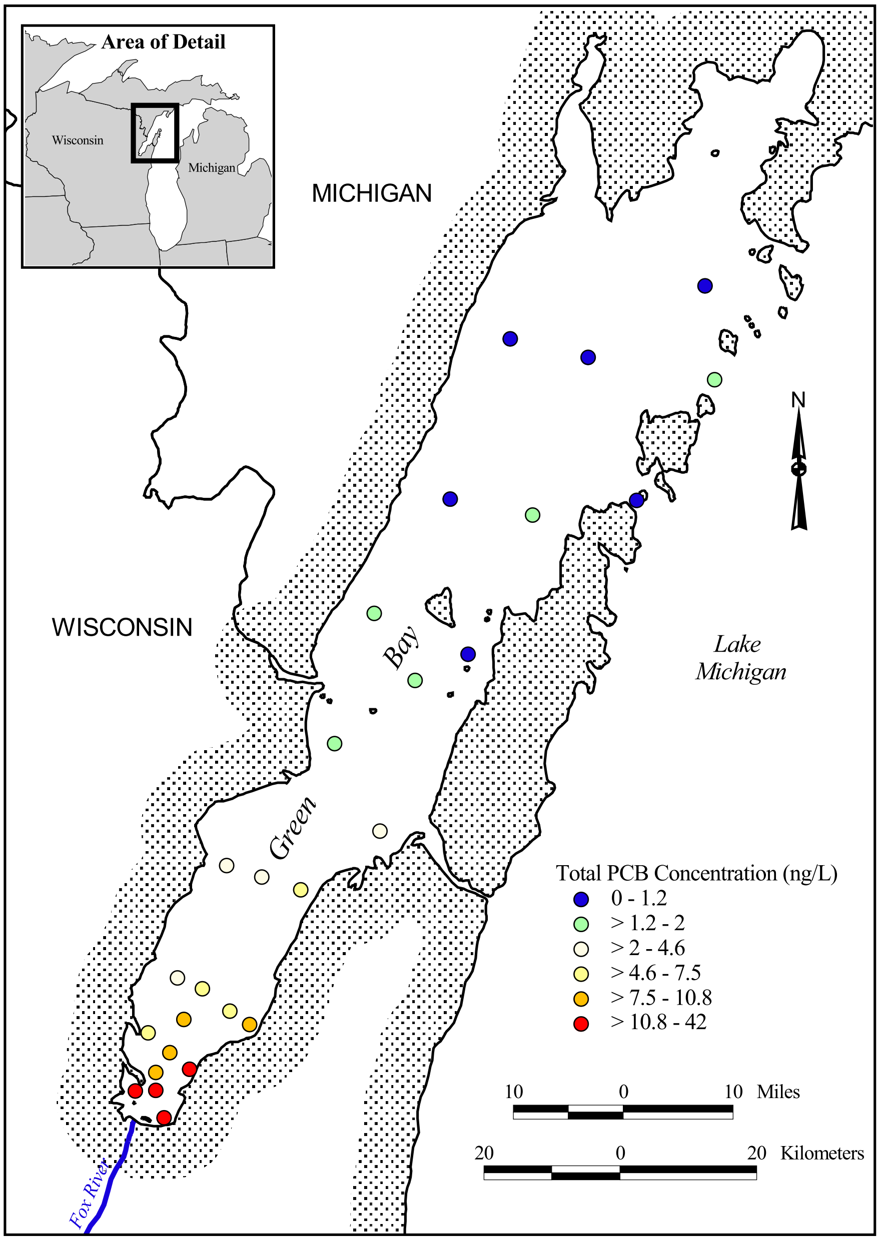
Station[a]	May 1989	June 1989	July 1989	Sept. 1989	Oct. 1989	Feb. 1990	April 1990	Average
1	NA	26.0	24.9	40.4	47.8	8.73	103	41.8
2	11.7	31.5	28.5	23.2	31.5	10.6	102	34.1
3	43.3	27.0	15.1	24.7	44.2	7.45	9.38	24.4
4	9.31	21.5	6.84	11.0	10.4	9.09	5.75	10.5
5	5.74	8.98	5.84	11.8	6.20	3.51	4.37	6.63
6	4.67	10.2	14.2	13.9	9.79	7.92	6.92	9.65
7	30.3	19.6	23.1	9.67	24.0	13.5	18.2	19.8
8	8.56	4.63	12.0	7.99	20.7	5.01	7.04	9.42
9	3.39	3.94	4.57	6.39	5.58	4.18	3.68	4.53
10	4.30	4.89	11.2	4.67	15.2	4.97	2.79	6.85
11	6.87	7.22	8.80	6.37	12.5	5.79	4.72	7.46
12	17.7	13.0	13.1	10.4	7.32	6.39	7.17	10.7
13	6.22	2.97	2.96	3.10	3.93	3.09	3.65	3.70
14	3.57	2.08	3.34	1.57	9.25	3.21	2.59	3.66
15	5.42	7.28	1.96	1.60	9.16	3.51	5.95	4.98
16	2.82	1.16	1.31	1.24	2.19	2.24	1.80	1.82
17	6.40	5.94	1.46	1.08	3.65	3.93	4.30	3.82
18	3.35	1.31	1.34	1.06	3.66	1.73	1.43	1.98
19	1.77	0.910	1.11	0.977	2.80	1.67	1.52	1.54
20	NA	1.08	1.19	0.805	1.90	1.58	0.611	1.20
21	NA	0.919	0.497	0.741	2.06	NA	0.753	0.994
22	2.32	0.992	0.462	0.883	1.48	1.35	0.958	1.21
23	2.77	0.719	0.642	0.615	1.08	NA	0.870	1.12
24	1.40	0.825	0.798	0.812	1.04	NA	0.845	0.954
25	1.25	0.765	0.689	0.984	1.40	NA	0.666	0.959
26	3.11	1.16	0.651	0.715	1.10	NA	0.698	1.24
27	1.95	0.983	0.824	0.643	1.36	NA	0.735	1.08

a. See Figure 5-2 for station locations.

NA: No measurement taken.

Source: GBMBS data from the WDNR sponsored database at http://www.ecochem.net/FoxRiverDatabaseWeb/default.asp, downloaded July 1999.

Figure 5-3
Mean Total PCBs in Green Bay Surface Water, 1989 to 1990

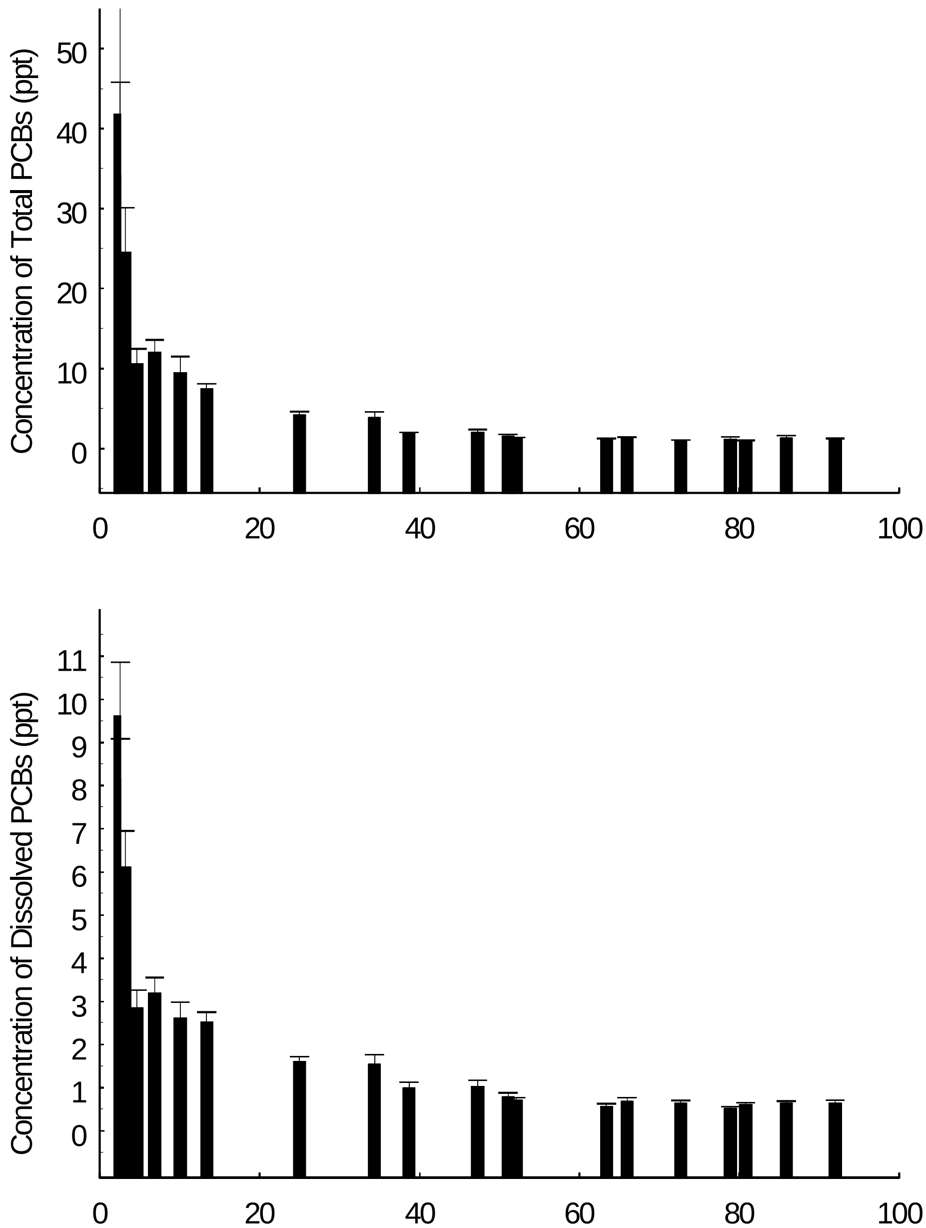


j:/projects/greenbay/fingerprint/newpcb.apr/Surface Water Data

Source: GBMBS data from the WDNR sponsored database at http://www.ecochem.net/FoxRiverDatabaseWeb/default.asp, downloaded July 1999.

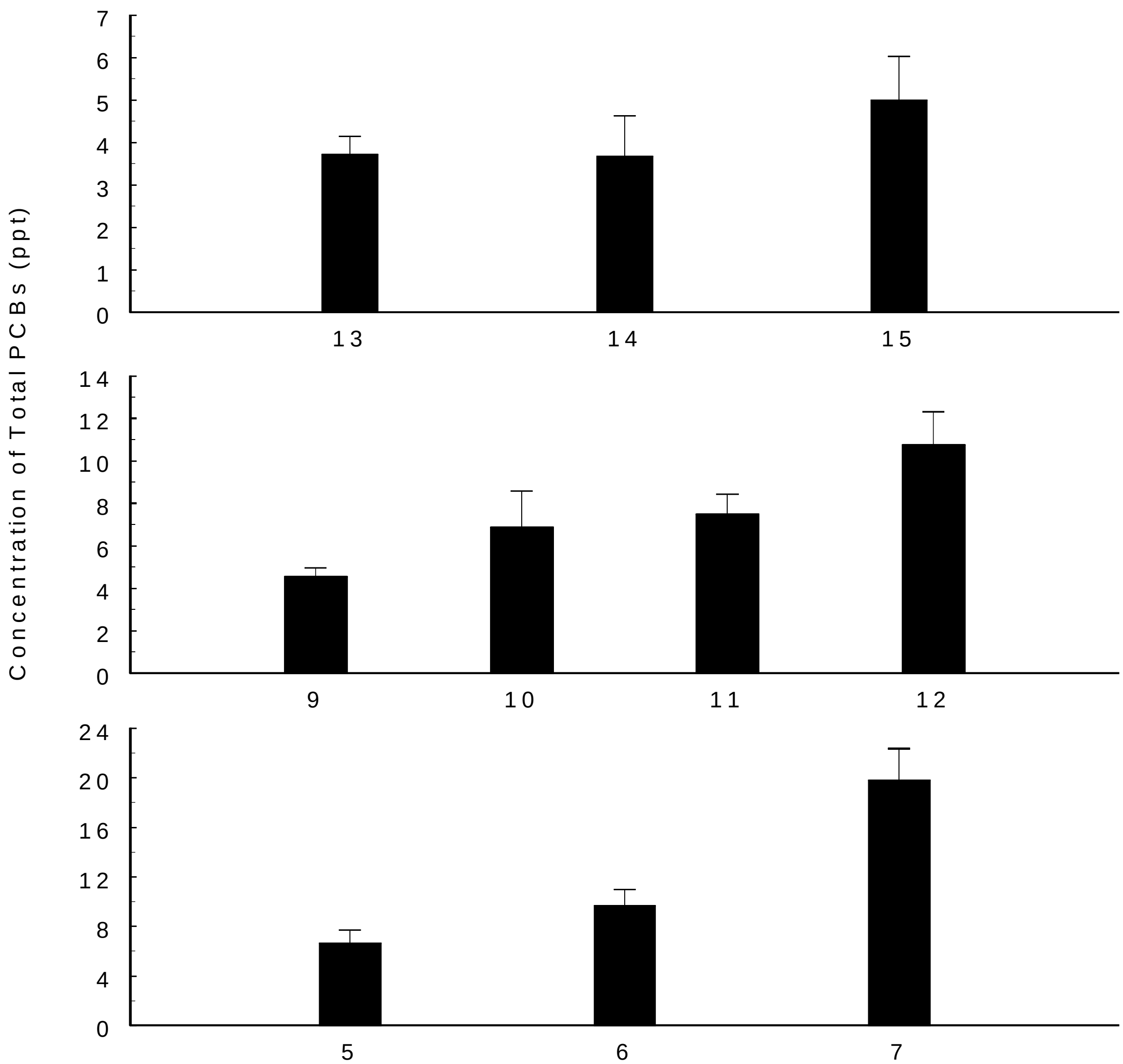
Figure 5-4
Distance from the Fox River Mouth Versus PCB Concentration in Green Bay Surface Water

Means plus one standard error are shown. PCB concentrations across three transects (stations 5, 6, and 7; stations 9, 10, 11, and 12; and stations 13, 14, and 15; see Figure 5-2) were averaged to obtain a single value for each.



Source: GBMBS data from the WDNR sponsored database at http://www.ecochem.net/FoxRiverDatabaseWeb/default.asp, downloaded July 1999.

Figure 5-5
Concentration of Total PCBs in Green Bay Surface Water at Three Horizontal Transects
Means plus one standard error are shown. Sample location numbers are shown in Figure 5-2.



Source: GBMBS data from the WDNR sponsored database at http://www.ecochem.net/FoxRiverDatabaseWeb/default.asp, downloaded July 1999**.**

concentration gradient from the bay to the lake. The highest PCB concentration measured in the northern half of Lake Michigan was at a near-shore location just south of the mouth of Green Bay, near the waterway connecting Green Bay and the lake at Sturgeon Bay. Thus, this data point may reflect the influence of Green Bay PCBs on Lake Michigan and movement of PCBs from the bay to the lake.

Similarly, data collected for the 1989-1990 GBMBS showed higher concentrations in outer Green Bay compared with Lake Michigan, and thus the mass balance models based on the data show net movement of PCBs from the bay to the lake. The decreasing PCB concentration gradient from the bay to the lake indicates that the bay surface water serves as a PCB source to Lake Michigan.

5.1.3 Fish

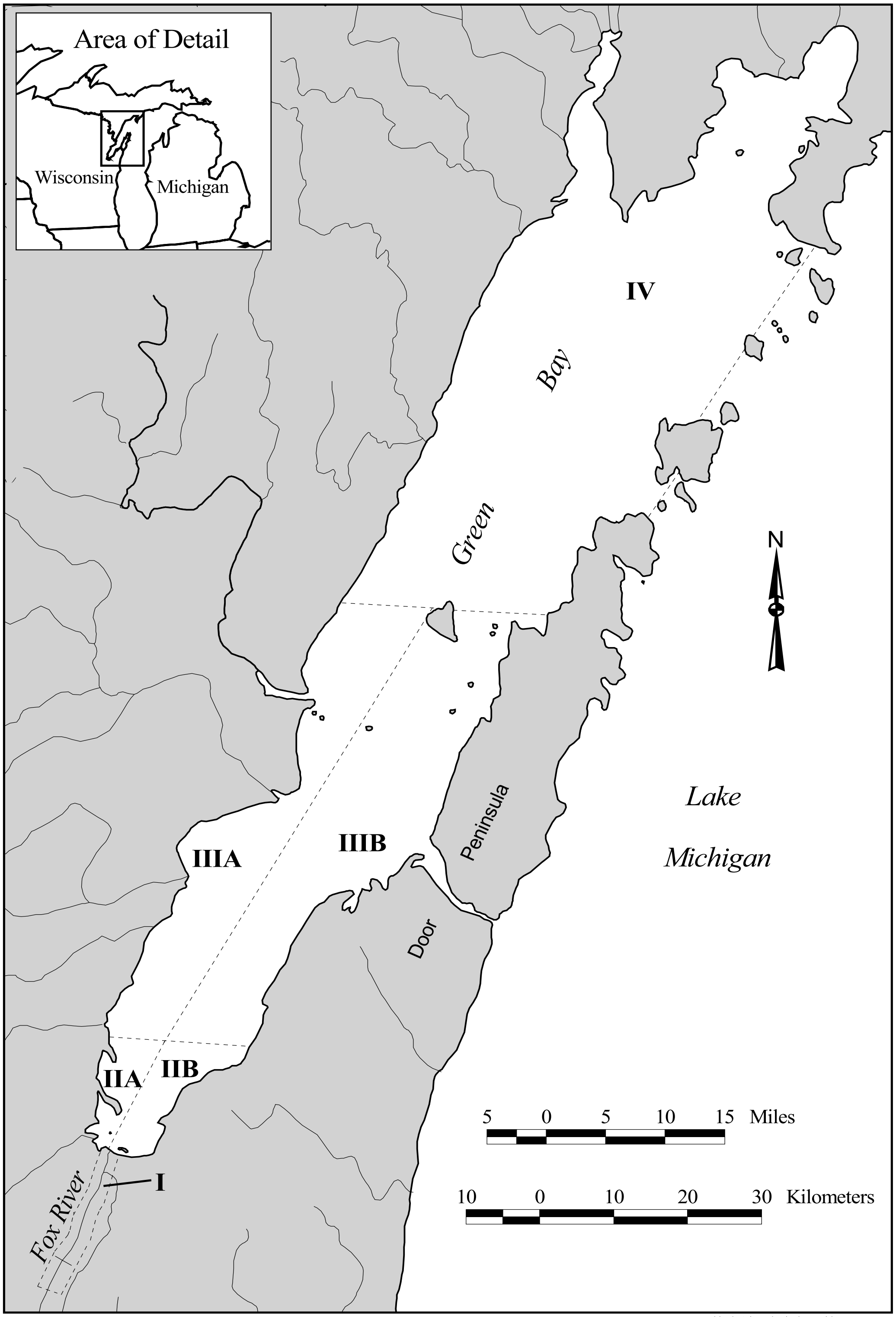
The most complete database available on the spatial distribution of PCBs in Green Bay fish comes from the GBMBS. Six species (alewife, brown trout, carp, gizzard shad, rainbow smelt, and walleye) were collected from numerous locations across Green Bay in 1989-1990 and analyzed for PCB congeners in whole-body samples (Connolly et al., 1992). Since the samples were all collected and analyzed using similar methods and during similar times, results for a given species from different locations provide a direct comparison of spatial PCB accumulation patterns.

Sampling locations across the bay were grouped into six different zones within the bay, shown in Figure 5-6. Zone 1 is the Lower Fox River downstream of DePere Dam; Zones 2A and 2B are the western and eastern halves, respectively, of the innermost portion of the bay; Zones 3A and 3B are the western and eastern halves, respectively, of the rest of the inner bay; and Zone 4 is the outer bay (beyond Chambers Island). Table 5-2 shows the number of samples of each species collected for each zone.

Total PCB concentrations in whole-body alewife, brown trout, carp, gizzard shad, rainbow smelt, and walleye measured as part of the GBMBS are shown in Figures 5-7 through 5-12. Total PCB concentrations were calculated as the sum of individual congener values. The total PCB concentrations shown are normalized to fraction lipid in the sample to control for variations in PCB concentrations due to variations in lipid content.

All of the fish species show similar spatial patterns of PCB concentrations. Concentrations are highest in the Lower Fox River and decline with increasing distance into the bay. In addition, concentrations within zones 2 and 3 along the eastern shore of the inner bay (zones 2B and 3B) are generally higher than those along the western shore (zones 2A and 3A). Therefore, the spatial pattern of PCBs in Green Bay fish is consistent with the patterns seen in sediment and surface water, demonstrating the pathway connection between sediment, surface water, and fish.

Figure 5-6
Fish Sampling Zones Used in GBMBS



j:/projects/greenbay/amls_aprs/gb_zones.apr

Table 5-2
1989-1990 GBMBS Fish Collection Sample Sizes

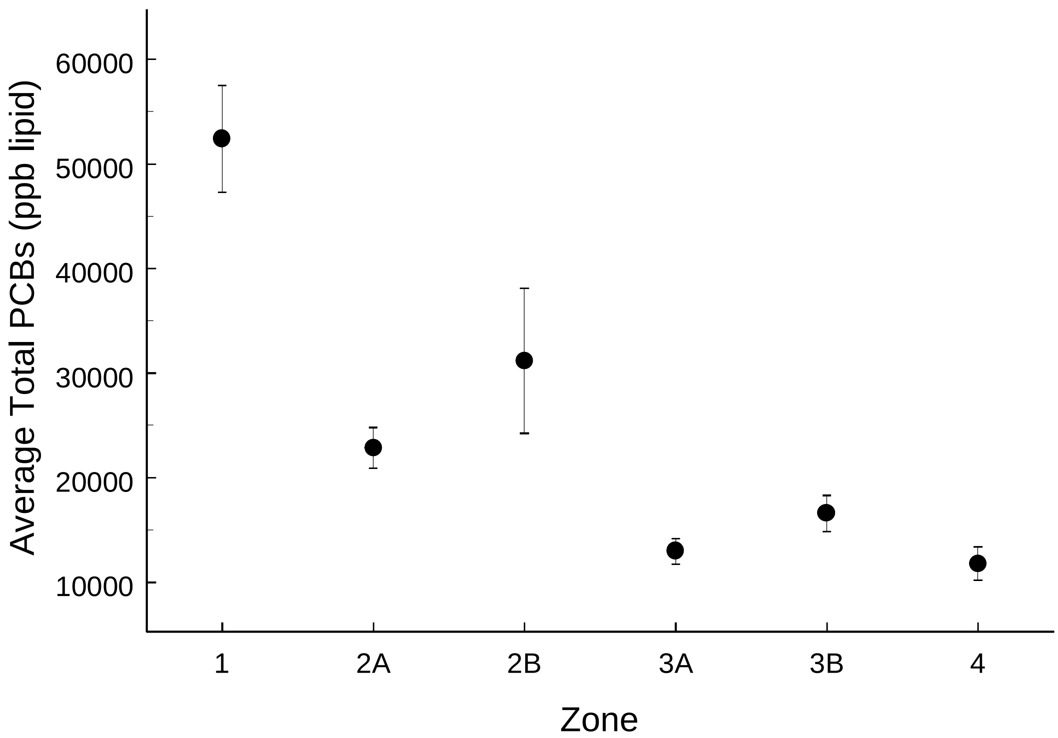
Species	Zone 1	Zone 2A	Zone 2B	Zone 3A	Zone 3B	Zone 4
Alewife	11	21	14	18	7	8
Brown trout	0	0	0	14	12	13
Carp	34	36	36	17	25	23
Gizzard shad	9	8	6	0	0	0
Rainbow smelt	0	14	15	20	20	18
Walleye	25	10	21	10	12	13

Source: GBMBS data from the WDNR sponsored database at http://www.ecochem.net/FoxRiverDatabaseWeb/default.asp, downloaded July 1999.

