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Sheboygan River and Harbor

Aquatic Ecological Risk Assessment

Prepared for:

United States Environmental Protection Agency

Chicago, Illinois

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AQUATIC ECOLOGICAL RISK ASSESSMENT

Volume 1 of 3

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LIST OF ACRONYMS

AVS	acid volatile sulfide
BSAF	biota sediment accumulation factor
bw	body weight
CEH	chick embryo hepatocyte bioassay
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act of 1980
cfs	cubic feet per second
CMDS	classical multidimensional scaling
COC	contaminant of concern
dw	dry weight
ERA	ecological risk assessment
EROD	7-ethoxyresorufin-Odeethylase
FDA	U.S. Food and Drug Administration
HQ	hazard quotient
IBI	Index of Biotic Integrity
LOAEL	lowest observed adverse effects level
NEC	no effects concentration
NOAEL	no observed adverse effects level
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PEL	probable effects level
PRP	potentially responsible party
QA/QC	quality assurance and quality control
RM	river mile
ROC	receptor of concern
SEM	simultaneously extracted metals
TEF	toxic equivalency factor
TEL	threshold effects level
TEQ	toxic equivalent
TOC	total organic carbon
Triad	sediment quality triad
TRV	toxicity reference value
UCL	upper confidence limit
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
WDNR	Wisconsin Department of Natural Resources
WHO	World Health Organization
ww	wet weight

1.0
INTRODUCTION

This document presents the aquatic ecological risk assessment (ERA) for the Sheboygan River and Harbor site in Sheboygan, Wisconsin, prepared for the U.S. Environmental Protection Agency (USEPA), Region V.

The Sheboygan River and Harbor Superfund site is located in east-central Wisconsin, extending approximately 14 mi (22 km) from slightly upstream of the Sheboygan Falls Dam to the river mouth and harbor at Lake Michigan. This area was designated as a Superfund site in 1986 primarily based on elevated concentrations of polychlorinated biphenyls (PCBs) detected in sediment and fish from the Sheboygan River. Three potentially responsible parties (PRPs) were identified: Tecumseh Products Company, Kohler Company, and Thomas Industries. In 1990, Diecast Corporation was identified as an additional PRP (WDNR 1995a).

ERAs are an integral part of the remedial investigation and feasibility study process designed to support risk management decisions at Superfund sites (USEPA 1997). ERAs evaluate the likelihood that adverse ecological effects are occurring or may occur as a result of exposure to one or more stressors (USEPA 1992). Adverse responses can range from sublethal responses in individual organisms to a loss of ecosystem function (USEPA 1997). This ERA is prepared in accordance with the interim final USEPA guidance document for designing and conducting ERAs at Superfund sites (USEPA 1997).

1.1 BACKGROUND

Historically, the primary contaminants of concern (COCs) in the Sheboygan River are PCBs. A primary source of this contamination to the river is the Tecumseh Products Company, a die-casting plant adjacent to the river in Sheboygan Falls (Figure 1-1). Contamination of fish by PCBs was initially identified in 1977 by the State of Wisconsin during its statewide monitoring program (WDNR 1995a). In 1978, concentrations in fish 3 mi (5 km) upstream from the harbor were found to exceed the U.S. Food and Drug Administration (FDA) action level, resulting in the issuance of food consumption advisories (Environ 1995). In 1987, a waterfowl consumption advisory was issued based on exceedances of the FDA action level (WDNR 1995a). Investigations of the river showed the highest concentrations of PCBs in sediment immediately downstream from Tecumseh. Tecumseh used hydraulic fluids containing PCBs from about 1966 to 1971, and materials containing Aroclor 1248 and 1254 were inadvertently released onto soils near the site. Tecumseh excavated 2,050 m^3 of PCB-contaminated soil in 1979 (WDNR 1995a). From 1989 to 1991, sediment from areas of the river most contaminated with PCBs was removed or armored. The first round of removal and armoring was done as part of the alternative specific remedial investigation process to pilot test remediation alternatives. The second round of removal actions was part of an emergency process to remove deposits where PCB concentrations posed risks to human health. Deposits containing elevated PCB concentrations are still present in the Sheboygan River.

Additional potential point sources of contamination to the Sheboygan River are the Kohler Company Landfill and a former coal gasification plant. The Kohler landfill was operated between 1950 and 1975 for the disposal of chrome plating sludges, enamel powder, hydraulic oils, solvents, and paint wastes. The landfill was designated as a federal Superfund site in 1984. Results of a remedial investigation of the landfill completed in 1991 showed that landfill wastes contained volatile organic compounds, polycyclic aromatic hydrocarbons (PAHs), phenolic compounds, PCBs, and trace elements including chromium, cadmium, lead, copper, antimony, and zinc (WDNR 1995a). These studies did not establish a pathway to the river from the landfill.

The former coal gasification plant, located along the east bank of the river (Figure 1-1), was operated from 1872 to 1929 by the Wisconsin Public Service Corporation (WDNR 1995a). The plant is the suspected source of PAHs detected in sediments of the Sheboygan River near the Pennsylvania Bridge and the Eighth Street Bridge (WDNR 1995b). Thomas Industries, one of the PRPs for the Sheboygan River and Harbor site, is a manufacturer of paint spraying equipment (WDNR 1995a). Information on potential contaminant sources from Thomas Industries was not available.

1.2 OBJECTIVES

In the Superfund program, ERAs provide the risk information necessary for risk managers to make informed decisions regarding substances designated as hazardous under the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA; see 40 CFR 302.4). According to the Office of Solid Waste and Emergency Response Directive 9285.7-17, ERAs are prepared 1) to identify and characterize the current and potential threats to the environment from a hazardous substance release, and 2) to identify cleanup levels that would protect natural resources from risk (USEPA 1997).

Thus, objectives of this ERA are twofold: 1) to evaluate risk posed to aquatic organisms and piscivorous birds and mammals exposed to toxic substances in the Sheboygan River and Harbor, and 2) to derive concentrations of PCBs and other COCs in sediment that would be protective of the Sheboygan River ecosystem as assessed through surrogate receptor species. In addition, this ERA includes recommendations regarding the monitoring that will be needed to establish a baseline prior to remedial action and to assess long-term remedy effectiveness (Appendix H).

The focus of this ERA is to estimate the present level of risk to the aquatic organisms and piscivorous birds and mammals of the Sheboygan River and Harbor from exposure to contaminated sediments, water, and biota. To estimate risk, tissue and sediment data from recent studies, including the 1994–1995 Sheboygan River food chain and sediment contaminant assessment conducted by the Wisconsin Department of Natural Resources (referred to herein as the WDNR food chain study, 1996a) and data collected specifically for this ERA, are evaluated in combination. In addition, other relevant data collected on Sheboygan ecological communities by WDNR in recent years are included to provide an overall context for the ERA. Thus, the recommendations made regarding protective sediment concentrations and future monitoring needs reflect what is currently known about the aquatic and piscivorous species in the Sheboygan River and Harbor aquatic ecosystem.

To address flood plain soils that have also been contaminated within the site, USEPA is conducting a terrestrial ERA using the American robin as the surrogate species. Earthworm and soil samples were collected for the robin study in November 1997. In combination, this ERA and the terrestrial assessment address contamination in environmental media of the river and harbor and in the floodplain soils. The combination is important because of the dynamic interchange between floodplain soils and the river.

1.3 DOCUMENT ORGANIZATION

This report is organized in eight sections. Section 1.0 provides an introduction to the risk assessment, background information on the site, and objectives of the ERA. Section 2.0 presents results from the problem formulation phase of the ERA, including discussions of resources at risk; selection of COCs; fate, transport and ecotoxicity of COCs; selection of receptors of concern (ROCs); profiles of ROCs; the conceptual site model; assessment and measurement endpoints; and risk hypotheses. Section 3.0 presents the evaluation of risk to benthic invertebrates using the sediment quality triad (Triad) approach. Section 4.0 evaluates concentrations of PCBs in sediment and fish tissue, examines the relationship between PCB concentrations in sediment and fish tissue, and characterizes risk to fish. Section 5.0 presents results of the food web model and evaluates risk to piscivores. Section 6.0 discusses protective sediment concentrations for ROCs. Section 7.0 discusses overall ecological significance to the Sheboygan River and Harbor. References are contained in Section 8.0.

Figures and tables are bound separately in Volume 2.

The following appendices are bound separately in Volume 3:

- *Appendix A: Analytical Data* — laboratory data from the 1997 ERA and the WDNR food chain study
- *Appendix B: Toxic Equivalent Calculations*
- *Appendix C: Laboratory Report, Freshwater Sediment Toxicity Testing Program*
- *Appendix D: Benthic Community Data*
- *Appendix E: Life History of* Limnodrilus hoffmeisteri *and* L. cervix
- *Appendix F: Parameterization of the Time-Dependent Food Web Bioaccumulation Model*
- *Appendix G: Impacts on Lake Michigan Salmonids*
- *Appendix H: Recommendations for Long-Term Monitoring*
- *Appendix I: Analytical Methods*
- *Appendix J: Taxonomic Methods*

2.0
PROBLEM FORMULATION

The problem formulation focuses the risk assessment and establishes the goals, breadth, and major issues for consideration (USEPA 1992,1997). This section presents the final problem formulation. It contains sections on resources potentially at risk; the selection of COCs and their fate, transport, and ecotoxicity; the selection of ROCs and species profiles; and a conceptual model with complete exposure pathways, assessment and measurement endpoints, the study rationale, and risk hypotheses. The study rationale section presents an overview of the toxic equivalency factor (TEF) theory and the rationale for the additional field sampling conducted in August 1997 to supplement past studies.

2.1 ENVIRONMENTAL SETTING

The Sheboygan River and Harbor site covers 14 mi (22 km) of the river from Sheboygan Falls to Lake Michigan, including Sheboygan Harbor at the river mouth. The Sheboygan River basin drains a total of about 725 km^2 and includes 2 major tributaries, the Onion and Mullet Rivers (WDNR 1995a). Land use upstream of the site is primarily agricultural and related open space. Adjacent to the site, land is used primarily for industrial, residential, and recreational purposes. The Sheboygan River within the study area can generally be characterized as a warm water stream with fairly low gradients and shallow, turbid water with naturally high concentrations of suspended solids. Visibility is generally less than 30 cm and the water color is brown.

A variety of aquatic habitats are present within the river study area. The Sheboygan River and Harbor site was divided into six river segments for the purposes of study design and data evaluation for the food chain study conducted by WDNR (1995b). These segment designations were also used for this ERA. The segment descriptions are as follows (see also Figure 1-1):

***Segment 1 ¾ Reference area, upstream of Sheboygan Falls Dam**:* Other than agricultural inputs, there are no known industrial sources of contaminants to this area. Contaminants measured in sediment from this area were expected to be representative of background levels. This segment has an average width of 22 m with typical riffle, pool, and run habitats. Pools are generally between 0.5 and 1.5 m deep; the amount of rocky substrates and fish cover are considered good for fish habitat (WDNR 1996b).

Segment 2 ¾ Estimated river mile (RM) 13.9 to 11.2, from Sheboygan Falls Dam downstream to River Bend Dam: This segment includes the Tecumseh Plant, and historically has had higher concentrations of PCBs than any other segments. Aquatic habitat in this segment is dominated by long slow runs with very few riffle areas due to the impounded nature of the segment. This river segment is generally between 20 and 30 m wide with water depths ranging from 0.6 to 1.2 m. The riparian zone in much of this segment is thick scrub brush and deciduous forest, with substantial forest canopy over the river.

Segment 3 ¾ RM 11.2 to 9.9, between River Bend Dam and Waelderhaus Dam: Sediment in this area is contaminated with lower concentrations of PCBs than in Segment 2. This area is an important depositional zone downstream from the PCB source. The aquatic habitat is similar to that of Segment 2, described above.

Segment 4 ¾ RM 9.9 to 5.0, from Waelderhaus Dam to the area where the Kohler Company settling pond discharges to the river: Concentrations of PCBs in the sediment of Segment 4 are lower than Segments 2 and 3, and similar to Segment 5 based on historical data. This segment was not sampled for the ERA because of similarities to Segment 5 with respect to sediment contamination and limited accessibility. This segment is characterized predominantly by riffles and runs with sediment deposited intermittently in a thin layer along the river banks. The width averages 30 m and water depth is generally between 15 and 60 cm.

Segment 5 ¾ RM 5.0 to 1.6, from the Kohler Company settling pond discharge to the 14th St. Bridge: This segment includes the Kohler Company historic discharge mixing zone and the Kohler Landfill Superfund site. Contamination by metals is generally higher from RM 0 to 3 than in upstream portions of the river. River Segment 5 is a long, free flowing segment, 20 to 30 m wide in the upper section between RM 5 and Esslingen Park and 30 to 60 m wide in the lower section between Esslingen and Kiwanis Parks. The upper section is dominated by riffle, pool, and run habitats generally less than 1.5 m deep. Runs are dominated by rubble and gravel substrates considered to provide good to excellent fish habitat and cover. The lower section of Segment 5 flattens, widens, and deepens as the river approaches Lake Michigan; very few riffle areas are present in this area.

Segment 6 ¾ RM 1.6 to 0, from the 14th St. bridge to Sheboygan Harbor in Lake Michigan: This segment includes the former coal gasification plant site at approximately RM 1.1. Concentrations of PCBs in sediment are lower than in upstream segments, and PAH contamination is high adjacent to the former coal gasification site. Contamination by metals is generally higher from RM 0 to 3 than in upstream portions of the river. The segment is generally between 50 and 80 m wide and 2 and 7 m deep. Flows are slow and much of the shoreline is developed with light industry, marinas, and residential areas. This area is a substantial depositional zone due to the slow moving water.

2.2 RESOURCES POTENTIALLY AT RISK

Potential ecological receptor species considered for this ERA are benthic invertebrates, fish, and birds and mammals that depend on aquatic resources of the Sheboygan River. This section provides a general description of benthic invertebrates, fish, birds, and mammals that reside in or around the Sheboygan River.

2.2.1 Benthic Species

The benthic and epibenthic community in riffles of the study area are dominated by several families within Ephemeroptera (mayflies), Trichoptera (caddis flies), Coleoptera (aquatic beetles), Diptera (midges), and Pelecypoda (freshwater clams). The soft depositional zones are dominated by oligochaete worms. An important epibenthic crustacean found in the study area is the species of crayfish *Orconectes virilis* (WDNR 1990, 1993).

The oligochaetes represent the group most likely to be potential receptors due to their ubiquitous distribution and numerical dominance within the benthic community, ingestion of nine times their body weight of sediment per day (Slepukhina 1984), and multi-year life spans. They are also an important group trophically, serving as an important food source for numerous fish in the river.

Oligochaetes are common in mud and debris substrate in streams and lakes. The most abundant populations are found in organically enriched environments, although they occupy a wide niche (Pennak 1978). Many oligochaete species are pollution tolerant (Pennak 1978; Lauritsen et al. 1985). Regionally, oligochaete dominated communities have been documented at the south end of Green Bay, Wisconsin, near the mouth of the Fox River (Howmiller and Scott 1977), and throughout the organically enriched areas of Lake Michigan (Lauritsen et al. 1985).

2.2.2 Fish

Fisheries surveys have identified year-round populations of warm-water resident fish species and seasonal populations of cold-water anadromous fish species in the Sheboygan River that are potential receptors of contamination (WDNR 1996b). The three dams in the study area do not have fish passage facilities and therefore restrict the movement of fish between stream segments. However, resident species can be swept from upstream segments to downstream segments during periods of high flows or flooding. Therefore, many of the resident fish are found in all segments of the river while anadromous fish are restricted to Segments 4, 5, and 6 below the Waelderhaus Dam (Nelson pers. comm. 1997).

WDNR conducted a fish community survey of the Sheboygan River in 1994 that evaluated fish and habitat indices in Segments 1 and 5 in the study area and five other segments upstream of the study area (WDNR 1996b). Fish habitat was evaluated using the Fish Habitat Rating - Rivers system (Simonson et al. 1994), and the fish community was evaluated using the Index of Biotic Integrity (IBI; Lyons 1992). The evaluation methods consider the physical attributes of the river and composition of the fish community; they do not consider chemical contamination. The survey concluded that the quality of fish habitat was good to excellent and the IBI rating was good in both segments.

2.2.2.1 Resident Fish

The major resident fish species observed in the study area during a fish community survey conducted in 1994 are presented in Table 2-1 (WDNR 1996b). This survey sampled River Segments 1 and 5 in the study area.

Two of the most common groups of resident fish in the Sheboygan River study area are the centrarchids (sunfish and bass) and cypriniformes (carps, minnows, and suckers). The most common centrarchids were smallmouth bass and rock bass; these species have been observed in all segments sampled in the study area. Other centrarchids observed, though not as commonly, included several sunfish such as bluegill, pumpkinseed, and black crappie (WDNR 1996b). The centrarchids are nearshore spring spawners that are often associated with aquatic vegetation, structure, or pools downstream of riffles. Young-of-the-year appear in late spring to summer and all life stages are present within the river. Young-of-the-year and young juveniles are expected to have the least amount of movement within the river during normal flows, but this has not been studied or confirmed. There is also evidence to suggest that the younger life stages are more likely to be swept substantial distances downstream during flood events (Nelson pers. comm. 1997). The smaller centrarchids such as black crappie and rock bass are opportunistic benthic and pelagic feeders, feeding on a variety of benthic organisms, aquatic insects, crustaceans, and small fish. The smallmouth bass is a piscivorous predator that primarily feeds on larger fish or macroinvertebrates such as crayfish (Scott and Crossman 1973).

Several large species of cypriniformes including common carp, white sucker, and redhorse were numerically very common and abundant in total biomass in both segments sampled in the study area in 1994 (WDNR 1996b). Carp were found in a variety of habitats including deeper riffles, runs, and pools with or without structure. White sucker and redhorse were most often observed in deeper pools just below riffles not associated with vegetation or structure. All of these species are spring spawners and all life stages can be expected in the study area. Carp, sucker, and redhorse are primarily large benthic feeding fish that live and feed in direct contact with the sediments (Scott and Crossman 1973).

Several small minnows were numerically dominant in the fish survey conducted in 1994 and included common shiner, sand shiner, and horneyhead chub (WDNR 1996b). During the WDNR food chain study longnose dace were also observed. These species can be expected in most segments of the river. They prefer riffle environments and feed primarily on small benthic and epibenthic invertebrates (Scott and Crossman 1973).

Other larger piscivores such as walleye, northern pike, and channel catfish were not commonly observed in the river. Walleye and channel catfish, both of which are common lake residents, may be more common in segments below the Waelderhaus Dam, while northern pike have been observed in several segments upstream of the study area in quiet, shallow water with aquatic vegetation. All of these species are spring spawners and all life stages are likely to be found in the river, although walleye and catfish may be transient as adults. Walleye and northern pike are upper-trophic level predators that feed primarily on fish. Channel catfish are opportunistic benthic feeders, although larger adults can be piscivorous (Scott and Crossman 1973). Lake trout, a lake-dwelling salmonid, was documented in Segment 6 in 1976 and 1984 (WDNR 1997) but this species is not expected to reside in the lower river for extensive periods because of its preference for deep lake environments.

2.2.2.2 Anadromous Fish

Two groups of anadromous fish are present in the Sheboygan River––Pacific salmonids which include coho salmon, chinook salmon, and steelhead trout; and the clupeids (herring), which include alewife and gizzard shad.

The Pacific salmonids are not indigenous to the Great Lakes and are maintained by a stocking program administered by WDNR. Juveniles are released into the lower river below Waelderhaus Dam where they rear until they reach smolt size, then they migrate to the open waters of Lake Michigan where they spend their adult life. After 2 to 5 years in the lake, the salmonids return to the lower river during spawning runs. However, suitable spawning habitat is not present in the lower river, thus successful spawning does not occur. In the spring, three strains of steelhead trout are planted in the lower river ––late summer, early winter, and spring varieties; the seasonal designation indicates the time at which the spawning run occurs in the river. Chinook and coho salmon return to the lower river during the fall months. This management program would indicate that either planted juveniles or adults on spawning runs are present in the lower river year-round

(Eggold pers. comm. 1997). Juvenile salmonids are opportunistic, feeding on benthic invertebrates and insects. Adults in the lake are top predators in the aquatic food web, feeding primarily on alewife and other forage fish. Adults do not feed during their spawning runs in the river (Scott and Crossman 1973).

In 1987, WDNR discontinued its stocking program because of sediment contamination by PCBs. In 1990, the agency initiated a salmonid PCB accumulation study to assess the viability of reintroducing a salmonid stocking program. Juvenile steelhead trout and coho salmon were released in the river below the Waelderhaus Dam and were sampled at intervals and analyzed for PCBs. PCB tissue analyses were also conducted on the returning coho salmon and steelhead trout. The results indicated that higher concentrations of PCBs accumulated in juveniles released in the lower river in the fall than in reference areas; these fish resided in the river through the winter and outmigrated during the spring. PCBs did not accumulate in juvenile fish that were stocked in the spring and that quickly outmigrated. Total PCB concentrations in skin-on fillets of sub-adult and adult coho salmon and steelhead trout in the Sheboygan River did not differ significantly from concentrations in sub-adult and adults returning to a reference river (Eggold et al. 1996). Because of these results, the salmonid stocking program (spring release) in the Sheboygan River was reintroduced in 1994 (Eggold pers. comm. 1997).

2.2.3 Birds

A list of bird species associated with aquatic habitats of the river is presented in Table 2-2. Most of the migratory waterfowl species listed in Table 2-2 are found primarily in the harbor area (e.g., Northern pintail, Northern shoveler, lesser scaup). The harbor area also supports bird species associated with open areas, such as gulls, terns, cormorants, and, more rarely, ospreys (Patnode pers. comm. 1998a). Other waterfowl species are year-round residents, such as mergansers, mallards, black ducks, and Canada geese, and can be found throughout the study area. The most common bird species associated with upriver habitats are swallows and wood ducks. Both kingfishers and great blue herons can be found throughout the study area, but they are not as abundant as most of the species listed above because of their larger home range requirements. The only known colony of black-crowned night herons in the Sheboygan River basin is found in the study area near New Jersey Avenue (Patnode pers. comm. 1998a). The only threatened or endangered terrestrial species known to inhabit the Sheboygan River and Harbor area is the American peregrine falcon (Katsma pers. comm. 1997). An active peregrine falcon nest exists near the Edgewater Power Plant at the mouth of the river. There are no officially recognized critical wildlife refuges within the Sheboygan River area (Patnode pers. comm. 1997).

In 1979 and 1985, WDNR collected several species of birds within the riparian zone of the Sheboygan River adjacent to the study area and analyzed tissues for PCBs (Katsma pers. comm. 1997). Concentrations ranged from 100 to 200 mg/kg in tissues collected from herons, kingfishers, and sandpipers.

WDNR has collected tree swallows for the past three years, analyzing tissues for PCBs. Tree swallows feed heavily on aquatic insects emerging from the river. In the study area, tree swallows were found to accumulate as much as 2 to 3 mg/kg of PCBs in 10 days by feeding on emergent insects. PCB concentrations between 3 and 10 mg/kg were observed in eggs. In 1995, impaired hatching and induction of liver enzymes in 12 day old nestlings were documented. Growth and juvenile development were generally normal if clutches got past the hatching stage. Tree swallows are now being banded to document movement of adults. Data indicate that if one or two nests fail, the birds will move upriver to another site (Patnode pers. comm. 1997).

2.2.4 Mammals

A list of mammal species associated with aquatic habitats of the river is presented in Table 2-2. Muskrat and raccoon are the most common mammalian species associated with aquatic habitats. Beaver and mink are very rare below the Waelderhaus Dam (Patnode pers. comm. 1998a). According to WDNR (1995a) mink populations are well below what would normally be expected for the available habitat, and in fact no mink were captured during a trapping study conducted along the river. It is likely that mink observed in the study area either originally escaped from fur farms, or have emigrated into the area from noncontaminated areas. Wildlife experts at WDNR believe that sufficient habitat exists to support a moderate wild mink population (Patnode pers. comm. 1997). Threatened or endangered mammal species are not expected to be found within the study area (WDNR 1995a). Historical data for concentrations of PCBs measured in wildlife from the Sheboygan River area are presented in Table 2-3.

2.2.5 Reptiles

In 1996, WDNR began a snapping turtle study, examining PCB concentrations in eggs and performing enzyme and histopathology studies. PCB concentrations in eggs collected from the lower Sheboygan River have ranged from 8 to 28 mg/kg compared to less than 0.1 mg/kg in eggs collected from the upper basin. Hatching success at the male-determining temperature was reduced in clutches with total PCB concentrations higher than 15 mg/kg. Gross deformities have been observed in 2 turtles, but were not correlated with PCB concentrations. Liver enzyme activity in 8-month-old, PCB-contaminated hatchlings is significantly suppressed. Two clutches collected above Sheboygan Falls have been contaminated. To better understand and monitor movement of the adult females, eight have been radio-equipped. Approximately 180 hatchlings have been tagged with microchips and returned to the site of female capture and egg collection.

Recapture and sampling of these individuals is planned to monitor survival, growth, and PCB bioaccumulation (Patnode pers. comm. 1998b).

2.3 CONTAMINANT OF CONCERN SELECTION

This section describes the process of selecting COCs for benthic invertebrates, fish, birds, and mammals. Separate approaches were used for each group of organisms; specific methods and results for each group are described in this section. The initial list of contaminants considered for the ERA included PCBs, PAHs, metals, pesticides, and dioxins and furans.

2.3.1 Pesticides, Dioxins, and Furans Analysis

Data collected on pesticides, dioxins, and furans for the 1997 ERA were used for selecting COCs because limited data were available from previous studies. Pesticides were not detected in sediment in 1987 (BBL 1990) and were only detected at very low concentrations (5.8 *m*g/kg dieldrin and 7.3 *m*g/kg DDE) in one of the 18 sediment samples collected and analyzed for this ERA in 1997 (Appendix A-1, Table A1-2). The quality assurance and quality control (QA/QC) review of the data indicated that the identification of pesticides in this sample may have been due to coelution with specific PCB congeners eluting at the same retention time (Appendix A-2). Because of their tenuous identification, and because pesticides were very rarely identified in sediment, the decision was made to eliminate them as COCs and to focus efforts for the ERA on contaminants expected to pose the greatest risk.

Dioxins and furans were also eliminated during the COC screening process. During historical sampling, two sediment samples were collected and analyzed for dioxins and furans in 1987. In one of those sediment samples, only 2,3,7,8-TCDD was analyzed, but was not detected at a detection limit of 120 *m*g/kg wet weight (ww) (BBL 1990). In the other sediment sample, collected from 6 to 8 ft deep in the harbor, tetra- through octa-chlorinated dioxin congeners were not detected at a detection limit of 250 *m*g/kg ww (BBL 1990). Although sediment benchmarks are not available for the protection of benthic invertebrates, these detection limits are orders of magnitude higher than proposed sediment benchmark concentrations of 0.06 *m*g/kg dry weight (dw) and 0.10 *m*g/kg dw associated with low and high risk to fish, respectively (USEPA 1993a). Thus, the potential for impacts on benthic invertebrates from dioxins and furans could not be eliminated from consideration based on historical data. Thus, a phased sampling approach was conducted as part of the August 1997 ERA sampling effort to explore the concentrations of dioxins and furans in a cost-effective manner.

Three composite smallmouth bass samples collected from Segment 2 were analyzed for dioxin/furan congeners as part of this ERA to determine if dioxins and furans should be retained as COCs and analyzed in all fish and sediment samples. These samples were chosen because the highest concentrations of PCBs in fish and sediment have been reported in Segment 2, and dioxins and furans have been reported as contaminants in some PCB mixtures (DeVault et al. 1989; Eitzer 1993; Hebert et al. 1994).

The fish tissue results were calculated using the toxic equivalent (TEQ) approach. A TEQ is developed for each sample as the sum of the dioxin-like toxicity of the PCB congeners and dioxin/furan congeners to yield a single concentration equivalent to the toxicity of a similar concentration of 2,3,7,8-TCDD (Equation 2-1).

$$TEQ = SUM(TEFi[Congener]i) \qquad \textbf{Eq. 2-1}$$

Where TEQ is the weighted sum of dioxin-like toxicity, TEFi is the toxic equivalency factor (TEF) for Congener i, and [Congener]i is the wet weight concentration of a dioxin-like congener measured in tissue and sediment.

The TEQ approach is based on results of numerous studies of laboratory animals and cell culture bioassays which demonstrate that some of the most toxic planar halogenated hydrocarbons cause similar adverse effects but have different potencies. In this approach, a comparison of the toxicities of key planar halogenated hydrocarbons with the toxicity of 2,3,7,8-TCDD is used to develop a TEF. A number of sets of TEFs are available; those selected for this ERA are presented in Tables 2-4 and 2-5. The rationale for TEF selection is described below.

For fish, studies on early-life-stage rainbow trout mortality have been conducted to determine TEFs for dioxin-like PCB congeners by injecting graded doses of the congeners into newly fertilized eggs (Walker and Peterson 1991; Zabel et al. 1995a). In these studies, TEFs were calculated as 2,3,7,8-TCDD LD50/congener LD50. These TEFs were used in this ERA because they were derived for rainbow trout based on *in vivo* measurement of a population-relevant toxicity endpoint — larval survival following egg exposure. For congeners not included in these two studies, TEFs from the World Health Organization (WHO 1997) were used. The WHO compilation represents the work of an international program designed to develop internationally-agreed-upon TEFs.

For mammals and birds, TEF schemes were applied to concentrations of PCB congeners in their diets. No TEF system is available specifically for mink (Leonards et al. 1995). From the studies conducted to determine which TEF system is the best predictor of toxicity in mink, it was concluded that none of the available systems stands out above another. The various TEF systems including the system developed by Safe (1993), the

International TEFs (Ahlborg et al. 1994), and the H4IIE bioassay system all provide similar results (Leonards et al. 1995; Tillitt et al. 1996).

While all the TEF systems for mammals provide similar results when evaluating reproductive effects in mink, the International TEFs were used in this assessment. The International TEFs were selected because 1) they were developed using a consensus approach and a broad data base of results from 1,146 studies, 2) the tests from which the TEFs were developed underwent rigorous scrutiny and evaluation, and 3) the TEFs were designed for use in risk assessments with endpoints that are ecologically relevant such as embryo mortality in *in vivo* studies (Ahlborg et al. 1994; Tillitt pers. comm. 1997). This last point is significant because mink are highly sensitive to adverse reproductive effects when exposed to elevated PCB concentrations (Eisler and Belisle 1996; Wren 1991).

