Sheboygan River Food Chain and Sediment Contaminant Assessment

Final Project Report
U.S. Environmental Protection Agency
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INTRODUCTION

The purpose of this report is to document the results of the Sheboygan River Food Chain and Sediment Contaminant Assessment. This project was completed by the Wisconsin Department of Natural Resources (WDNR) with funding assistance from the U.S. EPA Great Lakes National Program Office (Grant #GL-995681).

The International Joint Commission, in response to the 1987 Amendments to the Great Lakes Water Quality Agreement identified the lower 14-mile section of the Sheboygan River as a Great Lakes Area of Concern (AOC). This means that the Sheboygan River AOC is considered one of the 43 most contaminated areas in the Great Lakes drainage basin. In response to this designation, the WDNR in conjunction with area citizens developed Remedial Action Plans (RAPs). The first Sheboygan River RAP document (WDNR, 1989) outlined the sources of contaminants to the AOC. The second RAP document (WDNR, 1995a) refined the source information and recommended actions to clean up the contaminated areas and evaluate the results. Through the RAP process, guidelines required the advisory committees to evaluate potential impairments to the 14 beneficial uses of waterways identified by the International Joint Commission (IJC). For the Sheboygan AOC, nine of the 14 beneficial uses were considered impaired. Contaminated sediments directly or indirectly contribute to seven of the impaired uses. This study combines many recommendations contained in the RAP documents to determine the contribution, composition and distribution of contaminants within the AOC.

Contaminated sediment is a major contributor of pollutants to the Sheboygan River AOC and Lake Michigan. Several programs including U.S. EPA's Superfund and WDNR's Environmental Repair Program (ERP) have initiated actions within the AOC that are beginning to address contaminated sediment. These individual programs have narrowly defined, program specific objectives. On the other hand, RAP committees determined that an ecosystem approach was necessary to achieve long-term goals. The focus should encompass the processes and progress achieved through the Superfund and ERP programs, yet go beyond their limitations to benefit the entire lower section of the river from the Sheboygan Falls dam to the harbor.

In order to design an effective and comprehensive restoration strategy for the Sheboygan River, ecosystem impacts from contaminants must be understood. Corrective actions to eliminate ecosystem impacts associated with contaminated sediment will also achieve significant progress towards delisting impaired uses in the AOC. Many recommendations put forth by the RAP committees reflect the need to determine baseline conditions in the AOC by identifying the contribution, composition and distribution of contaminants associated with river sediments. This project implemented several recommendations identified by the RAP committees through an integrated, coordinated and collaborative effort to establish needed baseline conditions for the food chain from which to evaluate the performance of future clean up actions.

CONTAMINANTS OF CONCERN

The primary contaminants of concern in the Sheboygan River AOC are polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs) and heavy metals. Because of their stability and persistence in the environment, PCBs are still with us today. Their hydrophobic and lipophilic properties allow for rapid accumulation in organisms through the food chain. Fish and waterfowl consumption advisories are in effect for the Sheboygan River. A do not eat advisory for all resident fish species (including carp, walleye, smallmouth bass, catfish, northern pike, rock bass, bluegill and crappie) is in effect for the Sheboygan River Area of Concern (WDOH & WDNR, 1998). In 1987, the WDNR suspended stocking of trout and salmon after it was discovered that the stocked fish were accumulating high levels of PCBs before leaving the river. WDNR staff completed an experimental stocking study of trout and salmon (Eggold et al., 1994) which concluded that trout and salmon stocked in the spring migrate to Lake Michigan soon after stocking. Since these fish spend little time in the river, PCB accumulation concentrations of returning fish were not different from those in reference streams. Conversely, the fish stocked in the fall over winter in the river and accumulate high amounts of PCBs in their tissues. The returning fish had tissue PCB concentrations higher than fish stocked in reference streams. In response to the study, the WDNR resumed stocking trout and salmon in the Sheboygan River only in the spring.

Populations of mink within the Sheboygan River AOC are well below what normally would be expected given the available habitat. Small mammal trapping by the WDNR in 1993 recovered no mink within the AOC. Occasional mink are seen in this area. However, they are suspected as transients that are not breeding in the area (Katsma, 1994). Mink depend on a diet of fish and invertebrates, and may be accumulating contaminants from these food sources through the food chain (Patnode, 1995). Reproductive problems in mink are suspected because of their low population levels and the high quality of available habitat. Studies have shown that reproduction has been severely reduced when mink are exposed to PCBs (Aulerich et al., 1971; 1973; Aulerich & Ringer, 1977).