Brazner and DeVita (1998) conducted a study on contaminant concentrations in young-of-the-year littoral fishes in Green Bay. Their results are consistent with the findings of the GBMBS on spatial patterns of PCB contamination in Green Bay fish: PCB concentrations were highest in fish near the Fox River mouth and declined along a gradient from the inner to the outer bay.

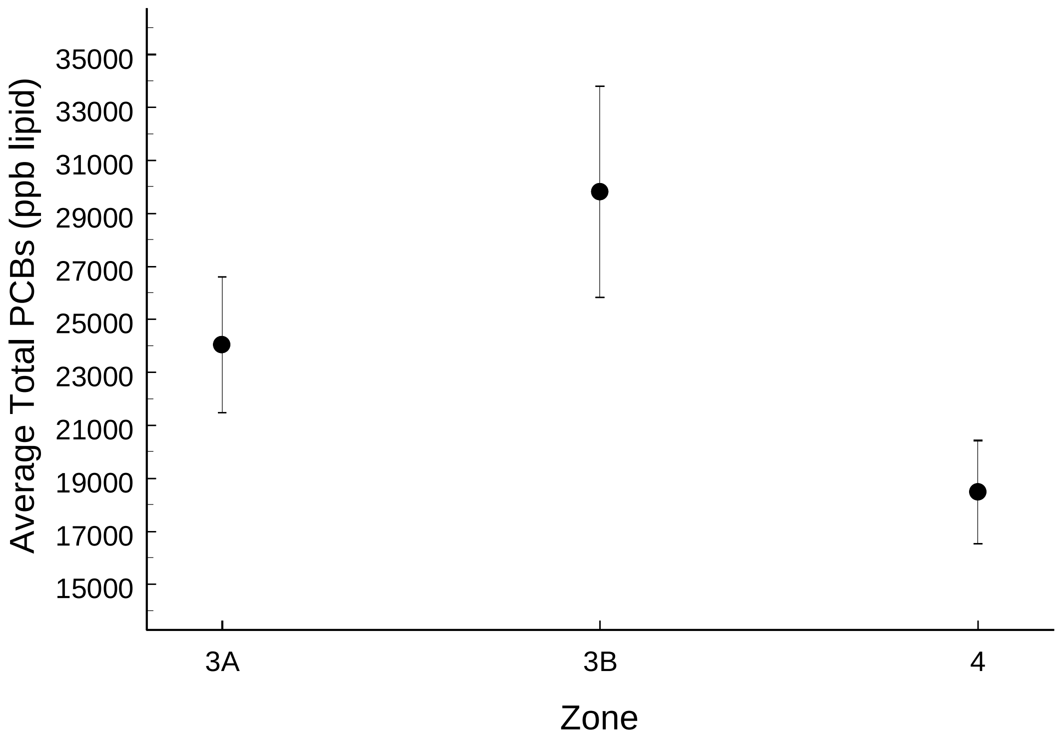
In conclusion, the spatial pattern of PCB contamination in Green Bay fish is consistent with the patterns observed in sediment and surface water. Concentrations are highest in fish sampled closest to the mouth of the Lower Fox River and decline with distance from the mouth. PCB concentrations are also higher in fish sampled along the eastern shore of the inner bay than in those sampled along the western shore. These data are consistent with a link between PCB accumulation in fish and PCB concentrations in surface water and sediment, indicating that the transport of PCBs throughout the bay via the surface water pathway results in the exposure and accumulation of PCBs in Green Bay fish.

Figure 5-7
Total Lipid-Normalized PCB Concentrations in Green Bay Alewives, 1989. Bars equal plus or minus one standard error about mean. Zone locations are shown in Figure 5-6.



Source: GBMBS data from the WDNR sponsored database at
http://www.ecochem.net/FoxRiverDatabaseWeb/default.asp, downloaded July 1999**.**

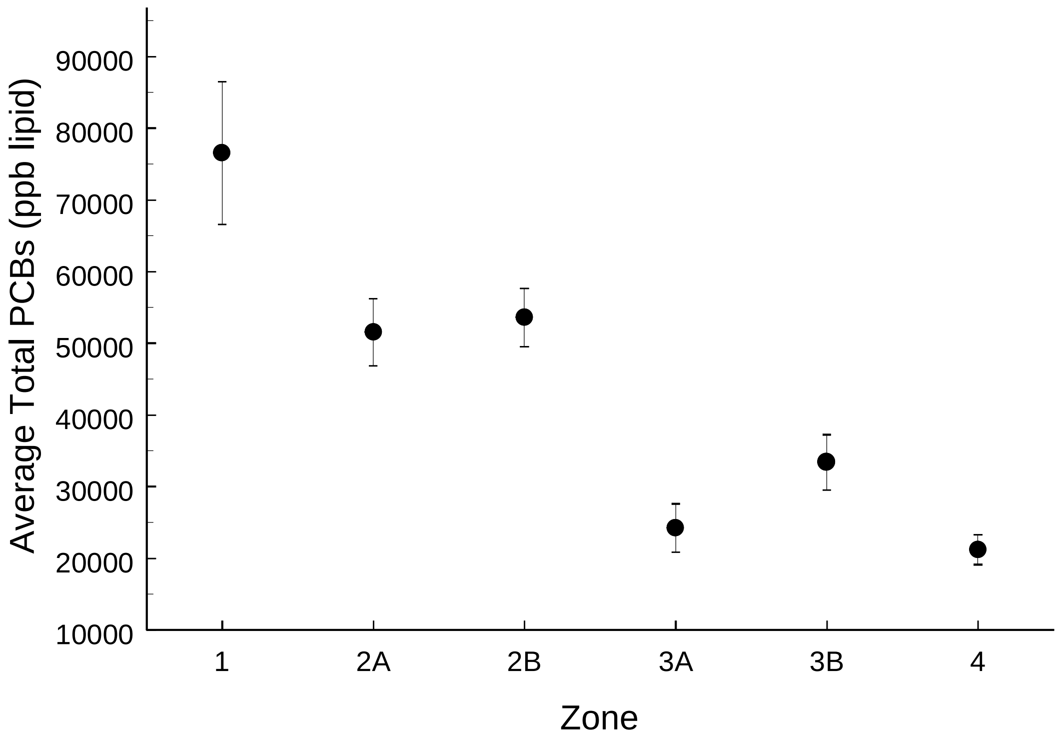
Figure 5-8
Total Lipid-Normalized PCB Concentrations in Green Bay Brown Trout, 1989. Bars equal plus or minus one standard error about mean. Zone locations are shown in Figure 5-6.



Source: GBMBS data from the WDNR sponsored database at http://www.ecochem.net/FoxRiverDatabaseWeb/default.asp, downloaded July 1999**.**

Figure 5-9

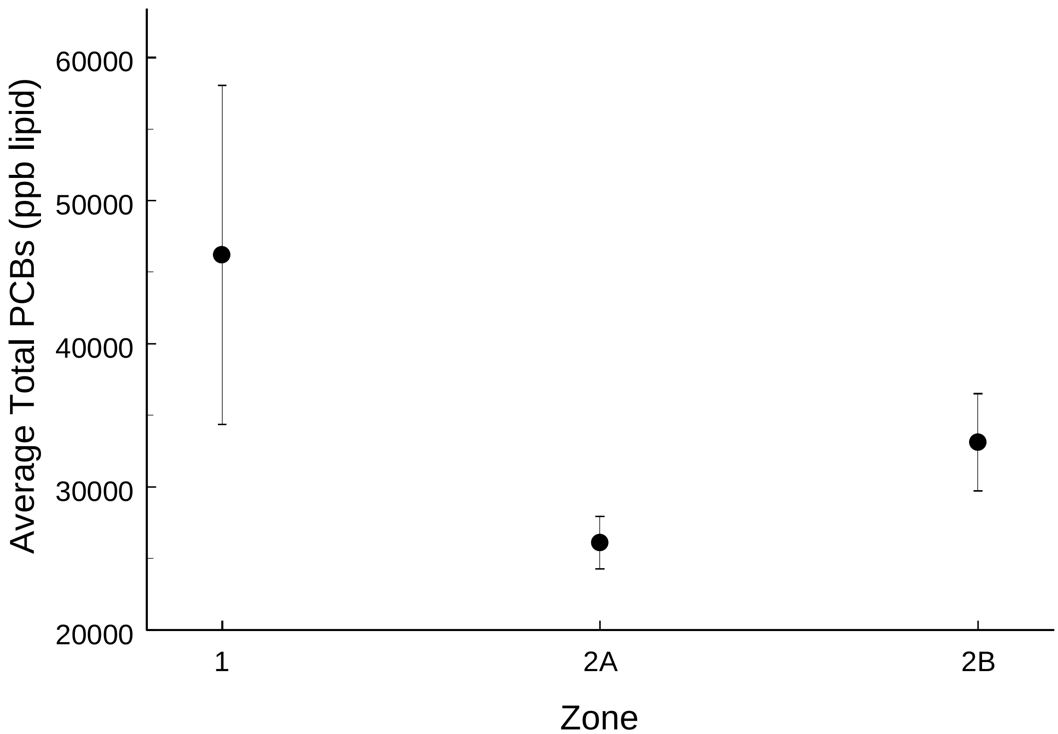
Total Lipid-Normalized PCB Concentrations in Green Bay Carp, 1989. Bars equal plus or minus one standard error about mean. Zone locations are shown in Figure 5-6.



Source: GBMBS data from the WDNR sponsored database at http://www.ecochem.net/FoxRiverDatabaseWeb/default.asp, downloaded July 1999**.**

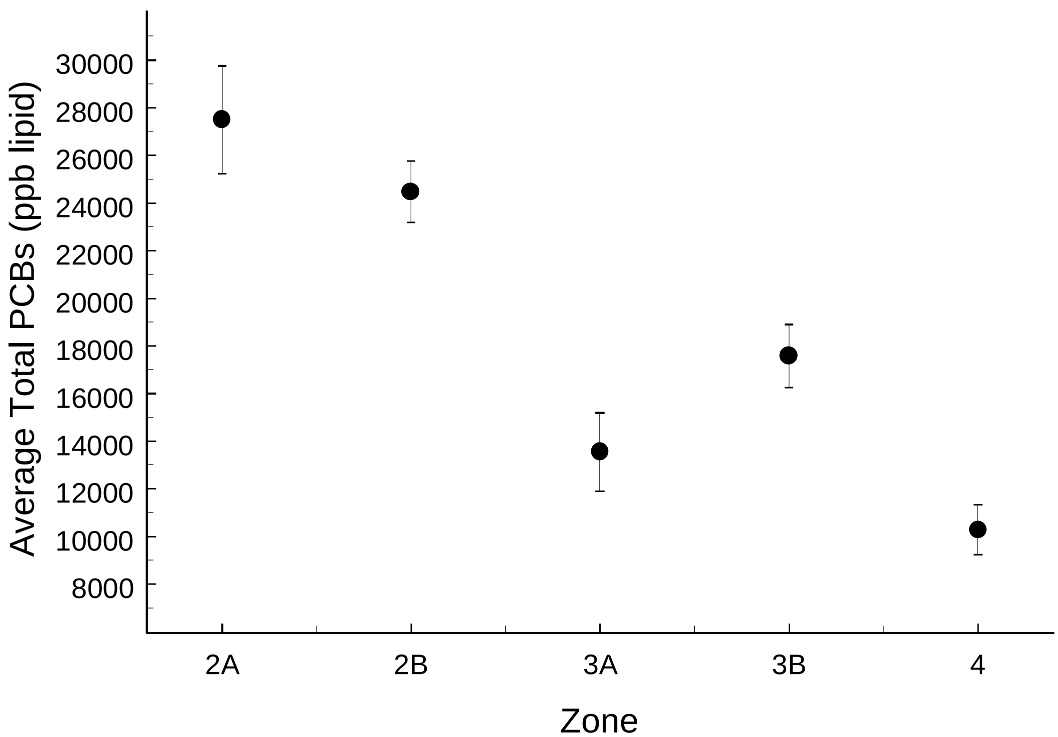
Figure 5-10

Total Lipid-Normalized PCB Concentrations in Green Bay Gizzard Shad, 1989. Bars equal plus or minus one standard error about mean. Zone locations are shown in Figure 5-6.



Source: GBMBS data from the WDNR sponsored database at http://www.ecochem.net/FoxRiverDatabaseWeb/default.asp, downloaded July 1999**.**

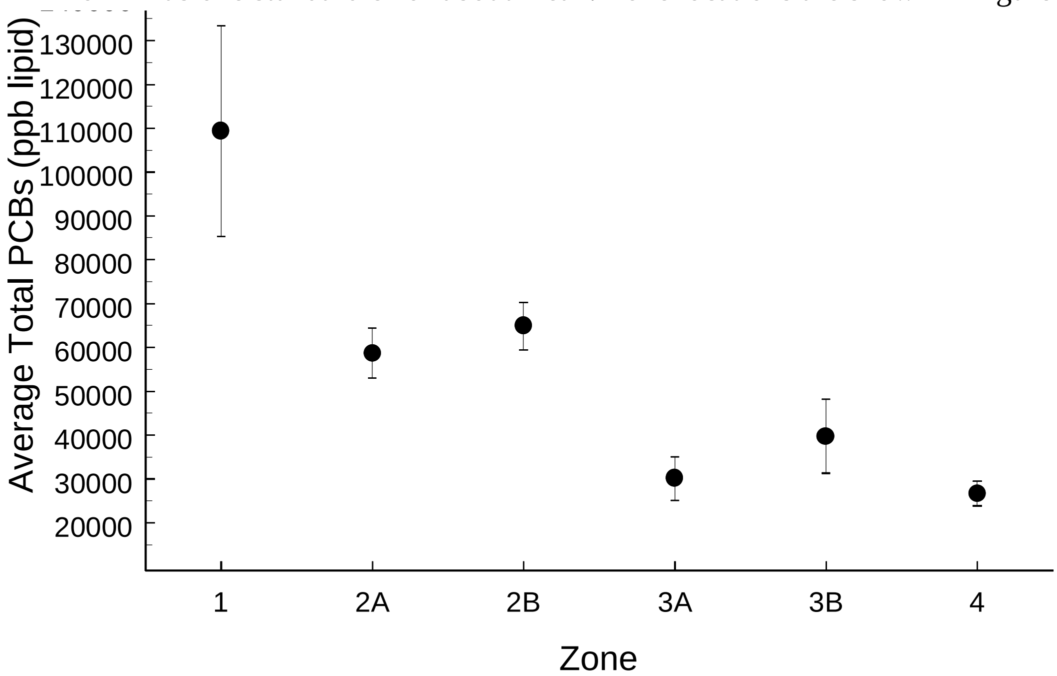
Figure 5-11
Total Lipid-Normalized PCB Concentrations in Green Bay Rainbow Smelt, 1989. Bars equal plus or minus one standard error about mean. Zone locations are shown in Figure 5-6.



Source: GBMBS data from the WDNR sponsored database at http://www.ecochem.net/FoxRiverDatabaseWeb/default.asp, downloaded July 1999.

Figure 5-12

Total Lipid-Normalized PCB Concentrations in Green Bay Walleye, 1989. Bars equal plus or minus one standard error about mean. Zone locations are shown in Figure 5-6.



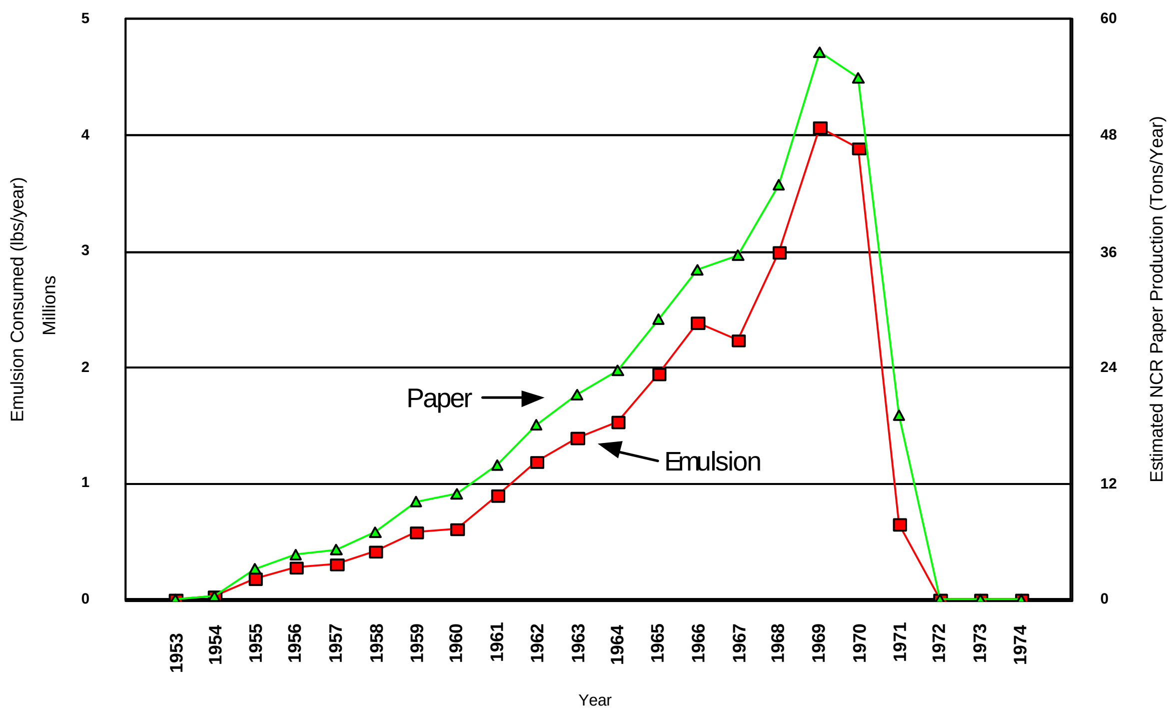
Source: GBMBS data from the WDNR sponsored database at http://www.ecochem.net/FoxRiverDatabaseWeb/default.asp, downloaded July 1999.

5.2 PCB TEMPORAL PATTERNS IN GREEN BAY

As described in Chapter 2, PCB releases into the Fox River were low in the early 1950s, increased dramatically through the 1960s, then declined sharply in the early 1970s (Figure 5-13).

The temporal pattern of PCB contamination in Green Bay resources is expected to lag behind the pattern of PCB releases into the Fox River, since the PCBs must move from the initial release points into the bay. Also, since PCBs are long-lived in environmental systems, they will decline in the environment at a rate much slower than the rate of decline in initial releases to the Fox River. The temporal trend analyses presented in this section provide a description of the time lag and decline rate of PCBs in the bay relative to the timing of initial releases into the Fox River.

Figure 5-13
NCR PCB Emulsion Consumed (lbs/year) and Paper Produced (tons/year) at the Appleton Coated Paper Mill



Temporal trends are examined through PCB concentrations in dated sediment cores and through historical data on PCB concentrations in fish tissue. The temporal evaluation demonstrates that:

- In general, PCB concentrations in Green Bay have declined since the 1970s, coinciding with decreases in PCB releases from paper companies.

- The specifics of the temporal decline vary by fish species, zone, and time period.
- PCB concentrations in fish beyond the innermost portion of the bay do not show a decline between 1989 and 1996.
- PCB transport pathways continue to operate in the Lower Fox River/Green Bay system, and Green Bay fish continue to be exposed to PCBs.