It should be noted, however, that there is a poor correlation between species sensitivity to reproductive toxicity and endpoints which have been documented as mediated by aryl hydrocarbon (Ah) receptors, such as P450IA1 induction (Moore and Peterson 1996). For example, at a given dose, rodents (which are commonly used in testing) experience a higher induction of 7-ethoxyresorufin-Odeethylase (EROD) activity than mink but undergo less severe reproductive impacts than mink. Therefore, TEFs derived using the traditional “animal models” (i.e., rats and mice) are likely to underestimate toxicity in mink.

A set of TEFs has been developed specifically for birds. Researchers have shown that results of the H4IIE bioassay correlate well with hatching success of double-crested cormorants (Tillitt et al. 1992) and other piscivorous birds (Giesy et al. 1994b). However, another bioassay has recently been developed to measure EROD activity in chick embryos which have been shown to be highly sensitive to dioxins and related compounds (Brunström 1990). The chick embryo hepatocyte (CEH) bioassay was developed to derive the 2,3,7,8-TCDD equivalent concentrations in eggs of wild herring gulls and great blue herons (Kennedy et al. 1996). This study demonstrated that the responses of two biological endpoints, EROD induction and porphyrin accumulation, were highly correlated with the 2,3,7,8-TCDD equivalent concentrations calculated using the TEFs derived from the CEH bioassay.

The TEFs identified in Kennedy et al. (1996) were used in this ERA to quantify exposure and characterize risk to great blue herons because 1) the bioassay was developed to evaluate the relative potency of 2,3,7,8-TCDD equivalent contaminants for birds, and 2) the TEFs developed from the CEH bioassay and used to evaluate adverse effects in the great blue heron were highly correlated with the measured biological effects.

Using the method described above, the dioxin/furan TEQ concentrations based on fish TEFs in the 1997 ERA ranged from 0.94 to 1.3 ng/kg ww and the total TEQ concentrations ranged from 11 to 21 ng/kg ww (Table 2-6). These concentrations are lower than 50 ng/kg ww, a screening concentration for fish tissue proposed by USEPA to represent low risk to fish (USEPA 1993a). The contribution of the dioxin/furan TEQ concentration to the total TEQ concentration ranged from 6.3 to 8.5% in the three fish samples (Table 2-6). Because of their relatively low contribution to the total TEQ concentration, dioxins and furans were not carried through the risk assessment as COCs for fish. Since additional fish and sediment were not analyzed for dioxins and furans, potential risks to benthic invertebrates from these compounds were not evaluated further. Because of the low concentrations found in fish, the likelihood of risks to benthic invertebrates was not sufficient to warrant the high cost of dioxin and furan analysis in additional sediment samples.

Dioxins and furans were not considered COCs for birds and mammals because of the relatively low contribution of dioxins and furans to the total TEQ concentration based on either bird or mammal TEFs. As shown in Tables 2-7 and 2-8, dioxins and furans contributed less than 1% to the total TEQ concentrations for birds and mammals, and therefore would not contribute significantly to the total risk.

2.3.2 Screening of Contaminants of Concern for Benthic Invertebrates

Historical sediment data used for the benthic invertebrate screening are presented in Table 2-9. Although removal actions have been conducted in some areas of the river, it was not clear from the documents available which samples were collected from areas that had been remediated. Therefore all data were included for screening. This approach is also protective in case remedies did not remove contaminants.

Contaminants considered potential COCs included metals, PCBs, and PAHs. A contaminant was considered a COC if its maximum on-site concentration detected in the sediments of the Sheboygan River exceeded the sediment benchmark concentration. Threshold effects level (TEL) values from USEPA (1996a) were used as sediment benchmarks to evaluate direct sediment exposure to benthic organisms (Table 2-10). These TELs were derived from freshwater exposures of *Hyalella azteca* using 28-day survival, growth, and reproductive endpoints. TELs were calculated as the geometric mean of the lower 15th percentile concentrations of the effects data and the 50th percentile concentration of no-effects data. The TEL values were selected as protective COC screening criteria because they are considered to represent sediment concentrations rarely associated with adverse effects to benthic organisms.

All potential COCs had maximum concentrations that exceeded their respective benchmarks and therefore were retained as COCs for benthic organisms. The metals included as COCs were arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc. Concentrations of PCBs and PAHs in the sediments exceeding the screening criteria were widespread and of high magnitude. Metal concentrations exceeded the benchmarks at fewer locations and at lower magnitude.

2.3.3 Screening of Contaminants of Concern for Fish

Metals, PCBs, and PAHs were also potential COCs for fish. COCs were retained if the 95% upper confidence limit (UCL) concentrations of contaminants in fish from site-related areas exceeded mean concentrations in fish from reference areas by more than 1.5 times. Data used for screening fish for PCBs were PCB congener data for smallmouth bass collected for this ERA in 1997. For metals, data used were those collected by WDNR in 1994 for white sucker in a reference area and in Segment 6 (Schrank et al. 1997), because this was the most complete data set available for metals in fish.

The 95% UCL concentrations for PCBs in fish from Segments 2, 3, and 5 were substantially higher than mean concentrations from the reference area, so PCBs were retained as COCs (Table 2-11). The only metals detected in fish from the reference area or Segment 6 were copper, mercury, and zinc. The 95% UCL concentrations of metals detected in fish from the site area did not exceed the respective mean concentrations in reference area fish enough to warrant inclusion of any metals as COCs for fish.

PAHs were not analyzed in fish collected for the WDNR food chain study in 1994 or for this ERA. PAHs are expected to be extensively metabolized by fish (Eisler 1987a). However, a recent study reported higher concentrations of PAH biliary metabolites in white suckers collected from the lower Sheboygan River compared to white suckers collected from an upstream reference location (Schrank et al. 1997). The white suckers collected from the lower river also showed biochemical indicators of exposure to PAHs. Therefore, PAHs were retained as COCs for fish.

2.3.4 Screening of Contaminants of Concern for Birds and Mammals

For mammals and birds, potential COCs were mercury, PCBs , and PAHs, per discussions with USEPA and WDNR. PCBs were automatically included as COCs because of the elevated fish tissue and sediment concentrations at the study site. Mercury and PAHs were evaluated using a two-phased screening approach to determine if they should be retained.

The first screening phase was conducted to compare site-specific sediment and tissue concentrations with reference area concentrations. If the COC was not eliminated based on the background screen, it was carried through to the next screening phase. The second phase, a risk-based approach, was conducted using the approach presented in Sample et al. (1996), which involves calculating dietary benchmarks for potential COC and receptor species combinations. If the site-specific tissue concentration exceeded the dietary benchmark, the contaminant was considered a COC and carried through the ERA.

Mercury and PAH sediment and tissue data from WDNR's food chain study, including data on emergent and larval invertebrates and crayfish, and sediment and fish data from the 1997 ERA were used in the screening process. In addition, mercury data for white suckers collected from a reference area and from Segment 6 were used (WDNR 1997; Schrank et al. 1997).

2.3.4.1 Phase I Screening: Background Comparison

Initially, the site-specific 95% UCL concentration of mercury and PAHs in the sediments were compared to the concentrations from the reference area as shown in Table 2-12. It was not possible to calculate the 95% UCL for PAHs for river Segments 2 and 3 for data collected in 1997 because only one sample was collected in each of these segments. In this case, the measured concentrations of PAHs, as shown in Table 2-12, were used for comparison to the reference area.

Results of the sediment screening approach indicated that both mercury and PAHs should be evaluated by screening the site-specific tissue concentrations against reference area concentrations. The 95% UCL concentration of mercury in the sediments measured in Segment 2 exceeded the mean reference area concentration measured both in the WDNR food chain study and in the 1997 ERA (Table 2-12). Additionally, the 95% UCL concentrations of PAHs exceeded the mean reference area concentrations in most river segments.

The tissue screening assessment was conducted in the same manner as the sediment screening. For each river segment represented, the site-specific 95% UCL concentrations of mercury and PAHs in tissues were compared to the mean concentrations in the reference area.

Based on the results of the tissue screening (Table 2-13), mercury was eliminated from further analysis. The site-specific tissue concentrations in larval insects and fish exceeded the reference area concentrations by a maximum of 1.4 times, which was not considered high enough to warrant Phase II screening. However, individual PAH concentrations in invertebrate tissue from the site exceeded the reference area concentrations by as much as 9 times, as shown in Table 2-14, so PAHs were retained for comparison to benchmarks.

2.3.4.2 Phase II Screening: Dietary Benchmark Comparison

In Phase II of the screening process a dietary benchmark was calculated for PAHs for mammals. Water data were not evaluated in the assessment because data were not available. This screening process follows the general method used in the Sample et al. (1996) benchmark screening assessment approach. The dietary benchmark is a PAH concentration in the piscivore diet that is equivalent to a no observed adverse effects level (NOAEL) as shown in Table 2-15. Initially a food factor was calculated using food ingestion and body weight parameters (Table 2-15). Food ingestion rates were calculated by developing a site-specific diet using literature and site-specific information, and incorporating the energetic requirements of the piscivores in relation to the energy content of their prey (USEPA 1993b; Tables 2-16 and 2-17). A PAH dietary benchmark was calculated specifically for mink, the mammalian species selected as an ROC for this ERA (Section 2.5).

Before the PAH dietary benchmark was developed, the literature was searched for dietary toxicity test-based NOAELs for mink. A NOAEL equivalent concentration for the piscivore diet was then derived for PAHs (Table 2-18). This assessment, while highly conservative, is appropriate for selecting COCs for a receptor species and was developed based on the following assumptions:

- ROCs reside at, and therefore forage exclusively from, the contaminated site
- 100% of the food ROCs consume is contaminated
- 100% of the COC is bioavailable
- ROCs consume 100% of each tissue type, thereby consuming only the most contaminated tissue

NOAELs were not available for every PAH for mink. The only PAH dietary study available for mammals (mice) was conducted with benzo(a)pyrene. Since NOAELs were not available for all PAHs for mammals, the NOAEL for benzo(a)pyrene was used to calculate the mink dietary benchmark to which all PAH tissue concentrations would be compared (Table 2-18).

To screen for mink, the maximum site-specific PAH tissue concentrations in prey were compared to the mammal dietary benchmark. Because this benchmark screening approach is highly conservative, the maximum value was used rather than the 95% UCL tissue concentration. As a result of this screening, PAHs were not included as COCs for mink because the maximum tissue concentrations in prey items (Table 2-14) were less than the mammalian dietary benchmark (Table 2-15).

It was not possible to calculate a dietary benchmark for the great blue heron since an acceptable dietary toxicity test using PAHs was not available for birds. Since it was not possible to screen PAHs for the great blue heron using the benchmark screening approach, they were screened in a qualitative manner. The ranges of PAH concentrations measured in emergent and larval invertebrates collected from the Sheboygan River during the food chain study were 0.0011 to 0.044 mg/kg ww and 0.0071 to 0.038 mg/kg ww, respectively. (PAHs were undetected in crayfish at a detection limit of 0.007 mg/kg ww and were not measured in fish.) These concentrations are at least 3 orders of magnitude lower than the concentrations reported to cause hepatic effects in mallards (Patton and Dieter 1980), although the mixture fed to mallards in the Patton and Dieter (1980) study contained only 3 of the PAHs measured in tissues collected from the Sheboygan River. Furthermore, since consumption of aquatic insects alone will not likely result in adverse effects in great blue heron because aquatic insects do not constitute a significant portion of the prey items in the great blue heron diet, PAHs were eliminated as COCs for birds.

As a result of the phased COC screening, PCBs were the only COCs that were evaluated in the ERA for birds and mammals.

2.3.5 Summary of Contaminants of Concern Selected for the ERA

Table 2-19 summarizes the COCs evaluated in this ERA for each receptor group. PCBs are considered COCs for benthic invertebrates, fish, birds, and mammals. Effects of PAHs will be evaluated for benthic invertebrates and fish. Metals are considered COCs for benthic invertebrates only.

2.4 CONTAMINANT FATE, TRANSPORT, AND ECOTOXICITY

This section contains transport and fate information for selected COCs. Section 2.4.2 presents ecotoxicity information for COC and ROC combinations identified in Table 2-19.

2.4.1 Contaminant Fate and Transport

The ultimate fate and transport of contaminants in the Sheboygan River system will depend on a wide range of characteristics of the river system and on the physical and chemical properties of the individual contaminants. In the following discussion, a brief overview of potentially important physical characteristics of the Sheboygan River is presented followed by a more detailed discussion of the fate and transport of the classes of contaminants that have been selected as COCs—PCBs, PAHs, and metals.

2.4.1.1 Characteristics of the Sheboygan River

Water Flow ¾ Dissolved contaminant concentrations and compounds associated with dissolved organic matter in the water column will be transported rapidly throughout the system as a result of the river flow.

The Sheboygan River has a mean annual discharge of approximately 7.3 m^3/sec (258 cubic feet per second [cfs]) based on data collected from 1942 to 1986. Recorded flows at the U.S. Geological Survey (USGS) gauging station have ranged from a minimum of 0.028 m^3/sec (1 cfs) in August 1922 to a maximum flow of 217 m^3/sec (7,680 cfs) in March 1975 (David 1990).

The Sheboygan River is subject to seasonal flooding with peak flows typically occurring in March and April. Figures 2-1a through 2-1h show annual hydrographs of the river measured at Sheboygan from 1989 through 1997. Unusually high flows of 3,000 to 4,000 cfs were recorded in April 1993 and June 1996 and 1997.

Transport of contaminants associated with dissolved organic carbon can also be important. Relatively high dissolved organic carbon concentrations were measured in the Sheboygan River between April 1994 and October 1995 (average dissolved organic carbon = 8.0 mg/L). The presence of dissolved organic carbon has been shown to increase the mobility of organic contaminants such as PCBs (Brownawell and Farrington 1986) and decrease the bioavailability of these contaminants (McCarthy et al. 1985).

Sediment Transport ¾ In addition to water flow, sediment particles are resuspended and transported downstream. The suspended particulate loading also follows a seasonal pattern with the highest concentrations of suspended material measured during the spring floods in March and April when increased flow rates result in sediment resuspension.

The Sheboygan River is characterized by alternating riffle areas and deposits of fine sediments along the shorelines with coarser sediments midstream. Some deposits are quite large, in particular above the River Bend and Waelderhaus Dams, near Kiwanis Park, and near the Eighth Street Island in Sheboygan. During large storms and flood events, these deposits may be resuspended and redistributed within the river or transported into the harbor. The Sheboygan River deposits approximately 23,000 m^3 of sediment a year into the harbor (David 1990).

Atmospheric Transport ¾ The atmosphere can function either as a source or a sink for contamination in a river system. The relative concentrations of volatile compounds (e.g., mono- and dichlorobiphenyls) in the water column and the atmosphere will determine the importance of atmospheric deposition as a potential source of contamination relative to losses of volatile compounds due to evaporation.

In the following sections, the relative importance of specific transport and exposure pathways will be discussed for each group of compounds.

2.4.1.2 Polychlorinated Biphenyls

PCBs are a class of 209 different compounds referred to as congeners. PCB congeners are chlorinated biphenyls with one to ten chlorines attached to a biphenyl nucleus. The chemical and physical properties of the individual congeners are largely determined by the number of chlorines and the positions of the substituted chlorines. As the degree of chlorine substitution increases, the aqueous solubility and vapor pressure of the specific congeners decrease.

The fate and transport of PCBs in environmental systems is controlled by distribution or partitioning of PCBs between sediment, suspended particulates, surface water, and biota. The observed partitioning of nonionic organic chemicals, such as PCBs, is due to sorption to organic phases, including porewater dissolved organic carbon and sedimentary organic matter. The extent to which congeners are associated with organic matter relative to their dissolved aqueous concentrations is related to their levels of chlorination. The more chlorinated congeners have stronger tendencies to be associated with particulate and dissolved organic matter than the less chlorinated congeners.

PCBs were marketed as Aroclors, complex mixtures of individual PCB congeners. Aroclors are named according to their average chlorine content. For example, Aroclor 1248 contains 48% chlorine by weight and Aroclor 1254 contains 54% chlorine by weight. The different chlorine concentrations of each Aroclor are reflected in its congener composition. For example, Aroclor 1221 contains a larger proportion of less chlorinated, di- and trichlorobiphenyls relative to Aroclor 1254 which contains a higher proportion of the more chlorinated, penta- and hexachlorobiphenyls.

From 1959 to 1971 PCB-containing hydraulic fluids were used at the Tecumseh Products site by either Die Cast Corporation or Tecumseh Products. From 1959 through 1969, these fluids contained Aroclor 1248 and from 1970 to 1971 a fluid was used which contained a mixture of Aroclor 1254 and 1248. Among other operational activities, Tecumseh Products constructed a dike sloping 45 degrees into the river using contaminated soil from the Tecumseh plant. These activities introduced PCBs into the river system and the PCBs have been redistributed throughout the river by natural processes.

Bioaccumulation of PCB congeners occurs as a result of the partitioning of the congeners between an organic phase (the organism's lipid content) and aqueous solution. Therefore, bioaccumulation is highly dependent on the organism's lipid content and trophic level, and on the hydrophobicity of the PCB congener. Octanol-water partition coefficients for PCBs range from log K_{ow} 4.09 to 8.18 (Hawker and Connell 1988). Connell (1991) has shown that bioaccumulation can be predicted from octanol-water partition coefficients when the K_{ow} lies between 2 and 6. Chemicals with log K_{ow}<2 usually bioaccumulate more than would be expected from their K_{ow} values; chemicals with log K_{ow} >6 tend to bioaccumulate less than expected (Connell 1991).

Biomagnification occurs when the concentration of a chemical increases in increasing trophic levels. Thomann (1989) extensively evaluated the relationship between the K_{ow} of a chemical and its potential for biomagnification. Thomann concluded that biomagnification through the food chain is unlikely to occur for chemicals with log K_{ow} < 5, but is likely for chemicals with log K_{ow} between 5 and 6.5. Biomagnification remains important for chemicals with log K_{ow} values up to 8, although other factors, such as top predator growth rates and bioconcentration by phytoplankton, take on greater significance (Thomann 1989). If metabolization occurs, then these correlations are not applicable.

Although PCBs are generally persistent, they can be degraded *in situ* to a limited extent by resident microorganisms. Evidence for anaerobic reductive dechlorination of PCBs, similar to that reported by others (Brown et al. 1987a,b; Quensen et al. 1988; Rhee et al. 1993), has been reported for the Sheboygan River (David 1990; Sonzogni 1990; Sonzogni et al. 1991). Dechlorination reactions appear to be occurring only in sediments with total PCB concentrations greater than 50 mg/kg (David et al. 1994).

2.4.1.3 Polycyclic Aromatic Hydrocarbons

PAHs are a class of nonpolar organic contaminants characterized by their highly aromatic, fused ring structures. Environmental sources of PAHs include petroleum products and combustion residue (i.e. soot particles). Because of their low aqueous solubilities (0.0003 to 34 mg/L) and high octanol-water partition coefficients (log K_{ow} = 3.4–7.6), PAH compounds in aquatic systems tend to be associated with sediments and biota.

In the Sheboygan River, the fate and transport of PAHs will be largely controlled by sediment organic carbon content and dissolved organic carbon concentrations in the water column and sediment porewater. The extent to which an individual PAH compound will tend to be associated with either sediment or dissolved organic carbon depends on the relative hydrophobicity of the compound which can be predicted from its molecular weight.

Lower molecular weight PAHs — three aromatic rings or less — are more water soluble and more easily degraded. Higher molecular weight compounds will tend to predominate in sediments where they are subjected to burial, resuspension, and degradation reactions. The available literature suggests that higher molecular weight PAHs are degraded by microbes slower than lower molecular weight PAHs. Half lives for these compounds range from months to years. Furthermore, biodegradation probably occurs more slowly in aquatic systems than in soil (Clement 1985).

Uptake of PAH compounds by aquatic biota is rapid. However, PAH compounds are also quickly metabolized and eliminated from most fish. Invertebrates, especially mollusks, do not metabolize PAHs as efficiently and may accumulate high tissue concentrations (Eisler 1987a; Varanasi et al. 1989). Bioconcentration factors for those species that do not metabolize PAHs tend to increase as the molecular weights and the octanol-water partition coefficients of the PAHs increase.

2.4.1.4 Metals

Key factors that affect the partitioning and speciation, and thus the bioavailability, of sediment metals include Eh (redox conditions), pH, porewater hardness, and the organic carbon content of the sediment. The redox conditions, pH, and the porewater concentration of dissolved organic carbon influence the oxidation state and the dissolved speciation of the metal. Metals exhibit a range of binding affinities with both organic and inorganic phases present in the sediment resulting in varying concentrations of dissolved versus particulate metals. In addition, metals exhibit a range of stability constants with dissolved ligands which determines the ratio of complexed to freely dissolved species in solution.

Total sediment metals concentrations are generally not predictive of the bioavailability of these trace elements. Concentrations of certain metals in porewaters have been correlated with biological effects (Di Toro et al. 1990). For several divalent metals, a key partitioning phase controlling cationic metal activity and toxicity in sediments appears to be acid volatile sulfide (AVS; DiToro et al. 1990, 1992; Carlson et al. 1991; Allen et al. 1993; Ankley et al. 1993). Simultaneously extracted metals (SEM) and AVS measurements can be made to assess the potential bioavailability of SEM metals — cadmium, copper, lead, nickel, and zinc.

The model states that if the AVS concentration is greater than the SEM concentration, toxicity will not be observed (DiToro et al. 1990). In other words, if the SEM/AVS ratio is less than 1 or SEM minus AVS is less than 0, then sufficient AVS exists to bind all SEM and adverse effects in benthic invertebrates are not expected. In contrast, if the SEM/AVS ratio is greater than 1 or SEM minus AVS is greater than 0, sufficient AVS is not available to bind all the SEM; therefore, benthic organisms may be exposed to toxic concentrations of metals.

The bioavailability of metals that form stable complexes with organic compounds is particularly complex. For example, methylmercury compounds are extremely toxic and are efficiently bioaccumulated through aquatic food chains (Wiener and Spry 1996). Methylmercury is formed in aquatic sediments due to microbial methylation of inorganic mercury.

2.4.2 Ecotoxicity of Contaminants of Concern

This section discusses ecotoxicity of the COCs selected for each potential ecological receptor group. Relevant toxicological endpoints of PCBs are presented for benthic invertebrates, fish, birds, and mammals. For PAHs, endpoints are discussed for benthic invertebrates and fish. Relevant toxicological endpoints of metals are presented for benthic invertebrates.

2.4.2.1 Polychlorinated Biphenyls

Benthic Invertebrates¾ PCBs have a wide variety of effects on aquatic organisms. There are significant interspecies differences in sensitivities to PCBs, even among species that are closely related taxonomically (Eisler 1986a). Most studies of the effects of PCBs on benthic invertebrates have shown effects on mortality, growth, and reproductive impairment.

Fish¾ Effects of PCBs on fish include mortality, growth-related effects, behavior responses, biochemical alterations, and adverse reproductive effects. Of particular concern are the effects of dioxin-like PCB congeners, which have the same toxic mechanism as 2,3,7,8-TCDD (Walker and Peterson 1991; Zabel et al. 1995a). 2,3,7,8-TCDD and these dioxin-like PCB congeners cause early life stage mortality associated with blue-sac disease, which involves subcutaneous yolk sac edema (Wisk and Cooper 1990; Walker et al. 1991).

In addition, numerous field studies have reported increased mortality, pathologic anomalies, and biochemical changes in feral fish collected from ecosystems where PCBs have been reported and correlated with PCB tissue burdens (Niimi 1996). These observations include reduced hatchability and poor survival of larvae taken from feral organisms and reared in the laboratory (Mac and Schwartz 1992; Ankley et al. 1991). This impact is clearly important from an ecological perspective. Other impacts, such as behavioral responses and biochemical alterations, are more difficult to interpret, although some biochemical alterations may adversely affect reproduction (Sivarajah et al. 1978; Chen et al. 1986; Thomas 1988).

Birds¾ A substantial amount of research demonstrates that adverse reproductive effects occur in piscivorous bird populations exposed to PCBs and dioxins in the Great Lakes Region (Jones et al. 1993, 1994; Tillitt et al. 1992; Giesy et al. 1994a,b). The bulk of the research has focused on double-crested cormorants because deformities were first discovered in this species. Some work has recently been done to evaluate reproductive effects of PCBs in the great blue heron (Sanderson et al. 1994, 1997). Piscivorous birds display a number of symptoms similar to those observed in other avian species exposed to planar halogenated hydrocarbons in the laboratory including altered biochemical homeostasis, physical deformities, fetotoxicity, and teratogenesis. In addition to embryo mortality, PCBs cause edema and beak malformations often recognized as crossed beaks in double-crested cormorants (Firestone 1973; Schrankel et al. 1982; Brunström and Darnerud 1983: all as cited in Brunström 1990).

Mammals¾ Wildlife, especially mink, are particularly susceptible to adverse effects from exposure to specific PCB congeners, including the non-ortho and mono-ortho substituted PCBs, because their mechanism of action is similar to 2,3,7,8-TCDD (Leonards et al. 1995). Residues from PCBs can cause mortality or serious reproductive complications in mammals. Other clinical signs of PCB toxicity include anorexia, liver and kidney degeneration, and gastric ulcers, which have been observed in mink fed PCB-contaminated coho salmon (Wren 1991).

2.4.2.2 Polycyclic Aromatic Hydrocarbons

PAHs vary substantially in their toxicity to aquatic organisms. Lower molecular weight PAHs (2- and 3-ring compounds) such as naphthalene, fluorene, phenanthrene, and anthracene are acutely toxic to aquatic organisms. Acute toxicity increases with increasing alkyl substitution on the lower molecular weight compounds (Van Luik 1984). Many of the higher molecular weight compounds with 4–7 aromatic rings, such as chrysene and benzo(a)pyrene, are less toxic but demonstrably carcinogenic, mutagenic, or teratogenic to a wide variety of organisms including fish, amphibians, birds, and mammals (Moore and Ramamoorthy 1984; Eisler 1987a). Among aquatic organisms, acute toxicity is most pronounced among crustaceans and least among teleosts (Eisler 1987a).

Benthic Invertebrates ¾ Effects of PAHs observed in benthic invertebrates include inhibited reproduction, delayed emergence, sediment avoidance, and mortality (Eisler 1987a; Landrum et al. 1991). In a study of PAH toxicity to the amphipod *Diporeia*, the mechanism identified as most likely responsible for observed acute toxic responses to PAHs was narcosis (Landrum et al. 1991). Generally, aquatic invertebrates are less able to metabolize PAHs than aquatic vertebrates, although metabolization rates vary widely within and between phyla (Meador et al. 1995).

Fish ¾ PAHs are generally hydrophobic compounds and must be metabolized to more water-soluble forms before they are excreted. In most fish, PAHs are rapidly taken up, metabolized, and excreted so that concentrations found in edible tissues are generally low. The major route of elimination is through excretion into bile. The biotransformation and excretion rates can vary widely among fish species (Meador et al. 1995). Fish exposed to PAHs may be induced to produce higher levels of enzymes capable of transforming PAHs to more excretable but occasionally more carcinogenic metabolites (O'Connor and Huggett 1988).

Because fish rapidly metabolize and excrete PAHs, fish tissue residue concentrations of parent PAH compounds do not provide a useful measure of exposure to fish (Varanasi et al. 1989). Determining concentrations of PAHs in sediment is a useful measure of exposure because PAH-contaminated sediment has been linked to adverse effects in fish, including reproductive impairment, immune dysfunction, increased incidence of liver lesions, and other histopathological endpoints (Malins et al. 1987; Johnson et al. 1988; Varanasi et al. 1992). Fin erosion and liver abnormalities have also been observed in fish exposed to extracts from PAH-contaminated sediments (Fabacher et al. 1991). Other studies report sublethal effects on the cellular immune system (reduced macrophage activities) in fish exposed to PAH-contaminated sediments that could result in increased susceptibility to disease (Weeks and Warinner 1984,1986; Weeks et al. 1986). The most common diseases generally affect the liver, although cataracts and pollution-related disorders of the skin and gills may also occur (O'Connor and Huggett 1988).

2.4.2.3 Metals

Benthic Invertebrates¾ Toxicity of metals to benthic organisms ranges widely from slight reduction in growth rates to mortality. Mollusks are generally less sensitive than other aquatic phyla (Leland and Kuwabara 1985). The most sensitive life stages of benthic organisms are generally the embryonic and larval stages. In freshwater, increasing water hardness decreases the toxicity of cadmium, chromium, copper, lead, nickel, silver, and zinc. The form of metal also effects toxicity; for example, methylmercury is more toxic than inorganic mercury. The combination of metals in the environment may result in additive, synergistic, or antagonistic effects, with the overall effect depending on the toxicity of the metals in question, the specific physical and chemical conditions of the site, and internal synergistic or antagonistic effects within organisms. Table 2-20 presents the general ecotoxicological effects of specific metals on benthic organisms.

2.5 RECEPTOR OF CONCERN SELECTION

The following eight criteria were considered in the selection of ROCs (not in order of importance):

- Trophic level
- Feeding regime — bottom feeder vs. pelagic vs. piscivore
- Sensitivity to COCs
- Site use
- Availability of site data
- Human or ecological importance
- Availability and appropriateness of toxicological data

Based on the above criteria, six ROCs were selected — benthic invertebrates, smallmouth bass, white sucker, longnose dace, great blue heron, and mink. The following paragraphs provide rationale for the selection of these receptors.

Benthic invertebrate species were selected primarily because of their ecological importance and their sensitivity to COCs. Diverse and abundant benthic communities are necessary to maintain healthy aquatic populations farther up the food chain. Benthic species are sensitive to a wide array of contaminants. Particularly sensitive genera within the benthic community, such as amphipods, are among the first species to disappear in polluted areas (Lamberson et al. 1992). Toxicological data for many benthic invertebrate species are widely available. Many contaminants in sediment of the Sheboygan River have been shown to exceed benthic TELs in past studies (Table 2-10).

Three species of fish were selected as ROCs from different trophic levels and representing different feeding preferences. The smallmouth bass is representative of an upper-trophic-level, pelagic fish that is common at the site and is of human importance because of recreational fisheries. White sucker represents a bottom feeder, and longnose dace is an insectivore. A primary consideration in selecting these three specific species was the availability of data from the WDNR food chain study.

Salmonids were also considered as potential ROCs because 1) steelhead trout, chinook salmon, and coho fry are stocked in the lower river, 2) all are sensitive to the COCs, and 3) some historical data exist. However, they were not included because of 1) their low site usage — they leave the river soon after spring stocking in April and 2) the results of the 1987–1990 study in which juvenile and adult salmonids were analyzed and it was found that contaminant concentrations were not significantly higher than those found basinwide (Eggold pers. comm. 1997). These findings resulted in the removal of the anadromous fisheries ban. Instead of including salmonids as potential ROCs, it was decided to qualitatively discuss potential impacts to salmonids using historical data that are readily available (Appendix G) and to consider this information in the evaluation of ecological significance (Section 7.1).