A consumption advisory for waterfowl with PCB tissue contamination is in effect for portions of the Sheboygan River and Harbor. The advisory states that no one should eat mallard ducks using the Sheboygan River from the Sheboygan Falls dam downstream to the river's mouth at Lake Michigan. In addition no one should eat lesser scaup (bluebills) using the Sheboygan Harbor (WDNR, 1996).

PAHs are also accumulated by organisms somewhat, but tend to be more volatile and are readily metabolized by higher vertebrates. Schrank, et al. (1997) found that white suckers residing in the lower Sheboygan River accumulated significant amounts of PAHs and PCBs. These fish also exhibited some blood and tissue alterations suggesting impaired fish condition.

Heavy metals are also a concern from an accumulation and toxicity standpoint, but their presence in AOC sediments and biota is less understood than the organic contaminants.

FOOD CHAIN STUDY OBJECTIVES

The overall goal of this study is to establish baseline contaminant concentrations associated with sediments, water column and the biota within the Sheboygan River AOC, and to identify potential bioaccumulation factors between sediment, water column and biota. This project was designed to:

1. Provide baseline information for the Sheboygan River RAP's long-term trend monitoring strategy to evaluate the performance of future remedial actions and to delist impaired uses.
2. Determine the bioavailability of toxic substances and bioaccumulation of PCBs through the food chain in the AOC.
3. Evaluate spatial distribution of PCB congeners in AOC sediment and availability to aquatic organisms.
4. Provide needed information on PAH distribution and bioavailability in the Sheboygan River.
5. Provide information about the distribution and uptake of heavy metals in the Sheboygan River.

Each of these objectives includes evaluations of the:

1. Focus on the presence or absence of compounds between food chain elements (bioaccumulation objectives) or river segments (source or distribution objectives).
2. Differences (concentrations or mass) between food chain elements or river segments.

Review of the historical data relating to aquatic community composition provided the basis to identify a simplistic food chain for the Sheboygan River comprising resident species for use in this study. Each of the biotic components was carefully chosen to reflect food chain links to the contaminants available from the sediments and water column. Larval benthic macroinvertebrates were chosen to establish a primary link between sediments and water column contaminants to insectivorous fish. Adult macroinvertebrates were chosen to evaluate a potential link to the terrestrial community. Crayfish were chosen as an intermediate link to predator fish. Longnose dace are insectivorous and a potential food source to smallmouth bass. White suckers are omnivorous and were chosen (year 1+ and adults) as an intermediate food chain link. The young white suckers are also potential prey for smallmouth bass. Smallmouth bass are the highest link in the food chain chosen for this study. Year 1+ smallmouth bass feed on insects and small crayfish, while the adults are primarily piscivorous (Becker, 1983).

HISTORICAL SOURCES OF CONTAMINATION

The Sheboygan River RAP committees identified contaminated sediment as a significant source of PCBs, PAHs and heavy metals to the AOC and Lake Michigan. The study area contains two Federal Superfund Sites (Sheboygan River and Harbor and Kohler Landfill), that have contributed pollutants of concern to the Sheboygan River. A former coal gasification facility site in the City of Sheboygan is under investigation through WDNR's Environmental Repair Program. The following sections describe the known suspected sources of pollutants of concern to the Sheboygan River Food Chain and Sediment Contaminant Assessment study area.

Kohler Landfill Superfund Site

The Kohler Company Landfill was declared a Superfund site in 1984 after contaminated surface water runoff was detected. Kohler Company has operated this landfill since 1950 for foundry sand, core and pottery waste disposal. Certain cells were used for disposal of chrome plating sludges, enamel powder, hydraulic oils, solvents and paint wastes. The Remedial Investigation (RI) for this site was completed in 1990 (Blasland & Bouck, 1991). Wastes found in the landfill include volatile organic compounds (VOCs) including vinyl chloride, trichlorethane (TCE) and 1,2-dichlorethane (DCE), PAHs, phenolic compounds, and heavy metals including chromium, cadmium, lead, copper, antimony and zinc. Groundwater in the shallow aquifer beneath the site is also contaminated with these compounds and flows into the Sheboygan River rather than underneath it (Geraghty and Miller, 1992).

A Record of Decision (ROD) was issued in 1996 for landfill closure and the groundwater element. Construction of the remedy began in 1997 and was completed during the summer of 1998. The slope adjacent to the Sheboygan River and side slopes were capped and planted with vegetation (accounting for about one-half of the landfill). The north side of the landfill is currently operating and accepting foundry sands and pottery clays.

A perimeter drain along the south and east portion of the landfill (>2000 linear feet) was constructed to collect leachate from the shallow aquifer. The leachate is being collected in the drain and pumped to the City of Sheboygan Wastewater Treatment Facility for treatment. Long-term care of the collection system, groundwater and leachate monitoring will be provided by Kohler Company (Fauble, 1998).