5.2.1 Sediment

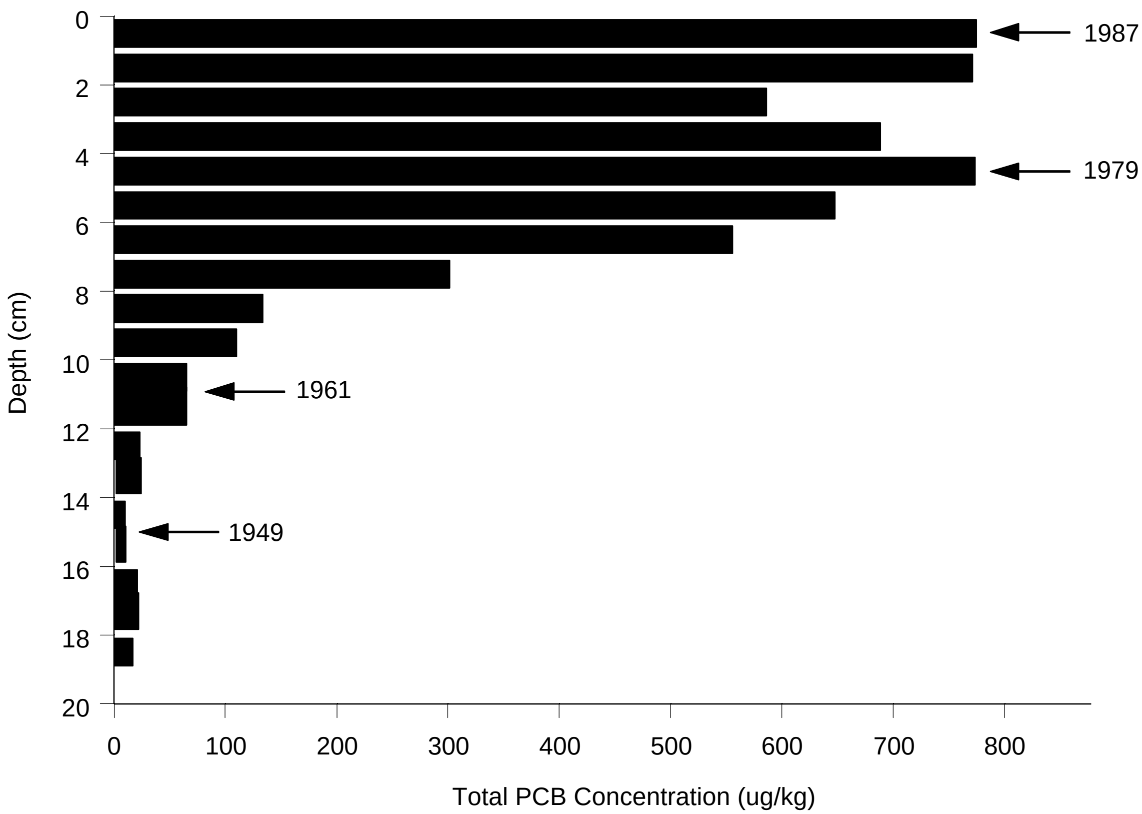
Hermanson et al. (1991) conducted a study on the historical patterns of PCB fluxes to Green Bay sediment using dated sediment cores. Sediment cores were collected from five locations in the inner bay, sectioned into 1 cm intervals (top 10 cm of the core) or 2 cm intervals (from 10 cm to the core bottom), and analyzed for PCBs, ^{210}Pb, and ^{137}Cs. The ^{210}Pb and ^{137}Cs measurements were used to assign dates to each of the core intervals corresponding to the date the material in the core was deposited. Cores were collected in 1981 and 1983, and thus provide information only through those dates.

Hermanson et al. (1991) concluded that their dated sediment core data demonstrate a decrease in PCB inputs starting in the late 1970s. In addition, some of their cores show maximum PCB concentrations at or near the surface (approximately corresponding to deposition during the year of collection, 1981). They also found that one of the sediment cores, from closest to the Fox River mouth, indicates the presence of contaminated Fox River dredge spoils disposed of in the bay in the 1960s. This conclusion is consistent with the dates of open-bay disposal of dredged Fox River sediments (WDNR, 1999a).

Manchester (1993) presents dating results for sediment cores collected as part of the GBMBS. The cores were sliced into 1 cm or 2 cm thick slices, and ^{210}Pb and ^{137}Cs dating techniques were used to assign years of deposition to each core slice. Manchester (1993) noted that most of the sediment cores from Green Bay did not have profiles that allowed for reliable dating, since extensive mixing of sediment layers confounded the dating analysis. Figure 5-14 plots total PCB concentration versus core depth and deposition date for Station 22, one of the few cores that had a relatively intact profile. Station 22 is located approximately 25 miles from the mouth of the Fox River, at a point approximately equidistant between the east and west shores of the bay.

Figure 5-14 shows that a dramatic increase in the concentration of PCBs being deposited began around 1961 at this location (PCB releases from Fox River paper companies began increasing significantly around 1954). From 1961 to 1979, PCB concentrations increased sharply, reaching a peak in 1979 (PCB releases from facilities are estimated to have peaked in 1970). Between 1979 and 1987 (the year the core was collected), PCB concentrations appear to have declined, then increased again to levels approximately equal to those in 1979. This core profile suggests an approximately 7 to 9 year lag between PCB releases into the Lower Fox River and deposition at

Figure 5-14
Total PCB Concentrations By Depth and Average Date of Deposition for Green Bay Sediment Core Station 22, Near the Oconto River Mouth.



Sources: PCB data are from the WDNR sponsored database (http://www.ecochem.net/FoxRiverDatabaseWeb/default.asp, downloaded July 1999). Deposition dates from Manchester, 1993.

this location (from 1954 to 1961 for the start of the increase, and from 1970 to 1979 for the peak). Once PCB concentrations reached their maximum in 1979, they remained high, consistent with the persistent nature of PCBs and the continuing release of mobilized contaminated sediments from the Fox River. Although the dates assigned to the core sections are approximate, they do indicate that PCB concentrations in the bay reached their maxima well after the releases from the paper companies were greatly reduced in 1971, and have remained high as PCBs continue to be mobilized and transported through the system.

Manchester also evaluated PCB congener profiles in Green Bay sediment cores. His evaluation showed that the congener pattern of PCBs is relatively constant at all depths. This consistency in congener patterns deposited over time indicates that the same type of PCBs has always been the dominant source to the system. Therefore, since the Fox River paper companies are the dominant

PCB source to the Fox River, and the Fox River is the dominant PCB source to Green Bay, these data indicate that the Fox River paper companies have always been the dominant source of PCBs to Green Bay.

5.2.2 Fish

Historical data on fish PCB concentrations in Green Bay were examined to evaluate potential relationships between temporal changes in fish PCB concentrations, PCB release dates, and sediment PCB accumulation. The evaluation of historical fish PCB concentration data can help determine the extent to which PCB pathways in the system continue to expose Green Bay fish to PCBs.

Data Sources

The historical pattern of PCB contamination in Green Bay fish was evaluated using the following four sets of data, which were combined into a single database for analysis:

- the State of Michigan fish contaminant monitoring database, which contains PCB data on a variety of fish species collected from the Michigan waters of Green Bay in 1993 (Michigan Department of Natural Resources, 1995)

- the State of Wisconsin fish contaminant monitoring database, which contains PCB data on a variety of fish species collected from the Wisconsin waters of Green Bay from 1971 to 1994 (WDNR, 1995)

- data collected during 1989-1990 as part of the GBMBS (described above in Section 5.1.3)

- data collected on walleye and brown trout PCB concentrations by the Service in 1996 as part of the NRDA (details on sampling, analytical methods, and results provided in Stratus Consulting Inc., 1999a).

A key issue in using these data is the comparability of the analytical results produced by the studies over time. For the State of Wisconsin fish contaminant monitoring program data, over 99% of the contaminant data were analyzed by the same laboratory, the Wisconsin State Laboratory of Hygiene (WSLH). The WSLH analytical procedures for PCBs are documented in the WSLH Organic Chemistry Unit Methods Manual Section 1410 (Wisconsin State Laboratory of Hygiene, 1997). The basic methods used by the WSLH have changed little since the WSLH first started analyzing fish tissue in the 1970s, except for a switch from hexane to dichloromethane for tissue extraction and the addition of a gel permeation sample cleanup step in the early 1980s (Tom Gibson, WSLH Organics division, personal communication). The WSLH uses separation on silica gel and Florisil columns and analysis on a packed column chromatograph equipped with an electron capture detector. Analytical instrumentation has improved significantly over time, allowing the WSLH to change their PCB reporting limit from 0.2 to 0.04 μg/g in 1993 (Tom Gibson, WSLH Organics division, personal communication).

Contaminant data in the Michigan database are from analyses done at the Health Risk Assessment Laboratory. Analytical procedures from the Health Risk Assessment laboratory are documented in the Quality Assurance Manual for the Health Risk Laboratory (Michigan Department of Community Health, 1997). The current methods include extraction using ethyl ether/petroleum ether 1:1 (v:v), separation on a silica gel column, and analysis on a packed column chromatograph equipped with an electron capture detector.

The Service designed the 1996 fish collection and analysis to provide results that can be compared directly to the GBMBS data collected in 1989-1990 (Stratus Consulting Inc., 1999a). The fish species targeted in 1996 (brown trout and walleye) correspond to species sampled in 1989-1990, and the fish were collected from similar locations in the bay. Furthermore, similar sample extraction and analytical methods for PCB and lipid content analysis were used in 1996 and 1989-1990 (Details provided in Stratus Consulting Inc, 1999a). Therefore, the methods used for the 1989-1990 GBMBS collection and the 1996 Service study can be considered comparable with each other.

Therefore, results from the 1989-90 GBMBS and 1996 Service studies are directly comparable to each other, and results from the separate State fish contaminant monitoring programs are probably internally consistent over time. However, the comparability of the GBMBS and Service data to the fish contaminant monitoring programs data is uncertain, and aspects of the temporal trend analysis that rely on comparison across State databases should be considered approximate only.

Methods for Temporal Trend Analysis

Based on the amount of PCB data available, the following five species were selected for the temporal analysis of PCB concentrations in fish: alewife, brown trout, carp, walleye, and yellow perch. Although many other Green Bay fish species have been sampled for PCBs, the number of samples and the spread of sampling effort over time for those species are much more limited than for the five species included in this analysis. Table 5-3 shows the total number of sample results available for the five selected species by year. No PCB concentration data are available for any of these species prior to 1975.

The analysis of spatial patterns of PCBs in Green Bay fish (Section 5.1.3) showed that PCB concentrations within a species vary by location of collection within the bay. Therefore, we conducted the temporal analysis of fish PCB concentrations on a zone-by-zone basis to minimize this potential source of variability. Data for each species were grouped into three location categories: Zone 2, which is the innermost part of Green Bay and includes GBMBS zones 2A and

Table 5-3
Number of Fish Samples Used in the Temporal Analysis of PCB Concentrations

Year	Alewife	Brown Trout	Carp	Walleye	Yellow Perch
1975			6		3
1976			9	4	5
1977					2
1978	2		4		1
1979	5	3	2	2	4
1980			3	1	
1981			16	7	
1982			5		
1983	4		6	2	4
1984	3	12	3		7
1985	2	47			
1986	2		5	3	
1987					
1988					
1989	68	59	159	103	
1990					
1991					
1992					3
1993		10			
1994					
1995					
1996		10[a]		24[a]	

a. Each sample was a composite of three to six fish.

2B; Zone 3, which is the rest of the inner bay and includes GBMBS zones 3A and 3B; and Zone 4, which is the outer bay and is the same as GBMBS Zone 4. PCB concentrations were normalized to fraction lipid in the sample to account for variation in wet weight PCB concentrations due to lipid content alone.

For each fish species and Green Bay zone, trends in PCB concentrations over time were evaluated using log-linear (i.e., exponential) or linear regressions. Log-linear regressions have been shown to accurately describe the temporal trend of PCBs in Lake Michigan fish (Stow et al., 1995). However, some of our data plots revealed a linear, rather than log-linear, relationship (as described below). In these cases, linear regressions were used to describe the trends. For some species and zones, data are only available for 2 years, 1989 (from the GBMBS collection) and 1996 (from the Service's NRDA collection). In these cases, PCB concentrations were compared between the two years using the Wilcoxon rank-sum test. A p-value of less than 0.05 was interpreted as statistically significant.

Alewife

Figure 5-15 shows the lipid-normalized PCB concentrations in alewives from Zones 2, 3, and 4. In all zones, most of the available alewife data were collected in 1989 as part of the GBMBS, and no data are available since 1989. In all three zones, log-linear regressions (shown on the plots) indicate a decrease in PCB concentrations over time, although the data are limited. The apparent trends in zones 2 and 4 are subject to single, high data points in 1979. Given the limited amount of data and the wide 95% confidence intervals (indicating a weak regression), it is difficult to make definitive conclusions regarding temporal trends in alewife PCB concentrations. Overall, the alewife data available for evaluating temporal trends are limited, but suggest a decline in PCB concentrations from the late 1970s to 1989.

Yellow Perch

PCB concentrations in Green Bay yellow perch over time are shown in Figure 5-16. Data are available only for Zones 2 and 3. In both zones, PCB concentrations show a decline over time consistent with an exponential decrease, through 1992 in Zone 2 and 1984 in Zone 3 (the last years for which data are available).

Walleye

Walleye PCB concentrations are shown in Figure 5-17. In Zones 2 and 4, data are available only from 1989 and 1996. In Zone 2, 1996 concentrations (mean of 63 μg PCB/g lipid) are statistically significantly lower than 1989 concentrations (mean of 34 μg PCB/g lipid) ($p = 0.001$, Wilcoxon rank-sum test). Concentrations are not significantly different between 1989 and 1996 in Zone 4 ($p = 0.11$, Wilcoxon rank-sum test).

In Zone 3, walleye PCB data are available from 1976 through 1996. A linear regression using all of the data indicates a slight decline overall in PCB concentrations, as shown by the regression line that slopes downward in Figure 5-17. However, the confidence interval about this line is broad, indicating that other temporal trends (no change or slightly increasing) may also be consistent with the data. The slightly downward regression over time appears to be driven by concentrations measured in 1989, which are lower than concentrations measured earlier. Because of the large number of data points collected in 1989 and 1996, we also compared the concentrations measured in these two years using the Wilcoxon rank-sum test. PCB concentrations were statistically significantly higher in 1996 than in 1989 ($p = 0.004$).

A possible covariate in the analysis is walleye size: as walleye size increases, the lipid-normalized PCB concentrations tend to increase under constant PCB exposure (Connolly et al., 1992). Thus, if there is a trend in the size of walleye sampled over time, this size trend could mask an

Figure 5-15

PCB Concentrations in Green Bay Alewife Over Time, by Zone. The solid line is the log-linear best-fit line, and the dotted lines mark the 95% confidence interval about the best-fit line.

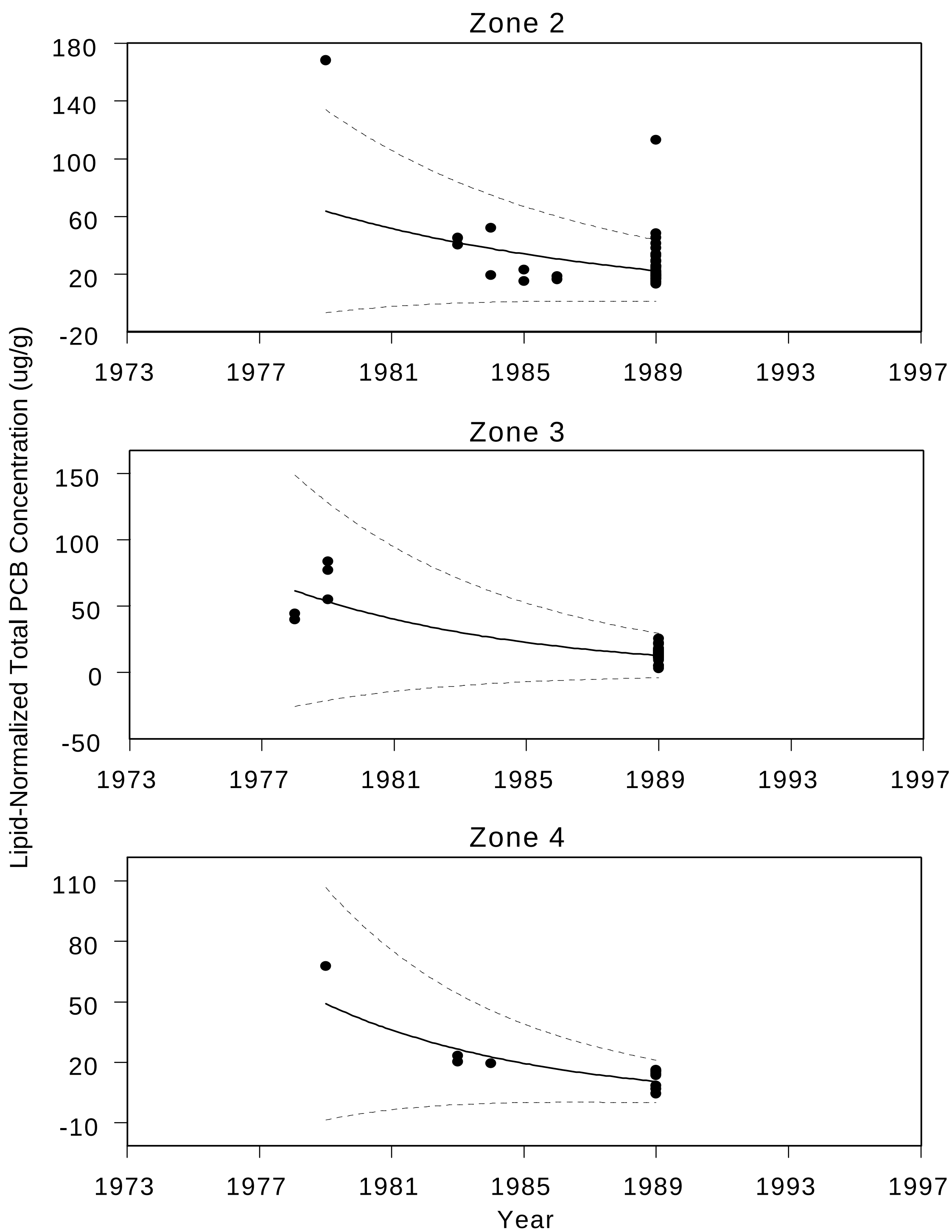


Figure 5-16
PCB Concentrations in Green Bay Yellow Perch Over Time, by Zone.
The solid line is the log-linear best-fit line, and the dotted lines mark the 95% confidence interval about the best-fit line.

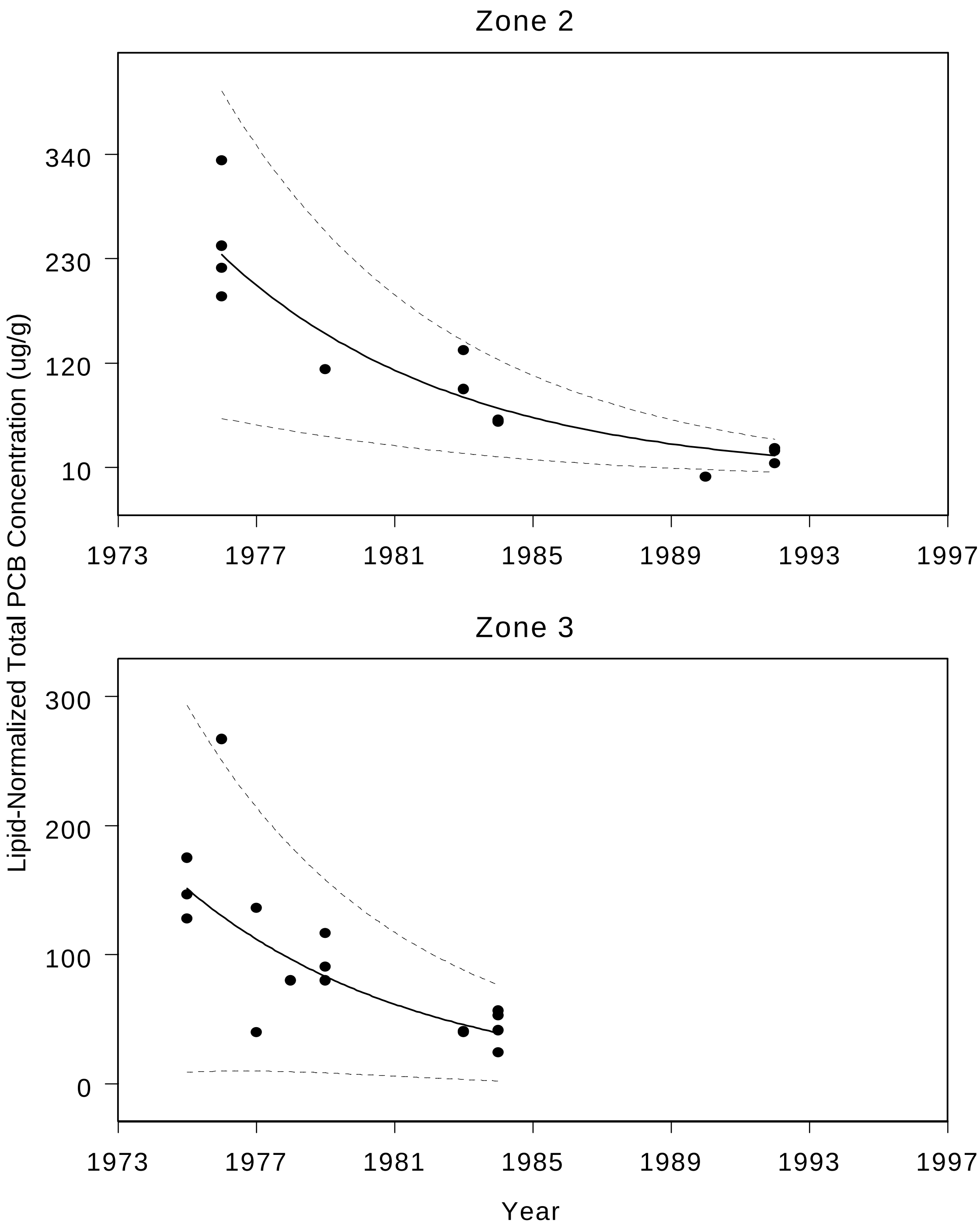
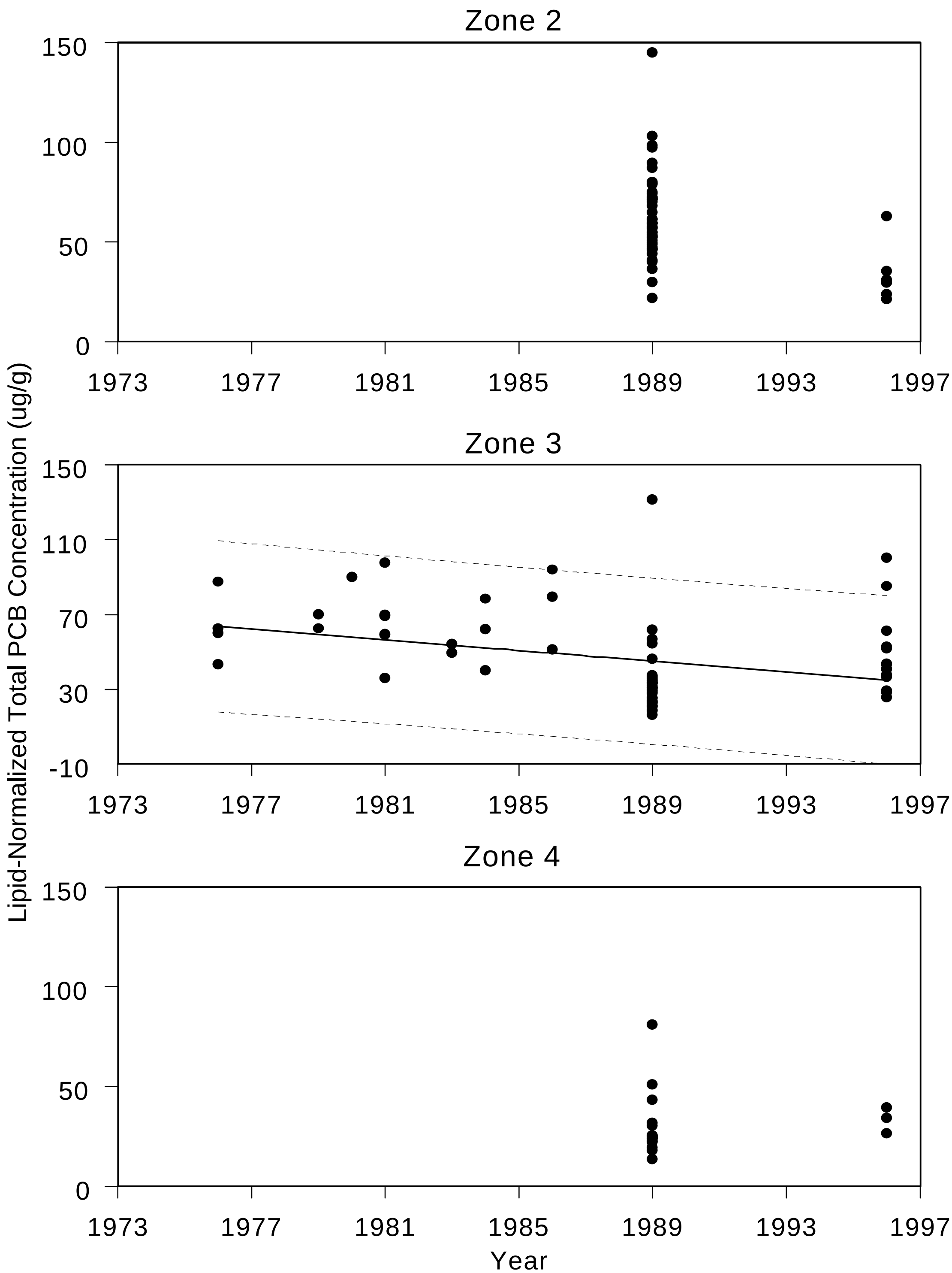


Figure 5-17
PCB Concentrations in Green Bay Walleye Over Time, by Zone.



underlying trend in PCB concentrations. However, not all of the PCB measurements shown in Figure 5-17 have a corresponding data point for the size of the walleye sampled. Without a link between fish size and PCB concentrations for individual samples, evaluating the potential effects of fish size on the temporal analysis of PCB concentrations is difficult. Therefore, we extracted from the database only those PCB measurements that have a corresponding value for fish weight. Plots of PCB concentrations for this subset of the data are shown in Figure 5-18 for the three zones. Plots of the corresponding fish weight data are shown in Figure 5-19 (plots based on fish length, rather than fish weight, are similar).