While the Sheboygan River habitats support a variety of wildlife species, this ERA focuses on piscivorous species. Great blue heron were chosen by USEPA to represent piscivorous avian species primarily because they have been sighted feeding within the study area. This species is susceptible to bioaccumulation of contaminants because it is at the top of the food chain, consuming fish and other aquatic organisms. A substantial amount of information is available showing that adverse reproductive effects and deformities occur in piscivorous bird species from exposure to PCBs and dioxins in the Great Lakes Region (Jones et al. 1993, 1994; Tillitt et al. 1992; Giesy et al. 1994a,b).

Mink were chosen by USEPA based on the observation that habitat types within the Sheboygan River watershed would be expected to support mink, but populations are well below what would normally be expected for the available habitat (WDNR 1995a). Mink are carnivorous, semi-aquatic animals on the top of the food chain, and thus may be expected to accumulate contaminants from ingestion of contaminated prey species. Mink are known to be extremely sensitive to PCBs and a decline of their populations in the United States and other regions of the world has been directly attributed to halogenated hydrocarbons (Giesy et al. 1994c; Osowski et al. 1995). Toxicological data are readily available for mink.

2.6 RECEPTOR OF CONCERN PROFILES

***Benthic Invertebrates*¾** Benthic communities present within the Sheboygan River provide considerable biomass to support ecological food webs and are important processors of organic matter and sediments. The benthic and epibenthic communities are largely immobile and reside in direct contact with the sediments and porewaters. Oligochaetes feed off detritus, while a small proportion of other benthic invertebrates are grazers, scraping algae off rocks.

***Smallmouth Bass* (Micropterus dolomieu)¾** Smallmouth bass are an abundant species in Segments 1, 2, 3, and 5 of the Sheboygan River and are commonly used as a monitoring species for PCB accumulation in the watershed. As reported in Section 2.2.1.2, smallmouth bass are upper trophic level predators that feed on larger fish or invertebrates such as crayfish. One study in Iowa found that the diet of the adult smallmouth bass included 20% insects, 30.5% crayfish, and 39% fish. The fish included several species of minnows, sunfish, darters, madtom catfish, and lampreys (Wydoski and Whitney 1979).

Several studies indicate that adult smallmouth bass tend to establish home ranges that they occupy on a seasonal basis (Ridgway and Shuter 1996; Todd and Rabeni 1989; Gerber and Haynes 1988) to year-round (Munther 1970). Home ranges for smallmouth bass populations in the Sheboygan River have not been investigated; however, a tagging study to track the movement of adult smallmouth bass was attempted. After a two month period, tagged fish could no longer be recovered in the location of capture suggesting that most of the fish had left the area (Nelson pers. comm. 1997). Definite patterns of diel activity have been documented in another watershed and were found to be affected by seasonal changes in water temperature. Fish remained in restricted home ranges for most of the year but tended to disperse in the spring. Seventy-five percent of these fish returned to their home ranges during the same year. Fish movements tended to be greater when temperatures were highest, averaging 120 m/day at 4ºC and 980 m/day at 27.5ºC (Todd and Rabeni 1989). Smallmouth bass prefer water temperatures between 21 and 27ºC (Wydoski and Whitney 1979). In two tributary streams of Lake Ontario, smallmouth bass tended to establish home ranges, where they resided throughout the summer, downstream from spring spawning areas (Gerber and Haynes 1988). This study also displaced fish from their home ranges and found that 26% of the fish returned to original home ranges. In the Snake River in Washington, 76% of tagged adults remained in the same area where they were originally tagged. Most of the rest of the fish moved less than 1,200 m from the tagging area (Munther 1970).

Movement of fish during different flow regimes has been examined to a limited extent. Todd and Rebeni (1989) found that during flood events in the Jacks Fork River, the movements of adult smallmouth bass did not differ from those observed during normal discharges. Simonson and Swenson (1990) studied critical stream velocities for young-of-year smallmouth bass. The study found that young recently risen from nest gravel (7–9 mm) were displaced from field nest sites and from laboratory flumes at stream velocities as low as 8 mm/sec. Nests in areas of higher stream velocities (15 mm/sec) failed to produce young. For larger young fish (16–71 mm), flows between 80 and 130 mm/sec did not result in downstream displacement.

These studies indicate that adult smallmouth bass in the Sheboygan River may establish a home range from the spring through the summer months, but may also range widely, particularly if water temperatures exceed about 27ºC. Although it appears that homing behavior appears to be common in the species, the incidence of straying or establishing new home ranges has ranged from about 25% in studies where fish were tagged on home ranges to over 70% in studies where fish were displaced.

It is also expected that juvenile or young-of-year smallmouth bass have smaller residential areas and may be quite restricted in their movements during normal flow conditions. However, there is also evidence that during very high flow or flood events, the smaller fish may be more easily displaced well downstream, including transport over dams (Lyons pers. comm. 1997a; Nelson pers. comm. 1997).

***White Sucker* (Catostomus commersoni)¾** White sucker are an abundant species in Segments 1, 2, 3, and 5 of the Sheboygan River, and have been used as a monitoring species for PCB accumulation. Ecological health effects in the watershed have also been evaluated using this species. In the study area, the species was most often associated with deeper pools downstream of riffles. Adult white sucker are a benthic dwelling, benthic feeding species that generally lives and feeds in direct contact with the sediments (Scott and Crossman 1973). The small downward pointing mouth and large protruding lips make the species uniquely adapted to "vacuum" feed on the river bottom, ingesting amphipods, larval aquatic insects, clams, snails, and plant material. One study found the percentage composition of the gut content of individual specimens to include 5–90% Chironomidae, 2–70% Trichoptera, 5–98% Entomostraca, and 5–85% Mollusca (Scott and Crossman 1973). Detritus can also be a component of the diet, but the quantity in white sucker foreguts was inversely related to benthic microcrustacean densities. The species can apparently separate detritus from invertebrates, suggesting that detritus is not ingested incidentally, but intentionally when preferred invertebrate prey are scarce (Ahlgren 1990).

Home ranges of white sucker have not been well studied; no such investigations have been conducted in the Sheboygan River (Nelson pers. comm. 1997). In some watersheds, the species has displayed distinct spawning migrations from lake to tributaries in the spring. In others, there do not appear to be large movements. The species can spawn in both streams and lakes (Scott and Crossman 1973). Based on their widespread occurrence in several segments of the Sheboygan River, it would be expected that white sucker between or above the dams would spawn, rear, and spend their lives within a segment. However, it is not known whether specimens below the Waelderhaus Dam are long-term residents.

***Longnose Dace* (Rhinichthys cataractae)¾** Longnose dace are a common species in Segments 1, 2, and 5 of the Sheboygan River (WDNR 1996a). The species is a riffle dweller preferring shallow, swift sections of streams. The species shape and small gas bladder are adapted to living among the stones on the bottom of swift streams. The diet of the longnose dace consists primarily of aquatic insect larvae and some algae. Conceivably, the algae are taken incidentally with the insects. Blackfly larvae that live in the swift sections of streams make up a large part of the longnose dace diet in some waters. Other insects include mayflies, stoneflies, and midges (Wydoski and Whitney 1979). The small size of the species, less than 4 in., would suggest a fairly small home range, but this has not been confirmed. The species has been documented to spend much of the spring and summer in riffles, but in some rivers they disappear from these shallow areas during the fall and winter, possibly moving to nearby, deeper pools when temperatures are cold.

The limited data would suggest that longnose dace in the Sheboygan River would occupy riffles from the spring to the fall and possibly move to pools during the winter as a refuge from cold temperatures. There is no evidence to indicate that the species has large seasonal movements. Populations in Segment 2, which is between dams and has only one substantial riffle, may be quite restricted in their movements.

***Great Blue Heron* (Ardea herodias) ¾** The great blue heron is a semi-aquatic wading bird whose distribution ranges from the coasts of southeast Alaska and northern British Columbia, through Canada and the U.S., and south to Belize and Guatemala. Spring migrants return to Illinois, Wisconsin, and central Minnesota in early February and continue moving into the U.S. and Canada through May. The great blue heron favors natural wetlands and riverbanks, but will nest on ocean shores, in brackish marshes and lagoons, and on lakes. These birds nest mostly in colonies of several hundred pairs and prefer islands or wooded swamps where they are isolated from predators, though they will also nest in hearty grasses or shrubs near water (Butler 1992).

Great blue herons feed by wading slowly in waters along shorelines to catch fish (Butler 1992). Other methods of feeding include probing — quickly moving the tip of the bill in and out of the water and substrate, pecking — picking items up from the substrate, plunging, hovering, standing, and even hopping to startle hard-to-find prey into moving. They hunt by sight both night and day and will often stand and wait for prey to approach them. Herons often feed in groups unless resources are limited (Kulshan 1978).

Because great blue heron are primarily fish eaters, their abundance in a particular habitat is positively influenced by the presence of small fish in shallow areas. The species of fish a heron chooses as prey depends on the size of the fish and the habitat in which the heron is foraging. A study of a population of herons in Wisconsin found that herons mostly select fish under 25 cm in length as prey (Kirkpatrick 1940). However, the size of fish caught by the herons has been shown to vary with habitat. Herons foraging in streams and rivers tend to catch a larger size range of fish, 8–23 cm and 8–33 cm, respectively, while heron foraging in lakes tend to capture fish from 20 to 28 cm in length (Alexander 1977).

Amphibians, invertebrates, reptiles, small mammals, and other birds may also be present in the diet of the great blue heron, especially in winter when the herons may move upland and forage in wet meadows and pastures (Butler 1992; Kulshan 1978). Small mammals, such as rodents, can play a large role in the diet of the great blue heron in early spring when the heron has just returned for the breeding season. This may be partially a result of still-frozen lakes and rivers (Collazo 1985).

***Mink* (Mustela vison) ¾** Mink are widespread through most of North America. This nocturnal, semi-aquatic, predatory mammal is associated with stream banks and riverbanks, lake shores, freshwater and saltwater marshes, and marine shore habitats. The amount of available wetland habitat determines mink distribution. Wetlands with irregular, diverse shorelines and dense vegetation provide the most suitable mink habitats (Allen 1986). Den availability may limit the number of mink a wetland area can support. Mink dens are found in cavities or rock piles above the water line, and in cavities of tree roots at the water's edge (Gerell 1967).

The home ranges of mink follow the shape of the water body on which they live. The size of the home range is directly affected by the amount and density of vegetative cover, so when vegetation is sparse, the home range is greatly expanded (Allen 1986). Females tend to use a more restricted area than males, whose foraging areas may overlap except during the breeding season from late February to early April (Linscombe et al. 1982). The home range may also be adapted depending on prey availability.

A great deal of work has been done to characterize and quantify the mink diet during different seasons and for mink from various locations. It is apparent that the importance of the prey items depends on the location and the season in which the dietary data were collected (Linscomb et al. 1982). Fish are an important part of the mink diet and are consumed in substantial quantities most of the year, though mink have a hard time catching fish in summer when waters are warmer (Erlinge 1969). Erlinge (1969) found that fish comprised between 70 and 80% of the mink's diet in a Swedish river in autumn, winter, and spring. However, during summer, fish made up only one-third of the food consumed. Frogs and crayfish are also consumed in large quantities by mink, particularly during warmer months when fish consumption decreases. Drought conditions aid in the availability of crayfish, while dry stream beds make it more difficult for mink to find frogs (Gerrell 1967; Korschgen 1958). Birds are also frequently preyed upon during the summer months (Gerrell 1967; Erlinge 1969). Mink will consume blackbirds, songbirds, and particularly waterfowl, including brooding females, ducklings, and eggs (Sargeant et al. 1973). Mink also consume small mammals during times when fish are most difficult to capture (Burgess and Bider 1980; Cowan and Reilly 1973).

2.7 CONCEPTUAL MODEL

The conceptual model describes how biota are exposed to site-related contaminants. The ultimate goal of the model is to clearly show complete exposure pathways and define assessment and measurement endpoints consistent with the transport, fate, and toxicological characteristics of the COCs. Figure 2-2 presents an overview of the conceptual model and this section describes its components.

2.7.1 Complete Exposure Pathways

In this section, potential exposure pathways are evaluated to determine which pathways are complete and important at the site. An exposure pathway is complete if a contaminant can travel from the source to ecological receptors and can be taken up by the receptors via one or more exposure routes (USEPA 1997). Often many pathways are complete, but are of varying importance. It is therefore important to identify the key pathways that reflect maximum exposures within the ecosystem and constitute exposure pathways to ecological receptors sensitive to the contaminant (USEPA 1997). As described in Section 2.3, pathways of PCBs, PAHs, and metal to benthic invertebrates are relevant at this site. For fish, pathways of PCBs and PAHs are of key concern, and for piscivore species, pathways of PCBs are important.

For benthic invertebrates, direct contact with water or sediment by the gills or integument are the primary exposure pathways (USEPA 1997). For lower trophic-level fish, diet and direct contact with water or sediment by the gills are the primary exposure pathways (USEPA 1997). For higher trophic-level fish, diet can be an important exposure pathway for COCs that are bioaccumulated or biomagnify, such as certain PCB congeners. The aquatic food web for the Sheboygan River is presented in Figure 2-3, which shows the number of levels through which bioaccumulation, and possibly biomagnification, may occur. Uptake of PCBs from diet is the most important pathway for consumers higher in aquatic food chains (Thomann 1981; Oliver and Niimi 1988), although uptake from direct contact with sediment can also occur (Thomann et al. 1992). Also, direct bioconcentration from PCBs in water may be significant.

The primary exposure pathway for mammalian and avian species is through consumption of prey that have bioaccumulated site-related PCBs (Figure 2-3). Incidental sediment ingestion during feeding may also be an important exposure pathway for mink. Fish, emergent macroinvertebrates, and crustaceans serve as exposure points via trophic transfer of contaminants to receptor species. For instance, mink consume up to 68% of their total diet as fish, aquatic invertebrates, and crustaceans during spring, summer, and early fall. Their diet shifts with the changing season to more terrestrial prey such as small mammals and birds. Inhalation and dermal absorption pathways were not considered significant for mink and great blue heron.

2.7.2 Assessment and Measurement Endpoints

As defined in USEPA (1992), assessment endpoints are explicit expressions of the actual environmental values that are to be protected, such as ecological resources. These resources include those necessary for ecosystem function, those providing critical habitat and fisheries, and those perceived as valuable by humans, such as endangered species (USEPA 1997). Assessment endpoints are generally tied to the response of ecological receptor species to environmental stresses. Unless an ecological ROC is listed as a protected or endangered species, assessment endpoints are selected that are relevant to population-level rather than individual effects.

Because many organisms die before they reach reproductive potential or maximum growth, risk assessment is designed to evaluate population-level effects (Barnthouse 1993). Many adverse effects have been observed in piscivorous birds from the Great Lakes including biochemical homeostasis, gross anatomical deformities, and reproductive effects of fetotoxicity and teratogenesis (Tillitt et al. 1992). According to Giesy et al. (1994b), adverse effects which can be most directly linked to population-level effects in birds are embryo lethality and developmental deformities. PCBs have long been linked to reproductive failure in mink. Reproductive failure and reduced kit survival are associated with low levels (1 mg/kg) of various PCBs in mink diets (Wren 1991). Therefore, reproductive endpoints are considered to be protective of the long-term survival of piscivores and were selected for this risk assessment. Assessment endpoints for the Sheboygan River and Harbor site include:

- Maintenance of a healthy benthic community with respect to diversity and abundance in the Sheboygan River and Harbor to serve as a sufficient food supply for aquatic, mammalian, and avian species

- Protection of fish species from reproductive impairment and other adverse effects

- Protection of piscivorous mammals from adverse reproductive effects

- Protection of piscivorous birds from adverse reproductive effects

Measurement endpoints are measurable biological responses to a stressor that can be related to the valued characteristics chosen as the assessment endpoints (Suter et al. 1993; USEPA 1992; although this definition may change—see USEPA 1996b; USEPA 1997). Measurement endpoints can be directly investigated in field studies, and can include both measures of effect and measures of exposure. Data from measurement endpoint investigations are used to characterize risk.

The measurement endpoints and risk characterization approaches include:

- A Triad approach will be used to assess the health of the benthic community in comparison to reference stations and control sediments.

- PCB concentrations in fish tissue samples from this ERA and the WDNR food chain study will be compared to literature toxicity thresholds for tissue residue PCB concentrations associated with adverse reproductive effects in fish.

- To evaluate exposure of fish to PAHs, data from Schrank et al. (1997) will be reviewed and site-sediment concentrations of PAHs will be compared to sediment concentrations associated with adverse effects in fish (WDNR 1992a).

- A food web model will be used to estimate the dietary dose to piscivorous mammals and birds from the concentrations of PCB congeners in prey items. These estimates will be compared to literature toxicity thresholds for PCBs. Data from the WDNR food chain study, including fish, crayfish, and invertebrate tissue concentrations, will also be used.

Measurement and assessment endpoints are presented along with the risk characterization approaches in Figure 2-4.

2.7.3 Study Design Rationale

This section describes the study design rationale for the 1997 ERA sampling event and describes how these additional data complement the historical data collected by WDNR to provide a thorough risk evaluation.

2.7.3.1 Benthic Species

The Triad uses a weight of evidence approach to assess the health of the benthic community. The Triad consists of three synoptic measures—bulk sediment chemistry, sediment laboratory bioassays, and benthic community structure analyses. Historical synoptic Triad data were not available, so it was determined that a new sediment data set would need to be collected as part of this ERA for a complete Triad analysis. Data from previous sampling events (BBL 1990, 1995; WDNR 1996a) were used to screen for COCs and to choose sampling locations for the Triad.

Sampling locations were chosen to represent a range of concentrations for each of the COCs — PCBs, PAHs, and metals. PCBs were given the lowest priority in choosing sampling locations for benthic invertebrates because higher trophic-level species are typically more sensitive to PCBs and risk to those species was therefore considered more likely to control remedial decisions. PAHs were considered more likely to cause impacts to the benthos than metals because PAH concentrations exceeded screening guidelines to a greater degree (Table 2-10). The choice of sampling locations is discussed in detail in Section 3.1, which describes the approach for the benthic invertebrate assessment.

2.7.3.2 Fish

To evaluate reproductive impairment and other adverse effects in fish from PCBs, a congener analysis was conducted to provide information needed for the TEQ approach described in Section 2.3.1. Synoptic sediment data were also collected to relate PCBs in sediment to risks for fish.

WDNR conducted a food chain study in 1994 and 1995 which provided useful data for this risk assessment approach. In their study, WDNR collected smallmouth bass (adults and young-of-year), white sucker (adults and young-of-year), and longnose dace from a reference area (Segment 1) and Segments 2, 3, and 5 of the Sheboygan River. They also collected sediment samples from these locations. Fish were collected in October 1994 and sediment samples were collected in February 1995 and both were analyzed for PCB congeners.

Additional fish and sediment sample collection for this ERA was designed to build on the WDNR food chain study and to 1) provide lower detection limits (0.1 to 1 ng/kg ww) for PCB congener analysis to allow more accurate TEQ calculations, 2) make synoptic collections of fish and sediment, 3) collect dioxin and furan data for COC screening in a subset of fish samples, and 4) relate current conditions to the WDNR food chain study data. For the 1997 ERA, juvenile smallmouth bass were collected from the same river segments as in the WDNR food chain study.

The risk assessment for fish presented in this document integrates PCB congener data collected in 1997 with the WDNR food chain study data, and estimates risk based on total PCBs and TEQ approaches.

Other than the collection of sediment data for PAH analysis, no additional data were collected to evaluate risks to fish from PAHs, although risks may be present. Instead, an indirect approach was selected which focuses on a review of an existing study of white suckers (Schrank et al. 1997) and a sediment benchmark analysis proposed by WDNR (1992a).

2.7.3.3 Piscivores

Risk to piscivorous species was evaluated by estimating a dietary dose to mink and great blue heron from concentrations of contaminants in prey and sediment. Total PCBs and TEQs calculated from congener data were used. During the study design process, it was determined that data collected from the WDNR food chain study and proposed data collected for the 1997 ERA would be used for the piscivore risk assessment. In addition to fish and sediment, the WDNR food chain study collected and analyzed crayfish and aquatic invertebrates for PCB congeners; these data were also used for the 1997 piscivore ERA.

2.7.4 Risk Hypotheses

A set of risk hypotheses was generated to direct data evaluation and analysis for the ERA. Using what is known about the modes of action and toxicities of the COCs to the selected ROCs, the following hypotheses were developed:

- The sediment in Segments 2 through 6 of the Sheboygan River site contains elevated concentrations of COCs that are toxic to benthic invertebrate species.

- The sediment, biota, and water in Segments 2 through 6 of the Sheboygan River site contain elevated concentrations of PCBs that are causing reproductive impairment in fish.

- The sediment in Segments 2 through 6 of the Sheboygan River site contains elevated concentrations of PAHs that are causing adverse effects in fish.

- The sediment in Segments 2 through 6 of the Sheboygan River site contains elevated concentrations of PCBs which are known to biomagnify in aquatic food chains. Consequently, exposure of piscivorous birds (represented by the great blue heron) to PCBs through food web exposure pathways has resulted in adverse reproductive effects.

- The sediment in Segments 2 through 6 of the Sheboygan River site contains elevated concentrations of PCBs which are known to biomagnify in aquatic food chains. Consequently, exposure of piscivorous mammals (represented by mink) to PCBs through food web exposure pathways has resulted in adverse reproductive effects.

These hypotheses can be tested by:

- Evaluating results of the Triad analysis for signs of significant adverse effects and positive correlative relationships among chemical concentration, sediment toxicity, and adversely altered benthic community structure.

- Comparing the concentrations of PCBs measured in fish to NOAEL concentrations reported in the literature and to concentrations associated with adverse effects on fish reproduction or other ecologically relevant adverse effects.

- Comparing concentrations of PAHs in the sediments to PAH concentrations reported in the literature to be associated with adverse effects in fish.

- Conducting wildlife exposure food web modeling to predict doses of PCBs to great blue heron and comparing these doses to NOAEL and lowest observed adverse effects level (LOAEL) doses reported in the literature.

- Conducting wildlife exposure food web modeling to predict doses of PCBs to mink and comparing these doses to NOAEL and LOAEL doses reported in the literature.

3.0
BENTHIC INVERTEBRATES EVALUATION

This section evaluates risk to the benthic invertebrates using the Triad approach. The Triad, sampling strategy, and methods are described, followed by an evaluation of the exposure of benthic invertebrates to COCs. Exposure is estimated by sediment chemistry analysis of depositional areas. Sediment benchmark concentrations from the literature representing effects on benthic invertebrates are presented. Measured effects on benthic invertebrates are evaluated based on the results of toxicity tests and the benthic community analysis. The results from the sediment chemistry, toxicity tests, and benthic community analysis are then integrated into a Triad evaluation to characterize risk to benthic invertebrates.

3.1 APPROACH

The Triad is described in this section, followed by the sampling strategy.

3.1.1 Sediment Quality Triad

The Triad, originally developed by Long and Chapman (1985), is an integrated, effects-based approach to characterizing sediment quality.

As applied in this study, the Triad integrates the synoptic measures of sediment chemistry, sediment toxicity, and the in-field measure of benthic community structure into a holistic evaluation of benthic community health. All three measures are considered useful since the composition of the benthic community can be altered by the presence of chemical contamination and by a number of natural conditions such as habitat, current velocity, light penetration, temperature, and substrate type, as well as by non-chemical anthropogenic impacts such as dredging.

Sediment exhibiting elevated chemical concentrations is an indication that an area has been affected by anthropogenic activities. Toxicity in a laboratory toxicity test is an indication that under controlled conditions, the concentration and form of the contaminants can disrupt biological systems. Synoptically measured alterations in the benthic community structure are an indication that the contaminants are causing effects under field conditions. Sediments that demonstrate a high degree of concordance among all three measures are considered to have degraded sediment quality because of chemical contamination, which poses a risk to the benthic community. This may also adversely impact higher trophic-level species that rely on the maintenance of an abundant and diverse benthic community for food. Lower concordance among all three measures indicates a lower probability of adverse effects due to COCs.

3.1.2 Sampling Strategy

The selection of 18 Triad stations in the Sheboygan River was guided by historical data (Table 2-9). Depositional areas with elevated PAH concentrations were emphasized, followed by areas with elevated PCBs or metals. This section provides additional details regarding specific sampling location rationales.

Stations T07 and T08 (Figure 3-1) were selected for examination of PCB effects. These stations were selected as depositional areas likely to have high PCB concentrations (Aartila pers. comm. 1997). Metals and PAHs are likely to be low at these stations based on their overall distribution in this segment of the river.

For determining the effects of metals, Stations R-73 and R-79 from the previous BBL (1990) study were selected and designated as Stations T09 and T10, respectively, for this study (Figure 3-1). These stations were chosen based on elevated concentrations of metals and expected low concentrations of PAHs. PCB concentrations at these stations were previously somewhat elevated (7–14 mg/kg; BBL 1990).

In addition to the 4 stations described above, 10 stations were selected to examine effects from PAHs. These stations were selected primarily in Segment 6 (T12 through T20), with one in Segment 5 (T11), to provide a range of PAH concentrations, and in an attempt to choose stations with relatively low concentrations of metals and PCBs. These Triad stations were chosen to represent Stations 5A, 6A, 6C, 6D, 6DUPPAH, and 6E from the WDNR food chain study, historical Stations H12 and H15, and historical stations just downstream of the Pennsylvania Avenue Bridge and just upstream of the island near Camp Marina.

A total of four reference stations (T01 to T04) were sampled upstream of the Sheboygan Falls Dam—one located just upstream of the dam, and the other three located farther upstream near Route 23. Their locations were chosen to represent the range of grain size compositions, total organic carbon (TOC) concentrations, and habitats expected at downstream sampling sites in the Sheboygan River.

3.2 METHODS

This section presents sampling and statistical methods for sediment sampling, toxicity testing, and benthic community analysis. The statistical and analytical methods used for the Triad analysis are presented in Section 3.3, which integrates the results of sediment chemistry, toxicity testing, and benthic community analysis.

3.2.1 Triad Sampling Methods

Sediment samples for chemical analysis and toxicity testing were collected with an Ekman or Petite Ponar grab sampler from the 0 to 10 cm sediment horizon at the 18 stations described above (Figure 3-1) as specified in the work plan, except for the following deviations. Although the historical station R-73 was targeted for sampling to be designated Station T09, the south side of the railroad bridge was sampled instead. Also, the work plan stated that an Ekman sampler would be used, but a Petite Ponar sampler was used instead at Stations T01 through T12 (Figure 3-1) because of the sandier sediment encountered in the upper river. The Eckman grab would only close completely in soft, silty sediments. The decision to change samplers is not expected to affect the results since the same depth of sediment was subsampled from both types of samplers. To obtain sufficient sediment volume for analysis requirements, successive grab samples were collected within a 3 m radius of the initial sampling location. Sediment grab samples were homogenized and distributed into appropriate sampling containers for chemical analysis and toxicity testing.

Sediment sampling for the benthic community analysis was conducted at each of the Triad stations using a Petite Ponar grab sampler. Five discrete replicate benthic samples were collected at each station. Each replicate was sieved using a 0.5-mm mesh screen and filtered site water was used to prevent inclusion of water-column organisms. The only exception was Station T19 where efficient use of remaining daylight and personnel dictated the use of unfiltered site water. This decision did not affect the final results for this station because the two individual water-column organisms were deleted for these samples, as was routinely done for all samples. It is fairly common for water-column organisms to become entrained in the grab sampler as it descends to the bottom. The presence of these organisms can often be reduced by using filtered water during field processing of the samples. Non-benthic organisms can also adhere to debris that forms part of the sample matrix and that is why organisms that are not part of the benthic community are deleted from the final data set. Three additional benthic samples were collected for WDNR using a 0.25-mm screen — one each at Stations T03, T08, and T10— for possible comparison with previous WDNR benthic data collections using the same mesh size. No results are reported from these samples.

Sediment was analyzed for PCBs (Aroclor analyses), pesticides, metals, PAH compounds, AVS, SEM, grain size, total solids, and TOC, according to methods presented in Appendix I.

A quality assurance review was conducted of the laboratory data to verify that the laboratory QA/QC procedures were documented and that the quality of the data were sufficient to meet the project data quality objectives and support the use of the data for its intended purposes. Data validation was completed to a slightly modified version of

USEPA Level 2 specifications to include Puget Sound Estuary Program protocols (USEPA 1995c; PSEP 1991). The level of effort included completing a 10% review of data and calculation checks for all calibration and quality control data, compound quantification and identification, verification of 100% of transcriptions, and a 10% calculation check of positive identification reported by the laboratories (Appendix A-2).

3.2.2 Toxicity Test Methods

Two separate bioassays were performed with sediment from each Triad station using the freshwater amphipod *Hyalella azteca* and the freshwater midge *Chironomus riparius*. Sediment samples for toxicity testing were collected between August 12 and August 18, 1997.

The tests and QA/QC were conducted according to American Society for Testing and Materials standards (ASTM 1996). Adverse effects were evaluated by measuring survival and growth in 14-day old *H. azteca*, and survival and growth in midges *C. riparius* at the third instar (a stage in larval development) at test initiation. In both tests, organisms were exposed to sediment from 14 site-related stations and four reference stations for a 10-day period. A negative control using clean silica sand and a positive control using a reference toxicant was performed for each test. The reference toxicant was zinc sulfate for *H. azteca* and potassium chloride for *C. riparius*. Six replicates were tested for each station or control.

The *H. azteca* test was initiated on August 26, 1997 and terminated on September 5, 1997. The *C. riparius* test was initiated on September 5, 1997 and terminated on September 15, 1997. No deviations from the workplan were encountered during toxicity testing.

Four endpoints were measured in the bioassays—survival and growth of *H. azteca* and *C. riparius*. Growth is represented by final biomass, because the initial biomass is a constant for a given test series. Total biomass and mean individual growth (total biomass divided by the number of survivors) were both considered for use as the growth endpoint. Both endpoints are linked with the survival results. Low survival results in lower total biomass. On the contrary, low survival in a replicate may result in less competition and more food, and therefore higher mean individual growth. For the Triad analysis, negatively correlated endpoints may lead to contradictory results, so total biomass was chosen as the growth endpoint. For the benchmark discussion in Section 6.1.2, statistical significance of both growth endpoints was considered.

The 14 station means for each endpoint were statistically compared to the corresponding pooled reference mean and to the negative control mean. Data were first evaluated for approximate normality and homogeneous variance. In cases where the data did not conform to these assumptions, transformations were applied to the data prior to statistical analysis. Two approaches were used for statistical comparisons. For comparisons to pooled reference stations, Bonferroni multiple comparisons were used. The Bonferroni procedure controls the experiment-wise error rate—that is the probability of at least one false positive for all 14 comparisons. Because of the large number of comparisons, 14, the Bonferroni experiment-wise error rate or alpha-level was set at 0.10. This corresponds to a pair-wise error rate of approximately 0.007 for the comparisons between sites and reference. Statistical significance from negative control samples was assessed using multiple *t*-tests with pairwise alpha-level set at 0.05. Thus, the probability of a false positive for each negative control comparison is set at 5%.