In Zone 2, the weight of fish sampled is not different between 1989 and 1996 ($p = 0.35$, Figure 5-19). Therefore, the PCB concentration comparison shown in Figure 5-18 (for the data subset with known weights) is not confounded by differences in fish weight between the two years. The PCB concentrations shown in Figure 5-18 are statistically significantly lower in 1996 than in 1989 ($p = 0.0025$). Therefore, this re-analysis that takes fish size into account confirms that PCB concentrations in Zone 2 walleye were lower in 1996 than in 1989.

In Zone 4, fish collected in 1996 were larger than those collected in 1989 ($p = 0.024$, Figure 5-19). The comparison of PCB concentrations for only those fish with corresponding weight values (Figure 5-18) shows that the measured PCB concentrations were not different between 1989 and 1996 ($p = 0.26$). Therefore, although PCB concentrations are not different in Zone 4 walleye between 1989 and 1996, the larger size of the fish collected in 1996 potentially confounds the analysis. Whether the size differences between the two years are large enough to mask an underlying PCB difference cannot be determined from the available data, because the number of samples are too few to develop weight/PCB relationships for the two years.

The weight plot for Zone 3 walleye over time (Figure 5-19) suggests that weight of fish sampled has increased over time (positive slope for the regression line). Additionally, a comparison of only fish collected in 1989 and 1996 shows that the fish collected in 1996 were larger than those collected in 1989 ($p < 0.001$). Therefore, weight should be controlled for in the analysis to account for changes in fish weight that could affect PCB concentrations measurements.

The amount of data for Zone 3 walleye in 1989 and 1996 is sufficient for a comparison of PCB concentrations between only those fish that fall within a common size range. We trimmed the 1996 data to include only those fish with weights less than the largest 1989 fish sampled, and trimmed the 1989 data to include only those fish larger than the smallest 1996 fish sampled. This trimming produced weight distributions that were not different between the two years ($p = 0.59$), allowing us to control for weight. Using these trimmed datasets, PCB concentrations were not different between 1989 and 1996 ($p = 0.73$). Therefore, when weight is controlled for in the analysis, the data do not show a change in PCB concentrations between 1989 and 1996 in Zone 3 walleye.

Figure 5-18
PCB Concentrations in Green Bay Walleye Over Time, by Zone, for Samples with a Corresponding Measurement of Fish Weight

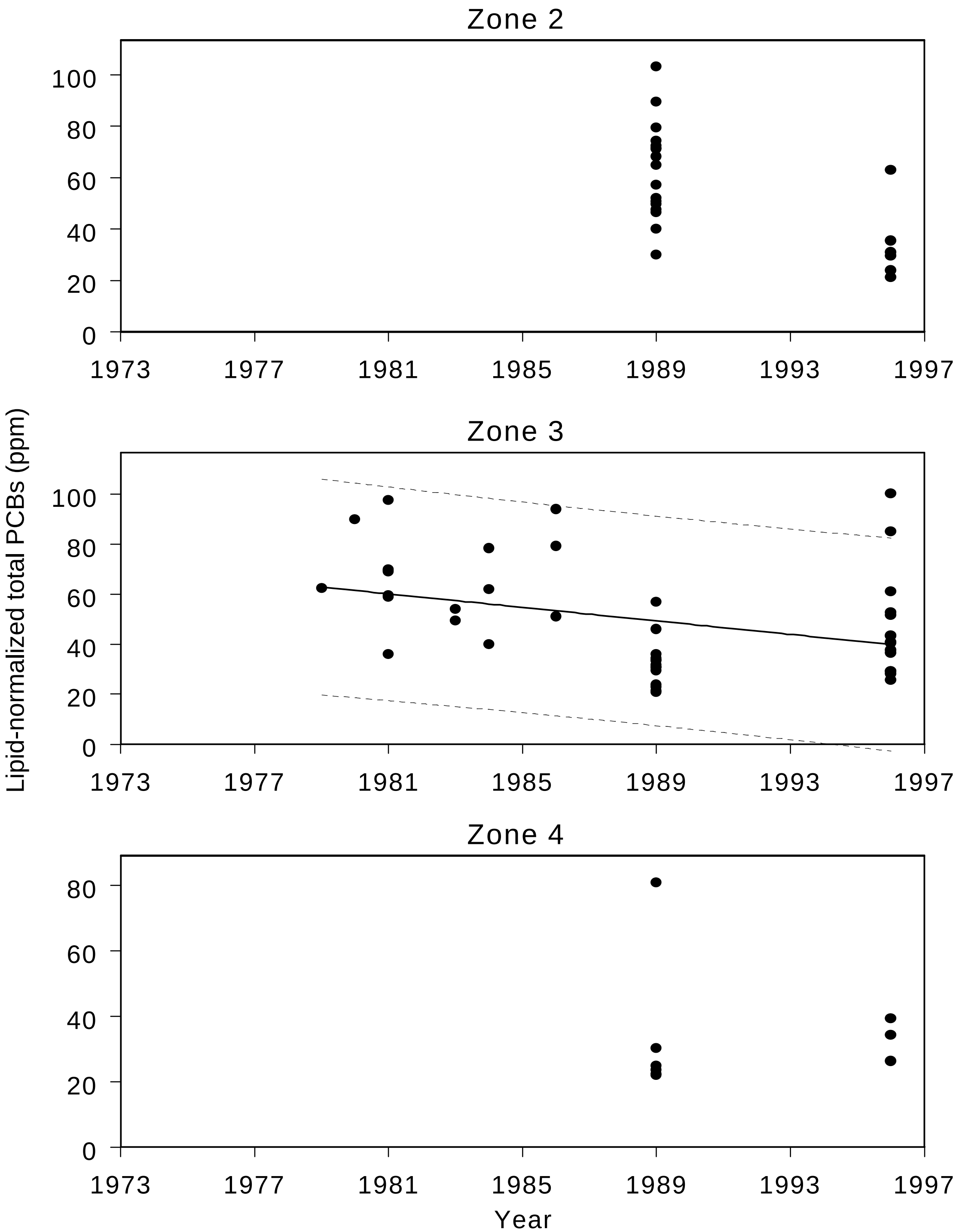
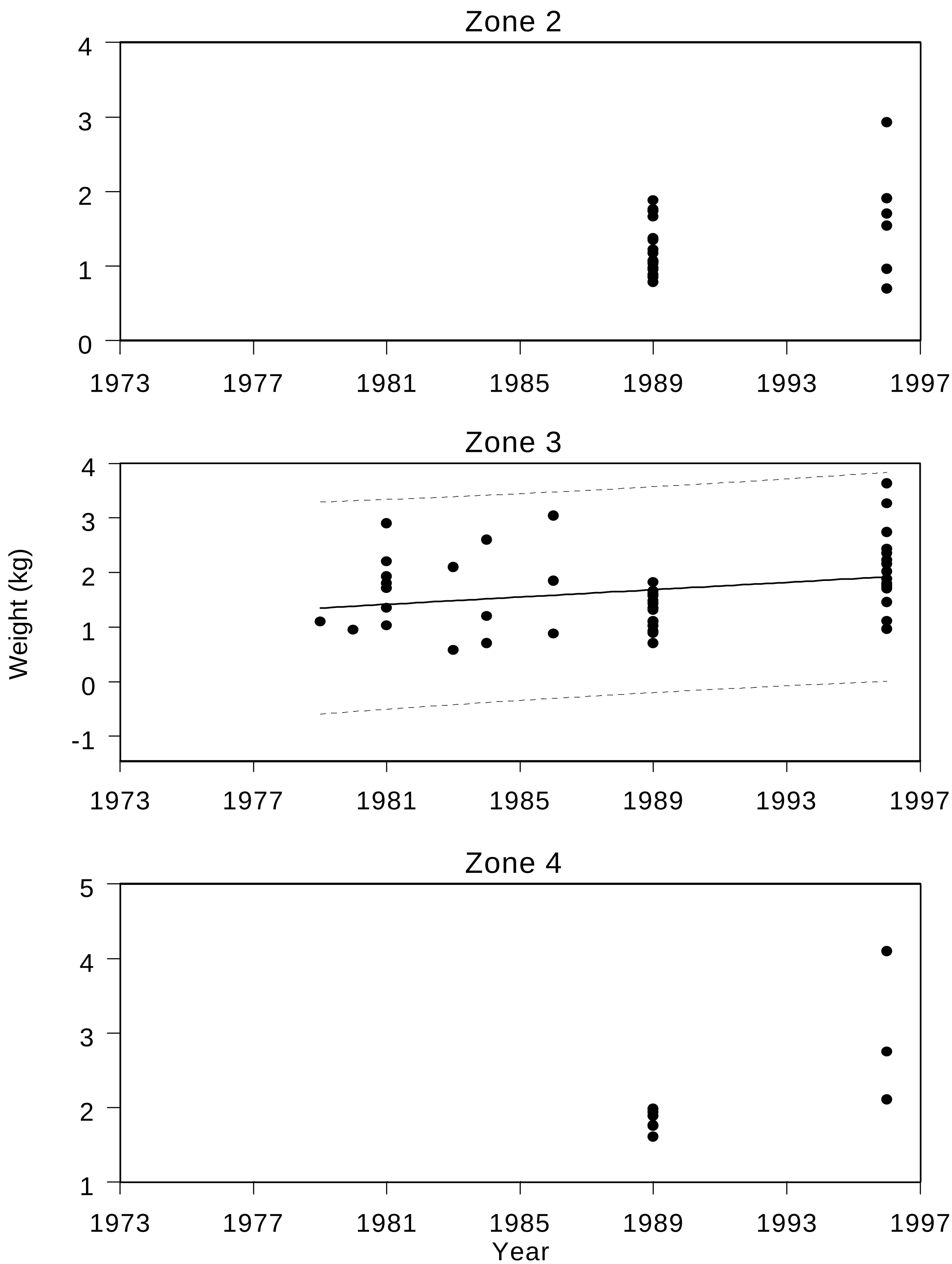


Figure 5-19
Weights of Green Bay Walleye Corresponding to the PCB Data Shown in Figure 5-18



Walleye Conclusions

The available data demonstrate that the overall temporal patterns of PCBs in Green Bay walleye are the following:

- In Zone 2, PCB concentrations decreased from 1989 to 1996, the only years for which data are available. This decrease is confirmed when walleye size, a potentially confounding variable, is taken into account in the analysis.

- In Zone 3, a slight decline in PCB concentrations is observed from the 1970s through 1996, although the data show considerable variability. Measured PCB concentrations are not different between 1989 and 1996 when walleye size is taken into account.

- In Zone 4, PCB concentrations are not different between 1989 and 1996 (the only years for which data are available). However, walleye collected in 1996 were larger than those collected in 1989, potentially biasing the 1996 results upward relative to the 1989 values.

Brown Trout

PCB concentrations in Green Bay brown trout over time are shown in Figure 5-20. Data are only available for Zones 3 and 4. The trend in Zone 3 PCB concentrations over time is similar to that in Zone 3 walleye concentrations over time, with a slight decrease apparent, although the data show considerable variability.

However, the weights of Zone 3 brown trout sampled increase with time (Figure 5-21). To evaluate whether this difference in the weight of fish sampled over time could affect the interpretation of the PCB trend over time, we plotted weight versus PCB concentration for each of the four years with the most Zone 3 brown trout data (1984, 1985, 1989, and 1996). These plots, shown in Figure 5-22, indicate that a strong relationship between lipid-normalized PCB concentrations and weight does not exist for any of the years. The strongest trend appears to be for 1996, with PCB concentrations actually declining with increased fish weight. Since there is no relationship between weight and PCB concentrations for Zone 3 brown trout, the increase in the weight of Zone 3 brown trout sampled over time does not confound the temporal analysis of PCB concentrations over time.

For Zone 4 brown trout, all but one data point was collected in 1989 or 1996 (Figure 5-20). Therefore, we evaluated the data by comparing concentrations in 1989 with those in 1996. Zone 4 concentrations were not different between 1989 and 1996 ($p = 1.0$). The weights of brown trout sampled in 1989 and 1996 were also not statistically significantly different ($p = 0.29$). Therefore, although the amount of data are limited, they show that PCB concentrations in Zone 4 brown trout are not different between 1989 and 1996.

Figure 5-20
PCB Concentration in Green Bay Brown Trout Over Time, By Zone

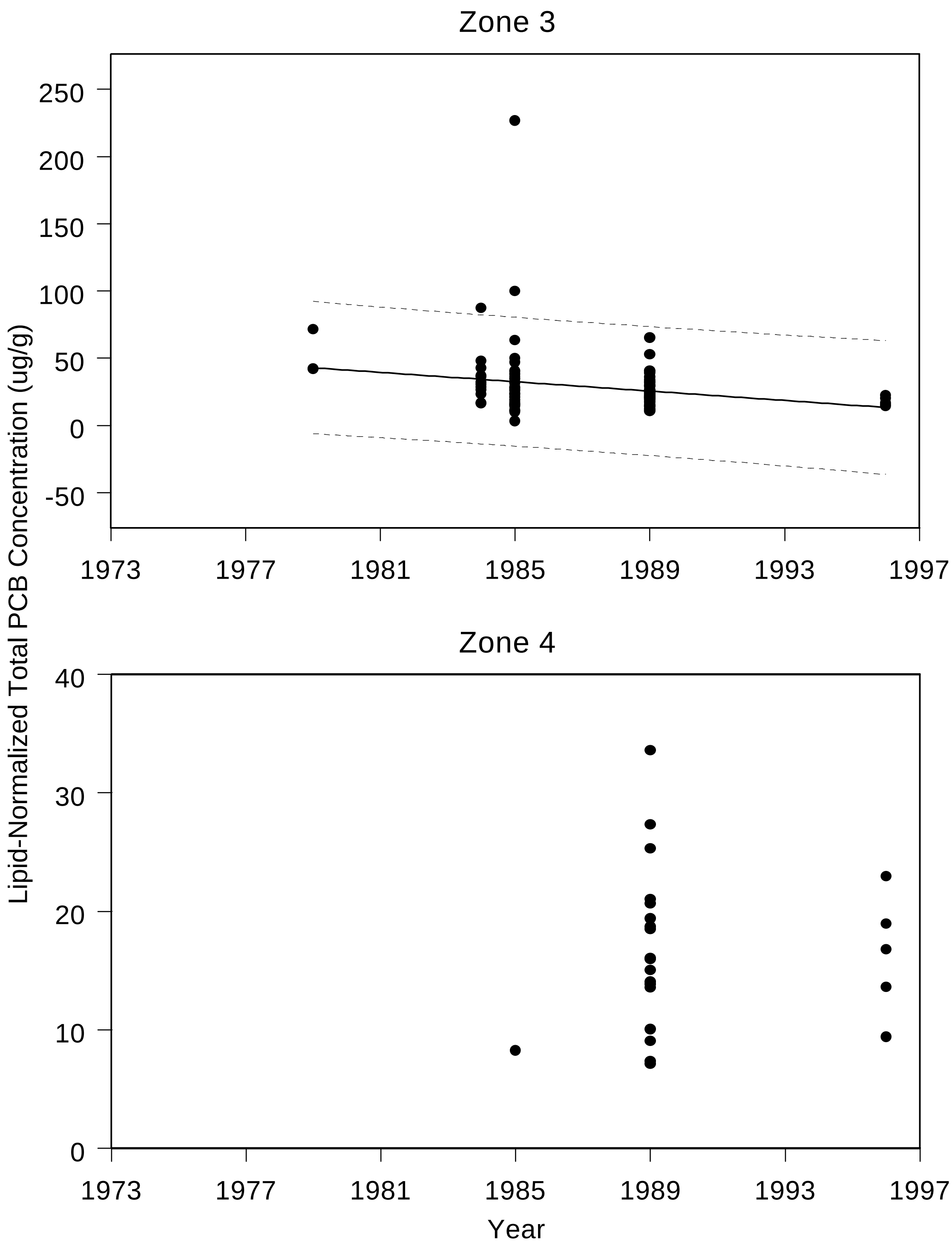
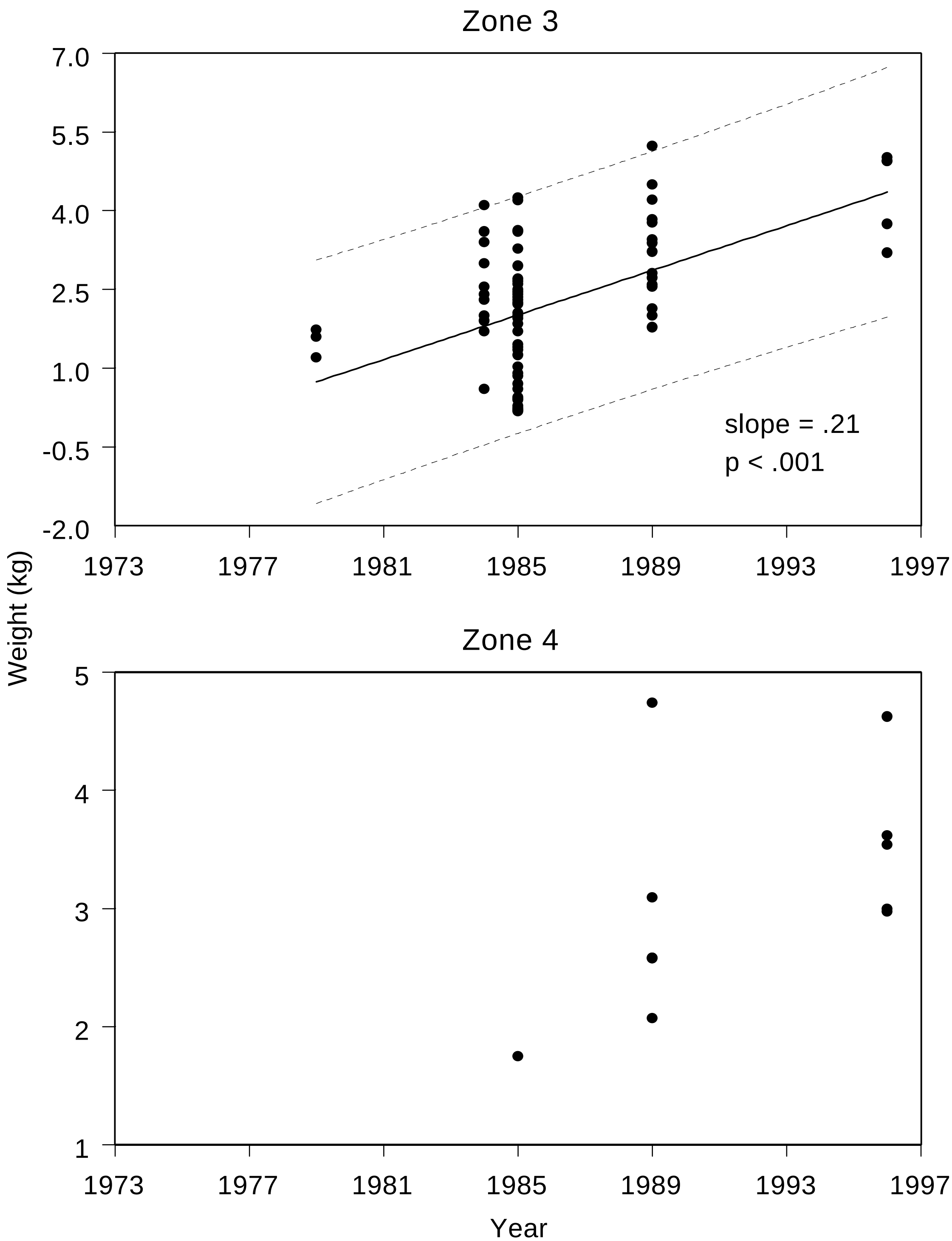


Figure 5-21
Weights of Green Bay Brown Trout Sampled for PCBs



Carp

Green Bay carp PCB concentrations over time are shown in Figure 5-23. Data are available only for Zones 2 and 3, and no data are available after 1989. In both zones, linear regression shows a decline in PCB concentrations over time, with the decline steeper in Zone 2 than in Zone 3 (although note the differences in the y-axis scales, which makes the decrease in Zone 3 appear much steeper relative to Zone 2 than it is). The weight of carp sampled does not change over time (data not shown). Therefore, carp PCB concentrations show a decline from the 1970s through 1989 in both Zone 2 and Zone 3.

Conclusions

Table 5-4 summarizes the results of the temporal analysis of PCB concentrations in Green Bay fish. In general, the data indicate that PCB concentrations in Green Bay fish have declined since the 1970s, coinciding with decreases in PCB releases from paper companies. However, the temporal pattern varies by species, zone, and time period:

- PCB concentrations show a stronger and more consistent decline in forage fish (e.g., yellow perch and perhaps alewife) than in predator fish (walleye and brown trout). Possible explanations for this difference include shifts in walleye and brown trout diet over time, and increased "lag time" for the reductions in PCBs to be detectable in the longer lived predatory species.

- PCB concentration declines are more prominent in Zone 2 than in zones 3 and 4 (e.g., walleye and brown trout). A possible explanation for this trend is that the signal of decreased PCB loadings from the Lower Fox River may take longer to reach the portions of the bay that are farther from the river.

- Except in the innermost portion of the bay, PCB concentrations do not show a decline between 1989 and 1996.

These conclusions show that Green Bay fish continue to be exposed to PCBs well after the timeframe of most of the direct PCB releases from paper companies. In some cases, the level of exposure appears to have remained relatively constant over the last 10 to 15 years. Therefore, PCB transport pathways are continuing in the Lower Fox River/Green Bay system.

5.3 CONCLUSIONS

PCB concentrations in sediment, surface water, and fish of Green Bay are highest in the inner bay and decrease with increasing distance from the Fox River mouth. PCBs are most concentrated on the eastern side of the inner bay, where Green Bay circulation patterns are

Figure 5-22
Weight Versus PCB Concentration for Zone 3 Brown Trout for the Sampling Years 1984, 1985, 1989, and 1996
Lines are linear regression lines.

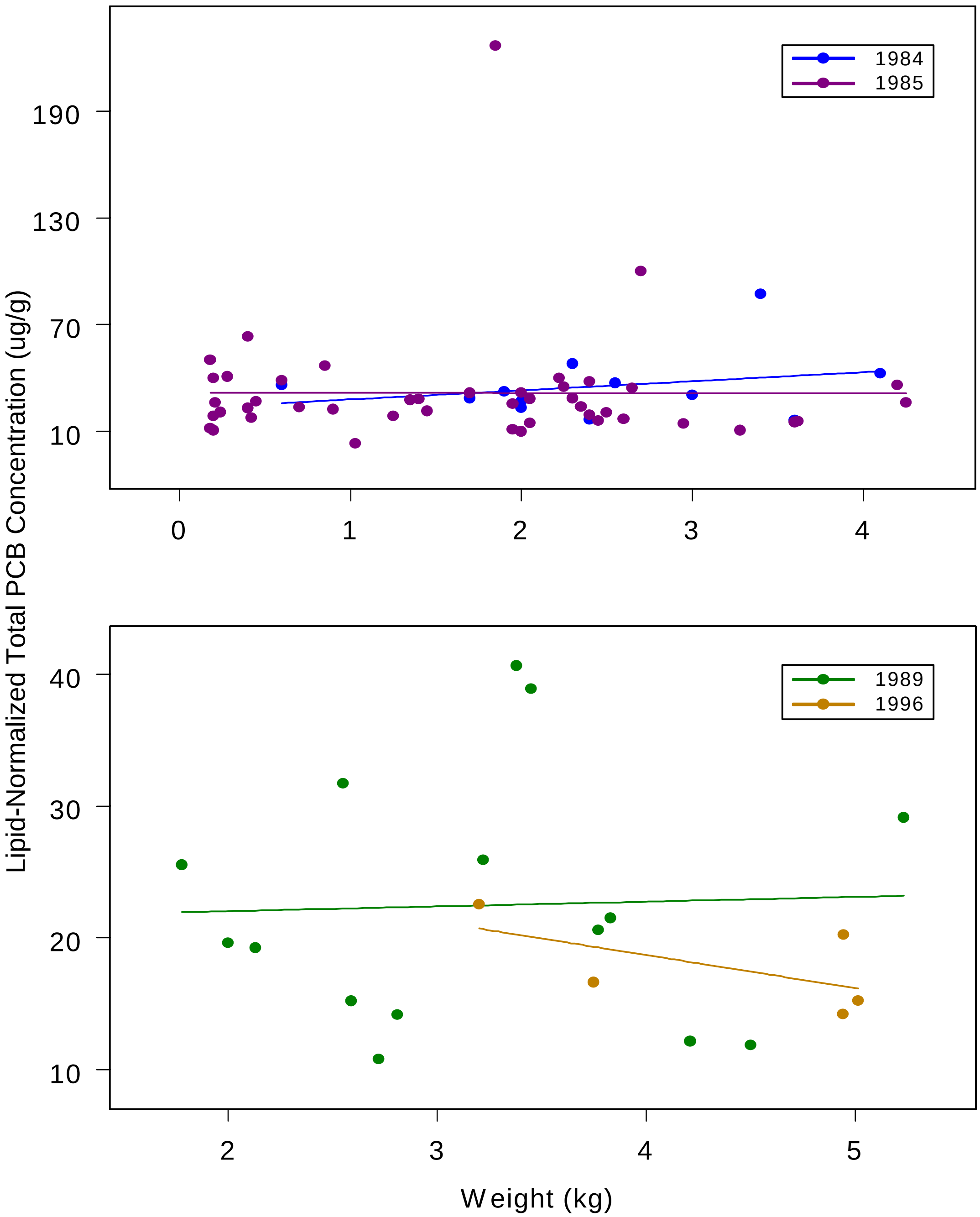


Figure 5-23
PCB Concentration in Green Bay Carp Over Time, By Zone

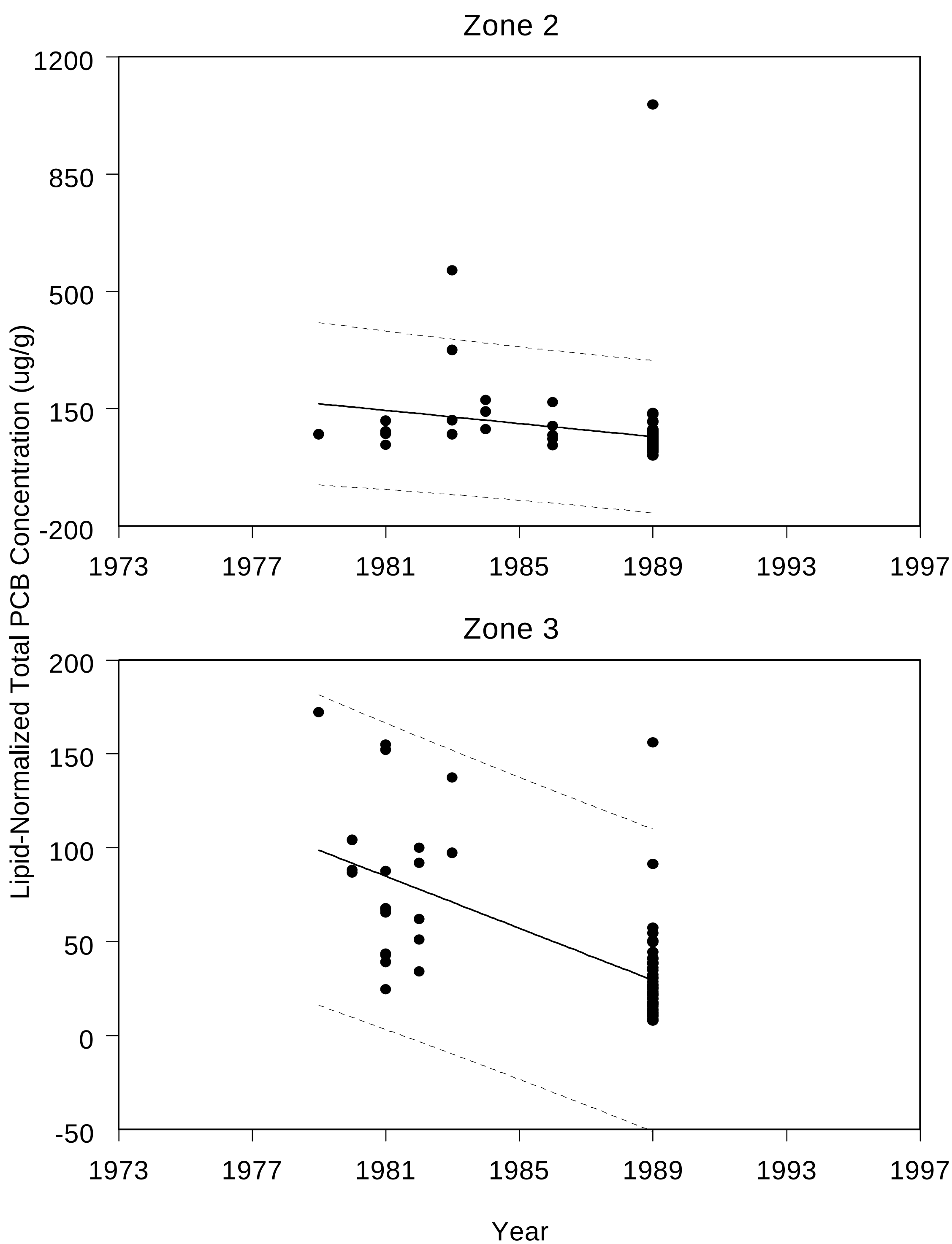


Table 5-4
Summary of Temporal Analysis of PCB Concentrations in Green Bay Fish

Species	Conclusion
Alewife	‣ Zone 2: Possible PCB decrease, 1978 to 1989, but limited data ‣ Zone 3: PCB decrease, 1978 to 1989 ‣ Zone 4: Possible PCB decrease, 1978 to 1989, but limited data
Yellow perch	‣ Zone 2: PCB decrease, 1976 to 1992 ‣ Zone 3: PCB decrease, 1975 to 1984
Walleye	‣ Zone 2: PCB decrease, 1989 to 1996 ‣ Zone 3: Slight PCB decrease, 1976 to 1996; No PCB decrease, 1989 to 1996 ‣ Zone 4: No PCB decrease, 1989 to 1996, but size a potentially confounding factor
Brown trout	‣ Zone 3: Possible PCB decrease, 1979 to 1996 ‣ Zone 4: No PCB decrease, 1989 to 1996
Carp	‣ Zone 2: PCB decrease, 1976 to 1989 ‣ Zone 3: PCB decrease, 1975 to 1989

expected to carry contaminated water and sediment discharged from the Fox River. Therefore, the spatial distribution patterns of PCBs in Green Bay, as indicated by analysis of PCBs in sediment, surface water, and fish, are consistent with the conclusion that the Fox River is the primary source of PCBs to the bay. The consistency of spatial patterns in sediment, surface water, and fish also demonstrates the pathway linkage between these resources.

Temporal trends in Green Bay PCB contamination were examined through PCB concentrations in dated sediment cores and through historical data on PCB concentrations in fish tissue. The temporal evaluation demonstrates that:

- In general, PCB concentrations in Green Bay have declined since the 1970s, coinciding with decreases in PCB releases from paper companies.

- The specifics of the temporal decline vary by fish species, zone, and time period.

- PCB concentrations in fish beyond the innermost portion of the bay do not show a decline between 1989 and 1996.

- PCB transport pathways continue to operate in the Lower Fox River/Green Bay system, and Green Bay fish continue to be exposed to PCBs.

CHAPTER 6
PCB CONGENER PATTERNS IN GREEN BAY

6.1 INTRODUCTION

This chapter presents an evaluation of the PCB congener patterns present in the sediments of Green Bay. PCB congeners are the individual PCB compounds that comprise PCB mixtures. Different sources of PCBs often have different PCB congener patterns. By evaluating the relative amounts of different congeners present in the sediments of Green Bay, we can evaluate the potential original source(s) of the PCBs to the bay.

The evaluation of PCB congener patterns in environmental samples is not straightforward. Several physical and biological environmental processes, as described in Section 6.2, can alter the congener patterns of the original mixtures once released into the environment, making source identification more difficult. In this chapter, we use multi-variate statistical techniques to evaluate quantitatively the PCB congener patterns in Green Bay sediment. The results of the evaluation demonstrate that:

- A shift in PCB congener patterns that is consistent with the Fox River being the dominant PCB source to Green Bay occurs from the Lower Fox River to inner Green Bay to outer Green Bay, as PCBs become more environmentally weathered the further they are transported away from the river mouth.

- PCBs in the outer bay have originated primarily from the inner bay and not from Lake Michigan. The PCB congener pattern in the sediments of outer Green Bay is more similar to the pattern in inner Green Bay than to the pattern in Lake Michigan. Furthermore, the PCB congener pattern in the outer bay is inconsistent with the transport and weathering of Lake Michigan PCBs, but is wholly consistent with the transport and weathering of PCBs from the inner bay.

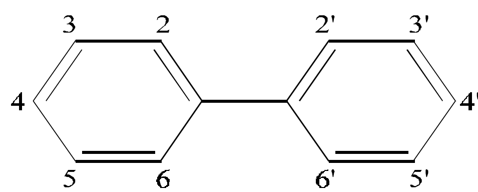
PCB congener patterns in Green Bay are therefore consistent with Fox River paper companies as the primary source of PCBs to inner and outer Green Bay, and with the movement of PCBs from the outer bay into Lake Michigan.

6.2 ENVIRONMENTAL CHEMISTRY OF PCB CONGENERS

PCB formulations used in industrial processes, such as the Aroclor 1242 released from Fox River paper companies, are actually mixtures of many different individual PCB compounds called congeners. Each congener has a different number and position of chlorine atoms substituted on the biphenyl "backbone" (Figure 6-1). A total of 209 PCB congeners are possible, although commercial mixtures such as Aroclor 1242 are dominated by a subset of the 209 congeners (Figure 6-2).

PCBs are persistent in the environment and degrade very slowly (Erickson, 1997). However, PCB congeners differ in their environmental persistence because of differences in their physical properties. As a result of this differential congener persistence, the congener patterns observed in environmental media often do not match the patterns in the Aroclor formulations that were originally released. This section briefly summarizes information on the fate of PCB congeners in the environment to provide a context for our evaluation of congener patterns in Green Bay.

Figure 6-1
Biphenyl Molecular Structure



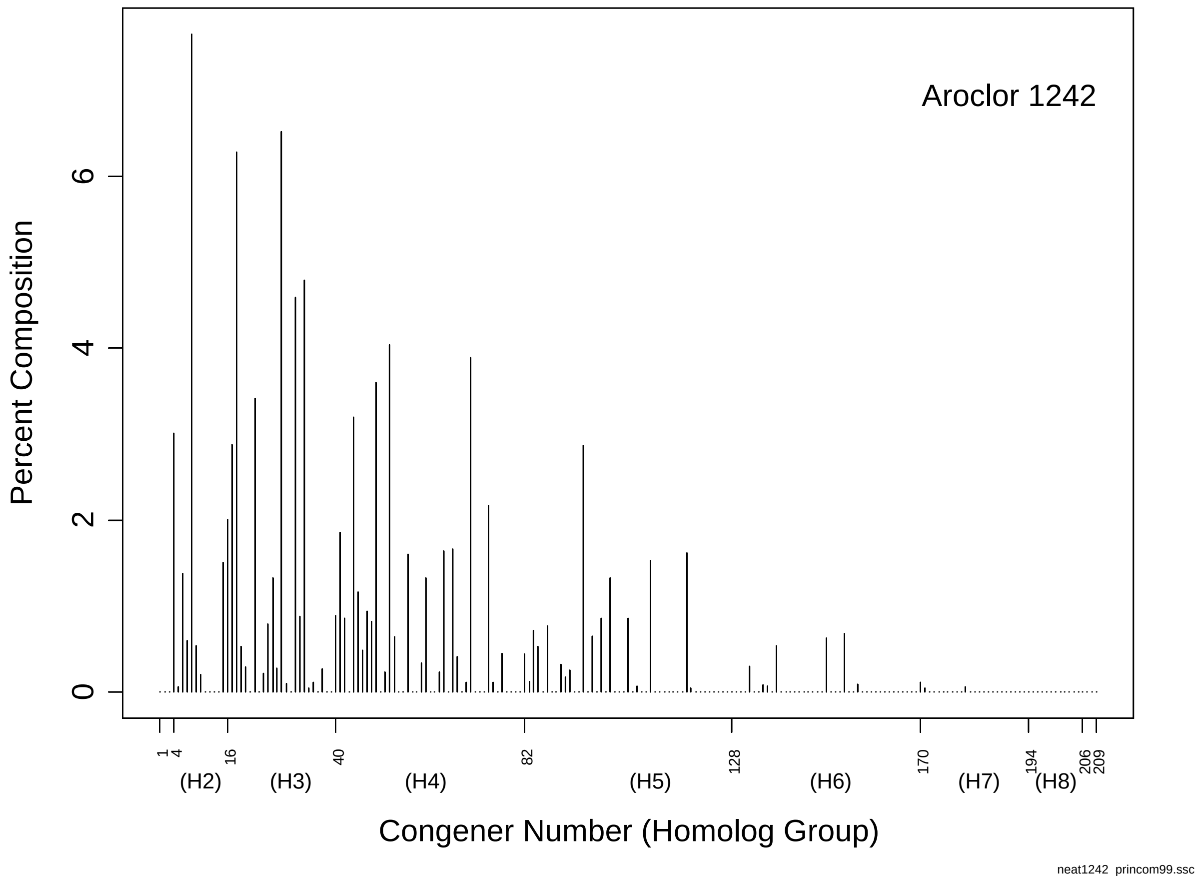
Microbial PCB Degradation

PCBs can undergo degradation by microbial communities under both aerobic (i.e., in the presence of oxygen) and anaerobic (i.e., with no oxygen present) conditions. Aerobic microbial degradation acts primarily on selected lower chlorinated congeners, producing carbon dioxide, water, and chloride ions (Erickson, 1997). Di-ortho substituted congeners (i.e., congeners with chlorine atoms at both the 2 and 2' positions in Figure 6-1) tend to be resistant to aerobic degradation (Brown and Wagner, 1990).

Anaerobic dechlorination has been documented in sediments from several PCB-contaminated aquatic systems (Brown and Wagner, 1990). Anaerobic microbes preferentially attack higher chlorinated congeners, removing chlorine atoms and producing lower chlorinated daughter PCBs (Brown et al., 1987). Since anaerobic conditions predominate in aquatic sediments, anaerobic dechlorination tends to be more important that aerobic degradation in aquatic sediments (Brown et al., 1987; Erickson, 1997). The anaerobic dechlorination process is congener-specific; some congeners are more susceptible to dechlorination than others, depending on the number and position of chlorine atoms on the parent molecule (Rhee et al., 1993). Some evidence indicates that the ability of microbial communities to dechlorinate different congeners is site-specific, with different river systems showing different patterns of dechlorination (Brown et al., 1987). The specific daughter PCBs produced by anaerobic dechlorination may also be specific to different microbial communities (Brown et al., 1987).

Figure 6-2
PCB Congener Composition of Aroclor 1242

Congeners are numbered from 1 to 209 based on the number and position of chlorine atoms. In general, higher congener numbers have more chlorine atoms. Data source: Schulz et al., 1989.



Many environmental factors affect the rate of microbial degradation of PCBs (Liu et al., 1996). Under most environmental conditions, microbial degradation of PCBs is both slow and incomplete (Erickson, 1997). PCB sediment concentration is a primary factor, with degradation rates increasing with PCB concentration (Abramowicz et al., 1993). For example, dechlorination occurs in Hudson River sediments generally only when total PCB concentrations are above approximately 30 μg/g (U. S. EPA, 1997). At sediment concentrations less than approximately 20 μg/g PCBs, as occur in Green Bay, microbial dechlorination is very slow and insignificant (Abramowicz et al., 1993).

PCB Weathering

We define weathering as processes that do not chemically alter the congeners, but redistribute the congeners among different environmental compartments, such as sediment, water, and the atmosphere. Since different congeners have different physico-chemical properties (e.g., vapor pressure, water solubility, adherence to sediment particles, etc), they have varying propensities to partition between environmental compartments. The constant re-distribution of PCBs among environmental compartments results in predictable shifts in congener patterns within the environmental media of a system.

Although PCBs are hydrophobic and tend to adhere to sediment particles, the lower chlorinated congeners, such as monochlorobiphenyls and dichlorobiphenyls, have higher water solubilities than the higher chlorinated congeners (Mackay et al., 1992). Thus when PCBs equilibrate between sediment and water, the water becomes enriched in the lower chlorinated congeners, and the sediment becomes enriched in the higher chlorinated congeners. This process has been documented in theoretical calculations (Burkhard et al., 1985), laboratory simulations (Eadie et al., 1990; Eadie et al., 1992) and field studies (Manchester, 1993; Eisenreich et al., 1994).

A similar phenomenon occurs between water and the atmosphere. The lower chlorinated congeners have higher vapor pressures and tend to volatilize more readily than the higher chlorinated congeners (Mackay et al., 1992). Thus, the atmosphere tends to become enriched in the lower chlorinated congeners relative to the water column. The lower chlorinated congeners can then be carried by air currents and re-distributed throughout the environment. This continuous process has produced a "global fractionation" of PCB congeners, in which the PCBs transported via air currents to northern latitudes are enriched in the lower chlorinated congeners (Muir et al., 1996).

Because of solubilization and volatilization, as sediment is transported from the original PCB source it tends to become more and more enriched in the higher chlorinated congeners. In general, the farther a sediment particle is transported from near a PCB source, the more times the congener partitioning process occurs and the more enriched in higher chlorinated congeners the sediment becomes. This pattern of increasing enrichment of higher chlorinated congeners in sediments farther from a PCB source has been documented at several PCB sites, including Lake Hartwell in South Carolina (Farley et al., 1994), the Hudson River (Bopp et al., 1981), and New Bedford Harbor (Bergen et al., 1998).