3.2.3 Benthic Community Analysis Methods

Laboratory processing consisted of sieving the formalin-preserved samples into 70% ethanol, sorting the organisms from the sample matrix, and identifying the macroinvertebrates. The sorting efficiency criterion of 95% stipulated in the work plan was met or exceeded in all cases. Twenty percent of each sample was re-sorted during the QA/QC check to verify the 95% criterion. A sample passed if the number of organisms found during the QA/QC check did not represent more than 5% of the total number of organisms found in the entire sample. If the number of organisms found was greater than 5% of the total number, the entire sample was re-sorted and re-submitted for QA/QC until it passed the 95% criterion.

Organisms were identified to the lowest practical taxonomic level. The work plan called for oligochaetes to be identified to class Oligochaeta. Preliminary data indicated that most of the stations were dominated by oligochaetes, so the taxonomic resolution of this group was increased from class to family. The methods used for taxonomic identification and a list of the taxonomic keys are provided in Appendix J.

Two benthic metrics were chosen to compare benthic community health among stations—species abundance and richness. These metrics were selected because they are considered robust indicators of benthic community health (Plafkin et al. 1989). Note that more than 20 other metrics were examined for relationships and no clear trends were observed. Data were first evaluated for approximate normality and homogeneous variance. In cases where the data did not conform to these assumptions, transformations were applied to the data prior to statistical analysis. Statistical significance from reference stations was assessed using Bonferroni multiple comparisons. For each benthic metric, there were 14 planned statistical comparisons—14 site stations versus the mean of reference stations. The experiment-wise alpha-level was set at 0.05, resulting in a pair-wise Bonferroni Type I error rate of approximately 0.004.

3.3 BENTHIC INVERTEBRATE EXPOSURE

In this section, exposure of benthic invertebrates to COCs is assessed using sediment data collected in 1997. These data were collected throughout the Sheboygan River to represent a range of exposure to different types of contaminants and to integrate sediment concentrations with toxicity and benthic community structure measured in co-located samples. This section summarizes sediment chemistry results for selected COCs for benthic invertebrates—PCBs, PAHs, and metals. In addition, results for SEM, AVS and conventional parameters are presented. All chemistry results as reported by the laboratory, including data qualifiers, are presented in Appendix A-1. The laboratory data were evaluated in terms of completeness, holding times, instrument performance, accuracy, precision, method reporting limits, and field quality control samples. During the quality assurance review, no data were rejected and all data were considered useable as reported (Appendix A-2).

3.3.1 Polychlorinated Biphenyls

Concentrations of PCBs in sediment are shown in Table 3-1. Seven PCB Aroclors were analyzed (1016, 1221, 1232, 1242, 1248, 1254, and 1260). Total PCBs were calculated by summing all detected concentrations of Aroclors plus one-half the detection limit for undetected Aroclors, only if that Aroclor was detected in another sample. PCBs were not detected at any of the reference stations, but total PCB concentrations were estimated at 0.029 to 0.030 mg/kg dw using the PCB summing methodology described above. These total PCB concentrations are less than the TEL and probable effects level (PEL) concentrations for total PCBs. At site-related stations, the PCBs were reported as Aroclors 1232, 1242, and 1254 and as total PCBs.

To determine PCB concentrations on an Aroclor basis, the observed pattern of congener composition in a sample is compared to patterns observed for Aroclor standards. The Aroclors that most closely match the pattern observed in the sample are selected for quantitation. The accuracy of the quantitation is determined by the extent to which the selected Aroclors match the observed congener pattern.

The highest total PCB concentration reported was for Station T07 in Segment 2, and it exhibited a unique compositional pattern. The PCB mixture detected in this sample was quantitated as Aroclor 1232. All other sediment samples collected for the Triad study contained mixtures that were quantitated as mixtures of Aroclor 1242 and Aroclor 1254.

In the case of Station T07, the pattern observed in the sediment sample did not closely match any of the Aroclor standards. In addition, gas chromatography/mass spectrometry analysis was conducted with this sample to confirm the presence of PCB congeners. The predominance of lighter congeners (di- and trichlorobiphenyls) resulted in the selection of

Aroclor 1232 as the Aroclor with the closest match. A detailed review of the chromatogram for this sediment sample revealed that the pattern of congeners observed at Station T07 (Appendix A-1, Table A1-6) could not be solely attributed to Aroclor 1232. Therefore, the total PCB concentration reported for this sample has a higher level of uncertainty associated with it since it was quantitated based on a fairly dissimilar pattern.

The extremely high concentrations of several less-chlorinated congeners resulted in a hundred-fold dilution of the sample for Station T07. If the sample contained Aroclors 1242 and 1254 at concentrations similar to those seen in the other samples from Segment 2, they would not be quantifiable because of the dilution of the sample.

In all other Triad sediment samples, the only Aroclors that were reported were Aroclors 1242 and 1254, a finding consistent with Aroclors detected in previous investigations (BBL 1990). Except for Station T07 which had a total PCB concentration of approximately 760 mg/kg, the total PCB concentrations ranged from 0.19 to 1.9 mg/kg with the highest concentration measured at Station T08, located between the River Bend Dam and the Waelderhaus Dam. There was no apparent downstream gradient below Station T08.

3.3.2 Polycyclic Aromatic Hydrocarbons

Total PAH concentrations were summed from individual compounds using the same methods described previously for PCBs. The lowest concentrations of PAHs were found in the four reference stations and at Station T07 (Table 3-2). The highest total PAH concentrations, ranging from 2.2 to 7.2 mg/kg, were detected at Stations T11 through T20. Fluoranthene and pyrene were the PAH compounds most frequently detected at the highest concentrations. PAH concentrations at reference Stations T01 and T04 were higher than many of the PAH-specific TELs, but did not exceed the PAH-specific PELs (Table 3-2).

3.3.3 Metals, Simultaneously Extracted Metals, and Acid Volatile Sulfides

Generally, concentrations of metals were relatively low and there did not appear to be any strong concentration gradients (Table 3-3). At Station T07, the highest concentrations of chromium, mercury, and silver were found, although these concentrations were not substantially higher than at other areas. SEM/AVS exceeded one only at Stations T19 and T20, but only slightly (1.21 and 1.66, respectively), indicating that SEM metals are generally not bioavailable at concentrations toxic to benthic organisms (Section 2.3.2). Concentrations of metals at reference stations did not exceed metals TELs or PELs (Table 3-3).

3.3.4 Grain Size, Total Organic Carbon, and Solid Content

Sediment texture consisted primarily of sand, silt, or clay (Table 3-4). At 10 of the 18 stations, more than 50% of the sediment was made up of silt and clay, with percentages as high as 90% at Station T10. TOC content ranged from 4.4 to 8.3%. Solids content of sediment ranged from 34 to 74%.

3.4 EFFECTS ON BENTHIC INVERTEBRATES

This section presents sediment benchmark concentrations representing effects to benthic invertebrates from the literature. Also presented are results from the site-specific toxicity tests and benthic invertebrate community analysis conducted for the 1997 ERA.

3.4.1 Sediment Benchmarks

Sediment benchmark concentrations used throughout this ERA were obtained from data generated by the Assessment and Remediation of Contaminated Sediments program (USEPA 1996a), with the exception of values for mercury and total PCBs, which are from Smith et al. (1996). The values derived by Smith et al. (1996) were based on a more comprehensive biological effects database for sediment which included the data generated by the Assessment and Remediation of Contaminated Sediments program. The benchmark values used the TEL, PEL, and the no effects concentration (NEC) based on both 14-day and 28-day *H. azteca* toxicity test data (survival, growth, and reproductive endpoints; Table 3-5).

TELs and PELs were calculated using the following procedure (USEPA 1996a):

> Concentrations observed or predicted by different methods to be associated with effects were sorted and the lower 15 percentile (ERL) and 50 percentile ERM concentrations of the effects data set were calculated. In addition, the 50 percentile (No Effects Range Median; NERM) and 85 percentile (No Effects Range High; NERH) concentrations of the effects data set were calculated. The TEL was calculated as the geometric mean of the ERL and NERM, whereas the PEL was calculated as the geometric mean of the ERM and NERH. The NEC is calculated as the maximum concentration of a chemical in a sediment that did not significantly adversely affect the particular response (e.g. survival, growth, or maturation) as compared to the control.

The definitions of TEL, PEL, and NEC, as presented by USEPA (1996a) are:

- TEL—a concentration below which toxic effects are rarely observed

- PEL—a concentration above which toxic effects are frequently observed

- NEC—analogous to an apparent effects threshold value, which is defined as a sediment concentration of a given chemical above which statistically significant effects are always observed

The TEL values calculated from the 28-day *H. azteca* results were used for screening COCs for benthic invertebrates (Section 2.3.2); the 28-day PELs were used as part of the Triad, and all benchmarks—TELs, PELs, and NECs for 14-day and 28-day *H. azteca* tests—were used in the discussion of the derivation of protective sediment concentrations for benthic invertebrates (Section 6.1.2).

3.4.2 Toxicity Test Results

This section presents results from each of the toxicity tests and addresses the statistical significance of site samples compared to negative control and reference samples. The detailed laboratory report is presented in Appendix C. Table 3-6 displays the mean and standard deviation for each toxicity endpoint by station.

Overall, the ranges of percent silt and clay and TOC in the reference sediment samples were representative of the composition of downstream site samples (Table 3-4). The grain size composition in the reference samples ranged from 12 to 61% silt and clay; site samples ranged from 16 to 90% silt and clay. The TOC concentrations in the reference samples ranged from 4.9 to 8.3%; site samples ranged from 4.4 to 6.3% TOC. Grain size and toxicity were not significantly correlated.

***Hyalella azteca*¾** Survival in site stations ranged from 0 to 92% (Table 3-6), and in reference stations from 47 to 95%. Mean survival in the negative control was 97%, meeting the criterion for test acceptability as outlined in ASTM (1996). Because of unequal variances and skewness in the data distribution, survival data were rankit transformed prior to statistical analysis. Survival was 0% at Station T07, which was the only station classified as toxic based on survival when compared to the reference stations. Based on multiple *t*-tests, three reference stations and nine site stations had significantly reduced survival as compared to the negative control—Stations T02, T03, T04, T07, T10, T11, T13, T14, T15, T16, T18, T19, and T20. No stations were statistically different from the reference based on total growth, although the growth endpoint at Station T07 could not be assessed because survival was 0%. Stations T13 and T14 were significantly less than reference for individual growth. Based on multiple *t*-tests, Station T14 had significantly lower total biomass and station T13 had significantly lower individual biomass when compared to the negative control.

The 96-hr LC50 for the zinc reference toxicant in the positive control was 145 μg/L Zn (95% confidence limits of 130 and 162 μg/L Zn). Water quality variables were within acceptable ranges with the exception of dissolved oxygen which dropped below the recommended 40% saturation in four replicates (T11, T13, T14, and T19) on day 7 of the test. Subsequent aeration brought the dissolved oxygen levels up to near saturation for the remainder of the test.

Total sulfides and interstitial ammonia can cause toxicity in sediment bioassays and therefore are measured at test initiation and termination as a QA/QC requirement. Total sulfides concentrations in the overlying water of the test sediments ranged from 0 to 0.015 mg/L S and were below effects levels established in previous testing. Total interstitial ammonia ranged from <0.1 to 29.5 mg/L NH_3. Ammonia concentrations were less on day 10 than day 0. Spiked ammonia sediment tests previously conducted at the EVS North Vancouver laboratory found the 14-day LC50 for interstitial ammonia to range from 41 mg/L NH_3 to greater than 100 mg/L NH_3 for *H. azteca*. The interstitial ammonia concentrations in the Sheboygan River sediment samples were below these effects levels (see Appendix C).

***Chironomus riparius*¾** Survival in site stations ranged from 0 to 93% and in the reference stations from 68 to 95% (Table 3-6). Mean survival in the negative control was 97%, meeting the criterion for test acceptability as outlined in ASTM (1996). Because of evidence of a non-normal distribution, survival data were arcsin transformed prior to statistical analysis. Survival was 0% at Station T07, which was the only station classified as toxic based on survival when compared to the reference stations. Based on multiple *t*-tests, Stations T02, T03, T04, T07, T09, T10, T11, T14, T17, and T20 had survival significantly lower than the negative control. No stations were statistically different from the reference or negative control based on total growth, although the growth endpoint could not be evaluated at Station T07 because survival was 0%. Individual biomass was significantly less than reference for Stations T12, T16, and T18.

The 96-hr LC50 for the potassium chloride reference toxicant in the positive control was 5.4 g/L KCl (95% confidence limits of 4.2 and 6.8 g/L KCl), which is within the laboratory range of 4.5 ± 3.0 g/L KCl (mean ± 2 standard deviation). Water quality variables were within ranges with the exception of dissolved oxygen which dropped below the recommended 40% saturation in seven replicates on day three. Subsequent aeration brought the dissolved oxygen levels up to near saturation for the remainder of the test.

Total sulfides and interstitial ammonia can cause toxicity in sediment bioassays and therefore are measured at test initiation and termination as a QA/QC requirement. Total sulfides concentrations in the overlying water of the test sediments ranged from 0 to 0.001 mg/L S and were below effects levels. Total interstitial ammonia ranged from <0.1 to 31 mg/L NH_3. Ammonia concentrations were less on day 10 than day 0. Spiked ammonia sediment tests previously conducted at the EVS North Vancouver laboratory found the 14-day LC50 for interstitial ammonia ranged from 126 to 168 mg/L NH_3 for *C. riparius*. The interstitial ammonia concentrations in the Sheboygan River sediment samples were below these effects levels (see Appendix C).

3.4.3 Benthic Community Analysis Results

Table 3-7 displays the means and standard deviations for total abundance and species richness by station. Because of evidence of a non-normal distribution, total abundance data were rankit transformed prior to statistical analysis. Station T07 had significantly reduced abundance relative to reference conditions. There were no other significant results. The full data set is presented in Appendix D.

The taxonomic list of organisms found at all stations is presented in Table 3-8. Taxonomy results indicated clear dominance of the class Oligochaeta, with more than 90% oligochaetes at most stations, and extremely low diversity within this class throughout the study area, despite changes in sediment types and habitats. Mean oligochaete densities ranged from 4,240 to 7,200 individuals/m^2 at the reference stations and 10,500 to 45,500 individuals/m^2 at site-related stations, with the exception of T07, which had a density of only 400 individuals/m^2.

The oligochaete populations were composed almost exclusively of immature individuals. Further investigation indicated that all oligochaetes were represented by the single family Tubificidae. A limited number of stations were selected to qualitatively assess oligochaete species composition in an attempt to assign immature individuals to discreet species based on the presence of a few mature individuals as is routinely done in the literature (Kennedy 1966). Only two species, *Limnodrilus hoffmeisteri* and *Limnodrilus cervix*, both members of the family Tubificidae, were present. Because both species of *Limnodrilus* were present at most of the stations examined, it was not possible to assign immature individuals to a particular species.

3.5 SEDIMENT QUALITY TRIAD ANALYSIS

The Triad integrates the individual measures listed in Table 3-9 into a holistic evaluation of sediment quality. The Triad data were analyzed in three ways:

- A collective evaluation of Triad endpoints (Section 3.5.1)
- A ranking of stations based on their performance across endpoints (Section 3.5.2)
- Multidimensional scaling to visually compare the cumulative effect of all results for each station (Section 3.5.3)

Together, these three approaches provide a thorough, integrated analysis of the benthic endpoint data. Each of these methods of analysis and a synthesis of the Triad results are presented in the following sections.

3.5.1 Analysis of Statistical Differences

A station is considered to be a "hit" on a given leg of the Triad if it shows significant differences from reference conditions for at least one endpoint on that leg. Determination of significant differences for toxicity and benthic community structure endpoints was described in Sections 3.4.2 and 3.4.3. Evaluation of sediment chemistry differences is described below.

Sediment chemistry metrics were obtained for PAHs, metals, and PCBs (as Aroclors) as follows. For PAHs and metals, the concentration for each analyte was divided by its PEL value, then the quotients were summed for total PAHs and total metals at each station. For PCBs, the Aroclor concentrations were summed first, then divided by the PEL for total PCBs. There were no sediment chemistry replications within a station, so direct statistical comparisons with references were not possible. Instead, prediction intervals around reference station values were used to determine significant differences. If the reference station values for each chemical endpoint—PAHs, metals, and PCB Aroclors—are assumed to come from the same normal distribution, a 95% prediction interval can be formed for this reference distribution. Then, if the sediment concentration at a particular station is from the same reference distribution (the null hypothesis), there is a 95% probability that the value will fall into the reference station prediction interval. A site station is considered different from reference for an individual chemistry endpoint if it falls outside of the 95% reference prediction interval, and if at least one individual analyte is above its PEL value for that endpoint. No PCB Aroclors were detected at any of the reference stations, so only the PEL exceedance was used to determine PCB differences. All stations, except Station T10, showed significant differences from reference conditions for at least one of the three sediment chemistry endpoints.

Table 3-10 provides a synthesis of the three legs of the Triad. The only station with hits in all three legs of the Triad was Station T07. Thus the probability of adverse benthic impacts due to COCs is highest at this station. All other stations had either one or two hits, and thus the probability of benthic impacts related to COCs at these stations is lower, and is related to the magnitude of the exceedances.

3.5.2 Triad Ranking

3.5.2.1 Method

The ranking method is a simple approach for displaying the relative performance of each station based on the nine endpoints listed in Table 3-9. The 18 Triad stations were ranked for performance of each endpoint. Ranking of Triad data has been successfully employed by Kreis (1988) and Canfield et al. (1994) to discriminate sites based on sediment quality. The ranking system used for this ERA is as follows:

- Sediment chemistry: Stations were ranked based on the degree to which the concentrations of COCs exceeded benchmark PELs as described in Section 3.5.1. For each endpoint, the station with the highest metric value received a rank of 1, most affected, and the station with the lowest metric value a rank of 18.

- Toxicity data: Stations were ranked separately for each of the four endpoints based on the measured test response. For example, for the *H. azteca* survival endpoint, the station with the lowest survival received a rank of 1, most affected, and the station with the highest survival received a rank of 18.

- Benthic community structure: Stations were ranked for total abundance and richness using the same approach as that used for the toxicity data. For example, the station with the lowest abundance received a rank of 1, most affected, and the station with the highest abundance received a rank of 18.

The average rank across endpoints orders the stations from poorer quality to better quality, relative to each other. The final weighted average Triad rank was computed using equal weighting for each leg of the Triad—sediment toxicity, benthic community structure, and sediment chemistry. Within each leg of the Triad, each individual endpoint was weighted equally.

The weighted average rank was used to evaluate the overall performance of each station. Stations with very low and very high average ranks have the greatest degree of concordance among endpoints. For example, low average ranks indicate poorer performance in all endpoints, identifying stations with poorer sediment quality. Stations with intermediate average ranks could have either intermediate performance for all endpoints, or high performance for some endpoints and low for others, producing an intermediate average rank. In either case, the characterization of sediment quality at these stations is less conclusive.

In many studies, the average ranks do not clearly sort stations into poorer, intermediate, and better groups. Critical values or cutoff points chosen from the distribution of average ranks can be useful for identifying which stations are considered poor performers relative to the other stations. For this study, critical values, in the form of confidence intervals, were developed by generating a random distribution of weighted average ranks, and comparing values from this distribution with the average ranks calculated for the 18 stations. First, a random average rank was generated as the weighted mean of nine random integers valued from 1 to 18. These integers represent a set of possible rank values for each of the nine endpoints. Note that they are generated with replacement, that is ranks can be repeated for a site. The weighted average of the set of random ranks represents a possible performance when there is no concordance among endpoints. A set of 10,000 such random average ranks was generated using a personal computer and a random number generator. This method formed an estimate of the random average rank distribution. From this distribution, the average rank values can be determined, which is unlikely to have occurred by chance alone. For example, suppose that the 10th percentile from the random average rank distribution is chosen as the critical value. The probability of getting an average rank less than this number, when there is no concordance among the endpoints, is less than 10%. A station with an average rank less than the 10th percentile of the distribution of randomized average ranks is implicated as an affected station because it must have consistently poor performance in many endpoints.

3.5.2.2 Results

Sediment chemistry, sediment toxicity, and benthic community structure data from the 14 stations in Segments 2, 3, 5, and 6 and the 4 reference stations in Segment 1 above Sheboygan Falls Dam were integrated into a Triad analysis using the ranking approach described above. The results of the station ranking are presented in Figures 3-2 and 3-3 and Table 3-11. Based on the overall station rank, only station T07 is clearly impacted relative to other stations; it falls outside of the 90% confidence interval with a consistently low rank. Stations T01 (a reference station), T08, T09, and T12 appear to be of higher quality than the other stations; they fall outside of the 90% confidence interval with consistently high ranks. Stations T13, T14, T16, and T19 are possibly impacted, since they fall outside of the 80% confidence interval with consistently low ranks. Station T03 is possibly of higher quality; it falls outside the 80% confidence interval with a consistently high rank. The remaining 8 stations, including two reference stations, fall into the intermediate range.

The ranking method works well for combining information across endpoints with different scales. Critical values can be used to quickly identify the stations with worst quality.

However, the magnitude of the differences between the stations is lost in this simple ranking approach.

3.5.3 Classical Multidimensional Scaling

3.5.3.1 Methods

Similar to cluster analysis, classical multidimensional scaling (CMDS) can be used to represent the similarity between stations (Johnson and Wichern 1992). CMDS attempts to preserve the distance and relative position that were observed between stations in the original multi-dimensional problem (represented by the 9 Triad endpoints listed in Table 3-9) within a two- or three-dimensional plot. The actual value of the coordinates on the CMDS plot is meaningless; it is only the relative positions of stations in this plot that are of interest. The proximity of stations in the CMDS plot reflects the similarity of stations based on the 9 Triad endpoints. CMDS produces the best possible estimate of location in two- or three-dimensions, but the distances among all stations are not perfectly maintained. A good fit is not guaranteed, and caution is needed in interpreting these lower-dimensional displays. In most cases, a three-dimensional plot provides a more accurate representation of actual distances than a two-dimensional image.

3.5.3.2 Results

For this study, endpoints were transformed as standard deviations from the mean before calculating the distances between stations, so that endpoints with a larger magnitude would not dominate the analysis. For example, abundance may range from 1 to 1,000, while mortality ranges from 0 to 1.0; if these endpoints were not standardized, the distance between stations would clearly be driven by differences in abundance. For PCBs, the value for station T07 was removed before calculating the mean and variance, so that this one large value would not exert undue influence on the standardized values. Next, the Euclidean distance between each pair of stations (the square-root of the sum of nine squared differences) was calculated. There are 18 stations which results in 153 station pairs for which distance values were calculated.

To further understand the relationships among stations regarding impact, CMDS was performed on the 14 stations in the study area downstream of the Sheboygan Falls Dam and the 4 reference stations above the dam. Station T07 was so far from the main cluster of stations that it distorted the distance calculations. In order to maintain an accurate portrayal of the distances in two dimensions, Station T07 was removed from the CMDS analysis. Figure 3-4 shows the two-dimensional representation of distances between stations with Station T07 removed. By excluding this station from the pattern, other less prominent patterns can also be seen. The four reference stations, Stations T01, T02, T03, and T04, are all located in the upper right-hand corner of the plot, reflecting their good performance for chemistry endpoints. Station T08 is located in the lower right-hand corner of the plot, reflecting a good performance on all endpoints other than PCB concentrations. Station T13 and, to a lesser extent, Station T19 are outside of the main cluster in the opposite direction from the reference stations. These two stations performed poorly on the chemistry endpoints. This analysis identifies stations which are different from the main cluster of stations. When combined with knowledge of the performance of the different stations on individual endpoints, these stations can be marked as more or less impacted than the others.

3.5.4 Triad Synthesis

This section provides an overview of the Triad, considering all three methods of analysis. Overlap among the method results was evident for Station T07, which was clearly identified as impacted. For other stations, the three Triad results were more difficult to interpret.

A summary of the Triad findings:

- Station T07 is clearly impacted. Sediment from this station exhibited 100% mortality in the two toxicity tests and contained a very high PCB concentration of approximately 760 mg/kg (Section 3.3.1). It had the lowest benthic total abundance, and the second highest sum of PEL-normalized metal concentrations.

- Station T13 is also impacted, based on the CMDS analysis. This station has the highest sum of PEL-normalized metals concentrations and the third highest PAH concentration. It had the poorest performance for *H. azteca* growth and was low in benthic invertebrate species richness.

- Station T19 also showed evidence of being impacted; it had the highest total PAH concentration, the third highest PCB concentration, and was among the poorest performers for *H. azteca* survival.

In summary, the Triad results indicate that Stations T07 and T13 are clearly impacted, and Station T19 is moderately impacted. All site stations had at least one PEL exceeded and 10 of the 14 site stations had significant *H. azteca* mortality relative to the negative control. However, the widespread dominance of oligochaetes and the significant toxicity in the reference area samples relative to the negative control made it difficult to correlate effects with sediment chemistry.

3.6 UNCERTAINTY IN THE BENTHIC INVERTEBRATE ASSESSMENT

3.6.1 Benthic Exposure

To assess exposure of benthic invertebrates to COCs, 18 triad stations, including 4 reference stations, were selected from depositional areas to cover the range of COC concentrations and mixtures present at the site. Most of the 14 site stations were located in the lower river in Segments 5 and 6, with one station each in Segments 2 and 3. Although historical data were examined to assess patterns of COCs in the sediment to select the Triad stations, numerous flood events over the last decade may have redistributed contaminated sediment deposits.

Sediments were analyzed for a suite of contaminants including PCBs, PAHs, metals, and selected pesticides. The possible presence of unmeasured contaminants in the samples may have contributed to toxicity or altered benthic community composition. Of the pesticides that were measured, elevated detection limits due to matrix interference in some samples may have obscured elevated concentrations. In particular, detection limits for lindane and DDE were slightly higher than their TELs at reference stations. At several of the site stations, particularly Stations T07 and T08, many of the pesticide detection limits were higher than PELs because of matrix interference.

3.6.2 Toxicity Test Uncertainty

Interpretation of toxicity test results was complicated by the statistically significant reduced survival of both *H. azteca* and *C. riparius* at reference Stations T02, T03, and T04 compared to negative controls. None of the COCs were detected at concentrations higher than the respective TELs at reference Stations T02 and T03, while none of the PELs were exceeded at reference Stations T01 and T04. TELs were exceeded for three PAH compounds at Station T01 and eight PAH compounds at Station T04. As noted above, detection limits for two pesticides, lindane and DDE, were slightly higher than their TELs at all reference stations.

Since the COC concentrations at the reference stations were generally low, as described above, the observed toxicity and benthic structure results were unexpected. Quality assurance standards were met during the toxicity tests, so the results do not appear to be a result of the test protocol. Instead, the low survival of benthic invertebrates at reference Stations T02, T03, and T04 may indicate the presence of other stressors on the system, such as unmeasured contaminants. The poor *in situ* benthic performance at these stations lends credibility to this hypothesis. These stations are upstream of the study area where farm land near the river may contribute agricultural herbicides and pesticides that were not measured in the priority pollutant pesticide scan performed.

3.6.3 Benthic Community Analysis Uncertainty

Freshwater benthic communities, particularly in rivers, are generally highly spatially variable or patchy. In the depositional areas sampled in this study, the nearly uniform nature of the benthic community at both site and reference stations and the dominance by immature oligochaetes was considered unusual.

Although unusual, these results were not unprecedented. Similar results were obtained in a study conducted by WDNR in 1990 (Aartila 1996) in which benthic invertebrate data were collected from six depositional areas in the Sheboygan River, including an upstream reference area. Other studies have reported that tubificid populations were composed mainly of immature specimens during the summer months in England and in the Little Calumet River in Indiana (Block et al. 1982; Kennedy 1966). Routinely, up to 80% of the collected oligochaete material may contain immature specimens which cannot be identified to species (Adreani et al. 1984; Steinlechner 1987).

Most likely, a combination of environmental parameters contributed to the benthic community composition observed in this study. *L. hoffmeisteri*, the dominant species present in the samples, is very sensitive to population density, and maturation time is density-dependent within ranges found in the 1997 ERA sampling event (Mason 1994). (A literature review of *L. hoffmeisteri* is provided in Appendix E.) It is possible that increased population pressure prior to the ERA sampling suppressed the development of mature adults, yielding a population characterized by immature organisms. Another possible cause for the immature oligochaete dominance is the multiple high-flow events that occurred two months prior to the sampling event (Figure 2-1). During these events, intense scouring and/or re-deposition of the benthic habitat likely occurred, which could have dramatically altered the community structure leading to subsequent recolonization by immature organisms. A similar occurrence was documented in the Little Calumet River near Hammond, Indiana (Block et al. 1982).

4.0
FISH EVALUATION

Potential risks to fish from PCBs and PAHs are characterized in this section. The general approach and methods are described followed by exposure data, effects concentrations, and the risk calculation. Relationships between concentrations in fish tissue and sediment are explored, and an uncertainty assessment is also included.

4.1 APPROACH

Risks to fish from exposure to PAHs were evaluated by reviewing an existing study of white suckers (Schrank et al. 1997) and using a sediment benchmark approach proposed by WDNR (1992a). Risks to fish from exposure to PCBs were evaluated by comparing concentrations of PCBs in resident fish to tissue residue effects concentrations reported in the literature.

Exposure of fish to PCBs was evaluated by collecting additional congener-specific data for juvenile smallmouth bass in 1997 and integrating those data with historical congener-specific fish tissue data collected by WDNR in 1994 for the food chain study. The 1997 data were collected from the same river segments that data were collected from in 1994. Additional historical PCB fish tissue data are available from annual monitoring conducted by Blasland, Bouck & Lee, Inc., in 1994, 1995, and 1996. However, these data were not used because only single smallmouth bass were analyzed as scales-off, skin-on fillets; they were analyzed for Aroclors 1254 and 1248, a pattern inconsistent with the Aroclor 1242 pattern dominating the 1997 ERA samples; and the range of tissue concentrations of total PCBs—0.5 to 18 mg/kg ww—was within the range measured in the WDNR food chain study and the 1997 ERA sampling.

Sediment samples were also collected and analyzed for PCB congeners for the 1997 ERA to relate fish tissue concentrations to sediment exposure concentrations. The compositing scheme was designed to preferentially sample sediment deposits in segments from which fish were collected. Depositional areas were targeted for sampling. Although smallmouth bass may also reside and feed in riffle areas, these areas were not selected for sampling because the PCB concentrations in these areas are likely to be much lower than PCB concentrations in the depositional areas because of the larger grain size and lower TOC of sediment in riffle areas. Instead, concentrations measured in fish were related to the concentrations in sediments from the depositional areas, since these areas serve as likely sources of PCBs.