PCB Congener Fate in Green Bay

Microbial anaerobic degradation of PCBs in Green Bay is expected to be minimal, since sediment concentrations are below those levels where such processes occur in the environment. The lack of dechlorination is confirmed in sediment core profiles of Green Bay. Manchester (1993) found that congener patterns in Green Bay sediment cores were constant with depth, indicating that dechlorination of PCBs in the deeper, anaerobic sediments is not occurring.

The primary process acting on congener patterns in Green Bay is expected to be physico-chemical weathering. Detailed studies of the distribution of PCB congeners in Green Bay have been conducted on the sediment:porewater interface (Manchester, 1993), the surface water:suspended particulate:dissolved organic carbon interface (Eadie et al., 1992), and the atmosphere:surface water interface (Achman et al., 1992). All of these studies confirm that the physico-chemical weathering processes described above are occurring in Green Bay. These processes tend to enrich the higher chlorinated congeners in the sediments of Green Bay, with the enrichment increasing with increasing distance from the Fox River (Table 6-1).

Table 6-1
Processes Affecting Environmental PCB Congener Patterns

	Overall Effect on Congener Pattern		
Process	**Reduces Relative Amount of Lower Chlorinated Congeners**	**Increases Relative Amount of Lower Chlorinated Congeners**	**Comment**
Anaerobic dechlorination		X	Congener specific Most likely not occurring in Green Bay
Aerobic degradation	X		Congener specific Typically slow and incomplete
Volatization	X		Important process in Green Bay
Solubilization	X		Important process in Green Bay

6.3 METHODS

Our approach uses multivariate statistical techniques to summarize the PCB congener patterns present in sediments of the Lower Fox River, Green Bay, and Lake Michigan. We use the complementary techniques of principle components analysis (PCA) and k-means clustering to compare the congener patterns in four different areas: (1) Lower Fox River from Lake Winnebago to Green Bay; (2) inner Green Bay (i.e., southwest of Chambers Island); (3) outer Green Bay (i.e., northeast of Chambers Island); and (4) Lake Michigan. The multivariate statistical techniques allow us to quantitatively compare and assess the patterns observed among these four regions. We use these comparisons to determine which regions have similar congener patterns, and what features of the congener patterns cause the similarities. The degree of similarities and the features of the congener patterns responsible for the similarities are then interpreted in terms of PCB environmental chemistry to assess the data with respect to competing hypotheses about source attribution.

6.3.1 PCB Congener Data Sources

The locations of the sediment samples from which PCB congener data were used in the congener pattern analysis are shown in Figure 6-3. The sources of the data are the following.

- Data for the Lower Fox River and Green Bay are the results of sample collection and analysis conducted as part of the GBMBS from 1987 to 1990 (see Chapter 5 for a description). In addition, data from four Green Bay locations sampled in 1996 as part of the Lake Michigan Mass Balance Study were also included (L. Stanfield, U.S. EPA, personal communication, 1999).[1]

- Lake Michigan data are from two sources:

  - One sediment core sample collected from northern Lake Michigan in 1996 as part of the Lake Michigan Mass Balance Study (L. Stanfield, U.S. EPA, personal communication, 1999).[1] Although many more Lake Michigan sediment cores were collected and analyzed as part of this study, the data are not yet available.

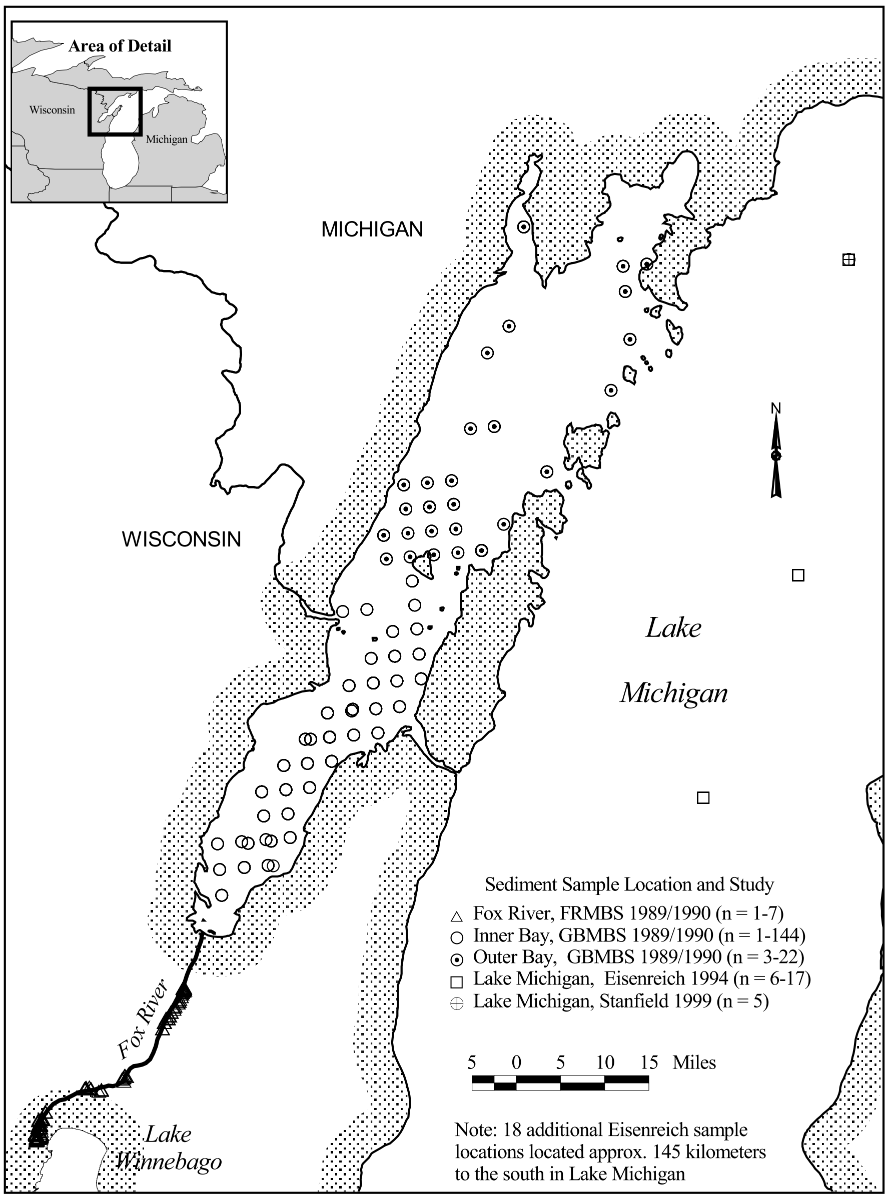
  - Eisenreich et al., 1994. In this study, sediment core samples were collected from 5 locations in Lake Michigan: three locations east of the passage between Green Bay and Lake Michigan (shown in Figure 6-3) and two locations in southern Lake Michigan.

Samples collected on different dates and from different depths at the same location were treated as independent samples. In this way, our analysis encompasses the full range of congener patterns observed in the individual core segments from all of the samples.

Chemical detection limits for congeners averaged 0.5 ng/g (dry weight). Many congeners could not be individually resolved due to coelution, which occurs when two or more congeners are indistinguishable by the analytical method used for quantification. Where necessary, we combined

1. "Lake Michigan Mass Balance Verified and Validated Data Sets." Created on July 23, 1999, by the U.S. Environmental Protection Agency.

Figure 6-3
Sediment Sample Locations in Fox River, Green Bay, and Lake Michigan



the results for individual congeners from one dataset into a group of congeners that matched the coelution pattern in a different dataset. Our database therefore contains the same sets of congeners and congener coelution groupings from all of the datasets. For simplicity of presentation, measurements of individual congeners and sets of coeluting congeners are hereafter both referred to as congeners. All congener concentration values were expressed as the percent of total PCB mass (by weight), where total PCB was defined as the sum of detectable congeners. Percentages were arcsine transformed, centered, and scaled to unit variance in all statistical analyses.

To avoid biases that could be associated with very low PCB concentrations and subsequent high analytical variability, we omitted samples which had total PCB concentration < 1 µg/kg or had fewer than 10 detectable congeners. In addition, specific congeners were omitted from the analysis if the median percent composition for that congener was <1% in all regions. As a result of these data inclusion criteria, the multivariate analyses used 41 distinct congeners to describe a total of 1175 samples: 167 from Fox River, 924 from Green Bay, and 64 from Lake Michigan. Total PCB concentrations found in these samples are presented in Figure 6-4.

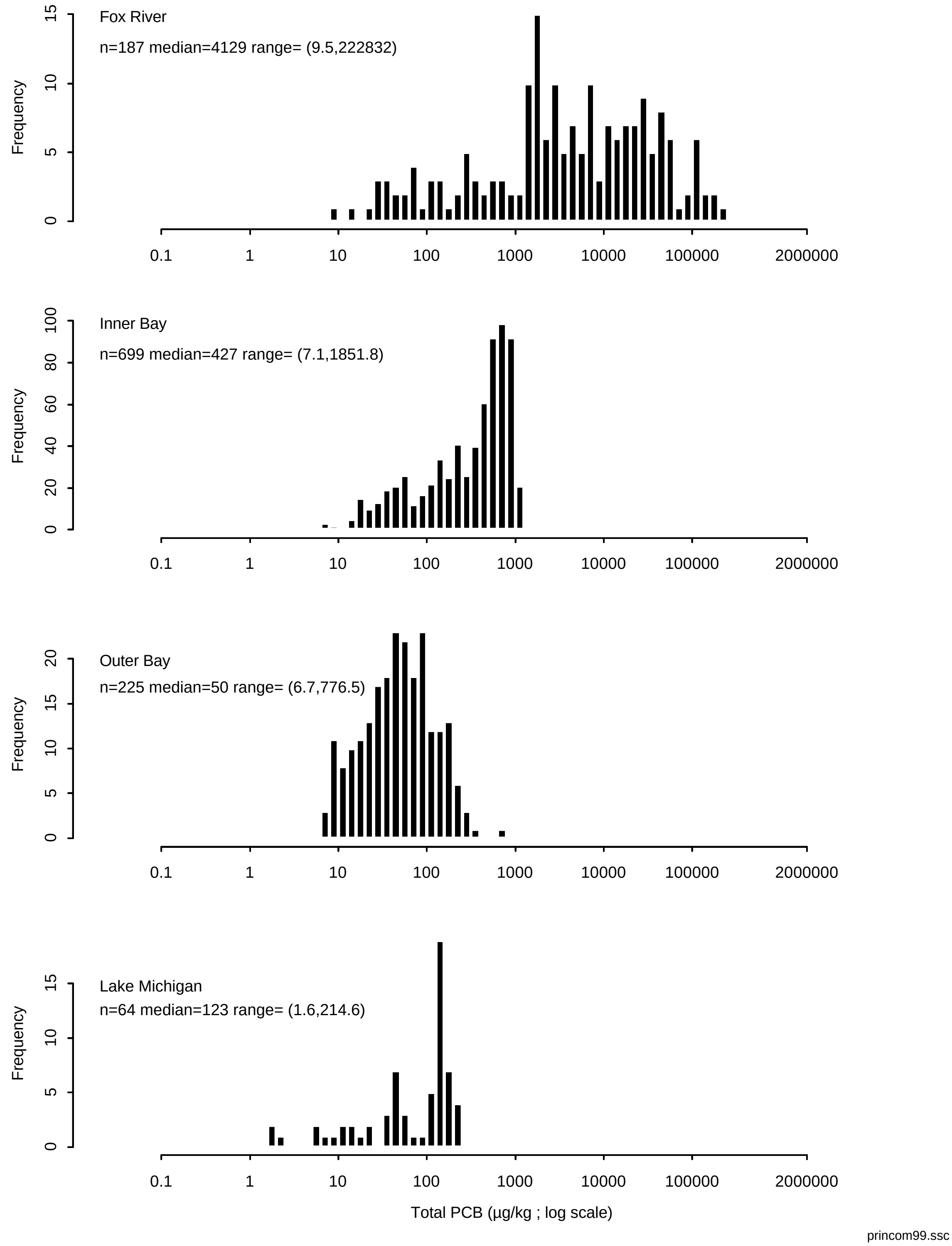
6.3.2 Multivariate Statistical Techniques

Each sediment sample has many PCB congener results associated with it, one result for each congener quantified. This type of data is termed multivariate data, since each sampling unit (i.e., the sediment sample) has associated with it many variables (i.e., concentrations of numerous different congeners). Multivariate statistical analysis techniques are designed to facilitate description of multivariate data by considering features that derive from the relationships among the variables and among the sampling units. A common objective of these methods is to cut through the complexity of numerous inter-related variables by highlighting important patterns that might not be noticed otherwise.

Multivariate statistical methods including principal component analysis (PCA) and a variety of other techniques have been employed to describe PCB congener profiles in environmental samples (e.g., Dunn et al., 1984; Focardi and Romei, 1987; Macdonald et al., 1992; Stalling et al., 1995; Magelssen and Elling, 1997; Rachdawong and Christensen, 1997). No particular method has emerged as a standard practice in the field. We employed PCA and k-means cluster analysis, methods which were selected for their ease of use and ability to capture different and complementary features of the data, namely. We consider these methods to be complementary and robust as a statistical approach for distinguishing PCB congener profiles, especially when applied in conjunction with information about the environmental chemistry properties of PCB mixtures.

PCA considers the variability contained in the original set of measured variables and yields a series of new, derived variables that are defined as combinations of the original variables. The derived variables are called "principal components," and they possess certain optimal statistical properties

Figure 6-4
Total PCB Concentrations in Sediment Samples from the Four Study Regions



with respect to their information content. The principal components effectively concentrate the total variability in the data (originally in the same number of dimensions as the number of variables) into a smaller number of new variables (and dimensions). The first principle component (PC1) is the combination of the original variables that explains the most variability in the data, the second principle component (PC2) is the combination that explains the most of the remaining variability, and so on. Thus the principle components provide statistical explanations of the total variability in the data, and can be used to describe and understand similarities and differences between individual samples with respect to the variability in the original variables. The results of PCA are typically depicted using plots showing the locations of the individual sample points in the newly defined principle components space. We also used euclidean distance in PC1 x PC2 dimensions as a quantitative dissimilarity measure, wherein we measured the distance in PC1 x PC2 space between each sample record and a reference point. We selected the mean of all outer Green Bay samples as the reference point to provide information as to whether the congener pattern in outer Green Bay samples is more similar to patterns in inner Green Bay samples or to those in Lake Michigan samples. This comparison can be used to infer the probable source of PCBs in the outer bay.

The k-means clustering method provides a cluster solution based on a predetermined number of clusters (Mardia et al., 1994; Ripley, 1996). We classified all samples into three clusters with the objective of determining the distribution of samples from different regions among the resulting groups. The distribution of samples from different regions among the three clusters provided a measure of group similarity. If the clusters resulting from this procedure are relatively homogenous with respect to sampling regions, we conclude that consistent regional patterns exist. If different regions are consistently assigned to the same cluster we also conclude that congener patterns found in sediments from those regions are substantially similar.

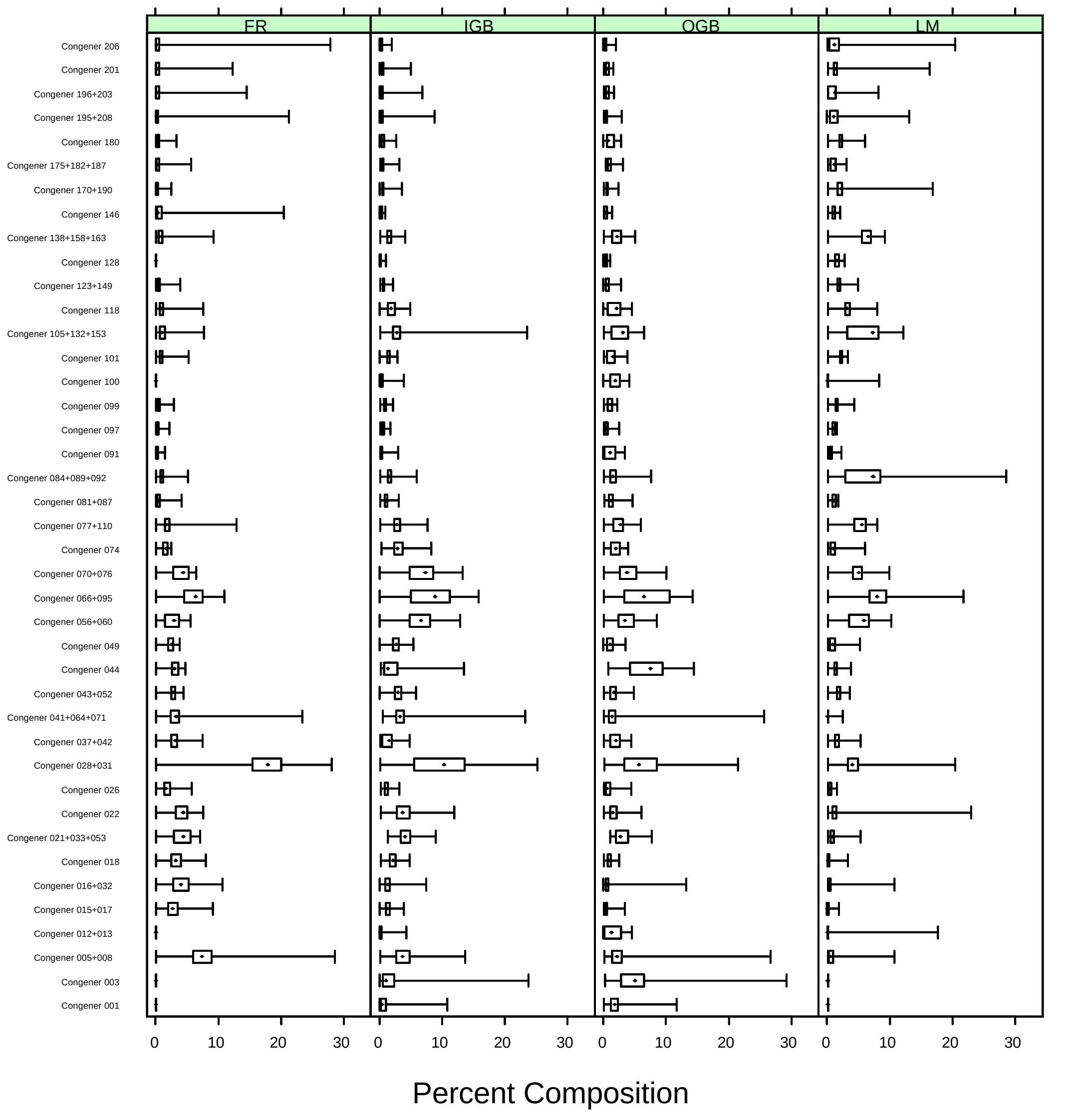
6.4 RESULTS AND DISCUSSION

6.4.1 Congener Profiles

Figure 6-5 presents the distribution of congeners measured in sediments from the Lower Fox River, inner Green Bay, outer Green Bay, and Lake Michigan. The congener profiles are generally similar in these four regions, although several important differences are apparent. The same congeners are among the most abundant in all of the regions, specifically 028+031, 056+060, 066+095, and 070+076. However, the Lower Fox River samples appear to be relatively enriched in the lower chlorinated congeners (those with low congener numbers), whereas Lake Michigan samples appear to be relatively enriched in the higher chlorinated congeners (those with high congener numbers). In addition, a small number of Lower Fox River samples are alsorelatively enriched in the higher chlorinated congeners, as indicated by the high maximum range of percent composition for congeners 146, 195+208, 196+203, 201, and 206. The congener composition in

Figure 6-5

Percent Composition of Selected PCB Congeners in Lower Fox River (FR), Inner Green Bay (IGB), Outer Green Bay (OGB), and Lake Michigan (LM). Congener numbers are given in left-most column. Bar ends are the minima and maxima, boxes are the interquartile range (25th % to 75th %), and symbols within the boxes are medians.



inner and outer Green Bay appear to be similar and fall between that of the Lower Fox River and Lake Michigan.

In the sections that follow, we examine specific features of the measured congener compositions using the multivariate statistical techniques described above.

6.4.2 Principal Component Analysis

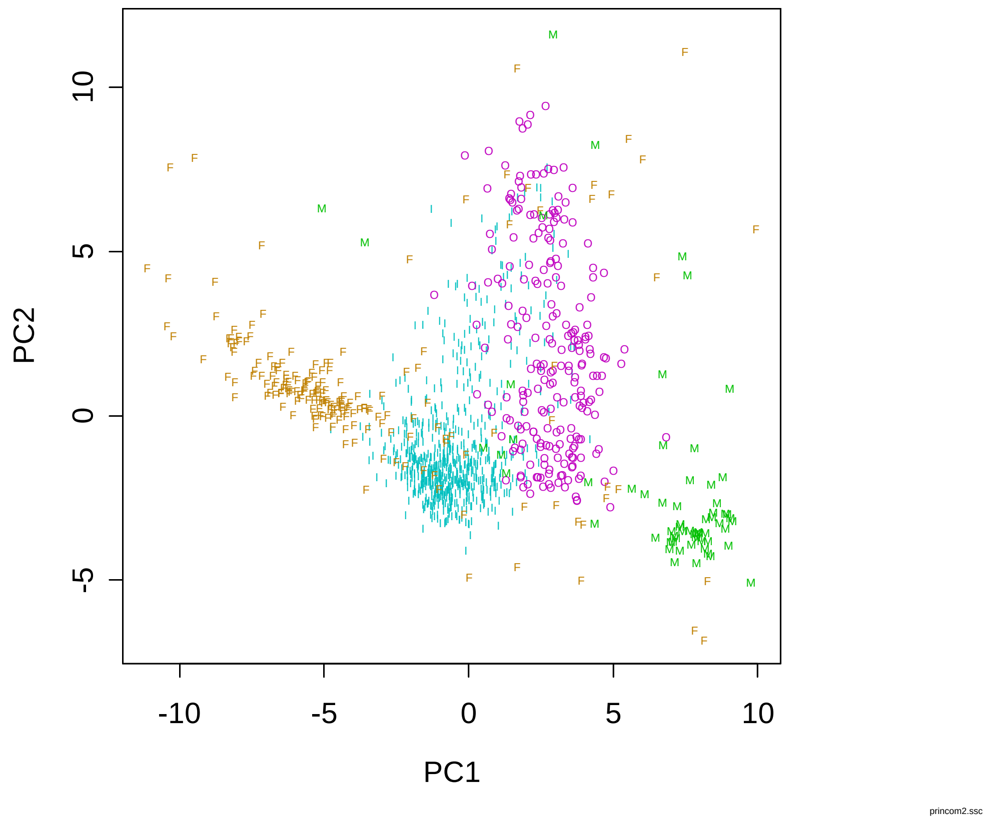
Figure 6-6 presents the plot of each sediment sample by PC1 and PC2 scores, and identifies the region from which each sample was collected. As can be seen in the figure, samples from within a region tend to group together. Thus, congener patterns tend to be similar within each of the regions, and somewhat distinct from the other regions. This result indicates that congener patterns are related to geographic location and thus can be used to discriminate between regions.

PCA identifies the overall degree of congener chlorination as the most important factor in explaining the variability in congener patterns between samples. Principal Component 1 (PC1), which by definition explains the largest percent of total variance in the data, explains 26% of the total variance among the 41 congeners. The congener loadings for PC1 are shown in Table 6-1, which demonstrates that congeners with numbers above approximately congener 77 have positive loading coefficients, whereas congener numbers less than 77 generally have negative loading coefficients. These loadings mean that samples with higher PC1 scores are relatively enriched in the more highly chlorinated congeners, whereas samples with lower PC1 scores are relatively enriched in the less-chlorinated congeners.

The frequency of PC1 scores in the four different geographic regions are shown in Figure 6-7. This figure depicts the relative abundance of different PC1 scores in sediment samples from the four regions. The relationship of the regions to each other on PC1 is consistent with the transport of PCBs from the Fox River, to inner Green Bay, to outer Green Bay and the weathering of the PCBs as they are transported. Lower Fox River samples are generally located at the low end of the PC1 scale, which reflects the greater relative abundance of lower chlorinated congeners in sediments from that region. Inner Green Bay samples are generally next lowest, indicating a loss of lower chlorinated congeners compared with Lower Fox River samples, but relatively more lower chlorinated congeners than in outer Green Bay. This loss of lower chlorinated congeners is consistent with the weathering of PCBs caused by evaporation and solubilization, as described in Section 6.2. Similarly, outer Green Bay samples tend to have higher PC1 scores than samples from lower Green Bay, indicative of weathering of PCBs as the PCBs are moved from inner to outer Green Bay.

The results of the PCA are consistent with studies on PCB weathering in environmental systems. The interpretation of PC1 scores as being representative of environmental weathering is in good agreement with laboratory studies on the weathering of Aroclor 1242. Brown and Wagner (1990)

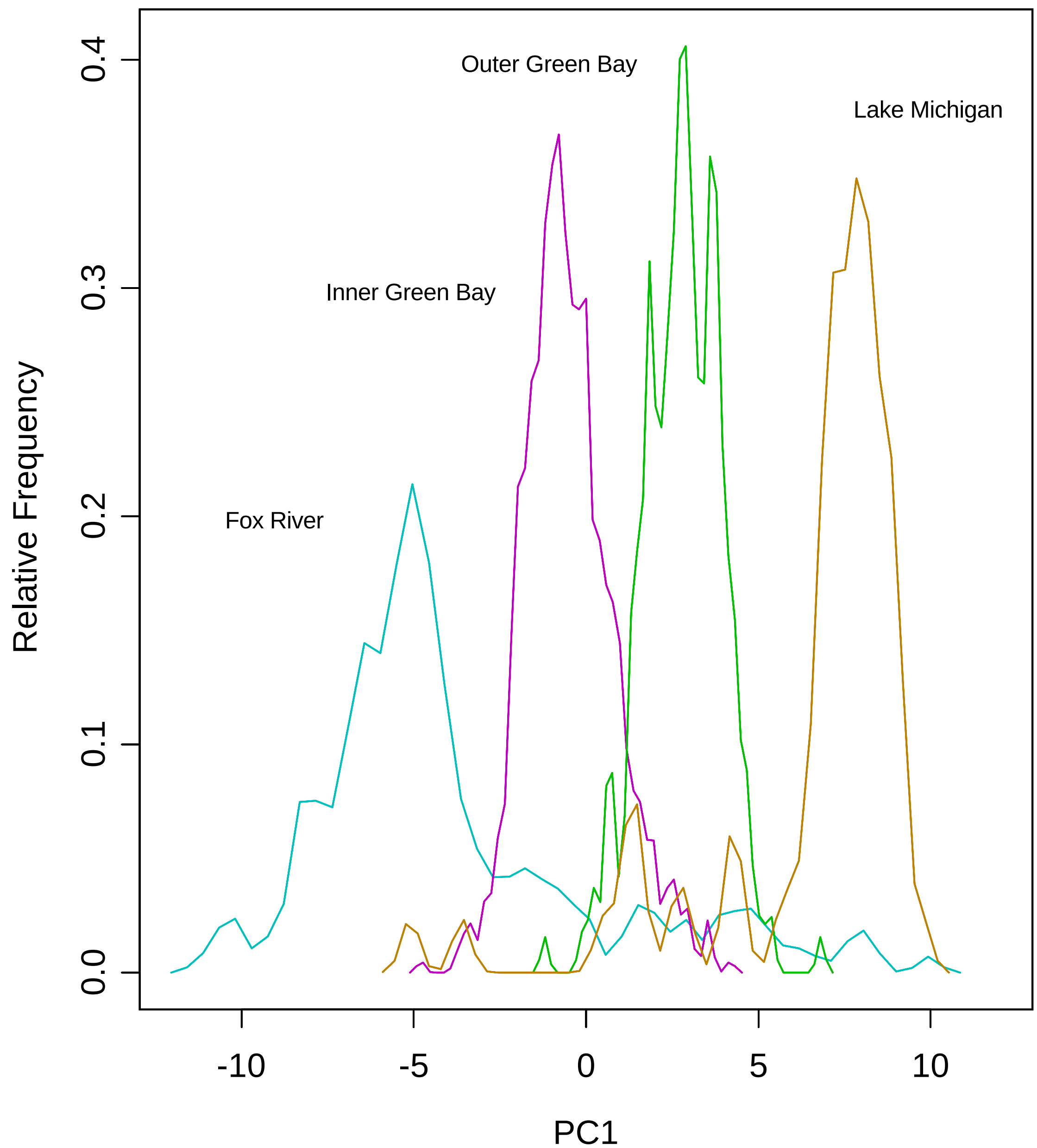
Figure 6-6
Graphical Ordination of Principal Components Derived from Congener Profiles (percent composition) in Sediment Samples from Fox River ("F"), Inner Green Bay ("I"), Outer Green Bay ("O"), and Lake Michigan (M"). PC1 and PC2 are defined in Table 6-1.



studied the relative loss of congeners from Aroclor 1242 when the Aroclor mixture was allowed to evaporate. They found that congeners with numbers above approximately 71 were relatively enriched as a result of evaporation (due to their lower vapor pressures), and congeners with numbers lower than approximately 71 were preferentially lost (due to higher vapor pressures). Brown and Wagner (1990) also concluded that the pattern they observed for evaporation of Aroclor 1242 is the same as that for solubilization from sediment into water, and therefore can be used to represent all environmental weathering processes. The split at approximately congener 71 corresponds closely with our PC1 loadings, where the break between positive loadings and negative loadings occurs between congeners 74 and 77+110. Therefore, the pattern of lower to higher PC1 scores from the Lower Fox River to inner Green Bay to outer Green Bay to Lake Michigan is wholly consistent with the environmental weathering of Aroclor 1242 released into the Lower Fox River and transported through the system.

Another important feature of the PCA is the fact that the congener pattern in outer Green Bay samples is more similar to the pattern in inner bay samples than to the Lake Michigan pattern.

Figure 6-7
Relative frequency of PC1 scores in Fox River (n = 187), inner Green Bay (n = 699), outer Green Bay (n = 225), and Lake Michigan (n = 64). Increasing values of PC1 generally correspond with greater proportion of highly chlorinated congeners.



princom99.ssc pc1dim.wmf

Figure 6-7 shows a clear gap between the bulk of Lake Michigan samples and the outer Green Bay samples along PC1. This difference in congener patterns is further illustrated in Figure 6-8, which presents the distance, in terms of PC1 and PC2 space, of samples relative to the mean of outer Green Bay samples. This figure shows that the median distance between the outer bay and inner bay congener patterns is 3.8 units, compared with a median distance of 8.1 units between outer bay and Lake Michigan patterns. This comparison demonstrates that the PCB congener pattern in outer bay samples is closer to the inner bay pattern than to the Lake Michigan pattern. This similarity in congener patterns indicates that outer bay PCBs likely originated from the inner bay rather than from Lake Michigan.

Further evidence of the inner bay being the source of outer bay PCBs comes from the relative positions of the outer bay and Lake Michigan samples along PC1. Lake Michigan samples are enriched in the higher chlorinated congeners relative to outer Green Bay samples. Because weathering acts to increase the proportion of higher chlorinated congeners, the transport (and subsequent weathering) of Lake Michigan PCBs to outer Green Bay would not result in the congener pattern observed in outer Green Bay. The congener patterns observed in outer Green Bay and Lake Michigan samples are consistent with the transport and weathering of outer bay PCBs into Lake Michigan, and inconsistent with the transport of Lake Michigan PCBs into the outer bay.

The congener pattern observed in outer Green Bay samples could include the mixing of PCBs from inner Green Bay and Lake Michigan. However, the contribution of Lake Michigan PCBs is most likely very small relative to PCBs from the inner bay, for two reasons: (1) the strong similarity between the inner and outer bay congener patterns; and (2) the fact that weathering of PCBs during surface water transport to the outer bay from either the inner bay or Lake Michigan would tend to shift PC1 scores to the right, decreasing the contribution of Lake Michigan PCBs to the outer bay PC1 scores. Thus the outer bay pattern is inherently consistent with transport of inner bay PCBs, and only a small fraction of PCBs from Lake Michigan could be mixed with inner bay PCBs in the outer bay to produce the PC1 scores observed in the outer bay.

PC2 explains 18.5% of the total variance in the data. PC2 is characterized by large positive loadings on congeners 12/13, 37/42, 44, 91, and 100, and smaller positive loadings on congeners 1, 3, and those greater than 170 (Table 6-2). Loadings on other congeners are negative. We are unable to explain PC2 either in terms of environmental processes that can alter congener patterns (weathering, aerobic or anaerobic degradation) or in terms of differences in parent Aroclors. Therefore, PC2 apparently addresses other sources of variation in the data, potentially from analytical variability or variations due to low concentrations or frequency of detection in the samples.

Figure 6-8
Euclidean Distance between Points in PC1xPC2 Space Relative to the Mean Value among Inner Green Bay Samples among Four Study Regions

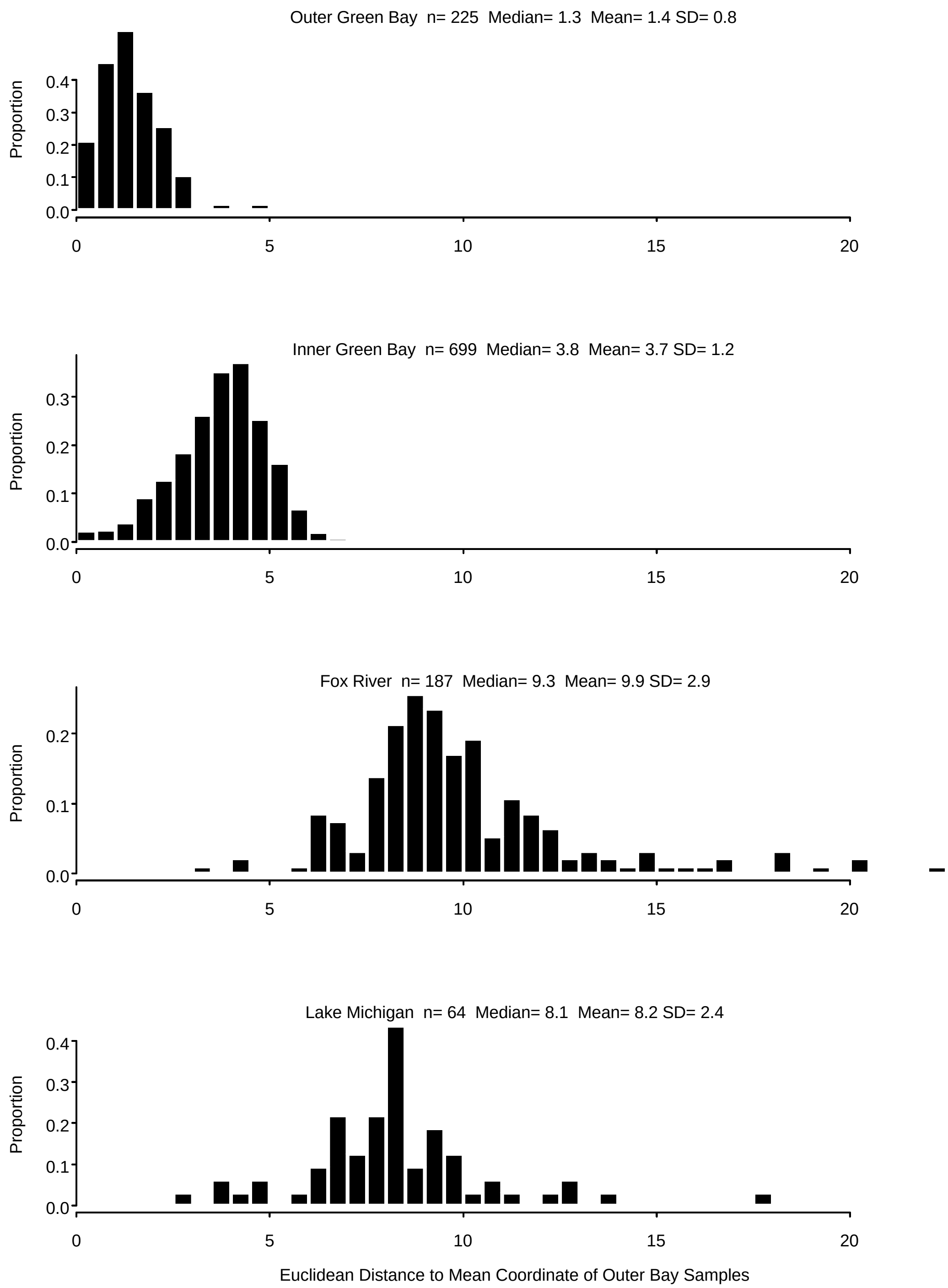


Table 6-2
Principal Component Loadings for PC1 and PC2

Congener/Congener Coelution Set	PC1	PC2
Proportion of Variance (%)	**26.1%**	**18.5%**
Cumulative Proportion (%)	**26.1%**	**44.6%**
PCB 001	0.0971	0.1499
PCB 003	0.1027	0.1571
PCB 005+008	-0.223	0.0029
PCB 012+013	0.1121	0.1827
PCB 015+017	-0.2599	-0.0036
PCB 016+032	-0.2124	0.0366
PCB 018	-0.2498	-0.0803
PCB 021+033+053	-0.1732	0.0097
PCB 022	-0.1798	-0.1388
PCB 026	-0.2047	-0.0078
PCB 028+031	-0.1863	-0.0745
PCB 037+042	-0.0569	0.1235
PCB 049	-0.1456	-0.1628
PCB 056+060	-0.0035	-0.2301
PCB 066+095	-0.0025	-0.2137
PCB 070+076	-0.0398	-0.2452
PCB 074	-0.0634	-0.2214
PCB 077+110	0.1031	-0.2686
PCB 081+087	0.1328	-0.0519
PCB 084+089+092	0.1563	-0.1201
PCB 091	0.1197	0.1324
PCB 097	0.1205	-0.2276
PCB 099	0.1661	-0.2025
PCB 100	0.1237	0.1675
PCB 101	0.1161	-0.2646
PCB 105+132+153	0.176	-0.2368
PCB 118	0.1305	-0.2667
PCB 123+149	0.1727	-0.1913

Table 6-2 (cont.)
Principal Component Loadings for PC1 and PC2

Congener/Congener Coelution Set	PC1	PC2
PCB 128	0.2311	-0.0567
PCB 138+158+163	0.2288	-0.1675
PCB 146	0.0493	0.0276
PCB 170+190	0.2021	-0.0403
PCB 175+182+187	0.1961	0.1187
PCB 180	0.1983	0.0652
PCB 195+208	0.1573	0.0853
PCB 196+203	0.1444	0.1179
PCB 201	0.1672	0.084
PCB 206	0.1221	0.0879

6.4.3 Cluster Analysis

The results of the cluster analysis, in which the sediment samples are clustered into groups of similar congener patterns, are consistent with the PCA analysis. The cluster analysis indicates that inner Green Bay and outer Green Bay congener patterns are the most similar among patterns in the four regions. Clustering the sediment samples into three groups results in one classification group consisting largely of Lower Fox River samples (group 1), one group consisting of inner and outer Green Bay samples (group 2), and one group consisting largely of Lake Michigan samples (group 3) (Table 6-3). The clustering indicates that >99% of inner Green Bay and outer Green Bay samples are sufficiently similar to be classified into the same cluster (Table 6-3). This result is consistent with the PCA analysis, which showed that outer Green Bay samples are more similar in their congener pattern to inner Green Bay samples than to Lake Michigan samples.

Of the Lower Fox River samples, 13.4% are clustered into group 3 with the majority of the Lake Michigan samples. This grouping of some Lower Fox River samples with most of the Lake Michigan samples indicates that a small number of Lower Fox River samples are enriched in higher chlorinated congeners. As discussed previously in Section 6.4.1, some Lower Fox River samples have relatively high proportions of congener numbers 146, 195+208, 196+203, 201, and 206. These congeners, which contain from six to nine chlorine atoms, are indicative of Aroclors 1254 and 1260 rather than 1242 (Erickson, 1997). Evidence of isolated areas of higher chlorinated congener in Lower Fox River is also reported by ThermoRetec Consulting Corporation and N.R.T. Inc. (1999).

Table 6-3
Classification of Sediment Samples from Four Regions into Three Groups Based on k-Means Clustering Using PCB Congener Profiles

Region	Percent of Region's Samples in Classification Group		
	1	2	3
Lower Fox River (n = 187)	79.1%	7.5%	13.4%
Inner Green Bay (n = 699)	0.7%	99.3%	0.0%
Lake Michigan (n = 64)	3.1%	7.8%	89.1%
Outer Green Bay (n = 225)	0.0%	99.1%	0.9%

6.5 CONCLUSIONS

This chapter presents the results of two multivariate statistical approaches to evaluating the PCB congener patterns in the sediments of the Lower Fox River/Green Bay system. The analysis of congener patterns demonstrates the following:

- The observed congener patterns are consistent with the Lower Fox River being the primary source of PCBs to both inner and outer Green Bay. There is a spatial shift in congener patterns that is consistent with the transport and weathering of PCBs from the Lower Fox River to inner Green Bay to outer Green Bay.

- PCBs in outer Green Bay most likely were not transported from Lake Michigan. The PCB congener pattern in outer Green Bay is more similar to the pattern in inner Green Bay than to the pattern in Lake Michigan. Furthermore, the outer Green Bay pattern is unlikely to have been derived from the weathering of the pattern observed in Lake Michigan. Based on the PCB congener patterns, it is more likely that Lake Michigan PCBs originated from outer Green bay.

CHAPTER 7
PATHWAY DETERMINATION AND CONCLUSIONS

7.1 PATHWAY DETERMINATION

This report presents a determination of PCB pathways for surface water, sediment, and aquatic biota resources of the Lower Fox River/Green Bay system. The determination is consistent with the Department's regulations for conducting NRDA at 43 CFR Part 11. The report determines the pathways through a combination of the following [43 CFR §11.63(a)(2)]:

(1) Demonstration of the presence of PCBs in pathway resources. Chapter 5 describes the spatial and temporal patterns of PCB contamination in sediment, surface water, and fish of Green Bay, and Chapter 6 describes PCB congener concentration patterns in terms of PCB pathways within the system.

(2) Use of GBMBS models that show that surface water, sediment, and aquatic biota serve as PCB transport pathways in the system. Chapter 3 summarizes the application of the GBMBS models to the determination of pathway.

In determining the pathways, the following were considered:

- The chemical and physical properties of the PCBs when being transported in the environment [43 CFR §11.63(a)(1)(I)]. The GBMBS models are based on detailed physico-chemical characterization of' PCBs, including water solubility, adherence to different types of particles, volatilization, and uptake and elimination in biota. In addition, Chapter 6 presents an analysis of PCB congener fate as a function of PCB environmental chemistry characteristics.

- The mechanism of transport of PCBs [43 CFR §11.63(a)(1)(ii)]. Chapter 4 describes the Green Bay water circulation patterns that transport PCBs in the surface water column. Furthermore, the GBMBS models are based on information on mechanisms of PCB transport in the system.

- Combinations of pathways that, when viewed together, transport the PCBs to exposed resources [43 CFR §11.63(a)(1)(iii)].

The conclusion of the pathway determination analysis is that there are three pathways by which PCBs released from Fox River paper company facilities are transported to exposed natural resources in the Lower Fox River/Green Bay environment:

(1) Surface Water/Sediment Pathway

- Surface water and sediment in the Lower Fox River downstream of the mills and in Green Bay has been exposed to PCBs.

- The areal extent of the transport and exposure includes the Lower Fox River downstream of paper company facilities, inner Green Bay, outer Green Bay, and Lake Michigan.

(2) Biological Pathway

- A variety of biota, including phytoplankton, zooplankton, benthic invertebrates, and fish, serve as PCB pathways, transporting PCBs through the food chain to predatory fish and birds.

- The migration of PCB-contaminated biota also serves as a transport pathway. Natural resources on the Reservation of the Oneida Tribe of Indians of Wisconsin are exposed to Lower Fox River/Green Bay PCBs through this pathway.

(3) Air Pathway

- Evaporation of PCBs from Green Bay and subsequent downwind transport serves as a pathway of PCB movement.

7.2 SUMMARY OF PCB FATE IN LOWER FOX RIVER/GREEN BAY

The ultimate transport and fate of PCBs in the Lower Fox River/Green Bay system can be summarized using estimates of the mass of PCBs distributed in different areas of the system. The great majority of PCBs in the system are contained in the bed sediments (as opposed to the mass in surface water, biota, and air). Therefore, estimates of the amount of PCBs in bed sediments are good approximations of the distribution of PCBs in the Lower Fox River/Green Bay system.