4.2 SAMPLING AND ANALYSIS METHODS

This section presents sampling and analysis methods for fish and sediment data used for the 1997 ERA and the WDNR food chain study.

4.2.1 Fish

4.2.1.1 1997 ERA

Juvenile smallmouth bass were collected in August 1997 from Segments 1, 2, 3, and 5 of the Sheboygan River. Young-of-year fish were not collected because few young-of-year smallmouth bass were found in Segments 2, 3, or 5 in the study area, although they were plentiful in Segment 1, the reference area. Fish composites were collected using a direct current stream electroshocker provided by WDNR. Three whole-body composites, each consisting of three to five individual smallmouth bass, were collected from each of the four specified segments at locations identified in Figure 3-1. After the fish were stunned by the electroshocker, they were netted and placed in a holding tank containing river water. Upon completion of fish collection at each river segment, fish lengths and weights were recorded and specimens were sorted by size.

Ten to 14 fish were collected from each of the four segments and composited to obtain three separate tissue samples for chemical analysis based on length (Table 4-1). The goal was to collect similar size ranges of juvenile fish in each study area segment. The smallest fish available were targeted for capture. Only juvenile fish in the size range from 11.6 to 19.4 cm, estimated as 1 to 2 years old, were captured in numbers sufficient for analysis.

Whole fish composites were wrapped in hexane-rinsed aluminum foil and double-bagged in plastic bags. Composite samples were analyzed for PCB congeners, dioxins and furans (a subset), lipids, and percent moisture, according to methods presented in Appendix I.

4.2.1.2 WDNR Food Chain Study

As part of the WDNR food chain study, smallmouth bass, white sucker, and longnose dace were collected in October 1994 from the same four segments of the river as in the 1997 ERA, Segments 1, 2, 3, and 5, using the same sampling methods. Two size classes of fish, adult and young-of-year, were collected for smallmouth bass and white sucker, whereas only one size class, adult, was collected for longnose dace. For each size class and fish species, three replicate samples were collected at each of the four segments. For smallmouth bass and white sucker, each replicate consisted of three to five similar-sized fish. For longnose dace each replicate consisted of 25 similar-sized fish. The range of mean replicate fish size for each fish species was 19.2 to 29.3 cm for adult smallmouth bass, 6.1 to 10 cm for young-of-year smallmouth bass, 23.6 to 34.8 cm for adult white sucker, 6.4 to 13.3 cm for young-of-year white sucker, and 5.3 to 12 cm for longnose dace (Burzynski, pers. comm. 1997). Whole-body fish composites were analyzed for PCB congeners and lipid content. Some of the WDNR food chain study samples were not analyzed for all coplanar congeners required for a complete TEQ calculation. Inclusion of these samples in composite averages would result in an underestimation of TEQs, thus, these samples were not included in the calculation.

4.2.2 Sediment

4.2.2.1 1997 ERA

Sediment samples were collected from the 0 to 10 cm horizon using a Petite Ponar grab sampler. A Petite Ponar sampler was used in place of an Eckman grab because of the sandy sediment encountered. The Eckman grab would only close completely in soft, silty sediments. The change in samplers is not expected to affect the results because the sampling depth was not affected.

Three to five composited sediment samples were collected in depositional areas in each of four study area segments, Segment 1, 2, 3, and 5 of the Sheboygan River (Figure 3-1). Three composited sediment samples were collected in each of Segments 1, 2, and 3; and 5 samples were collected in the larger Segment 5. Each sediment sample was a composite of three grabs collected within the depositional zone. To obtain depositional sediments throughout a segment, the 3 or 5 stations were located approximately equidistant throughout the entire segment. When a station location was reached in the field, the nearest depositional area was identified and the sediment was sampled. Depositional areas were selected using a metal probe to determine the depth of the deposit and sediments were examined visually to estimate silt content. Sediment samples were analyzed for PCB congeners, grain size, total solids, and TOC, according to methods presented in Appendix I.

4.2.2.2 WDNR Food Chain Study

Sediment samples were collected in February 1995 from locations shown on Figure 4-1 (sampling locations in the reference area are not shown). Each sample consisted of one discrete sediment core taken with a polycarbonate tube coring device. Only the biologically active zone of each core was retained for analysis, although one core from Segment 6 was sampled at depth for PAHs. The sediment samples were analyzed for PCB congeners, PAHs, selected metals, TOC, and grain size.

4.2.3 Data Validation

Data validation procedures for the 1997 ERA data were the same as for the Triad chemistry, described in Section 3.2. Methods for data validation conducted by WDNR for the food chain study were presented in the Sheboygan River Food Chain and Sediment Contaminant Assessment Quality Assurance Project Plan (WDNR 1995c). All chemistry results from the 1997 ERA, as reported by the laboratory, including data qualifiers, are presented in Appendix A-1. During the quality assurance review, the laboratory data were evaluated in terms of completeness, holding times, instrument performance, accuracy, precision, method reporting limits, and field quality control samples. No data were rejected as a result of this review and all data were considered useable as reported in Appendix A-2. Chemistry results for the WDNR food chain study, as received from WDNR, are presented in full in Appendix A-3. Summarized results from data validation of WDNR food chain data were not available.

4.3 FISH EXPOSURE

Exposure of fish to PCBs is evaluated in this section using fish tissue and sediment data collected for the ERA in 1997 and for the WDNR food chain study in 1994 and 1995.

4.3.1 Total Polychlorinated Biphenyl Concentrations

Total PCBs in tissue and sediment from both the 1997 ERA and the WDNR food chain study were calculated by summing all detected congener concentrations plus one-half the detection limit for undetected congeners. The same scheme was used to calculate total PCBs from Aroclors, except Aroclors that were not detected in any sample in the study area were not included in the sum.

4.3.1.1 Smallmouth Bass Tissue

The highest tissue PCB concentrations, up to 37 mg/kg ww, were measured in adult smallmouth bass collected from Segments 2 and 3 in 1994 (Table 4-2). The total PCB concentrations measured in juvenile smallmouth bass collected from Segments 2, 3, and 5 in 1997 ranged from 9.1 to 23 mg/kg ww and are similar to the total PCB concentrations measured in young-of-year smallmouth bass collected from the same segments in 1994 which ranged from 10 to 31 mg/kg ww. The total PCB concentrations measured in the adult fish in 1994 were generally higher, ranging from 16 to 37 mg/kg ww, than those measured in the young-of-year fish except in Segment 3, where the concentrations were similar for the two size classes of smallmouth bass.

4.3.1.2 Sediment

Total PCBs measured in sediment samples collected in Segments 2, 3, and 5 ranged from 0.47 to 38 mg/kg dw in the 1997 ERA sediment samples collected for the fish assessment (Table 4-3). The concentrations in Segments 2 and 3 were generally higher than those in Segment 5 and were highly variable, with ranges of 3.7–20 mg/kg dw and 3.2–38 mg/kg dw reported in Segments 2 and 3, respectively. PCB concentrations in sediment from the reference area (Segment 1) were more than two orders of magnitude lower, all less than 0.026 mg/kg dw.

Sediment samples were also analyzed for total PCBs in the Triad study as part of the 1997 ERA. In the Triad study sediment samples, total PCBs were calculated by summing Aroclor concentrations instead of summing individual congener concentrations as in the sediment samples collected as part of the fish assessment. The total PCB concentrations in the Triad samples were similar to those in the fish assessment samples in Segment 1, much higher in Segment 2, and slightly lower in Segment 3 (Table 4-3). The very high concentration, 760 mg/kg dw, measured in the Segment 2 Triad sample was expected since an area suspected of high PCB concentrations was targeted. Concentrations in Segment 6 Triad samples were much lower, 0.2–0.5 mg/kg dw, than in Segments 2, 3, and 5 and were less variable.

The range of total PCB concentrations in Segments 2, 3, and 5 measured in the 1997 ERA fish assessment (0.47–38 mg/kg dw) and in 1995 for the WDNR food chain study (1.0–15 mg/kg dw) were similar except for the concentration in sample S3-2 of 38 mg/kg dw. Total PCB concentrations were calculated from the sum of the individual PCB congener concentrations in both of these studies.

PCBs appear to originate in Segment 2 and be carried downstream to Segments 3 and 5, which is consistent with the conceptual model of the site

4.3.2 Polychlorinated Biphenyl Congener Pattern Analysis

4.3.2.1 Principal Polychlorinated Biphenyl Congener Identification

To compare sediment and fish tissue PCB congener concentrations and composition, the congeners that were most frequently detected and contributed the most to total PCB concentrations in fish tissue samples were identified (Table 4-4). These principal PCB congeners were identified on the basis of being detected in more than 75% of the samples and representing 2% of the total PCB concentration in at least one sample. The sum of the principal PCB congeners represents an average of 80.3% of the total measured PCB concentrations in the juvenile smallmouth bass tissue samples collected in the 1997 ERA.

Note that these congeners were not selected on the basis of their toxicological significance.

4.3.2.2 Polychlorinated Biphenyl Congener Analysis of 1997 Sediment Samples

Figures 4-2a and b show the comparative PCB congener patterns in the 1997 sediment samples collected for the fish assessment study with and without samples S2-2 and S3-2 since the high PCB congener concentrations measured in these samples require a scale that obscures the congener pattern of the remaining samples. In general, the compositional pattern is consistent among these three segments, with a prevalence of tri- and tetrachlorinated congeners in Segments 2, 3, and 5 consistent with a relatively unweathered PCB mixture.

The highest average PCB congener concentrations were measured in Segment 2 for all congeners except 017, 047/048, 091, and 149 (Figure 4-3a). High concentrations of these congeners measured in one sample, S3-2, from Segment 3 resulted in maximum mean concentrations of these congeners for Segment 3. The congener patterns in the segments were not affected by the organic carbon normalization of the congener concentration (Figure 4-3b).

The contribution of the less chlorinated, tri- and tetrachlorobiphenyls was greater in Segments 2, 3, and 5 than in Segment 1 (Figure 4-4). The contribution from the pentachlorobiphenyl congeners was relatively similar in all segments. The more chlorinated hexa- and heptachlorobiphenyl congeners contributed a greater percentage of the total concentration in Segment 1 sediments than in sediments from Segments 2, 3, and 5, although the concentrations of these congeners were much lower in Segment 1. The difference in compositional pattern between Segments 2, 3, and 5 and Segment 1 suggests a different source of PCBs for Segment 1.

4.3.2.3 Polychlorinated Biphenyl Congener Analysis of 1997 Smallmouth Bass Tissue

The three fish composite samples collected per segment for Segments 1, 2, 3, and 5 showed very little within-segment variability in PCB congener patterns, thus the patterns obtained by averaging the within-segment composites are compared to assess differences among the segments (Figure 4-5). The differences between Segment 1 fish tissue composition and Segments 2, 3, and 5 fish tissue compositions are similar to the differences seen between the sediment compositions of the reference area and the study area segments. The congener composition profiles for the smallmouth bass collected in Segment 1 contained a higher percent of the highly chlorinated hexa- and heptachlorobiphenyl congeners than the congener composition profiles for fish collected from Segments 2, 3, and 5. The contribution of the less chlorinated, tri- and tetrachlorobiphenyl congeners was greater in the fish collected from Segments 2, 3, and 5 than in the fish collected from Segment 1.

The highest PCB congener concentrations were measured in Segments 2 and 3 (Figure 4-6a). The fish collected from Segment 2 contained relatively high concentrations of four pentachlorobiphenyl congeners, 085, 087, 097, and 110. This result is consistent with the Triad sediment samples collected in Segment 2. The concentrations of all other principal congeners were higher in Segment 3 than in Segment 2. The lowest concentrations downstream of the reference area were measured in the Segment 5 samples. The relationships between the average concentrations for each segment were not affected by the lipid normalization (Figure 4-6b).

4.3.3 Comparison with WDNR Food Chain Study

4.3.3.1 Principal Polychlorinated Biphenyl Congener Identification

A subset of the principal PCB congeners identified in Section 4.3.2.1 was used to compare the fish tissue and sediment congener concentrations measured for the 1997 ERA with data collected for the WDNR food chain study in 1994 (Table 4-5). The congeners were selected on the basis of being detected in more than 75% of the samples and contributing at least 2% of the total PCB concentration in at least one fish tissue sample in both the 1997 ERA and the 1994 WDNR food chain study.

4.3.3.2 Sediment Polychlorinated Biphenyl Congener Concentrations and Composition

The average sediment PCB congener concentrations reported in the 1997 ERA and the WDNR food chain study are similar when the concentrations are presented on a dry weight basis (Figures 4-7a, 4-8a 4-9a, 4-10a). However, there are differences between the organic carbon normalized concentrations reported in the two studies (Figures 4-7b, 4-8b 4-9b, 4-10b). The organic carbon normalized concentrations reported by WDNR are higher than the concentrations measured during the ERA for Segments 1, 2, and 5. This difference is due to the substantially lower organic carbon content in the sediments collected in 1994 relative to those collected in 1997.

The congener composition was remarkably consistent among the river segments in 1994 (Figure 4-11b). In contrast, the profiles measured in 1997 are much more variable, particularly in terms of the contribution from the less chlorinated tri- and tetrachlorobiphenyl congeners (Figure 4-11a) although exclusion of Sample S3-2 reduces the variability among the segments. The magnitude of the contribution from these congeners to the total concentration is fairly similar in the two datasets.

4.3.3.3 Smallmouth Bass Tissue Polychlorinated Biphenyl Congener Concentrations and Composition

In 1994, two size classes of smallmouth bass were collected for measurement of tissue PCB congener concentrations, young-of-year and adults. In 1997, juvenile smallmouth bass were collected and analyzed for congener concentrations.
In Segment 1, the adult fish collected in 1994 contained higher PCB congener concentrations than the young-of-year collected in 1994 or the juvenile fish collected in 1997 for all congeners. This was also the case for Segment 2 with the exception that juvenile fish collected from Segment 2 in 1997 contained the highest concentrations of three pentachlorobiphenyl congeners—087, 097, and 110 (Figures 4-12a, 4-13a). Otherwise, the juvenile fish collected in 1997 and the young-of-year collected in 1994 had similar concentrations. The relationship between the different size classes was not affected by lipid-normalization of the congener concentrations (Figures 4-12b, 4-13b).

The differences between concentrations observed in young-of-year and adult smallmouth bass from Segments 1 and 2 are not as apparent in Segments 3 and 5, although the congener concentrations measured in the young-of-year are still generally less than the concentrations in adults for both the wet weight and lipid-normalized concentrations (Figures 4-14a, 4-14b, 4-15a, 4-15b). The concentrations in the juveniles in these segments overlapped those in the adults and young-of-year fish, suggesting little difference between 1994 and 1997.

The composition of PCBs in fish from the reference area was very different than in fish from Segments 2, 3, and 5 (Figure 4-16). The composition of the reference area fish samples was dominated by penta-, hexa- and heptachlorobiphenyl congeners, although the concentrations of these congeners were approximately two orders of magnitude lower than the concentrations in the other segments.

The congener composition in the juvenile smallmouth bass in 1997 differed from the composition observed by WDNR in young-of-year and adult smallmouth bass in 1994. The 1994 samples contain consistently higher concentrations of two pairs of coeluting congeners, 031/028 and 047/048, than the 1997 samples. This difference was apparent in every segment in both the fish and the sediment congener compositions. It is probable that this difference is because of differences in the analytical methods employed in the two studies, rather than an actual change in congener composition between 1994 and 1997.

4.3.4 Toxic Equivalent Concentrations

Concentrations of PCB congeners in juvenile smallmouth bass tissue can also be expressed as TEQ concentrations which describe dioxin-like toxicity to fish, as described in Section 2.3.1. (See Appendix B for TEQ data and calculations.) Average TEQ concentrations for PCBs of 0.14, 15, 16, and 6.1 ng/kg ww were calculated for Segments 1, 2, 3, and 5 respectively (Table 4-6).

As shown in Table 4-6, the three congeners that contributed the greatest percentage of the total TEQ concentration for each segment were 077, 118, and 126. These congeners contributed 92 to 93% of the total TEQs. This section describes the spatial distribution of these congeners to assess the potential exposure in each of the segments.

4.3.4.1 Sediment Concentrations and Composition

The highest concentrations of Congeners 077, 118, and 126 were measured in the two sediment samples with the highest total PCB concentrations in Segments 2 and 3, Samples S2-2 and S3-2 (Table 4-7). The contribution of each of these congeners to the total PCB concentration is fairly consistent among sediment samples from all segments implying TEQ exposures proportionate to total PCBs except for sample S3-2. In sample S3-2, the important TEQ congeners are a lower percentage of the total PCBs, although as noted, the concentrations of the individual congeners are high.

4.3.4.2 Smallmouth Bass Fish Tissue Concentrations and Composition

The highest concentrations of PCB Congeners 077, 118, and 126 were also observed in Segments 2 and 3 in juvenile smallmouth bass tissues collected for the 1997 ERA (Table 4-8). Generally the percent total PCB concentration of these congeners was similar among the segments implying a relatively consistent relationship between TEQ concentrations and total PCBs in tissue. Note that the signature of sediment sample S3-2, where the TEQ congeners contributed relatively less to the total PCB concentrations, was not reflected in fish tissue from Segment 3.

4.3.4.3 Comparison with Toxic Equivalent Concentrations Calculated from the WDNR 1994 Fish Tissue Data

TEQ concentrations calculated for fish collected in the WDNR food chain study (Table 4-9) were similar to those calculated for juvenile smallmouth bass collected in 1997 (Table 4-6) in Segments 2, 3, and 5, with PCB Congeners 077, 118, and 126 again comprising the bulk of the total TEQ concentrations. In fish from site-related segments, TEQs for adult, juvenile, and young-of-year smallmouth bass were generally higher than those for longnose dace and white sucker, although the total TEQs in Segment 5 were similar for the longnose dace and smallmouth bass. The TEQs for the smallmouth bass were similar for all age groups except in Segment 2, where the total TEQ concentration for the adult smallmouth bass (38 ng/kg ww) was over twice that of the juvenile and young-of-year smallmouth bass (15 and 14 ng/kg ww, respectively).

In Segment 1, the reference area, the TEQ calculated for the juvenile smallmouth bass was much lower than in the WDNR fish tissue, predominantly because of the higher detection limit of Congener 126 in the WDNR study. In the Segment 1 WDNR fish tissue samples and in many of the WDNR fish tissue samples collected from Segments 2, 3, and 5, Congener 126 was not detected at this higher detection limit. The TEQ concentration for Congener 126 in each of these samples was reported as one-half the detection limit; thus Congener 126 constitutes a large percentage, 28 to 96%, of the total TEQ concentration in these samples.

4.4 EXPOSURE MODELING AND ASSESSMENT FOR FISH

In this section, two methods commonly used to relate concentrations of PCB congeners in fish to concentrations in sediment are discussed, including biota sediment accumulation factors (BSAFs) and bioaccumulation modeling. The relationship between PCB concentrations in tissue and in sediment is important from an exposure perspective and in providing information for future decisions regarding sediment remediation.

4.4.1 Biota Sediment Accumulation Factors

Site-specific BSAFs (kg of organic carbon/kg of lipid) are calculated for nonpolar organic compounds using the formula:

$$BSAF = \frac{C_f / f_1}{C_s / f_{oc}} \qquad \textbf{Eq. 6-1}$$

where:

C_f	=	contaminant concentration in fish
f_1	=	lipid fraction in fish tissue
C_s	=	contaminant concentration in sediment
f_{oc}	=	organic carbon fraction in sediment

BSAFs are derived on a site- and species-specific basis, using empirical data (USEPA 1995d). They incorporate the effects of metabolism, biomagnification, growth, and bioavailability.

4.4.1.1 Biota Sediment Accumulation Factor Methodology

BSAFs for total PCBs were calculated using the 1997 ERA PCB congener data, the WDNR food chain study PCB congener data, and a combination of the two data sets (Table 4-10a). BSAFs for TEQs were calculated using the 1997 ERA data (Table 4-10b).

BSAFs were calculated for Segments 1, 2, 3, and 5 separately because the dams between Segments 1 and 2, 2 and 3, and 3 and 4 prohibit upstream fish passage, although fish passage downstream can occur during floods. Within each segment, fish composites were first lipid normalized then averaged. For sediment, composite samples from the 1997 ERA or single samples from the WDNR food chain study were first TOC normalized, then averaged over the segment. The BSAF using the combined data was calculated by pooling all lipid normalized and TOC normalized data by segment.

Confidence intervals were calculated using bootstrapping, a statistical technique. Bootstrapping is based on the idea that the data at hand are an adequate representation of the population distribution (Manly 1997; Efron and Tibshirani 1993). Many samples of the same size as the original data set are drawn, with replacement, from the available fish and sediment concentrations. The BSAF is calculated for each bootstrap sample. A 90% confidence interval is formed by the 5th and 95th percentiles of the distribution formed by these BSAFs. These intervals were then corrected for bias in the bootstrap sample. The confidence intervals presented in Tables 4-10a and 4-10b were derived using 1,000 bootstrapped samples from the available sediment and tissue concentrations for each segment. The intervals are quite wide, reflecting the large variability in the data, particularly in the sediment concentrations.

4.4.1.2 Biota Sediment Accumulation Factor Results

The results of the BSAF calculations are presented in Tables 4-10a and 4-10b. BSAFs calculated for total PCBs for juvenile smallmouth bass collected in 1997 ranged from 3.1 in Segment 3 to 14 in Segment 1 with confidence intervals ranging from 1.2 to 23. BSAFs for TEQs covered approximately the same range, 3.2 to 14, but were more uncertain with confidence intervals ranging from 1 to 66. For all three fish species collected in the WDNR food chain study, BSAFs ranged from 0.4 to 18, with wide confidence intervals ranging from 0.2 to 43. When the two data sets are combined, the BSAFs show a smaller range from 1.6 to 6.1 with closer confidence intervals, 0.89 to 8.8.

In general the confidence intervals are wide, primarily because of variability in sediment concentrations. In particular, for the 1997 data set with only three sediment composites, a single sample with a high sediment concentration can dramatically affect the overall BSAF. Figure 4-17 shows the range of BSAF values calculated for total PCBs using the bootstrap method and the 1997 ERA sediment and smallmouth bass data. Figure 4-18 shows BSAF bootstrap distributions for total PCBs when sediments from the WDNR food chain study samples are combined with 1997 ERA sediment and smallmouth bass data.

For both data sets, BSAFs calculated for Segment 1, the reference area, were generally much higher and variable than for the site-related segments. BSAFs for Segment 2, nearest Tecumseh Products Company, were generally the lowest. BSAFs from Segments 3 and 5 tended to be intermediate. The TEQ BSAFs calculated using 1997 data basically matched this pattern for all segments except Segment 3, which was very high, similar to the reference BSAF.

The lower BSAFs in the site-related segments relative to the reference area may reflect the more variable concentrations of PCBs in the site segment sediments if sediment with the highest PCB concentrations were selectively sampled.

The range of BSAFs measured for smallmouth bass, longnose dace, and white sucker is comparable to the range reported for freshwater fish and total PCBs in the literature. In Parkerton et al. (1992), median BSAFs are reported for smallmouth bass, yellow perch, carp, brown bullhead, catfish, and sunfish ranging from 2.3 (in yellow perch) to 11.1 (in carp). MacDonald et al. (1993) report a BSAF range of 3.8 to 15.5 for smallmouth bass in seven Ontario lakes.

4.4.2 Bioaccumulation Modeling of the Fish/Sediment Relationship

This section describes the methodology and assumptions used to mathematically describe the relationship between PCB concentrations in juvenile smallmouth bass tissue and PCB concentrations in river sediment utilizing a time-dependent food web model.

4.4.2.1 Modeling the Aquatic Fate of Polychlorinated Biphenyls

A number of modeling approaches are available to describe the relationship between PCB concentrations in Sheboygan River sediments and the PCB concentrations observed in resident fish. The simplest equilibrium partitioning models assume chemical equilibrium in environmental media relative to fugacity, that is contaminant concentrations in environmental media are expected to be proportional to the organic carbon or lipid contents of the media. However, field and experimental studies indicate that aquatic biota, particularly higher trophic-level organisms, are capable of bioaccumulating PCBs at higher concentrations than would be expected from direct equilibrium partitioning between environmental media (Zaranko et al. 1997). Therefore, biomagnification through trophic transfer is an important process that must be considered (Zaranko et al. 1997; Morrison et al. 1996).

4.4.2.2 Description of the Bioaccumulation Model

In order to address the complex and congener-specific relationship between PCB concentrations in sediment and biota, a non-equilibrium time-dependent model was formulated to describe the bioaccumulation of PCB congeners by filter feeding and detritivorous benthic invertebrates and fish. The food chain bioaccumulation model is a dynamic interpretation of the steady state bioaccumulation model originally developed by Gobas (1993) and recently revised to include biomagnification in benthos (Morrison et al. 1997). The model is based on the premise that predominant routes of chemical uptake are through water and consumption of contaminated food, while chemical elimination processes include loss to the water via the gills, loss by fecal egestion, loss by metabolic transformation, and “loss” via growth dilution (Morrison et al. 1997). Furthermore, the model is designed to describe the fate of individual PCB congeners by incorporating congener specific environmental fate data.

The original Gobas models have been verified in a number of aquatic ecosystems and have demonstrated good performance (Gobas 1993; Gobas et al. 1995; Morrison et al. 1996, 1997). The model applied in this study represents an improvement over previous models since it incorporates time-dependent processes, does not assume equilibrium partitioning between sediment and benthic invertebrates, and accounts for benthic invertebrate feeding preferences and strategies. The model was modified from the steady-state equations presented in Morrison et al. (1997) by incorporating changes in organism weight, lipid content, and diet composition over the life span of the organism and by simulating multiple generations or age classes of organisms (Gobas et al. 1995). The model code was further modified by Gobas (pers. comm. 1997a) to accept sediment concentration inputs rather than chemical loadings. The model contains steady-state relationships for all biotic compartments except phytoplankton, accounts for biomagnification, and does not rely on kinetic rate constants (Morrison et al. 1996, 1997).

4.4.2.3 Model Parameterization

Because the model is available in a generic format, it was adjusted to reflect site-specific conditions in the Sheboygan River using conventional chemical, biological, and environmental data. Successful application of the model required reliable data to describe physical attributes of the environment, chemical concentrations in the food web, and food web structure (Morrison et al. 1997). This section outlines the data used to parameterize the model and important modeling assumptions.

Assumption 1: Metabolic transformation of the PCB congeners is negligible.

Metabolic transformation may be ignored since it is considered to be an insignificant route of chemical elimination for most PCBs (Morrison et al 1996; Swackhamer and

Skoglund 1993). Invertebrates and fish have very limited abilities to biotransform PCBs, and when metabolism has been observed in these animals, it has been restricted to lower chlorinated PCB congeners (Morrison et al. 1997) that were not modeled in this ERA.

Assumption 2: Chemical equilibrium exists between river sediments and water.

While the model is designed to model disequilibrium between river sediments and overlying water, recent waterborne PCB concentrations were not available in this study. However, in river ecosystems it is reasonable to initially assume equilibrium between sediment and water (Gobas pers. comm. 1997b).

Assumption 3: The Sheboygan River has achieved a long-term, kinetically controlled steady-state between PCBs in sediment and biota.

Although the model describes time-dependent processes for the food web, the concentrations in sediments were assumed to be constant over the duration of model simulations in this study, which is using PCB congener data from the August 1997 sediment sampling program. Therefore, the modeling implicitly assumes that the observed sediment and tissue concentrations are indicative of a long-term, kinetically controlled steady-state condition, rather than pronounced short-term changes in environmental conditions. The assumption of a prolonged steady-state condition is reasonable given the relatively long chemical half-life in river sediments (Morrison et al. 1996).

Assumption 4: The PCB concentrations measured in sediment from the four Sheboygan River segments are representative of exposure to the juvenile smallmouth bass sampled in those segments.

Since the three dams within the study area lack fish passage facilities, the movements of fish are constrained, although fish passage across the dams is still possible under certain conditions. Furthermore, juvenile smallmouth bass were selected for modeling since they are expected to have greater site fidelity than adults. However, although juveniles are expected to have a relatively low degree of movement, these younger life stages may be more susceptible to being carried downstream during storm events. A major storm occurred in the Sheboygan watershed two months prior to the sampling period; this may have caused translocation of juveniles between segments. Since these perturbances cannot be quantified, the modeling assumes that these events had negligible impact on fish locations, and that sampled fish are representative of the corresponding sediment samples within each segment.

Model parameterization consisted of three major components: 1) chemical properties of selected PCB congeners, 2) environmental properties of media such as organic carbon content, lipid content, and organism weights, and 3) trophic relationships. The parameterization of these components was based on both the literature and site-specific data, and is detailed in Appendix F.

4.4.2.4 Model Application and Verification

Although the model is most suitable for the congener-specific modeling of PCBs, modeling of all 209 PCB congeners was not feasible. Fortunately, a few individual congeners contributed the vast majority of the dioxin-like TEQ concentrations in smallmouth bass tissues. As shown in Table 4-11, three PCB congeners, 077, 118, and 126, collectively contributed more than 90% of the total measured TEQ concentrations, based on toxicity to fish, in all river segments sampled in 1997. When the TEF system for mammalian toxicity (WHO 1997) was applied (Table 4-12), PCB Congeners 105, 118, 126, and 156 contributed more than 90% of the total TEQ concentrations. When the TEF system for avian toxicity (Kennedy et al. 1996) was applied, PCB Congeners 066, 077, 105, 118, 126, and 156 contributed more than 90% of the total TEQ concentrations in all segments except Segment 1, the reference area (Table 4-13). For fish, mammal, and bird TEQs, the percent contribution of each congener varied somewhat between segments, but did not vary considerably within segments. From a modeling perspective, this is desirable, since it indicates that the contamination footprint in fish tissues within each river segment is relatively homogeneous. Also, dioxins and furans measured in Segment 2 collectively contributed less than 8% of the total TEQ concentration. Therefore, the six PCB congeners that were more important in terms of dioxin-like toxicity, 066, 077, 105, 118, 126, and 156, were selected to model.

Model validation was conducted by comparing model simulations of PCB concentrations in juvenile smallmouth bass tissue with measured PCB concentrations in fish sampled in August 1997. Since the patterns of PCB concentrations and TEQ concentrations differed considerably among river segments, each of the six selected congeners was modeled separately for each of the four sampled river segments. Since the model predicts concentrations specifically for juvenile smallmouth bass and the observed data represent composites of different ages of fish, a system of weighting model predictions was required. Based on age-length relationships in smallmouth bass, the sampled fish, ranging in length from 11.6 to 19.4 cm, are expected to represent second-year (age 1+) and third-year (age 2+) smallmouth bass (Scott and Crossman 1973; Lyons pers. comm. 1997b). The length of 15.5 cm was estimated to be the cutoff between second- and third-year smallmouth bass. Therefore, model results for second- and third-year fish were weighted according to the number of fish in each composite of each age. The calculations used to weight model-predicted values are presented in Table 4-14, along with a comparison to observed tissue concentrations.