The WDNR used the results of extensive sediment sampling to estimate that approximately 39,400 to 47,300 kg of PCBs are contained in Lower Fox River sediments (Chapter 4). Sediment sampling in Green Bay conducted as part of the GBMBS provided an estimate of 8,500 kg PCB in Green Bay sediments (Chapter 5). Although both estimates can be considered only approximations, these estimates indicate that the sediments of the Lower Fox River contain a larger mass of PCBs than the sediments of Green Bay. Therefore, to the extent that PCB transport processes are still operating on sediment PCBs in the Lower Fox River, PCBs will continue to be transported into Green Bay.

The total of the estimated PCB mass contained in the sediments of Lower Fox River and Green Bay (47,900 to 55,800 kg) is much less than the WDNR's estimate of the total mass of PCBs released from Fox River paper companies, 300,000 kg (Chapter 2). This large difference indicates that PCBs have been lost from the system. PCBs could be lost from the system via complete degradation (not just dechlorination, which merely transforms one PCB into another PCB) or transport out of the system. Given that complete PCB degradation does not occur to a large extent in most aquatic systems (Erickson, 1997), it is very unlikely that the large mass difference between PCBs released and PCBs in the system can be accounted for by PCB degradation.

The transport of PCBs out of the Lower Fox River/Green Bay system most likely accounts for most of the PCB mass difference. The GBMBS models estimated that surface water transport to Lake Michigan and volatilization to the atmosphere and subsequent downwind transport were the two dominant mechanisms by which PCBs are lost from the Lower Fox River/Green Bay system. Both of these processes would tend to transport PCBs from Green Bay into northern Lake Michigan.

Therefore, a simple mass balance approach indicates that the ultimate fate of much of the PCBs released from Fox River paper company facilities is transported out of the Fox River/Green Bay system to Lake Michigan.

7.3 REPORT CONCLUSIONS

The conclusions of the evaluation of PCB pathways are the following:

1. *PRP paper manufacturing and processing facilities released large quantities of PCBs into the Lower Fox River.*

▸ Based on reviews of historical facility records, industrial processes and waste disposal practices, and PCB concentrations in paper products and waste, paper company facilities along the Lower Fox River released approximately 300,000 kg of PCBs into the Lower Fox River.

2. The Fox River is the dominant source of PCBs to Green Bay.

▸ The GBMBS estimates that in 1989, the Fox River was the source of 92% of the PCBs that entered Green Bay from all tributary or atmospheric sources.

▸ The spatial pattern of PCBs in Green Bay sediment, surface water, and fish is consistent with the Fox River being the primary source of PCBs to Green Bay.

- Detailed analysis of sediment congener patterns shows that PCBs in the inner and outer bays of Green Bay have congener patterns more similar to Fox River patterns than to northern Lake Michigan patterns. Changes observed in the congener patterns throughout the bay are consistent with environmental weathering of the Aroclor 1242 released from Fox River paper company facilities.

3. *Surface water is the primary pathway by which PCBs are transported in the Lower Fox River/Green Bay system.*

- Measurements of PCBs in surface water (as both dissolved and suspended phases) document the movement of PCBs in the surface water column.

- The GBMBS models conclude that advective transport in surface water (i.e., movement with water currents) is the primary PCB transport pathway in the system.

4. *Fox River PCBs are transported throughout Green Bay.*

- Water circulates from the inner bay to the outer bay, carrying suspended sediment and PCBs with it.

- Outer bay sediment, water, and fish are contaminated with PCBs.

- The PCB congener patterns in inner and outer bay sediments are consistent with the Fox River being the source of outer bay PCBs.

5. *Fish and birds in Green Bay are exposed to PCBs via the food chain pathway.*

- A PCB bioaccumulation model, developed as part of the GBMBS, models food chain PCB uptake for several fish species, including gizzard shad, alewife, rainbow smelt, brown trout, and walleye. For all species, both surface water and dietary items are PCB exposure routes. Most of the accumulated PCBs come from the diet, particularly for walleye and brown trout.

6. *PCB concentrations in Green Bay have declined since the 1970s, but remain high because of the environmental persistence and continued environmental release of PCBs.*

- PCB concentrations in Green Bay sediment increased in the 1960s and 1970s, coinciding with Fox River paper company PCB releases.

- PCB concentrations in Green Bay fish have declined since the 1970s, coinciding with reductions in direct PCB releases to the Fox River.

- PCB concentrations in Green Bay fish have declined much more slowly than the decline in direct PCB releases from paper companies into the Fox River, demonstrating that PCBs are persistent in the environment and continue to be released and transported within the system.

7. PCBs are transported from Green Bay into Lake Michigan.

- A large exchange of water takes place between Green Bay and Lake Michigan, providing a PCB transport mechanism.

- PCBs in water have been measured at higher concentrations in outer Green Bay than in northern Lake Michigan, indicating a concentration gradient from the bay to the lake.

- The GBMBS models estimate a net movement of approximately 122 kg of PCBs from the bay to the lake via surface water advection in 1989. Additionally, the models estimate a net exchange of 158 kg from the water column to the air in 1989, and the prevailing southwesterly winds would tend to carry these volatilized PCBs toward Lake Michigan.

- Congener patterns are consistent with the transport and weathering of PCBs from Green Bay to Lake Michigan.

- A simple mass balance approach indicates that the ultimate fate of much of the PCBs released from Fox River paper company facilities is transport out of the Fox River/Green Bay system, to Lake Michigan.

CHAPTER 8
REFERENCES

Abramowicz, D.A., M.J. Brennan, H.M.V. Dorf and E.L. Gallagher. 1993. Factors influencing the rate of polychlorinated biphenyl dechlorination in Hudson River sediments. *Environmental Science and Technology* 27(6): 1125-1131.

Achman, D.R., K.C. Hornbuckle and S.J. Eisenreich. 1992. Volatilization of polychlorinated biphenyls from Green Bay, Lake Michigan. *Environmental Science and Technology* 27(1): 75-98.

Ahrnsbrak, W.F. and R.A. Ragotzkie. 1970. Mixing processes in Green Bay. *Proceedings of the 13th Conference on Great Lakes Research*, Buffalo, New York. pp. 880-890.

Appleton Papers, Inc. Year unknown. 100 Years: Locks Mill Centennial Anniversary, 1889-1989, Locks Mill, Combined Locks, Wisconsin.

Appleton Papers, Inc. 1987. The Birth of Carbonless: NCR Paper Brand. Appleton, Wisconsin, February 28.

Beltran, R.F. 1992. The Green Bay/Fox River Mass Balance Study Management Summary: Preliminary Management Summary. Prepared for the U.S. EPA, Great Lakes National Program Office. December. 24 pp.

Bergen, B.J., K.A. Rahn and W.G. Nelson. 1998. Remediation at a marine Superfund site: Surficial sediment PCB congener concentration, composition and redistribution. *Environmental Science and Technology* 32(22): 3496-3501.

Bierman, V.J., J.V. DePinto, T.C. Young, P.W. Rodgers, S.C. Martin, R. Raghunathan and S.C. Hinz. 1992. Development and Validation of an Integrated Exposure Model for Toxic Chemicals in Green Bay, Lake Michigan. Prepared by U.S. EPA, Large Lakes and Rivers Research Branch. Draft Final Report. September 1.

Bopp, R.F., H.J. Simpson, C.R. Olsen and N. Kostyk. 1981. Polychlorinated biphenyls in sediments of the tidal Hudson River, New York. *Environmental Science and Technology* 15(2): 210-216.

Brazner, J. and W. DeVita. 1998. PCBs, DDE, and mercury in young-of-the-year littoral fishes from Green Bay, Lake Michigan. *Journal of Great Lakes Research* 24(1): 83-92.

Brown, J.F., R.E. Wagner, H. Feng, D.L. Bedard, M.J. Brennan, J.C. Carnahan and R.J. May. 1987. Environmental dechlorination of PCBs. *Environmental Toxicology and Chemistry* 6: 579-593.

Brown, J.F. and R.E. Wagner. 1990. PCB movement, dechlorination, and detoxication in the Acushnet Estuary. *Environmental Toxicology and Chemistry* 9: 1215-1233.

Burkhard, L.P., D.E. Armstrong and A.W. Andren. 1985. Partitioning behavior of polychlorinated biphenyls. *Chemosphere* 14(11/12): 1703-1716.

Buser, D.J. 1985. Analysis of dated sediment cores from Lake Michigan's Green Bay for polychlorinated biphenyls. University of Wisconsin-Milwaukee Master's thesis.

Cogswell, S. 1998. Fishery Surveys on Seven Streams in the Oneida Indian Reservation, Wisconsin. 1998 Stream Assessments and Contaminant Collections. Green Bay Fishery Resources Office.

Cogswell, S. and D. Bougie. 1998. Duck Creek Fisheries Assessment: Final Report. Green Bay Fishery Resources Office Report 98-1. October 30.

Connolly, J.F., T.F. Parkerton, J.D. Quadrini, S.T. Taylor and A.J. Thumann. 1992. Development and Application of a Model of PCBs in the Green Bay, Lake Michigan Walleye and Brown Trout and their Food Webs. Prepared for the U.S. EPA, Large Lakes Research Station, Grosse Ile, Michigan. October 2. 200 pp.

DePinto, J.V. 1994. Role of mass balance modeling in research and management of toxic chemicals in the Great Lakes: The Green Bay Mass Balance Study. *Great Lakes Research Review* 1(1): 1-8.

DePinto, J.V., R. Raghunathan, P. Sierzenga, X. Zhang, V.J. Bierman Jr., P.W. Rodgers and T.C. Young. 1994. Recalibration of GBTOX: An Integrated Exposure Model for Toxic Chemicals in Green Bay, Lake Michigan. Draft Final Report. Prepared for the U.S. EPA, Large Lakes and Rivers Research Branch, Grosse Ile, Michigan. March 1. 150 pp.

Dunn, W.J.I., D.L. Stalling, T.R. Schwartz, J.W. Hogan, J.D. Petty, E. Johansson and S. Wold. 1984. Pattern recognition for classification and determination of polychlorinated biphenyls in environmental samples. *Analytical Chemistry* 56: 1308-1313.

Eadie, B.J., N.R. Morehead and P.F. Landrum. 1990. Three-phase partitioning of hydrophobic organic compounds in Great Lake waters. *Chemosphere* 20(1-2): 161-178.

Eadie, B.J., G.L. Bell and N. Hawley. 1991. Sediment Trap Study in the Green Bay Mass Balance Program: Mass and Organic Carbon Fluxes, Resuspension, and Particle Settling Velocities. NOAA Technical Memorandum ERL GLERL-75. Great Lakes Environmental Research Laboratory, Ann Arbor, MI. July. 29 pp.

Eadie, B.J., N.R. Morehead, J.V. Klump and P.F. Landrum. 1992. Distribution of hydrophobic organic compounds between dissolved and particulate organic matter in Green Bay waters. *Journal of Great Lakes Research* 18(1): 91-97.

Eisenreich, S.J., D.L. Swackhamer, D.T. Long and K. Golden. 1994. I. Organochlorines in Lake Michigan Sediments. A report to the Great Lakes National Program Office, U.S. EPA. 205 pp.

Eisler, R. 1986. Polychlorinated biphenyl hazards to fish, wildlife, and invertebrates: A synoptic review. *U.S. Fish and Wildlife Service Biological Report* 85(1.7): 72 pp.

Erickson, M.D. 1997 *Analytical Chemistry of PCBs*. Lewis Publishers, New York. 667 pp.

Exponent Environmental Group. 1998. Draft Technical Memorandum: Model Evaluation Workgroup Technical Memorandum 7b. Review of the Green Bay Food Web Model. Prepared for Fox River Model Evaluation Workgroup. July.

Farley, K.J., G.G. Germann and A.W. Elzerman. 1994. Differential weathering of PCB congeners in Lake Hartwell, South Carolina. *Environmental Chemistry of Lakes & Reservoirs* 237: 575-600.

Focardi, S. and R. Romei. 1987. Fingerprint of polychlorinated biphenyl congeners in samples of human subcutaneous adipose tissue. *Chemosphere* 16(10-12): 2315-2320.

Gottlieb, E.S. 1992. Variability of the Stratified Flow in the Passages Connecting Green Bay and Lake Michigan. Phd Thesis, University of Michigan.

Hagler Bailly Services, Inc. 1998. Lower Fox River/Green Bay NRDA: Initial Restoration and Compensation Determination Plan. Prepared for U.S. Fish and Wildlife Service. September 14.

Hawley, N. and J. Niester. 1993. Measurement of horizontal sediment transport in Green Bay, May-October, 1989. *Journal of Great Lakes Research* 19(2): 368-378.

Hermanson, M.R., E.R. Christensen, D.J. Buser and L.M. Chen. 1991. Polychlorinated biphenyls in dated sediment cores from Green Bay and Lake Michigan. *Journal of Great Lakes Research* 17(1): 94-108.

HydroQual Inc. 1995. Addendum to Green Bay Final Report Food Chain Model Projections. Prepared by HydroQual, Inc., Mahwah, NJ. November. Job Number ABTA0204.

HydroQual Inc. 1999. Hydrodynamics, Sediment Transport and Sorbent Dynamics in Green Bay. Prepared for Remediation Technologies, for Wisconsin Department of Natural Resources. March.

Kennedy, J.A. 1982. Water-mass structures and exchanges in Green Bay, Lake Michigan. University of Wisconsin-Milwaukee Master's thesis.

Lathrop, R.G., J.R.V. Castle and T.M. Lillesand. 1990. Monitoring river plume transport and mesoscale circulation in Green Bay, Lake Michigan, through satellite remote sensing. *Journal of Great Lakes Research* 16(3): 471-484.

Limno-Tech, Inc. and WDNR. 1998. Model Evaluation Workgroup Technical Memorandum 1: Model Evaluation Metrics. March 13.

Liu, X., R.C. Sokol, O.-S. Kwon, C.M. Bethoney and G.-Y. Rhee. 1996. An investigation of factors limiting the reductive dechlorination of polychlorinated biphenyls. *Environmental Toxicology and Chemistry* 15(10): 1738-1744.

LTI Environmental Engineering. 1998. Fox River and Green Bay PCB Fate and Transport Model Evaluation Technical Memorandum 2b: Compilation of Watershed Solids and PCB Load Estimates for Green Bay. Draft. Prepared by LTI, a division of Limno-Tech, Inc. August 7.

Macdonald, C.R., R.J. Norstrom and R. Turle. 1992. Application of pattern recognition techniques to assessment of biomagnification and sources of polychlorinated multicomponent pollutants, such as PCBs, PCDDs, and PCDFs. *Chemosphere* 25(1-2): 129-134.

Mackay, D., W.Y. Shiu and K.C. Ma. 1992. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Volume I, Monoaromatic Compounds, Chlorobenzenes, and PCBs*. Lewis Publishers, Ann Arbor, Michigan.

Magelssen, G.R. and J.W. Elling. 1997. Chromatography pattern recognition of Aroclors using iterative probablistic neural networks. *Journal of Chromatography A* 775: 231-242.

Manchester, J.B. 1993. The Role of Porewater in the Remobilization of Sediment-Bound Polychlorinated Biphenyl Congeners. PhD Dissertation for the Department of Chemistry, University of Wisconsin, Madison. Ann Arbor, Michigan: UMI Dissertation Information Service. 584 pp.

Manchester-Neesvig, J.B., A. A.W. and D.N. Edgington. 1996. Patterns of mass sedimentation and of deposition of sediment contaminated by PCBs in Green Bay. *Journal of Great Lakes Research* 22(2): 444-462.

Mardia, K.V., J.T. Kent and J.M. Bibby. 1994. *Multivariate Analysis*. Academic Press, New York. 518 pp.

Marti, E.A. and D.E. Armstrong. 1990. Polychlorinated biphenyls in Lake Michigan tributaries. *Journal of Great Lakes Research* 16(3): 396-405.

Martin, S.C., S.C. Hinz, P.W. Rodgers, J. Victor J. Bierman, J.V. DePinto and T.C. Young. 1995. Calibration of a hydraulic transport model for Green Bay, Lake Michigan. *Journal of Great Lakes Research* 21(4): 599-609.

Michigan Department of Natural Resources. 1995. Fish Contaminant Monitoring Database, 1983-1995. Provided to Hagler Bailly in electronic format by Bob Day, Michigan Department of Environmental Quality.

Michigan Department of Community Health. 1997. Quality Assurance Manual: Draft. Bureau of Laboratories, Chemistry and Toxicology Division. Health Risk Assessment Section.

Miller, G.S. and J.H. Saylor. 1985. Currents and temperatures in Green Bay, Lake Michigan. *Journal of Great Lakes Research* 11(2): 97-109.

Miller, G.S. and J.H. Saylor. 1993. Low-frequency water volume transport through the midsection of Green Bay, Lake Michigan, calculated from current and temperature observations. *Journal of Great Lakes Research* 19(2): 361-367.

Modlin, R.F. and A.M. Beeton. 1970. Dispersal of Fox River water in Green Bay, Lake Michigan. *Proc. 13th Conf. Great Lakes Res.* pp. 468-476.

Mortimer, C.H. 1978. Water Movement, Mixing, and Transport in Green Bay, Lake Michigan. A review with speculations prepared for the Green Bay Workshop: University of Wisconsin Sea Grant College Program, 14-16 September.

Muir, D.C., Alex Omelchenko, Norbert P. Grift, Dan A. Savoie, P. Wilkonson and G.J. Brunskill. 1996. Spatial trends and historical deposition of polychlorinated biphenyls in Canadian midlatitude and arctic lake sediments. *Environmental Science and Technology* 30(12): 3609-3617.

NCR Corporation. 1996. NCR Corporation's Response to the Department of Interior's Information Request, Dayton, Ohio, May 5.

Rachdawong, P. and E. Christensen. 1997. Determination of PCB sources by a principal component method with nonnegative constraints. *Environmental Science and Technology* 31(9): 2686-2691.

Rhee, G.Y., R.C. Sokol, C.M. Bethoney and B. Bush. 1993. A long-term study of anaerobic dechlorination of PCB congeners by sediment microorganisms: Pathways and mass balance. *Environmental Toxicology and Chemistry* 12(10): 1829-1834.

Ripley, B.D. 1996. *Pattern Recognition and Neural Networks*. Cambridge University Press, New York. 403 pp.

Schulz, D.E., G. Petrick and J.C. Duinker. 1989. Complete characterization of polychlorinated biphenyl congeners in commercial aroclor and clophen mixtures by multidimensional gas chromatography — electron capture detection. *Environmental Science and Technology* 23(7): 852-859.

Stalling, D.L., W.J.D. III, T.R. Schwartz, J.W. Hogan, J.D. Petty, E. Johansson and S. Wold. 1995. Application of soft independent method of class analogy (SIMCA) in isomer specific analysis of polychlorinated biphenyls. *American Chemical Society Symposium Series* 284: 195-234.

Steuer, J., S. Jaeger and D. Patterson. 1995. A Deterministic PCB Transport Model for the Lower Fox River between Lake Winnebago and Depere, Wisconsin. Wisconsin Department of Natural Resources PUBL WR 389-95. 290 pp.

Stow, C.A., S.R. Carpenter, L.A. Eby, J.F. Amrhein and R.J. Hesselberg. 1995. Evidence that PCBs are approaching stable concentrations in Lake Michigan fishes. *Ecological Applications* 5(1): 248-260.

Stratus Consulting Inc. 1998. Fish Consumption Advisories in the Lower Fox River/Green Bay Assessment Area. Prepared for U.S. Fish and Wildlife Service, U.S. Department of the Interior, and U.S. Department of Justice. Final Report. November 24.

Stratus Consulting Inc. 1999a. Association Between PCBs, Liver Lesions, and Biomarker Responses in Adult Walleye *(Stizostedium vitreum vitreum)* Collected from Green Bay, Wisconsin. Prepared by Barron, M.G., M. Anderson, D. Beltman, T. Podrabsky, W. Walsh, D. Cacela, J. Lipton, S.J. The, D.E. Hinton, J.T. Zelikoff, A.L. Dikkeboom, B.A. Lasee, S.K. Woolley, D.E. Tillitt, M. Holey, P. Bouchard and N. Denslow. April 13.

Stratus Consulting Inc. 1999b. Injuries to Avian Resources, Lower Fox River/Green Bay Natural Resource Damage Assessment. Prepared for U.S. Fish and Wildlife Service, U.S. Department of the Interior, and U.S. Department of Justice. Final Report. May 7.

Swackhamer, D.L. and D.E. Armstrong. 1987. Distribution and characterization of PCBs in Lake Michigan water. *Journal of Great Lakes Research* 13(1): 24-36.

Swackhamer, D.L. and D.E. Armstrong. 1988. Horizontal and vertical distribution of PCBs in southern Lake Michigan sediments and the effect of Waukegan Harbor as a point source. *Journal of Great Lakes Research* 14(3): 277-290.

ThermoRetec Consulting Corporation and N.R.T. Inc. 1999. Draft Remedial Investigation: Lower Fox River, Wisconsin. Prepared for Wisconsin Department of Natural Resources. February.

U.S. EPA. 1977. PCBs Involvement in the Pulp & Paper Industry. February 25. #EPA/560/6-77-005.

U.S. EPA. 1993. Wildlife Exposure Factors Handbook: Volume I of II. U.S. Environmental Protection Agency Report #EPA/600/R-93/187a.

U.S. EPA. 1997. Hudson River PCBs Superfund Site Reassessment: Data Evaluation and Interpretation Report, Executive Summary. February 13.

Velleux, M. and D. Endicott. 1994. Development of a mass balance model for estimating PCB export from the Lower Fox River to Green Bay. *Journal of Great Lakes Research* 20(2): 416-434.

Wisconsin Department of Natural Resources. 1995. Fish Contaminant Monitoring Database, 1971-1995. Provided to Hagler Bailly in electronic format by J. Amrhein, WDNR.

Wisconsin Department of Natural Resources. 1997. Workplan to Evaluate the Fate and Transport Models for the Lower Fox River and Green Bay. Draft. September 19. 9 pp.

Wisconsin Department of Natural Resources. 1999a. Model Evaluation Workgroup Technical Memorandum 2e: Estimation of Lower Fox River Sediment Bed Properties. March 31.

Wisconsin Department of Natural Resources. 1999b. Technical Memorandum 2d: Compilation and Estimation of Historical Discharges of Total Suspended Solids and PCBs from Lower Fox River Point Sources. Madison, Wisconsin, February 23.

Wisconsin State Laboratory of Hygiene. 1997. Wisconsin State Laboratory of Hygiene Organic Chemistry Unit Methods Manual, Section 1410: Tissue Analysis: Pesticide and PCB Residue in Tissue. pp. 1410-1 to 1410-10.