Predicted versus observed PCB congener concentrations are presented graphically in Figure 4-19. The figure illustrates that the model did a reasonable job of predicting concentrations of PCBs in juvenile smallmouth bass, although certain congeners and segments produced better fit. Overall, the model under-predicted concentrations more often than it over-predicted. Of the six PCB congeners modeled, 077 and 126 exhibited the best model fit. This is desirable since these two congeners, particularly Congener 126, are significant contributors to total TEQ concentrations for fish, mammals, and birds. When fish-based TEQ concentrations are considered, the congener with the poorest fit, 118, contributes the lowest amount to total TEQ concentrations—17%, 13%, 19%, and 23% in Segments 1, 2, 3 and 5 respectively. Of the four river segments, the best fit was achieved in the segment with the highest PCB congener concentrations, Segment 2, while the poorest fit was observed in Segment 1, the reference segment. In Segment 2, most model predictions were within a factor of two of observed composite concentrations for Congeners 077, 118, and 126. In the reference segment, PCB concentrations were underestimated by factors of approximately three to six; this lack of fit is not readily explainable and was also observed in the BSAFs (Section 4.4.1).

Nearly all of the predicted concentrations fell within a factor of five of the ideal fit. This level of model precision may be satisfactory for risk assessment purposes, where order of magnitude uncertainties are not unusual (Frakes et al. 1993). The quality of fit is encouraging in view of the fact that all model parameterization was conducted *a priori,* that is, no model parameters were calibrated to achieve improved fit. It should be noted that the observed data exhibit large differences in field BSAFs among segments (Section 4.4.1); these differences are not supported by corresponding differences in key model components, such as lipid contents, organic carbon contents, or trophic relationships. Therefore, it is possible that lack of fit may be explained by confounding factors related to sampling, rather than to differential levels of biomagnification across river segments.

There are a number of reasons why the model performed satisfactorily in this study:

- The site affinity of the juvenile smallmouth bass is high because of both natural movement limitations and artificial constraints imposed by the dams; therefore, migrations of fish were not a significant issue with the possible exception of downstream movement during flood events. Residence time has proven to be a major source of uncertainty in other modeling studies (Iannuzzi et al. 1996).

- The basic model equations, while generic in nature, have been extensively tested in the Great Lakes region (e.g., Lake Ontario, Western Lake Erie) for PCBs and are therefore readily applicable to the Sheboygan River.

- The negligible metabolism by fish of the PCB congeners studied eliminates a source of uncertainty, since significant metabolism by fish would affect both the depuration rate of PCBs and the concentration reached at steady-state.

- An abundance of site-specific data, including the WDNR food chain study and 1997 ERA data, were available to parameterize key model components such as lipid contents, high resolution PCB concentrations, and sediment TOC, to which the model is sensitive (Iannuzzi et al. 1996).

- Since the model is time-dependent, changes in dietary composition as fish age were explicitly incorporated. This may be particularly important for juvenile fish such as smallmouth bass, since dietary composition changes substantially over time in younger fish.

The results from this modeling exercise demonstrate important exposure pathways of PCBs to fish within the Sheboygan River and are used in Section 6.2 to estimate concentrations of PCBs in sediments that would be protective of fish.

4.5 EFFECTS ON FISH

This section presents the "benchmark" selection process for fish. To evaluate effects of PCBs on fish, concentrations of PCBs in fish associated with adverse effects were compiled from the literature. Literature was reviewed for PCB tissue residue effects concentrations with an emphasis on NOAELs and LOAELs for development, reproduction, and survival. PCB tissue residue effects concentrations were evaluated two ways to present the most complete picture possible—toxicity based on total PCBs and toxicity associated with dioxin-like PCB congeners using a TEQ approach, as described in Section 2.3.1.

In the following section, Section 4.6, these effects concentrations are compared to measured tissue concentrations in fish to evaluate potential risk. For PAHs, tissue effects concentrations are not relevant since fish rapidly metabolize and excrete PAH compounds (Varanasi et al. 1989). Instead, effects on fish from PAHs were evaluated from an exposure perspective, discussed in Section 4.6.2.

4.5.1 Total Polychlorinated Biphenyls Effects Concentrations

The literature was reviewed for studies which related concentrations of total PCBs in fish tissue to ecologically relevant effects in fish, specifically those associated with reduced reproductive success including larval fish mortality and larval growth. Eighteen studies were identified and details are presented in Table 4-15. Note that a large number of other studies are available that examined other endpoints such as biochemical alterations, some with lower effects concentrations. However, the ecological significance of these effects is more speculative.

The studies presented in Table 4-15 cover a wide range of test conditions, species types, and endpoints. The studies can be split into two groups. The first group comprises the studies with a field component. These studies include fish that have been exposed to PCBs and other contaminants under field conditions or fish that have been exposed to contaminated sediment or food that contained PCBs and may have also contained other contaminants. The second group of studies include laboratory studies with either dietary or water exposures to unweathered PCBs only.

In the ten studies with a field component, NOAELs and effects concentrations were all less than 14 mg/kg ww, except in the study by Bengtsson (1980) which reported an effects concentration of 170 mg/kg ww in whole body cyprinid minnows with number and hatchability of ova, delayed spawning, and premature hatching as the endpoints. The lowest effects concentration was 0.12 mg/kg ww in Baltic flounder ovary corresponding to a reduction in viable hatch (von Westernhagen et al. 1981). This effects concentration was lower than the range of NOAELs reported in these studies. However, it was similar to effects concentrations reported in three other field studies (Mac and Edsall 1991; Spies et al. 1985; and Hogan and Brauhn 1975).

For laboratory studies, two studies reported effects concentrations less than 32 mg/kg ww. Hendricks et al. (1981) reported an effects concentration of 1.6 mg/kg ww in rainbow trout eggs for reduced growth of fry, and Hansen et al. (1974) reported an effects concentration of 5.1 mg/kg ww in sheepshead minnow eggs for decreased fry survival. Otherwise, the effects concentrations ranged from 32 mg/kg ww to 429 mg/kg (assumed ww) for effects ranging from reduced egg hatch to fry mortality. Note that in the remaining laboratory studies, PCB concentrations were measured in a variety of tissues. In several studies, concentrations were measured in whole-body tissue; in others, concentrations were measured in back muscle or unspecified tissue. Effects concentrations were also measured in dead fry (Mauck et al. 1978) or as terminal residues (Nebeker et al. 1974). Also, the endpoints evaluated in several of these studies represent fry mortality and are likely to be much less sensitive than studies measuring concentrations in eggs and assessing reproductive endpoints such as hatching success and larval survival. The lack of consistency among these studies in terms of the tissues measured for PCB concentrations and the toxicity endpoints makes it difficult to interpret these studies in the same way as the studies that measured concentrations in eggs and evaluated reproductive effects endpoints.

Selecting a single tissue residue effects benchmark from this distribution of studies is subjective. As mentioned above and discussed further in the uncertainty section (Section 4.7.2), these studies represent a wide range of test conditions, exposures, types of PCBs, fish species, and effects endpoints. Therefore, the 10^{th} and the 50^{th} percentile effects concentrations were used in the risk characterization. Use of these percentiles does not imply that these concentrations are protective of all fish species. Instead, these percentiles are used as a guide to evaluate the potential for effects based on studies reported in the literature. The median (50^{th} percentile) value should be considered to represent a concentration above which effects are likely to be observed. These percentiles were calculated for effects concentrations measured in eggs and separately for the distribution of effects concentrations measured in tissue (mostly whole-body). For effects concentrations in eggs and ovaries, the 10^{th} and 50^{th} percentiles are 0.19 mg/kg eggs and 2.2 mg/kg eggs; for effects concentrations measured in tissues, the 10th and 50th percentiles are 25 mg/kg and 170 mg/kg. This division of effects concentrations is necessary so comparisons to measured whole-body tissue concentrations and calculated concentrations in eggs can be made in the risk characterization (Section 4.6). Only concentrations with observed effects were included in these distributions. A total of six NOAELs were also reported in these studies. The four NOAELs measured in eggs were within the range of effects concentrations measured in eggs and were very similar to the effects concentrations reported in the same four studies. One of the two NOAELs measured in tissue (5.3 mg/kg) was lower than the range of effects concentrations measured in tissue (13.7–475 mg/kg) and will also be evaluated in the risk characterization section.

4.5.2 Toxic Equivalents

Seven studies were identified with 2,3,7,8-TCDD fish tissue concentrations associated with reduced reproductive success and juvenile mortality or reduced growth (Table 4-16). Since the 2,3,7,8-TCDD concentration is equal to TEQ (i.e., its TEF is 1), these tissue concentrations are discussed as TEQ tissue concentrations. All studies were conducted in the laboratory, with no field component. Most of the studies involved waterborne exposures of eggs. NOAELs ranged from 23 ng/kg ww in lake trout eggs (Walker et al. 1994) to 1,190 ng/kg ww in northern pike eggs (Elonen et al. 1998). LOAELs ranged from 50 ng/kg ww in lake trout eggs (Walker et al. 1994) to 2,000 ng/kg ww in zebrafish eggs (Elonen et al. 1998).

Since the exposure conditions and endpoints for these studies were less variable than those for the total PCBs studies discussed above, the lowest NOAEL and lowest LOAEL were selected as benchmarks, 23 ng/kg and 50 ng/kg in lake trout eggs, respectively (Walker et al. 1994). Lake trout is the most sensitive species tested to date, and thus its NOAEL should be protective of all site fish.

4.6 FISH RISK CHARACTERIZATION

In this section, potential risks to fish are evaluated for PCBs and PAHs. For PCBs, measured total PCBs and TEQ concentrations in whole body tissue and calculated concentrations in eggs are compared to effects concentrations to evaluate the potential for adverse reproductive effects in fish. For PAHs, data from Schrank et al. (1997) were reviewed for cause and effects relationships and measured sediment concentrations of PAHs were compared to sediment concentrations associated with adverse effects in fish as cited in WDNR (1992a).

4.6.1 Potential Risks to Fish from Polychlorinated Biphenyls

To calculate potential risks to fish, a hazard quotient (HQ) approach was utilized to compare mean and 95% UCL concentrations of PCBs measured in fish collected in the 1997 ERA and in 1994 for the WDNR food chain study to effects and no effects concentrations reported in the literature. HQs are defined as the ratio of the measured concentration to the effects or no effects concentration.

HQ values of 1 or less are interpreted as an exposure resulting in negligible risk of adverse effects in receptor species. HQ values greater than one generally indicate risk, although they must be reviewed in the context of the degree of protectiveness and uncertainty built into the exposure calculations and effects studies.

To compare concentrations of PCBs measured in whole-body fish tissue from the Sheboygan River to no effects and effects concentrations reported in the literature, some conversions were required to calculate HQs. Two types of conversions were conducted—juvenile or young-of-year tissue concentrations were converted to predicted adult tissue concentrations and adult tissue concentrations were converted to predicted concentrations in eggs. These conversions were required because most of the no effects and effects concentrations were measured in adults or eggs.

Two factors, R_{C_1} and R_{C_2}, were used in these conversions, as shown in the equations below:

$$C_{adult} = R_{C_1} \times C_{\text{young-of-year or juvenile}}$$

$$C_{egg} = R_{C_2} \times C_{adult}$$

where R_{C_1} is the ratio of the mean concentration of TEQs or total PCBs in the adult to that in young-of-year or juvenile fish. For smallmouth bass, R_{C_1} is 1.5 for the adult to juvenile ratio and 1.3 for the adult to young-of-year ratio for total PCBs and is 1.9 for the adult to juvenile ratio and 3.6 for the adult to young-of-year ratio for TEQs based on the combined results of the WDNR food chain study and the 1997 ERA. For white sucker, the adult to young-of-year ratio is 1.1 for total PCBs and is 1.0 for TEQs. R_{C_2} is the mean concentration of PCBs in eggs of smallmouth bass and white sucker divided by the mean concentration of PCBs in adults observed by Niimi (1983); R_{C_2} is 1.2 and 0.57 for smallmouth bass and white sucker, respectively (Niimi 1983).

These conversions were applied to segment-specific mean and 95% UCLs of total PCB and TEQ concentrations measured in smallmouth bass and white sucker to predict adult and egg concentrations for the various size classes collected (Tables 4-17 and 4-18). Concentrations of PCBs measured in longnose dace during the WDNR food chain study were not converted because adults were collected and lipid ratios between adult dace and their eggs were not available. Thus, the concentrations in dace were only compared to whole-body no effects and effects concentrations for total PCBs.

4.6.1.1 Total Polychlorinated Biphenyls

HQs were calculated to evaluate potential risks to fish from total PCBs. HQs were calculated using predicted egg concentrations (Table 4-19) and measured and predicted concentrations in adult whole-body tissues (Table 4-20). HQs were calculated using the 10th and 50th percentile total PCB effects concentrations (Section 4.5). HQs were also calculated using the lowest whole-body no effects concentration because this concentration was lower than all the concentrations associated with effects in adult fish (Table 4-15). An analogous no effects concentration was not available for studies which measured total PCBs in eggs, that is, there was an effects concentration lower than the lowest no effects concentration; thus, HQs were not calculated for a no effects concentration in eggs.

HQs for smallmouth bass and white sucker were very high using the predicted concentrations in eggs (Table 4-19). For smallmouth bass in Segments 2, 3, and 5, they ranged from 95 to 290 with the 10th percentile effects concentration and from 8.2 to 25 using the 50th percentile effects concentration. HQs were generally higher in Segments 2 and 3 relative to Segment 5. For white sucker in these segments, HQs ranged from 16 to 58 and from 1.4 to 5.0 using the 10th and 50th percentile effects concentrations, respectively (Table 4-19). All HQs for white sucker in Segment 1 were less than or equal to 1, whereas they were less than or equal to 4.5 in Segment 1 for smallmouth bass.

HQs calculated using predicted or measured concentrations in adults relative to effects and no effects concentrations reported in whole-body tissues were much lower (Table 4-20). Relative to effects concentrations, the highest HQ for smallmouth bass was 1.8 and most were less than 1. All HQs relative to whole body effects concentrations were less than 1 for the white sucker and the longnose dace. Relative to the lowest whole body no effects concentration reported in the literature, however, the HQs based on the mean measured concentration exceeded 1 for all three species outside of the reference area, with maximum values of 8.5, 3.8, and 4.3 for smallmouth bass, white sucker, and longnose dace, respectively.

4.6.1.2 Toxic Equivalents

HQs for fish were also calculated for no effects and effects concentrations of dioxin-like PCB congeners using the TEQ approach. Predicted concentrations in smallmouth bass and white sucker eggs were compared to the lowest no effects and effects concentrations reported in the literature (Table 4-21). The range of HQs is similar to that reported for the whole-body no effects and effects concentrations for total PCBs, discussed above. For smallmouth bass in Segments 2, 3, and 5, the HQs ranged from 0.48 to 4.1 and from 0.22 to 1.9 using the lowest NOAEL and LOAEL, respectively. HQs were generally higher in Segments 2 and 3 relative to Segment 5, and HQs were less than 1 in Segment 1. All HQs calculated for the white sucker were less than 1 in all segments.

4.6.1.3 Combined Polychlorinated Biphenyl and Toxic Equivalent Assessment

The results for all three approaches used to calculate HQs for PCBs—based on total PCB concentrations in eggs, total PCB concentrations in whole-body adult fish, and TEQ concentrations in eggs—indicate potential reproductive effects in fish, particularly in Segments 2 and 3, where the PCB concentrations are most elevated. The risk appears to be greater for smallmouth bass than for either the white sucker or longnose dace, probably because smallmouth bass are at a higher trophic level and have higher relative lipid content in their eggs. The large range in HQ values derived from the three approaches reflects the high degree of uncertainty in the tissue residue effects benchmarks.

4.6.2 Potential Risks to Fish from Polycyclic Aromatic Hydrocarbons

PAHs were retained as COCs for fish because of previously measured concentrations of PAH biliary metabolites in white suckers collected from the lower Sheboygan River (Schrank et al. 1997). The presence of metabolites was indicative of exposure to PAHs. Schrank et al. (1997) collected white sucker from Segment 6 and evaluated fish health by measuring several biochemical parameters, histology of selected organs, and contaminant residues and metabolites. The study found that fish from Segment 6 had significantly lower hematocrits, significantly induced EROD activity, higher biliary metabolites of PAHs, higher tissue concentrations of PCBs, and a greater number of hepatic lesions and other histopathological abnormalities than reference fish. The study demonstrated that white suckers residing in the lower segments of the river absorbed PAHs and PCBs and also exhibited hematological, biochemical, and histological alterations.

Since it is difficult to determine whether these effects are because of PAH exposure, PCB exposure, or a combination of the two, the potential for impacts on fish due to PAHs was assessed in terms of the sediment PAH concentrations measured at Triad sampling stations throughout the river (Figure 3-1). Correlations between sediment PAH concentrations and neoplasms in feral fish, and/or the induction of neoplasms in bullheads by exposure to contaminated sediment extracts, support the hypothesis that some fish neoplasms and chronic responses result from exposure to carcinogenic chemicals, mainly PAHs, present in the fish's environment (Baumann et al. 1982; Black et al. 1980; Baumann 1984; Baumann et al. 1991). The sediment PAH concentrations measured at the Triad sampling locations were compared to sediment PAH concentrations measured at locations around the Great Lakes in which benthic fish had elevated tumor frequencies (Table 4-22). Note that these sites probably also contained PCBs as well. None of the measured PAH concentrations in the Sheboygan River exceeded the minimum concentrations of these compounds associated with elevated tumor frequencies in fish in the studies reported in Table 4-22. However, in a recent study of an estuarine flatfish species, the prevalence of liver lesions was correlated to sediment concentrations of total PAHs of 0.23–2.8 mg/kg dw (Horness et al. 1998). The elevated frequency of lesions and other alterations in white suckers collected from the lower Sheboygan River reported by Schrank et al. (1997) indicates that adverse effects may be occurring that are related to PAHs and possibly other contaminants, such as PCBs, in the river.

4.7 FISH UNCERTAINTY

To put potential risk to fish in context, uncertainty in evaluating fish exposure and COC effects must be evaluated. This section discusses these uncertainties.

4.7.1 Fish Polychlorinated Biphenyl Exposure Uncertainty

The major uncertainties affecting the assessment of fish exposure to PCBs include the sediment data used in the food web model and the calculation of TEQ concentrations.

Fish exposure to PCBs was assessed by measuring total PCBs (as a sum of congener concentrations) and dioxin TEQs (estimated from TEFs for coplanar PCB congeners) in fish and sediment composites. Collection of composite samples is a cost-effective way to include more samples from each segment, but it reduces the amount of information on the variability of individual samples.

The bioaccumulation modeling assumes that the measured sediment concentrations represent the average sediment exposure for fish in a given river segment. Collection of a limited number of sediment samples from an area such as the Sheboygan River that has highly variable PCB concentrations, particularly in Segments 2 and 3, has the potential for not accurately characterizing the overall exposure within a segment; for example, hot spots may be over- or under-represented. Since fish are exposed to sediment throughout an area, misrepresenting the distribution of sediment concentrations encountered by the fish may affect the development of predictive relationships to sediment (Section 6.2).

Depositional areas were targeted for sediment collection since they generally contain the highest PCB concentrations, and thus are critical in fish exposure. It is assumed that PCBs in the depositional areas are most important for determining the average PCB exposure to fish via all exposure pathways within a river segment. However, this emphasis should not be interpreted to imply that fish only reside or feed within depositional areas. Longnose dace, for example, are known to be riffle dwellers.

A few areas of uncertainty are specific to the calculation of TEQ concentrations. TEFs for fish are available for six dioxin congeners (including 2,3,7,8-TCDD which has a TEF of 1), 10 furan congeners, and 12 PCB congeners. In general, TEFs for the dioxin and furan congeners are much higher than those for PCB congeners. However, dioxin and furan congeners contributed only 6.3 to 8.5 percent of the total TEQ concentration in three juvenile smallmouth bass composite samples collected from Segment 2 (Table 2-6). Because they were not measured in fish samples from other river segments, dioxin and furan concentrations were not included in the TEQ calculations in this risk assessment. If it is assumed that dioxins and furans contribute the same percentage of total PCBs in all site fish, TEQ concentrations in fish may have been underestimated by approximately 8.5%.

In addition, all PCB congeners were measured for which TEFs for fish are available, except for Congener 081. Since it was not measured, the Congener 081 contribution to TEQ concentrations was assumed to be negligible. Assuming no metabolism or preferential bioaccumulation and exposure to an Aroclor 1248 type pattern, of which Congener 081 is about 0.02% by weight (Frame et al. 1996), Congener 081 would have contributed about 4.8% of the total TEQ based on the TEQ calculated for a Segment 2 fish composite, including contributions from dioxin and furan compounds. Thus, by not measuring Congener 081, TEQ may be underestimated by about 5%. Therefore, the TEQs used in the risk calculation for fish, which were calculated only for those PCB congeners measured, may be underestimated by approximately 13%.

TEQs calculated for the WDNR food chain study data may be biased high for the measured coplanar PCB congeners, because of the higher detection limits used for these congeners compared to the 1997 ERA PCB analysis and the use of one half the detection limit for undetected congeners in the TEQ calculation.

4.7.2 Fish Polychlorinated Biphenyl Effects Uncertainty

Determining tissue residue effects concentrations for fish based on the limited information available in the published literature is complicated by a number of factors including:

- Differences in species sensitivity
- Differences in tissues analyzed
- Conversions of concentrations measured in whole-body to concentrations in eggs
- Differences in exposure scenarios in laboratory and field studies
- Lack of consistency in the endpoints evaluated
- Differences in methods of PCB analysis

4.7.2.1 Differences in Species Sensitivity

For the evaluation of the reproductive impairment and survival effects from tissue residue concentrations of total PCBs, a number of published studies are available for a variety of fish species. A wide range of effects concentrations are reported in these studies. The exposure conditions, PCB measurements, and effects endpoints vary among these studies, making it difficult to evaluate the importance of interspecies differences in sensitivity to PCBs. In general, it appears that salmonids are more sensitive than minnows. Since the Sheboygan site provides habitat for a variety of fish species, effects concentrations were included from all relevant studies regardless of the specific fish species studied.

Toxicity data on dioxin exposure are not available to compare to estimated dioxin TEQs in Sheboygan River fish for any of the selected fish receptors. Elonen et al. (1998) recently showed that TEQ NOAELs for reproductive effects varied by as much as six fold in different freshwater fish species. The lake trout NOAEL used in this ERA is an order of magnitude lower than any of the NOAELs for the seven freshwater fish species studied by Elonen et al. (1998). Therefore, it is likely that using an effects concentration based on TEQs for lake trout is protective of site fish.

4.7.2.2 Tissue Type

Eight of the 19 effects concentrations for total PCBs and nine of the ten TEQ NOAELs are based on concentrations in eggs. Concentrations in "mature" eggs may be the most relevant concentration for assessing maternally transmitted PCBs to the developing embryo (Walker and Peterson 1994). Whole-body fish tissue was analyzed as part of the 1997 ERA sampling and the WDNR food chain study. Because many of the lowest total PCB effects concentrations and all but one of the TEQ NOAELs are based on concentrations measured in eggs, it is important to evaluate the uncertainty introduced through estimating the total PCB or TEQ concentration in eggs based on measurements of whole-body concentrations.

Mac et al. (1993) measured the concentrations of PCB congeners in adult whole-body tissue and eggs from lake trout from Lake Michigan. In these fish, the total PCB concentrations were 3 to 9 times higher in the whole-body samples than in eggs from the same fish. It is important to note, however, that the concentrations in whole-body lake trout and their eggs were approximately equal on a lipid normalized basis. Thus, the relative lipid contents of whole-body tissue and eggs may be a key factor in determining the relative PCB concentrations.

Studies used in the total PCBs effects analysis that measured PCB concentrations in eggs reported reproductive effects in a variety of fish species, including lake trout, rainbow trout, chinook salmon, sheepshead minnow, Baltic flounder, winter flounder, and starry flounder. The differences among species in relative distribution of lipid content in eggs versus whole-body fish may be an important factor in species sensitivity to lipophilic compounds like PCBs. For example, the percent lipid in whole-body adult lake trout is higher than that in their eggs, while the reverse is true for smallmouth bass. Additional research is required to resolve the toxicological implications of these species-specific relationships.

The conversion from PCB concentrations measured in whole-body samples of adult fish to the estimated concentration in eggs (Section 4.6.1) was based on a study conducted by Niimi (1983) that reported mean PCB concentrations in gravid female smallmouth bass and white suckers and mean PCB concentrations in eggs of these species. These mean concentrations had high associated standard deviations, which increases the uncertainty of this extrapolation. In addition, applying this conversion ratio to Sheboygan River fish that were collected in the summer and fall, as opposed to pre-spawning, is also somewhat uncertain.

4.7.2.3 Field vs. Laboratory

Both laboratory and field studies have advantages and disadvantages. While a true field study incorporates field conditions and exposure scenarios, cause-and-effect relationships can be difficult to verify because of the common presence of multiple contaminants. In laboratory studies, although cause and effect are easier to validate, field exposure conditions are not incorporated and complications associated with mixtures of contaminants are not addressed.

Most of the studies with a field component involved collection of mature female fish with eggs that were exposed to PCBs via maternal transfer; the eggs were brought to the laboratory where they were measured for various reproductive endpoints. In the field, exposure to elevated PCB concentrations would be quite different than that in the studies evaluated to determine effects concentrations. For example, developing larvae in the environment would continue to be exposed to PCBs in water and food.

Most of the laboratory studies are based on short-term exposure, and may underestimate exposure and risk. For example, of the TEQ benchmarks, many, including the lake trout NOAEL, were derived using 48-hour static water exposure of fertilized eggs.

Fish used in field studies to assess reproductive effects may have been exposed to a variety of contaminants in addition to PCBs. In the parts of the Sheboygan River, PAHs are also elevated and have a similar mechanism of action involving the activation of aryl hydrocarbon hydroxylase (Niimi 1994). Further research needs to be conducted on contaminant mixtures before the effects of multiple contaminant exposures can be fully understood.

4.7.2.4 Type of Endpoint

Reproductive endpoints, including hatching success and larval mortality and growth, are among the most sensitive and ecologically relevant endpoints, and thus these endpoints were the focus of the fish assessment. A variety of different reproductive endpoints such as egg hatchability, larval survival, fecundity, and larval growth, as well as different species, types of PCBs, and exposure scenarios were used in the studies included in the tissue residue effects analysis. Although there may be other sensitive and ecologically relevant endpoints such as the sublethal effects (delayed time to hatch, mild hemorrhaging, and moderate yolk-sac edema) observed in rainbow trout by Wilson and Tillitt (1996), associated tissue effects concentrations are not available.

4.7.2.5 Total Polychlorinated Biphenyls vs. Toxic Equivalents

With total PCBs, uncertainty arises from different analytical and summing techniques used to calculate total PCBs and from exposure of test species to different combinations of PCB congeners than the site-specific mixture at the Sheboygan River site. In addition, many of the laboratory effects studies included in the total PCBs assessment used unweathered Aroclor mixtures. Although coplanar PCBs are found at relatively low concentrations in the commercial Aroclor mixtures, several have been identified as important components of PCB tissue residues in aquatic biota and may be preferentially accumulated, particularly by higher-trophic-level organisms (Safe 1984; Hansen 1987; Kannan et al. 1988; Smith et al. 1990). Thus, PCBs in higher-trophic-level organisms may be more biologically active than the commercial mixtures (Parkinson and Safe 1987; Smith et al. 1990). However, utilizing the total PCBs approach is valuable because it exposes fish to all PCB congeners in combination. Some congeners not included in the TEQ scheme, such as Congeners 052, 128, 138, 153, and 180, which are often present in much higher concentrations than coplanar congeners, may also be responsible for reproductive effects (ACOE 1988).

The calculation of TEQs assumes additivity in the contribution of individual PCB congeners to the reproductive effects endpoints. While the additive, synergistic, or antagonistic interactions among congeners have not been clearly established for fish (Ankley et al. 1991), several recent studies (Zabel et al. 1995a,b; Newsted et al. 1995) have indicated that additivity is a reasonable assumption at environmentally relevant ratios. In addition, TEF values have been determined for only a few fish species (most values are based on studies with rainbow or lake-trout), and may be species-specific (Kim and Cooper 1997).

4.7.3 Uncertainty in the Polycyclic Aromatic Hydrocarbon Analysis

Although PAHs are known to cause adverse effects in fish, methodologies to quantify this risk are still being developed. The use of sediment concentrations associated with elevated rates of neoplasia in fish to screen sediment PAH concentrations has been used by some researchers, but still suffers from co-occurring contaminant issues. In addition, the database that was used for this purpose contained a limited number of values. Ecological significance of neoplasms in fish populations has yet to be firmly established, and no information is currently available for determining sediment effects concentrations for other, possibly more sensitive endpoints such as reproductive impairment and immune dysfunction.

5.0
PISCIVORE EVALUATION

Mink and great blue heron were selected as representative species to evaluate potential risk to piscivorous species residing at the Sheboygan River and Harbor Site. This section presents the approach used to model their exposure, the derivation of literature-based effects doses or toxicity reference values (TRVs), and the risk characterization and associated uncertainty.

5.1 PISCIVORE EXPOSURE ASSESSMENT

In Section 2.6, exposure profiles were presented that described habitat use, feeding behavior, and seasonal movements of each ROC. These factors are all important in regard to routes and duration of exposure. The following sections describe the development of a food web model to predict exposure and the data used in the assessment. Finally, data used to quantify exposure, including the rationale for the data selected, are presented.

5.1.1 Food Web Model Approach

The objective of this food web model was to predict the exposure to COCs that mink and great blue heron would encounter through feeding on aquatic organisms from the Sheboygan River. The food web modeling was used to calculate a total daily dose of the COCs as a result of consumption by the ecological receptor species.

The structure of the food web model is:

$$IR_T = \sum \frac{(C \times I \times BF)_x \times EF}{bw} \qquad \textbf{Eq. 5-1}$$

where:

IR_T = total rate of COC ingestion (mg/kg body weight [bw] day ww)
C_x = concentration of the COC in medium × (mg/kg ww)
I_x = rate of ingestion of medium (mg or kg/day ww)
BF_x = relative bioavailability factor of the COC from medium × (unitless)
EF = proportion of study area relative to entire home range of receptor species (exposure fraction, unitless)
bw = body weight of receptor species (kg)

The equation was expanded to specify each of the three ingested media identified:

$$IR_T = (C \times I \times BF)_{fish} + (C \times I \times BF)_{crayfish} + (C \times I \times BF)_{sediment/soil} \qquad \textbf{Eq. 5-2}$$

To parameterize the model, a substantial number of diet studies presented in USEPA (1993c) were reviewed and applicable studies retained based on the following criteria (Tables 5-1 and 5-2):

- Appropriate measurements were made (e.g., percent volume, percent frequency of occurrence)
- The data were collected from similar habitats
- The data were collected at an appropriate time of year

To address the assessment endpoint of reproduction, dietary studies that were conducted during this critical life stage were selected. For instance, the aquatic prey that were considered included those items that mink would be feeding on during the reproductive seasons of spring, summer, and early fall. The resulting parameters that were incorporated into this food web model are presented in Table 5-3.

In addition to the ingestion rates and dietary components previously discussed, temporal exposure and bioavailability were also considered. Mink, if present, would be expected to use the site for the entire year (chronic exposure) and the Sheboygan River shoreline would encompass their entire home range (exposure fraction 1.0). Great blue heron likely only use the site during the summer and migrate during winter; however, their exposure duration is also considered chronic because they are on-site for at least as long as the duration of the toxicity test (10 weeks) used to develop the avian TRV. An exposure fraction of 1.0 was also assumed for the great blue heron because the size of the site would likely exceed the size of the herons' home range or feeding territory during the summer.

5.1.2 Tissue Data Used in the Food Web Model

The study area was separated into three major river sections for the piscivore assessment. Segment 4 was excluded because it was not sampled. One section consists of Segments 2 and 3, and the other section consists of Segments 5 and 6. These river segments were treated separately because of distinctly different habitat types. Segment 1 was included as the reference area. Data collected from each river section were grouped accordingly. These river sections and data groupings will be referred to as Segments 2/3 and Segments 5/6.

The tissue concentrations used in the model were both the 95% UCLs of the means of the sections and the mean concentration to "bound" the exposure between an average and more conservative concentration. All data were converted to a wet weight basis in order to predict exposure of ROCs in the environment, and samples were only used in the TEQ calculations if all relevant TEF congeners were measured.

Tissue Data ¾ The data used in the food web model included total PCB concentrations in small mammals from Segments 5 and 6, crayfish, and fish collected by WDNR in 1994 as part of the WDNR food chain study and fish collected for the 1997 ERA. Because available information indicated that the diets of mink and great blue heron feeding in riverine environments (Alexander 1977) do not include macroinvertebrates, the emergent and larval insect data collected by WDNR were not used in the analysis.

The COC concentration data for smallmouth bass were evaluated to select data sets for use in the food web model. The smallmouth bass diet evolves as the fish grows until this species is ultimately piscivorous (Scott and Crossman 1973). This change in diet may affect the level at which contaminants are bioaccumulated. The smallmouth bass collected in WDNR studies and in the 1997 ERA encompassed a range of sizes and life stages including young-of-year, juvenile, and adult. Mink and great blue heron primarily consume small fish (Tables 5-4a, 5-4b); to avoid over-estimating the daily dose by incorporating tissue concentrations from large fish, the tissue data were evaluated and no consistent relationship was found between PCB concentrations in young-of-year or juvenile bass tissue and size. Therefore, only adult fish were excluded, because of size alone. The selected bass data were then combined with those from longnose dace and young-of-year white sucker for use in the model. Tissue data were grouped by river section (Segment 1, Segments 2/3, and Segments 5/6) to develop exposure concentrations. All tissue data and calculated exposure point concentrations used in the food web model are presented in Tables 5-5 and 5-6.

Sediment Data ¾ Because of the feeding behavior of ROCs and their prey, sediment was considered a minor component (2%) of the mink diet (Table 5-3) and not important in the great blue heron diet. All available sediment data were used to develop exposure point concentrations for mink (Table 5-7). The sediment data were converted from dry weight to wet weight concentration using the percent solids for each location collected in the 1997 ERA (percent solids data were not available for the WDNR food chain study). Sediment data and calculated exposure concentrations used in the mink food web model are presented in Table 5-7.

5.1.3 Dietary Exposure Results

Total dietary ingestion of TEQs and total PCBs was calculated using Equation 5-1 (Section 5.1.1) and the exposure parameters in Table 5-3. As described above, total dietary intake of total PCBs and TEQs was calculated for fish and crayfish, and total PCB intake was calculated for small mammals, the important prey items in the diet of the ROCs. The intake of PCBs through incidental sediment ingestion was also estimated for the mink. Results of the dietary exposure calculations are presented in Tables 5-8 and 5-9.

Mink¾ Mink feeding in Segments 2/3 of the Sheboygan River had the greatest estimated exposure to TEQs and total PCBs regardless of whether the concentrations were considered as the 95% UCLs or as the mean concentrations. Mink inhabiting the reference area had lower exposure to TEQs and two orders of magnitude lower exposure to total PCBs than mink inhabiting Segments 2/3 or Segments 5/6. The mink dietary exposure concentrations for total PCBs calculated using the 95% UCL were generally similar to those calculated using the mean concentrations at all locations.

Great blue heron¾ The pattern of TEQ and total PCB ingestion by the great blue heron was estimated to be similar to that of the mink, with the highest exposure from Segments 2/3 and the lowest from the reference area (Tables 5-8 and 5-9). It was estimated that great blue heron consume a TEQ concentration of approximately 100 ng/kg bw day more when total ingestion is calculated using the 95% UCL rather than the mean concentrations for Segments 2/3 and 5/6. The great blue heron dietary exposure concentrations for total PCBs calculated using the 95% UCL were similar to those calculated using the mean concentrations at all locations.

While feeding at the Sheboygan River, great blue heron ingest more TEQs than mink by approximately one order of magnitude. This difference is attributed to the higher TEFs for PCB congeners for birds than for mammals (Table 2-5).

5.2 EFFECTS ON BIRDS AND MAMMALS

This section presents a discussion of the studies that were the basis for the TRVs used to quantify effects in the mink and great blue heron. TRVs were compiled for both total PCBs and TEQs.

TRVs for the TEQs referenced to the toxicity of 2,3,7,8-TCDD, and total PCBs were selected from the literature and are summarized in Tables 5-10a and b. Details on the derivation of the TRVs are presented in Tables 5-11 and 5-12. The TRVs for TEQs and total PCBs were derived from recent studies in which mink and chickens, the surrogate for great blue heron, were fed carp collected from Saginaw Bay (Heaton et al. 1995; Summer et al. 1996 a,b).

The TRVs for mink were selected from a study conducted by Heaton et al. (1995). In this study, reproductive effects were evaluated by feeding adult mink carp collected from the mouth of the Saginaw River. PCB-contaminated carp were fed to mink in various proportions to arrive at a diet containing PCB concentrations of 0.015, 0.72, 1.53 and 2.56 mg/kg diet. Adult mink were fed the experimental diet for up to 182 days and kits were fed the same diet for 21 days. Even the lowest dietary dose resulted in a significant reduction in gestation duration, kit body weight, and kit survival at 3 and 6 weeks of age. The data generated in this study and the results of the H4IIE bioassay were used to develop NOAELs and LOAELs for total PCB and TEQ concentrations. The NOAEL was generated using the dietary total PCB concentration fed to the control group (0.015 mg/kg diet) with a corresponding TEQ concentration of 1.03 ng/kg. The NOAEL-based daily doses used to quantify exposure and characterize risk to mink from TEQs and total PCBs were 0.2 ng/kg bw day and 0.004 mg/kg bw day, respectively (Heaton et al. 1995; Tillitt et al. 1996). The LOAELs are 4 ng/kg bw day for TEQs and 0.146 mg/kg bw day for PCBs.

The TRVs developed for the great blue heron were derived from feeding studies conducted by Summer et al. (1996a,b). The studies were conducted with Babcock white leghorn chickens which were fed carp collected from Saginaw Bay at three treatment levels—control (no carp), low-dose (3.5% carp in diet), and high-dose (34% carp in diet). Control groups were fed the control diet for 2 weeks, and the low- and high-dose treatment groups were fed test diets from week 3 through week 10 (Summer et al. 1996a). The measured total PCB concentrations in the diet were 0.3, 0.8 and 6.6 mg/kg ww, respectively for the three treatments. The TEQ concentrations in the diet, derived using TEFs from the H4IIE bioassay, were 0.4, 4.5, and 45 ng/kg ww. The carp also contained various pesticides in concentrations ranging from <0.07 to 92.3 *m*g/kg ww.

The high-dose treatment resulted in an 18% decrease in the mean hatchability of eggs laid in weeks 6 through 10, and a 230% increase in overall deformity rate in embryos and chicks during weeks 1 through 10 compared with controls. There was no effect on hatchability in the low-dose treatment, but the overall deformity rate increased 36% compared with the control (Summer et al. 1996b). Based on these results, the high-dose treatment was considered the LOAEL, and the low-dose treatment the NOAEL. The categorization of the low-dose treatment as an approximation of the NOAEL is reinforced by considering the rates of multiple deformities—increased by 340% over the control in the high-dose treatment, but only by 36% in the low-dose treatment. The overall embryo and chick deformity rates during weeks 1 through 10 were 17% for the control group, 24% for the low-dose group, and 40% for the high-dose group (Summer et al. 1996b). The NOAELs were 0.046 mg/kg bw day for PCBs and 2.9 ng/kg bw day for TEQs; the LOAELs were 0.4 mg/kg bw day for PCBs and 28 ng/kg bw day for TEQs.

Because chickens appear to be more sensitive to PCBs than other avian species tested, uncertainty factors to account for species sensitivity were not used to adjust the NOAELs for great blue herons (USEPA 1993d).

The TEQ approach for PCBs was based on the assumption that the toxicity of individual PCB congener concentrations may be expressed in terms of the equivalent toxicity of a particular concentration of 2,3,7,8-TCDD. A number of TEF values have been developed to calculate 2,3,7,8-TCDD equivalent concentrations for fish, birds, and mammals exposed to PCB congeners. Since these TEF systems yield different TEQ concentrations for the same set of PCB data, it is very important to identify the TEF system applied and to ensure consistency in the application of the TEF values throughout the assessment.

As previously discussed (Section 2.3.4), TEFs developed by WHO (Ahlborg et al. 1994) and TEFs calculated using the CEH bioassay (Kennedy et al. 1996) were used to calculate 2,3,7,8-TCDD equivalent exposures for mink and great blue heron, respectively. These TEF values were selected primarily because 1) they are specific to birds and mammals, 2) a robust data set was incorporated to develop the mammalian values (Ahlborg et al. 1994), and 3) the CEH TEFs corresponded well with the 2,3,7,8-TCDD equivalent concentrations calculated from great blue heron egg residue concentrations and the CEH bioassay results. The application of these TEFs requires that toxicity benchmark values be calculated using equivalent TEF systems.

In the studies discussed above, the TEF values used in the dietary toxicity tests were estimated based on the H4IIE bioassay. Because the H4IIE-based TEF systems were used in these literature studies but the CEH-based and WHO systems were used in the exposure assessment, it was necessary to recalculate the TRVs to be consistent with the exposure assessment. TEQs were recalculated using the WHO and CEH TEFs in the piscivore assessment instead of the H4IIE-based TEFs used in the original studies (Table 5-13). The corresponding recalculated NOAELs and LOAELs are presented in Table 5-14. These recalculated NOAEL and LOAELs were used as the TRVs to quantify risk to mink and great blue heron in this ERA.

The potential error resulting from the use of inconsistent TEF systems in the TEQ calculations for exposure and effects assessment is large, since the calculation of a TEQ is sensitive to the TEF system applied. The CEH-based and WHO TEF systems assign higher TEFs for all dioxin-like PCB congeners, which dominated the TEQ in the tissues measured during the current study, relative to the H4IIE bioassay system (Table 5-15). As a result, identical PCB exposure concentrations yield total TEQs which are approximately 3 and 10 times greater than those calculated using the H4IIE TEFs (Table 5-13) for mammals and birds, respectively.

5.3 PISCIVORE RISK CHARACTERIZATION

In this section the total dietary exposure is compared with the NOAEL and LOAEL-based TRVs to determine the potential for adverse reproductive effects in mink and great blue heron. Using both NOAEL and LOAEL-based TRVs provides a range of the magnitude of exceedance for comparative purposes. Total dietary exposure calculated in Section 5.1.3 was compared with the TRV using an HQ approach (USEPA 1992, 1996b). The comparisons were expressed as a ratio of the predicted total exposure dose to the effects dose (Equation 5-3). The results of the HQ calculations are presented in Tables 5-16 and 5-17 and Figures 5-1 and 5-2.

$$HQ = \frac{IR_T}{TRV} \qquad \textbf{Eq. 5-3}$$

where:

IR_T	=	total rate of contaminant ingestion (ng/kg bw day ww for TEQs; mg/kg bw day ww for total PCBs)
TRV	=	Toxicity reference value (ng/kg bw day for TEQs; mg/kg bw day for total PCBs)

Mink **¾** Using the NOAEL TRVs, the mink HQs for TEQs were greater than 25 using either the mean or 95% UCL concentrations at all locations evaluated in the Sheboygan River, including the reference area (Table 5-16). The LOAEL-based mink HQs for TEQs ranged from 2.2 to 14 using the 95% UCL data. The TEQ HQs resulting from calculations with mean dietary concentrations were 59% to 86% of the 95% UCL concentrations.

Using the NOAEL-based TRVs for total PCBs, the HQs exceeded 600 for mink at Segments 2/3 and Segments 5/6. The HQs for total PCBs were 10 or less at the reference area regardless of whether the mean or 95% UCL concentrations were used (Table 5-17).

Great blue heron **¾** The HQs calculated for great blue heron TEQs were greater than 10 in both Segments 2/3 and Segments 5/6, using either the NOAEL or LOAEL-based TRVs and ranged up to 290 using the 95% UCL concentration and the NOAEL-based TRV (Table 5-16). As with mink, the HQ resulting from exposure to mean dietary concentrations were 59 to 87% of the HQs derived from the 95% UCL concentrations. The NOAEL- and LOAEL-based HQ values for great blue heron TEQs calculated for the reference area were all below 12.

For total PCBs, only the HQs for the NOAEL-based TRVs exceeded 10 in Segments 2/3 and 5/6 (Table 5-17). The NOAEL-based total PCB HQs were not substantially greater using the 95% UCL concentrations than using the mean concentrations.

Discussion ¾ The magnitude of the HQ values indicates that both mink and great blue heron are likely to suffer adverse reproductive effects as a result of feeding in the aquatic environment of the Sheboygan River based on the exposure assumptions used in the risk assessment. Considering the magnitude of the HQs using the NOAEL-based TRVs, and the exceedance of the LOAEL-based HQ for Segments 2/3, mink are likely suffering adverse reproductive effects from dietary consumption of PCBs, particularly in Segments 2/3 but also in Segments 5/6 and possibly in the reference area. This conclusion is consistent for exposure calculations using both 95% UCL and mean concentrations. Mink are highly susceptible to reproductive effects when exposed to low concentrations of PCBs in the diet as indicated by the low TRV for TEQs of 0.2 ng/kg bw day. A mink threshold dietary TEQ concentration of 1.9 ng/kg ww, as reported by Tillitt et al. (1996), was exceeded by both the mean and 95% UCL TEQ concentrations in all segments, adding to the weight of evidence that mink are being adversely affected. This data, coupled with the fact that WDNR has reported that no mink have been trapped in the area over the past several years, would suggest that mink are not reproducing in habitats along the lower Sheboygan River. The total PCB HQs for mink in Segments 2/3 and 5/6 are approximately 2 to 5 times greater than the TEQ HQs. In the reference area, the TEQ HQs for mink are greater than the total PCB HQs.

Using the TEQ approach, heron and mink appear to be at approximately equal risk of suffering adverse reproductive effects (Table 5-16). The NOAEL-based HQs for TEQs ranging from 130 to 290 clearly indicate a risk to great blue heron and other piscivorous birds feeding at the study sites. The likelihood of great blue heron to be at risk when feeding on aquatic organisms from the reference area is much lower than in Segments 2/3 and 5/6 based on the exposure assumptions used in this assessment. However, when TEQ concentrations in tissues measured from the reference area are directly compared to literature values there is some basis for concern; a NOAEL dietary TEQ concentration of 10 ng/kg reported by Summer (1992) was exceeded by one order of magnitude in fish collected from the reference area (Table 5-6).

For heron, the HQs calculated using the TEQ approach are approximately 3 to 4 times greater than the HQs calculated using the total PCB approach in Segments 2/3 and 5/6. The CEH assay is a reliable predictor of the potential for reproductive effects in birds and has been used to evaluate great blue heron. Since the congener-specific analysis provided a precise measure of the toxic congeners (except Congener 081), and a reliable TEF data set was used, the NOAEL-based HQs of 130 to 290 are cause for concern for piscivorous birds.

The dietary parameters used to predict exposure for this species are likely representative of the proportion of aquatic components in the diet. As with mink it is clear that great blue heron or other aquatic feeding birds would likely have lower reproductive rates if they consumed aquatic organisms from the Sheboygan River over a chronic exposure period.

5.4 PISCIVORE UNCERTAINTY

5.4.1 Piscivore Exposure Uncertainty

Uncertainty associated with the exposure assessment relates primarily to development of the food web model. The major uncertainties associated with the exposure assessment are as follows:

Tissue Data: Data were missing to quantify certain components of the mink and heron diet. For mink, amphibian tissue data were not available to estimate the dose associated with approximately 3% of the diet. Since these prey organisms are aquatic and dwell in riparian areas, they may also have elevated PCB tissue concentrations.

Assimilation Efficiency: To calculate the normalized ingestion rate for mink and great blue heron based on their diet, it was necessary to obtain the prey assimilation efficiency from the literature. These values were not always available. For instance, because the great blue heron/crayfish-specific assimilation efficiency was not available from the literature, it was necessary to select a rate from a similar combination of waterfowl/aquatic invertebrate. Use of surrogate assimilation efficiencies may affect the estimation of the normalized ingestion rates calculated for a receptor species.

Dietary Composition: The dietary composition of the receptor affects its normalized ingestion rate because each prey item has an associated gross energy (kcal/g ww) value, and each receptor/prey item combination has a different assimilation efficiency. Since site specific data were not available to develop the diets of mink and great blue heron, the dietary composition was developed from a literature review. The diet composition was based on only one study deemed to be the most representative of site conditions. Therefore, the total dietary PCB intake may be over- or underestimated.

Ingestion rate: Only one dietary study was used to develop dietary exposure parameters, and, based on reviews of other summaries of mink diet from various habitat types, fish ingestion varies from approximately 30 to 95% of the diet; therefore, estimating PCB ingestion assuming only consumption of fish might result in an overestimation of the PCB contribution from this pathway.

PCB congener data: PCB Congener 081 was not measured in fish tissue. This congener is one of the most toxic to birds. Since the Congener 081 TEF for birds is one of the highest, the total TEQ will be underestimated as discussed in Section 4.7. Exclusion of dioxins and furans likely only has a minor effect on the total TEQ (Table 2-6).

5.4.2 Piscivore Benchmark Uncertainty

Uncertainty associated with the TRVs that were selected relates primarily to the toxicity information available for the receptor species. The major uncertainty associated with the benchmark selection includes the following:

***Toxicity Reference Values*:** A dietary toxicity test using chicken as the test species was selected to predict risk to great blue herons. Because chickens are sensitive to the effects of PCBs, using them as a surrogate for the great blue heron may overestimate risk. An attempt was made to minimize the overestimation, however, by not adjusting the TRV using a species sensitivity or allometric scaling factor.

Carp collected from Saginaw Bay were used in the dietary toxicity test to develop the TRV for mink and great blue heron. In addition to PCBs, a number of pesticides were detected in those fish. It is not known if a synergistic effect of the chemical mixture influenced the response of mink in this study.

Toxicity Equivalency Factors: The particular TEF values selected may have a large influence on the total TEQ, depending on the congener pattern in the media under investigation. It is critical that the most appropriate TEF values be used to quantify exposure concentrations for a risk assessment, and that the same TEF values be used to calculated the effects and exposure concentrations. Different TEF systems may specify individual congener TEFs which vary by orders of magnitude. Some of this variability is the result of differences in congener-specific toxicity among receptors, e.g. birds versus rodents; other variability in TEFs may be attributed to uncertainty in receptor-specific TEFs.

Two sets of TEF values are available for birds—the WHO values (Ahlborg et al. 1994) and the CEH TEF values developed by Kennedy et al. (1996). The CEH TEFs were used in this ERA and not the WHO TEFs. To evaluate the potential impact of this decision, the following discussion presents the ramifications of not using the WHO TEFs and therefore, the overall effect on the calculation of risk to the great blue heron.

In the effects assessment, a threshold TEQ (TRV) for birds was recalculated using the CEH assay TEF system and the toxicity test congener data from the Summer et al. (1996a,b) study (see Section 5.2). This recalculated TEQ is 4 times greater (51.2 ng/kg) than it would be had the WHO TEF scheme been used (13.6 ng/kg); this results in a recalculated TRV (using data from Summer et al. 1996a,b) which is 3 times greater using the CEH TEFs than the recalculated TRV based on the WHO TEFs. This results in a total TEQ exposure concentration approximately 3 times higher when using the CEH TEFs rather than the WHO TEFs and the fish data from the current study. However, the final HQs are roughly equivalent because the recalculated TRV would also be 3 times higher. Therefore, in the effects assessment, the CEH assay was less conservative then the WHO TEFs developed for birds. When using congener data from fish collected during the current study and both sets of avian TEFs, the total TEQ calculated for the exposure assessment would have been 3300 ng/kg and 1200 ng/kg using CEH TEFs and WHO, respectively.

In this assessment the CEH TEFs were selected to quantify exposure to great blue heron. This particular TEF scheme does not have TEF values for all the dioxin and furans (Table 5-15). Therefore, using these TEFs to recalculate the TRV underestimates the effects dose to which the chickens were exposed, although probably not by much. For example, using the WHO TEF scheme, if TEFs for the dioxin and furan congeners were assumed to be zero, the resultant TEQ in the NOAEL diet only changes from 13.6 to 12.0 ng/kg.

The use of either TEF scheme has a few additional uncertainties. The use of TEFs does not account for antagonistic or synergistic interactions between congeners and therefore may underestimate the risk to wildlife. It should also be noted that the TEQ approach fails to account for toxicity of PCB congeners which have a different toxicological mechanism. Additionally, TEFs are not available for all congeners which have Ah receptor active compounds, therefore, the use of TEF may underestimate risk since an unknown TEF value is implicitly assigned a value of zero. For example, for PCB Congener 114, the WHO and H4IIE schemes have TEF values of 0.0001 and 0.000001, respectively, while a TEF for PCB Congener 114 is unavailable in the CEH TEF scheme. Therefore, if PCB Congener 114 is an important congener in the site-specific PCB mixture, the TEQ will be underestimated if the CEH TEF scheme is used.

6.0
PROTECTIVE SEDIMENT CONCENTRATIONS FOR RECEPTOR SPECIES

One of the objectives of this ERA is to identify concentrations of COCs in sediment that, if achieved over the home range of ROCs, would be protective of ROCs. Several possible methods are available to calculate these sediment concentrations for the protection of benthic invertebrates, fish, and piscivore health. These methods are explored in this section to provide risk managers with additional information to consider when evaluating remedial options.

6.1 BENTHIC INVERTEBRATES

Data from the Triad assessment and a comparison of that data to available freshwater sediment guidelines were considered for the derivation of contaminant concentrations in sediment that are protective of benthic invertebrates. This section presents an analysis of these two potential methods.

6.1.1 Triad Interpretation

A contaminant concentration-biological effects gradient could not be established, as discussed in Section 3.5. Therefore, the data collected for the Triad alone cannot be used to derive defensible contaminant concentrations in sediment for the protection of benthic invertebrates. However, as discussed in Section 6.1.2, the data are generally consistent with available sediment quality guidelines; therefore, these values can be used to provide guidance in establishing concentrations for the protection of benthic invertebrates. PCB concentrations in sediment that are protective of fish and piscivores are derived in Sections 6.2 and 6.3.

6.1.2 Comparison to Sediment Quality Guidelines

This section compares selected sediment quality guidelines, or benchmark concentrations, to the synoptic toxicity test and chemistry data from the Sheboygan River Triad assessment detailed in Section 3.5. The purpose of this comparison is to evaluate the potential utility of several sediment quality guidelines in predicting sediment toxicity in the Sheboygan River, to provide an indication of corresponding false positives and false negatives, and to determine if the site data are consistent with the guidelines derived from larger databases which include data from many freshwater sites.

These benchmarks were not developed for use as cleanup criteria, rather they were derived with varying intended interpretations, as described in Section 3.4.1. The intent of this discussion, therefore, is to provide risk managers with an overview of the potential ramifications of using different sediment quality benchmarks as protective sediment concentrations. For example, a TEL is meant to be a concentration below which toxicity is rarely observed. This does not mean that if toxicity is not observed in a sediment with COC concentrations greater than the TEL, that the TEL was not predictive.

6.1.2.1 Methods

USEPA (1996a) evaluated benchmark values relative to their potential to:

- Correctly classify toxic samples as toxic
- Correctly classify non-toxic samples as not toxic
- Incorrectly classify non-toxic samples as toxic
- Incorrectly classify toxic samples as not toxic

A sample is considered correctly classified if 1) the sample had a chemical exceedance of a benchmark and was toxic, or 2) the sample did not have a chemical exceedance of a benchmark and was not toxic. Samples are considered incorrectly classified if either 1) the benchmark comparison predicts toxicity but the sample is not toxic (false positive; Type I error), or 2) the benchmark comparison does not predict toxicity, but the sample is toxic (false negative, Type II error).

Table 6-1 shows toxicity-test results along with sediment benchmark exceedances for nine matrices—three sediment benchmarks (TEL, PEL, and NEC) for each of the three chemical groups evaluated (metals, PAHs, and PCBs). Toxicity was calculated in two separate ways, by statistical comparison to the reference samples and to the negative control. Total biomass was used as the growth endpoint rather than mean individual growth in this evaluation since individual growth and survival were negatively correlated.

TELs, PELs, and NECs used in this comparison were derived from the lowest of the 14- or 28-day *Hyalella azteca* bioassays described in USEPA (1996a) and as shown in Table 3-5. A benchmark is said to be exceeded if any of the COCs in its group exceed their respective benchmark. For example, if lead exceeded its TEL, the metals TEL was said to be exceeded. If none of the metals exceeded its TEL, then the metals TEL was said to be not exceeded.

A matrix is presented for each contaminant group and for each benchmark type based on a comparison to negative controls and reference stations (Tables 6-2 and 6-3). These matrices are then used to calculate the number of stations correctly classified and the number of false positives and false negatives. Results of both comparison methods are presented to show two possible ways of interpreting the toxicity data.

6.1.2.2 Discussion

By definition, TELs are intended to minimize false negative errors (Type II errors) as compared to PEL and NEC values. That is, the percent of samples that is toxic but contains COC concentrations lower than their respective TELs is minimized. This is important because the consequence of false negative errors in protective sediment concentrations is that toxic areas will not be identified for potential remedial action.

On the other hand, NEC values are intended to minimize false positive errors (Type I errors) as compared to TELs, and PELs are intended to fall in the middle, balancing Type I and II errors. Minimizing false positives is also important because the impact of these errors in decision making is that non-toxic areas will be identified as toxic and potentially remediated unnecessarily.

Thus, the ideal protective sediment concentration would minimize both false positive and false negative errors. As shown in Table 6-2, when evaluating toxicity based on the negative control comparison, the use of TELs for metals was better than PELs or NECs for correctly predicting toxicity and minimizing both false positive and false negatives. The use of either PELs or NECs for metals resulted in a high percentage of false negatives, thus underestimating risk. For PAHs, TELs and PELs were better at minimizing both the false positives and false negatives, whereas the use of the NEC would result in a high percentage of false negatives. For PCBs, use of any of the benchmarks resulted in relatively high percentages of correctly classified samples and relatively low percentages of false positives or negatives.

Statistical comparisons to reference were complicated by the high mortality observed in two of the reference stations, which resulted in only one of the site samples being classified as toxic. When toxicity is based on statistical comparison to the reference (Table 6-3), the use of TELs for metals would result in only 36% correctly classified and 64% false positives, which could overestimate risk to benthic invertebrates. Use of either PELs or NECs for metals would result in a high number of correctly classified samples and very low percentages of false positives and false negatives. For PAHs, the use of TELs or PELs would overestimate risk because of the high number of false positives, whereas use of the NECs would result in 79% correctly classified samples and relatively lower numbers of false positives and false negatives. All of the benchmarks for PCBs would overestimate risk because of the high number of false positives.

This assessment provides risk managers with an evaluation of the potential ramifications of applying benchmark values for metals, PAHs, or PCBs as sediment concentrations protective of benthic invertebrates.

6.2 FISH

This section presents the calculation of contaminant concentrations in sediment that are protective of fish. Because of the high uncertainty in the BSAFs calculated in Section 4.4.1, protective sediment concentrations were calculated using the time-dependent bioaccumulation model used to relate the concentration of PCB congeners in fish tissue to that in sediment, as discussed in Section 4.4.2. This method can be used to calculate a protective sediment concentration by setting the concentration in fish equal to an acceptable risk threshold and then back calculating a segment-specific contaminant sediment concentration for the protection of fish.

Assuming a consistent contribution of PCB Congeners 077, 118, and 126 within each segment, the acceptable aggregate TEQ contribution of these three congeners was determined as follows:

P_i = proportion of TEQ posed by PCBs 077, 118, and 126 in Segment *i*
TEQ_T = toxicity threshold total TEQ concentration (ng/kg fish eggs)
$P_i \times TEQ_T$ = TEQ_P (maximum acceptable TEQ from PCBs 77, 118, and 126 only)

For example, in Segment 3, the three PCB Congeners 077, 118, and 126 contributed approximately 93% of the total fish TEQ (Table 4-12); therefore the TEQ_P value would be determined by multiplying the total TEQ threshold by 0.93.

Assuming that each individual PCB congener contributes a consistent amount to total TEQ within each segment, as is apparent in the 1997 sampling data, then acceptable individual PCB congener concentrations may be back-calculated on a segment-specific basis. This is accomplished by using the proportion of TEQ posed by the specific congener in place of P_i in the above equation. The acceptable PCB congener concentration is the TEQ, for that congener only, divided by the TEF for that congener. The bioaccumulation model is used to back-calculate to a corresponding protective sediment concentration for each of the three specific PCB congeners.

Table 6-4 presents the derivation of protective sediment TEQ concentrations for fish using the Walker et al. (1994) study as an estimate of the threshold effects concentration in fish. Since concentrations in fish eggs are roughly proportional to tissue concentrations when expressed on a lipid weight basis (Gobas pers. comm. 1998), the TEQ NOAEL from Walker et al. (1994) derived for eggs was applied to fish tissue. This analysis assumes that the threshold effects concentration (wet weight) for TEQs in smallmouth bass eggs is equivalent to that observed in lake trout eggs in the Walker et al. (1994) study (23 ng/kg ww). Since smallmouth bass have higher egg lipid contents than lake trout, this threshold TEQ concentration in smallmouth bass would be lower on a lipid-normalized basis than that of the lake trout studies in Walker et al. (1994); nevertheless total concentrations (instead of lipid normalized concentrations) were conservatively used to establish a smallmouth bass benchmark because of uncertainty concerning the toxicological relevance of a lipid normalized egg benchmark.

Since the selected toxicological benchmark for TEQs in smallmouth bass is based upon egg concentrations rather than tissue concentrations, two adjustments were necessary in the development of a protective sediment concentration:

- Since egg concentrations reflect maternal transfer of contaminant, consideration was given to the relative concentration expected in adult tissues compared to eggs. Niimi (1983) showed that PCB concentrations (ww) in smallmouth bass eggs are on average 1.2 times greater than in adult tissue. Therefore, a scaling factor of 1.2 was applied to account for this difference.

- Maternal transfer of PCBs to eggs reflects partitioning between adult tissue and eggs. Since juvenile smallmouth bass were used in the sampling program and the bioaccumulation modeling, an adjustment is required to account for the fact that adult smallmouth tissue concentrations exceed those in juveniles. The 1997 ERA and WDNR food chain study indicated that the ratio of TEQ in adults to juveniles was 1.9 (Section 4.6); therefore this factor was applied to account for age-dependent bioaccumulation differences.

Both adjustments result in lower protective sediment concentrations (i.e., more protective); the combined scaling factor was 2.3. A sample calculation is provided below for PCB Congener 126 in Segment 3:

Threshold total TEQ in fish eggs (NOAEL TEQ) = 23 ng/kg egg ww

Congener portion of TEQ (i.e., proportion of TEQ contributed by PCB Congener 126 in Segment 3) ($P_{S3,\ PCB126}$) = 0.45

Congener partial TEQ (i.e., threshold TEQ for PCB Congener 126 in fish eggs in Segment 3) ($TEQ_{S3,\ PCB126}$) = NOAEL TEQ $\times$ ($P_{S3,PCB126}$) = 23 $\times$ 0.45 = 10.35 ng/kg egg TEQ

Fish PCB TEF value for PCB Congener 126 (TEF_{PCB126}) = 0.005

Egg benchmark concentration of PCB Congener 126 for smallmouth bass ($E_{S3,\ PCB126}$) = (TEQ_{S3}, PCB_{126})/ (TEF_{PCB126}) = (10.35)/(0.005) = 2,070 ng/kg egg = 2.07 μg/kg egg

Egg to adult tissue extrapolation: 2.07 μg/kg egg ÷ 1.2 (egg to adult tissue concentration ratio) = 1.73 μg/kg adult fish tissue value for PCB Congener 126 ($A_{S3,PCB126}$)

Adult to juvenile fish extrapolation: 1.73 μg/kg adult fish tissue ÷ 1.9 (adult to juvenile concentration ratio) = 0.91 μg/kg juvenile fish tissue value for PCB Congener 126 ($J_{S3,PCB126}$)

Lipid and organic carbon normalized biota-sediment accumulation factor for PCB Congener 126, calculated using food-web bioaccumulation model for juvenile smallmouth bass (Model $BSAF_{PCB126}$) = 3.078

Back-calculated protective sediment concentration for PCB Congener 126 in Segment 3 (NOAEL $PSC_{S3,\ PCB126}$) = ($J_{S3,\ PCB126}$ × Sediment TOC fraction) ÷ (Fish lipid fraction × Model $BSAF_{PCB126}$) = (0.91 μg/kg × 0.04) ÷ (0.029 × 3.078) = 0.41 μg/kg

As shown in Table 6-4, the protective sediment concentrations derived for all congeners in Segments 1 and 5 in the 1997 ERA sampling program are higher than the observed mean composite concentrations, indicating that the sediments within these segments of the Sheboygan River are unlikely to pose health risk to the resident fish species from dioxin-like effects of PCBs. The concentrations of Congeners 077, 118, and 126 in Segment 2, and PCB Congener 077 in Segment 3 were higher than the NOAEL-based protective sediment concentrations. The concentration of PCB Congener 077 in Segment 2 was also marginally above the LOAEL-based protective sediment concentration.

Bioaccumulation modeling for total PCBs was not conducted in this study. Modeling of the entire PCB mixture is possible and has been performed in similar studies; however the results are less reliable than congener-specific analyses since the 209 PCB congeners exhibit a variety of chemical properties which govern fate. For example, PCBs have octanol water partition coefficients that range from log K_{ow} 4.40 for monochlorobiphenyl to log K_{ow} 8.18 for decachlorobiphenyl (Rapaport and Eisenreich 1984; Hawker and Connell 1988). Therefore, modeling of total PCBs requires either congener-specific modeling of a large number of PCB congeners that contribute significantly to total concentration, or modeling of PCBs as a single contaminant. The latter approach requires simplifying assumptions and approximation of chemical fate properties for the mixture as a whole; the former approach is time intensive and costly.

Furthermore, when PCBs are modeled on a total basis, care must be exercised in the selection of toxicity benchmarks for use in establishment of a protective sediment concentration, since different PCB mixtures may have differing toxicological properties (Sections 4.5 and 4.7). Therefore, instead of conducting bioaccumulation models for total PCBs, total PCB protective sediment concentrations were estimated based on linear regression between individual congener concentrations and total PCBs in sediments, as discussed in Section 6.4.

6.3 PISCIVORES

Sediment contaminant concentrations protective of mink and heron can also be back-calculated using a combination of the food web model discussed in Section 5.1 and the bioaccumulation model discussed in Section 4.4.

6.3.1 Methodology for Calculation of Protective Fish Concentration for Piscivores

To calculate a protective sediment concentration for piscivores, a protective fish concentration is first required. The wildlife exposure food web model was used to develop a protective TEQ concentration in fish for piscivorous birds and mammals. The results of this calculation can be used as the input parameters to the fish bioaccumulation model to back-calculate to a protective sediment concentration.

6.3.1.1 Protective Fish Concentration

Protective fish concentrations were calculated for both mink and great blue heron. Fish consumption was the only dietary exposure pathway considered in this analysis because the purpose of the protective fish concentration calculation was to provide the key input parameters for the fish bioaccumulation model. The fish ingestion rates and TEQ TRVs are the same as those outlined in Sections 5.1 and 2.7.4, respectively.

A protective fish concentration was calculated using the following equation:

$$\text{Protective fish concentration} = \frac{bw \times TRV}{IR_{fish}} \qquad \textbf{Eq. 6-1}$$

Where:

bw = Body weight of the receptor species

TRV = TEQ toxicity reference value

IR_{fish} = Ingestion rate of fish

The fish tissue concentrations which are considered safe as consumptive values for mink and great blue heron are presented in Table 6-5.

6.3.1.2 Uncertainty

Great blue heron are primarily piscivorous but mink have a more varied diet, which includes fish, terrestrial species, and aquatic mammals. The amount of fish in the mink diet varies depending on the habitat, season, and availability of other prey. The revised food web model considers only fish; therefore, the actual protective sediment concentration will relate only to the fish component of the diet. This assumption may over or underestimate the total TEQ concentration to which mink are exposed depending on the TEQ concentrations in the other components of their diet, and the actual amount of fish consumed.

Mink and great blue heron feed on a variety of small littoral zone fish species. Contaminant concentrations in sediment that are protective of piscivores were derived using the fish bioaccumulation model, which was only developed for smallmouth bass; using this model made it necessary to assume that mink and great blue heron consume only smallmouth bass. This assumption may result in an under- or overestimation of exposure because other prey species may accumulate different contaminant concentrations in their tissues than smallmouth bass.

6.3.2 Fish Tissue to Sediment Extrapolation

The results of the piscivore food web modeling described above may be combined with the food-web bioaccumulation model to derive protective sediment concentrations for piscivores. As outlined in Section 6.2.2, the model may be used to back-calculate from "safe" fish tissue concentrations to a corresponding threshold concentration in sediments. There are two primary differences in the application of the bioaccumulation model to piscivores versus fish. The first difference is that the threshold concentration for piscivores is a concentration in their food rather than in their tissue. The second difference is in the TEFs applied to fish tissue concentrations; since fish, mammals, and birds exhibit different levels of toxic response to individual PCB congeners, different TEF schemes are used for fish (Walker and Peterson 1991), mammals (Ahlborg et al. 1994), and birds (Kennedy et al. 1996). The differences emphasize the importance of assessing PCB contamination on a congener-specific rather than total PCBs basis.

In deriving protective sediment concentrations using the food web model, a fundamental assumption is that the percentage contributions of individual PCB congeners must remain relatively consistent throughout each sampling segment. The fish tissue samples collected in August 1997 suggest that within each sampling segment, the pattern of congener-specific contributions to total TEQ is reasonably consistent (Appendix A-1, Table A1-7).

Consistency in PCB composition across sampling segments is less important since inter-segment differences may be accounted for by modeling PCBs on a segment-specific basis.

The relative importance of individual congeners (Section 2.3.1) varies for different piscivorous receptors (i.e., mammals and birds) because of the different TEF systems. Therefore, protective sediment concentration derivation for avian and mammalian piscivores requires the modeling of a different suite of PCB congeners for each receptor category. For mammals, contributions of greater than 5% of total TEQ are noted for PCB Congeners 126, 118, 156, 105, and 115 (in decreasing order of importance). In birds, contributions of greater than 5% of total TEQ are noted for PCB Congeners 066, 077, 105, 118, 126, and 128.

The following equations summarize the procedure that was employed to back-calculate sediment contaminant concentrations protective of piscivores from acceptable fish tissue concentrations. The BSAF value described is based on the food-web bioaccumulation model, rather than on the empirically observed field BSAF, as described in Section 4.4.1.

TEQ_T	=	threshold total TEQ concentration in dietary fish derived from piscivore food web model (ng/kg); note that the TEF system used to develop the benchmark TEQ concentrations must be consistent with that used to estimate the exposure TEQ
$P_{i,j,k}$	=	congener portion of TEQ (i.e., proportion of TEQ in Segment *i* posed by PCB Congener *j* for piscivore *k;* unitless fraction)
$TEQ_{i,j,k}$	=	congener partial TEQ (i.e., benchmark TEQ in Segment *i* from PCB Congener *j* for piscivore *k;* ng/kg fish)
	=	$P_{i,j,k} \times TEQ_T$ (ng/kg fish)
$TEF_{j,k}$	=	toxic equivalency factor for PCB Congener *j* for piscivore *k*
$C_{i,j,k}$	=	fish tissue benchmark in Segment *i* for PCB Congener *j* to protect piscivore *k*
	=	$TEQ_{i,j,k} / TEF_{j,k}$
$BSAF_{i,j}$	=	predicted biota-sediment accumulation factor (lipid and organic carbon normalized) in Segment *i* for Congener *j*, using the food-web bioaccumulation model for the prey fish species
$PSC_{i,j,k}$	=	($C_{i,j,k} \times$ Sediment TOC fraction) / (Fish lipid fraction $\times$ Model $BSAF_{i,j}$)

Results of the protective sediment concentration derivation for mink and great blue heron are provided in Tables 6-6 and 6-7, respectively. Results are provided for both NOAEL and LOAEL-based protective sediment concentrations. Although LOAEL-based protective sediment concentrations are not protective in the sense that they are based on a food concentration which is presumed to cause a significant adverse effect, they provide information to help bound the true threshold concentration. Because of the wide spacing of dose levels in the piscivore toxicity studies selected (NOAELs are 10 and 20 times lower than the LOAELs for birds and mammals, respectively), there is a wide range over which the threshold protective sediment concentration may lie. Therefore, while a protective sediment concentration based on the NOAEL should be protective of piscivore health, a protective sediment concentration between the NOAEL and LOAEL may or may not be protective, depending on the shape of the dose-response curve.

Unlike the fish health endpoint, piscivore protective sediment concentrations are exceeded for all congeners in Segments 2, 3, and 5, which is consistent with the high HQs for these receptors. For both birds and mammals, protective sediment concentrations are exceeded by the observed sediment concentrations by more than two orders of magnitude in some cases. Furthermore, for some congener and segment combinations, even observed background concentrations of PCBs exceed protective sediment concentrations based on NOAELs. The low protective sediment concentrations for piscivores reflect the high sensitivity of the test organisms, particularly when compared to fish. Because chickens and mink are known to be very sensitive to dioxin-like toxicity, it is unlikely that other piscivores would require lower protective sediment concentrations than those presented.

It is important to note that the protective sediment concentration values identified do not represent concentration thresholds that must be met by all sediments within a given segment. Instead, they represent mean exposure concentrations for fish species that are assumed to be protective for piscivores. Therefore, some river sediments may exceed the protective sediment concentration values, provided there are sufficient sediments below the protective sediment concentrations to compensate. Also, it may be acceptable for the protective sediment concentration for a specific congener to be exceeded by a small amount, provided that other congeners exhibit concentrations below their respective protective sediment concentrations, since the parameter of most interest is the total TEQ concentration. However, if the assumption of consistency in congener composition holds true within each segment, the ratio between observed sediment PCB concentrations and protective sediment concentrations should be approximately equal for all congeners. If this pattern is found to be consistent over time, in theory it is possible to monitor dioxin-like toxicity of Sheboygan River sediments using only a single congener, preferably one that contributes significantly to total TEQ, such as Congener 126. Another option is to use the congener data set to extrapolate to total PCB concentrations as discussed in Section 6.4.

6.4 PROTECTIVE SEDIMENT CONCENTRATIONS

The preceding sections focused on estimating protective sediment concentrations for fish, great blue heron, and mink on a congener-specific basis. With additional assumptions, protective sediment concentrations can also be estimated on a total PCBs basis.

NOAEL- and LOAEL-based total PCB protective sediment concentrations for each segment and each receptor were estimated using the protective sediment concentrations for each congener, as developed in Sections 6.2 and 6.3, and estimated linear regression coefficients. The regression approach is based on the consistent congener pattern observed in sediment and tissue within each segment (Section 4.3.2). However, the sediment sample in Segment 3 with 38 mg/kg dw total PCBs was not included in the regressions because its congener pattern was quite different from the other sediment samples, perhaps due to the influence of dechlorination processes. Samples from the reference area, which had very low total PCB concentrations and different PCB congener patterns, were also excluded from this analysis.

The estimated total PCB protective sediment concentrations are shown in Tables 6-8, 6-9, and 6-10. Protective total PCB concentrations in sediment ranged from 3.7 to 25 mg/kg dw for fish, from 0.14 to 0.97 mg/kg dw for great blue heron, and from 0.050 to 1.5 mg/kg dw for mink. An example of the linear regression is shown in Figure 6-1 and an example calculation is given below.

Example:

The estimated linear regression equation for Congener 77 (displayed in Figure 6-1) is:

$$Y = 130\ \textit{m}\text{g/kg} + 300X$$

$$\text{Concentration of total PCBs} =$$
$$130\ \textit{m}\text{g/kg dw} + (300 \times \text{concentration of Congener 77})$$

The LOAEL-based protective sediment concentration for Congener 77 in Segment 3 for great blue heron is 0.39 *m*g/kg dw (Table 6-9). Thus, the estimated total PCB protective sediment concentration for great blue heron in Segment 3 is:

$$130\ \textit{m}\text{g/kg dw} + (300 \times 0.39\ \textit{m}\text{g/kg dw}) = 250\ \textit{m}\text{g/kg dw or } 0.25\ \text{mg/kg dw}$$

The sediment sample in Segment 2 with 21 mg/kg dw total PCBs, sample S2-2, was weighted in the regressions because it is an extreme data point (see Figure 6-1). Although this sediment sample has the same congener pattern observed in the other sediment samples, it has a much higher total PCB concentration. That is, it has a much higher y-value (total PCBs) and a much higher x-value (congener concentration) than the other data points for each linear regression. If included without a weighting factor, it would exhibit undue influence on the estimated coefficients calculated using the ordinary least squares analysis. For this analysis, a value of 0.10 was chosen as the weight for this data point to reduce its influence on the regression estimate because the congener concentrations for sample S2-2 are approximately 10 times greater than the average congener values calculated without that sample.

Also note that because many of the estimates of total PCB protective sediment concentrations require extrapolation below the range of the observed congener data, this analysis assumes that the linear relationship extends into ranges of congener concentrations below those in the data set.

Somewhat different total PCB protective sediment concentrations were calculated for each of the receptors depending on which congener was used in the regression (Table 6-11). For fish, the protective sediment concentrations for total PCBs varied from 3.7 to 5.6 mg/kg dw and from 6.0 to 25 mg/kg dw for NOAEL and LOAEL endpoints, respectively. For great blue heron and mink, the NOAEL-based ranges were 0.14 to 0.72 mg/kg dw and 0.05 to 0.73 mg/kg dw, respectively. The LOAEL-based protective sediment concentration ranges were 0.23 to 0.97 mg/kg dw and 0.70 to 1.5 mg/kg dw for great blue heron and mink, respectively. While total PCB protective sediment concentrations also varied somewhat among Segments 2, 3, and 5, the range of variation was not large (Tables 6-8, 6-9, and 6-10). This is especially true when the uncertainty in the calculation is taken into account. Therefore, a single total PCB protective sediment concentration should be applied to the entire stretch of river from Segment 2 to the mouth of the river (i.e., segment-specific concentrations are not warranted). These total PCB protective sediment concentrations were developed to reflect an area-weighted average over the home range of the fish. For protection of mink and heron, the protective sediment concentrations should be applied over the home range of the forage fish in the size range consumed by these receptors.

7.0
SUMMARY

This section summarizes the results of the ERA, discusses the overall ecological significance of those results to the Sheboygan River and Harbor, summarizes the protective cleanup concentrations, and provides recommendations for future monitoring or study.

7.1 Ecological Significance to Sheboygan River and Harbor

The Sheboygan River and Harbor ecosystem includes a diverse range of species and functions, a subset of which was evaluated in this ERA. Since the ERA could not evaluate all species and all possible toxicological effects, important and representative species were selected as surrogates for the ecosystem and ecologically significant effects were emphasized. This section presents a summary of the results in terms of the assessment and measurement endpoints discussed in Section 2.7.

7.1.1 Benthic Invertebrates

A sediment Triad assessment was conducted that focused on depositional areas in the Sheboygan River, with all but two of the site stations located in the lower river Segments 5 and 6. The Triad comprises three synoptic measures and is used to assess the probability of adverse effects on the benthic invertebrate community. Of the 18 stations sampled, including the 4 reference stations, only 3 stations indicated a high probability of adverse effects based on a concurrence of the three Triad measures—Station T07, which contained very high PCB concentrations, high toxicity, and low benthic abundance; Station T13, which contained high metals and PAH concentrations, low *H. azteca* survival, and low benthic richness; and Station T19, which contained high PAH concentrations and showed low *H. azteca* survival. Other stations showed potential for effects based on one or two of the Triad measures, which indicates a lower probability of adverse benthic impacts at these stations. All 14 site stations had chemical concentrations that exceeded at least one PEL value and 12 of these stations had significant toxicity compared to the negative control in either one or both of the two toxicity tests for acute lethality.

Overall interpretation of the Triad was hampered by 1) low survival in both toxicity tests at three of the four reference stations even though TELs were only exceeded at two of the four reference stations for some of the PAH compounds, and 2) the widespread dominance of immature oligochaetes sampled throughout the river, including the reference area.

These two factors, which may have resulted from an overall physical site disturbance, allowed only very limited assessment of benthic effects.

In summary, interpretation of risk to benthic invertebrates in depositional areas and whether this risk is attributable to COCs was complicated by uncertainty in at least one of the Triad legs. Three site stations, Stations T07, T13, and T19, showed clear evidence of adverse effects in all three Triad legs, while 9 of the other 11 site stations showed evidence of adverse effects in the toxicity and chemistry measurements. Statistical comparison of toxicity-test acute lethality endpoints to the negative control samples indicates that toxicity is widespread, including at 3 of the 4 reference stations. The toxicity in the reference area combined with the relatively low contaminant concentrations suggests the possible importance of unmeasured contaminants.

7.1.2 Fish

The results for all three approaches used to calculate HQs for PCBs—based on total PCB concentrations in eggs, total PCB concentrations in whole-body adult fish, and TEQ concentrations in eggs—indicate potential reproductive effects in fish, particularly in Segments 2 and 3, where the PCB concentrations are most elevated and HQs are greater than 1 using all three analysis methods. The risk appears to be greater for smallmouth bass than for either the white sucker or longnose dace, probably because smallmouth bass are at a higher trophic level and have higher relative lipid content in their eggs. The large range in HQ values derived from the three approaches reflects the high degree of uncertainty in the tissue residue effects benchmarks. The very high HQs, up to 290, for smallmouth bass using predicted egg concentrations of total PCBs indicate that exposure to PCBs could result in reproductive impairment in some fish species in the Sheboygan River. However, since HQs for smallmouth bass based on whole-body total PCB concentrations and egg TEQ NOAELs and LOAELs are much lower, up to 8.5, the overall conclusion from this analysis is less clear (Section 4.7). The potential for risk to smallmouth bass in Segment 5 is about half of that in Segments 2 and 3; for white sucker and longnose dace, the risks in Segments 2, 3, and 5 appear to be similar.

Potential risks to fish from PAHs were also evaluated since Segment 6 contained elevated concentrations of PAHs in sediment and a study by Schrank et al. (1997) reported elevated PAH metabolites in white suckers collected from Segment 6 as well as hematological, biochemical, and histological alterations. Elevated concentrations of PCBs and DDE were also reported in the Segment 6 white suckers in Schrank et al. (1997). Assigning causal relationships to the biochemical alterations is not possible with the data available because PCBs and pesticides may also cause these alterations. Concentrations of PAHs measured in the sediment were below those correlated with elevated tumor frequencies in fish in WDNR (1992a). Although elevated tumor frequencies were observed, cause and effect relationships are not clear. The ecological significance of these effects is unknown.

Fish community studies indicate that fish populations and habitat are generally good for the area (WDNR 1996b). Using a fish habitat rating model (FHR-R, developed by Simonson et al. 1994), WDNR (1996b) rated fish habitat in Segments 1 and 5 from good to excellent. According to WDNR, Index of Biological Integrity values on the fish community in those areas were rated as good and a length frequency analysis of smallmouth bass sampled indicated a stable recruitment and a good quality size structure. However, it is possible that fish populations in the lower Sheboygan River could be supported by migration of upstream fish over the dams and that populations in segments between Segments 1 and 5 could be different.

Although salmonids were not addressed directly as ROCs in this ERA, they are important species in Lake Michigan which receives a portion of its PCBs load from the Sheboygan River. The Sheboygan River has annual spawning runs of chinook salmon, coho salmon, and steelhead trout. River Segments 5 and 6 provide important rearing habitat for the juveniles of these species as well as exposure to site-related contaminants. Studies have shown that juvenile coho salmon and steelhead trout would accumulate substantial concentrations of PCBs during their residence in the Sheboygan River, particularly if they overwinter in the river before migrating out to Lake Michigan. The level of PCB accumulation may indicate a risk to piscivores that feed on smolts leaving the river. Risks to salmonids from PCBs originating from the Sheboygan River, however, do not currently appear to be higher than risks to salmonids in Lake Michigan in general. This conclusion is based on an analysis of fish tissue of returning adult salmonids conducted by Eggold et al. (1996) that indicates that PCB concentrations are no higher in adult salmonids returning to the Sheboygan River than in adult salmonids returning to other rivers in the Lake Michigan basin.

7.1.3 Piscivores

Mink and great blue heron represented the piscivorous wildlife community in this ERA. The assessment endpoint presented for mink and great blue heron focused on the potential for reduced reproduction due to dietary exposure to PCBs. Segments 2 and 3 provide beneficial physical habitat for the riparian and aquatic wildlife community. They may also offer the most suitable foraging territory for wildlife, because of the riparian plant community which provides cover and reduces the amount of human disturbance. Segments 2 and 3 are the areas most contaminated with PCBs. The attractive physical habitat, coupled with the elevated degree of contamination, increases the potential for exposure and harm to piscivorous wildlife in Segments 2 and 3.

Adverse effects on the reproductive success of mink and great blue heron appear highly probable based on a comparison of predicted dietary doses for mink and great blue heron to TRVs derived from two studies in the literature. In Segments 2/3 and 5/6, HQs for mink based on TEQs ranged from 6.2 to 290 and HQs based on total PCBs ranged from 15 to 1,000. The absence of mink from the study area corroborates this finding, indicating that reproductive impacts are likely occurring since habitat within the study area does not appear to be a limiting factor.

In Segments 2/3 and 5/6, HQs for great blue heron based on TEQs ranged from 14 to 290 and HQs based on total PCBs ranged from 4.9 to 65. Although great blue heron are not nesting within or near the site, a breeding colony of black-crowned night heron—another piscivorous heron species—is present near New Jersey Avenue (Section 2.2.1). Great blue herons and black-crowned night herons have a similar natural history. Because of this, the black-crowned night heron colony is likely experiencing adverse reproductive effects as indicated by the high HQs for the great blue heron.

Piscivorous wildlife may consume anadromous fish smolts within the Sheboygan River or in Lake Michigan soon after the smolts outmigrate. PCBs that have accumulated in these fish may pose a risk to wildlife depending on the percentage of the diet the smolts comprise, which would require a more detailed analysis to address. It should be noted that this assessment focused on the characterization of risk only within the Sheboygan River. Although not evaluated, there may be risk to receptors in Lake Michigan from transport via the food web or from PCB loading in the water column, which contributes an average of 2 to 4% of the total PCB load (approximately 21–24 kg/year) to Lake Michigan (Marti and Armstrong 1990; Robertson 1996; Hall pers. comm. 1998).

A number of other wildlife species that reside within the study area were not considered in this ERA. WDNR and others continue to study the effects of PCBs in the Sheboygan River on both aquatic wildlife such as snapping turtles and insectivorous songbirds such as the American robin. The results of those studies will add to the weight of evidence to determine if PCBs are affecting the other ecological communities within the Sheboygan River study area.

7.2 PROTECTIVE SEDIMENT CONCENTRATIONS

Protective sediment concentrations are discussed for benthic invertebrates, fish, mink, and the great blue heron in this section. Protective sediment concentrations are intended to provide risk managers with information for selecting cleanup goals. This section summarizes the findings for benthic invertebrates, fish, and piscivores.

For the protection of benthic invertebrates in depositional areas, two avenues for protective sediment concentration derivation were evaluated: 1) protective sediment concentrations based on the results of the Triad study, and 2) comparison of measured toxicity and chemistry data to sediment quality guidelines. For most stations investigated, correlations among the three Triad legs were not sufficient to use the total Triad data set to evaluate protective sediment concentrations. Instead, three available freshwater sediment quality guidelines were evaluated to determine the likelihood of Type I or Type II errors if the guidelines were used as protective sediment concentrations for metals, PAHs, and PCBs. Site data were used to evaluate whether or not existing sediment quality guidelines could be used to correctly predict toxicity in short-term lethality test endpoints in two species of test organisms. This evaluation provides the risk manager with information on the likelihood that these guidelines over- or underestimate risks of metals, PAHs, or PCBs to benthic invertebrate species in depositional zones in the Sheboygan River.

For the protection of fish, the Gobas (1993) bioaccumulation model was used to back-calculate protective sediment concentrations for PCBs from no effects concentrations of specific congeners in juvenile smallmouth bass fish tissue. Based on the consistent PCB congener composition observed in sediment and juvenile smallmouth bass tissue within each segment (excluding the reference area), protective sediment concentrations for dioxin-like effects from total PCBs were estimated for Segments 2, 3, and 5 and ranged from 3.7 to 5.6 mg/kg.

For the protection of piscivores, the food web model and the bioaccumulation model were used in combination to calculate a range of protective sediment concentrations for mink and great blue heron based on NOAELs and LOAELs derived from the literature. In general, the congener-specific protective sediment concentrations for mink and great blue heron were similar, although the LOAEL-based protective sediment concentrations for great blue heron were somewhat lower for PCB Congeners 105 and 118. Most of the average congener concentrations measured in Segments 2, 3, and 5 were much higher than the protective sediment concentration range, indicating a high likelihood of risk to mink and great blue heron, especially near Segment 2. Congener concentrations were lower than or equal to protective sediment concentrations in the reference area, indicating that this area is unlikely to pose risks to mink and great blue heron. Using the same model discussed above for fish, total PCB protective sediment concentrations were estimated for mink and great blue heron; these concentrations ranged from 0.05 to 0.7 mg/kg for mink and from 0.1 to 0.7 mg/kg for great blue heron.

Therefore, based on the analyses presented in this risk assessment, cleanup goals similar to background sediment concentrations of PCBs in the Sheboygan River would be protective of ecological health (i.e., 0.050 mg/kg dw of total PCBs). This result corroborates the work previously conducted for the site (WDNR 1992b) and the conclusion previously stated by USEPA (1994) that recommended cleanup to background concentrations is appropriate for PCBs.

7.3 RECOMMENDATIONS

This section provides an outline of recommendations for a long-term monitoring program in the Sheboygan River and Harbor that can be used to evaluate the effectiveness of the selected remedial alternative in reducing risk to fish and wildlife from exposure to PCBs. This monitoring program should be developed in coordination with USEPA, WDNR, and the natural resource trustee agencies. Recommendations are made in this section and Appendix H to serve as a starting point for developing the program. The proposed monitoring program focuses on PCB concentrations in fish and sediment, because the greatest risks identified in this ERA were associated with PCB exposure to fish and wildlife. There are two basic objectives of the monitoring program:

- Provide the basis for evaluating the effectiveness of remedial actions by supplementing existing site data to establish a comprehensive pre-remediation baseline

- Generate data for periodic re-evaluation of potential fish, piscivorous-wildlife, and human exposure to residual PCBs and associated risks

The primary recommendations for the monitoring program include three main components: 1) resident fish monitoring of adult and young-of-year or juvenile fish; 2) caged fish studies using fathead minnows; and 3) sediment sampling. These recommendations were based in part on the availability of existing data from the Interim Monitoring Program (BBL 1996), the WDNR food chain study, and this ERA. Biological monitoring of floodplain areas, based on recommendations of the forthcoming floodplain ERA, should also be incorporated in the monitoring program. The plan for conducting the baseline monitoring event should be developed and implemented, at a minimum, one year prior to remedial action, recognizing that detailed monitoring programs for all components of the monitoring program may not be developed prior to the completion of the remedial design.

Additional details of the recommended long-term monitoring program are discussed in Appendix H, including a comparison of the recommended methods to those used in past studies and monitoring efforts as well as a discussion of other elements considered for the program.

8.0
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