Sheboygan River and Harbor Superfund Site

The Sheboygan River and Harbor was designated a Federal Superfund site in 1985 because of suspected PCB contamination in the river and floodplain. Results of the Remedial Investigation (RI) conducted for this site showed presence of PCBs, metals and several VOCs in the sediment and water column, and PCBs and heavy metals in floodplain soils (Blasland & Bouck, 1990). Sediment PCB concentrations in the river sediments between the Sheboygan Falls dam and the Waelderhaus dam ranged from no detect (ND) to 4500 ppm. Downstream of the Waelderhaus Dam PCB concentrations ranged from 1.9-220 ppm. Concentrations of metals in sediments were variable, but generally increased from upstream to downstream. Samples collected from floodplain soils generally followed the same patterns as the river sediments.

The sediments in the river section from the Sheboygan Falls Dam to the Waelderhaus dam were considered highly contaminated with PCBs and a threat to human health. Tecumseh Products Company (a responsible party for this Superfund Site) and the U.S. EPA cooperated to remove about 5000 cubic yards of contaminated sediment from the Sheboygan River. About 2500 cubic yards of sediments were placed in a confined treatment facility as part of U.S. EPA's Assessment and Remediation of Contaminated Sediment (ARCS) program. The remaining 2500 cubic yards were placed in a confined disposal facility located on Tecumseh property until final site remediation decisions are made through the Superfund process. Some additional sediment areas were "armored" in place using an experimental design developed by Blasland & Bouck Engineers. River monitoring to gauge the performance of removal actions included water column, sediment and caged fish sampling. Fourteen of the 18 areas excavated had post-removal sediment PCB concentrations below 40 ppm with an average of 13 ppm (Blasland & Bouck, 1992).

Coal Gasification Facility

The Wisconsin Public Service Corporation (WPSC) is the responsible party identified for a manufactured gas plant site under investigation by WDNR's Environmental Repair program. The former facility was located in the City of Sheboygan and operated between 1880 and 1930. During construction of a floating pier along the east bank of the Sheboygan River in 1990, builders found coal tar in the soil. Sources of pollution from this site include runoff from the gas plant (tars), contaminated groundwater and tar tanks which were previously underground but are now under water due to shoreline recession. WPSC conducted an environmental investigation of the site and concluded that both soil and groundwater contamination existed (Simon Hydro-Search, 1992). Groundwater at the site showed levels of arsenic, total cyanide and benzene above the state of Wisconsin enforcement standard. The coal gasification plant is the suspected source of PAHs found in downstream sediments near the Pennsylvania Avenue Bridge (Blasland & Bouck, 1990) and the Eighth Street Bridge (RMT, 1993).

METHODS AND MATERIALS

STUDY AREA

The Sheboygan River AOC is located in east central Wisconsin, about 55 miles north of the City of Milwaukee. The Sheboygan River headwaters are located in Fond du Lac County and the river flows east, southeast approximately 80 river miles before reaching the western shore of Lake Michigan in the City of Sheboygan (Figure 1). The river has an annual mean discharge of 250 cubic feet per second (cfs) and drains a 432 square mile area. The Sheboygan River has a diverse resident fishery and is classified as supporting a warmwater sport fish community with seasonal runs of Lake Michigan trout and salmon in the lower 10 miles of river. The study area consists of the reference site located above the Sheboygan Falls dam (segment 1), and five consecutive segments over 14 miles of river extending from below the Sheboygan Falls dam to the Sheboygan Harbor (Figure 2). The selected study segments and rationale are described in Table 1.

Table 1. Food Chain Study Segment Descriptions

Segment	Description
1	Reference site. No known sources of PCB, PAH or metals contamination. Most samples taken from the area near Meadowlark Road, 4.5 river miles upstream of Sheboygan Falls Dam. Mainly rural land uses adjacent to the stream. A good mix of pools, riffles and runs.
2	Rochester Park area. River mile 13.9 to 11.2. Area from Sheboygan Falls Dam in Sheboygan Falls downstream to Riverbend Dam in the Village of Kohler. Primary contaminants of concern are PCBs. This segment includes the upstream most source of PCBs in the Sheboygan River AOC, and the highest sediment PCB concentrations (WDNR, 1995; Blasland & Bouck, 1992). Adjacent land uses are park land and private ownership (natural riparian area). Dynamic river section. Contains a large riffle area, many deposition zones and pools.
3	Between Dams area. River mile 11.2 to 9.9. Between Riverbend and Waelderhaus Dams. Significant depositional zone downstream from Segment 2. Primarily PCB contamination. Contains a small riffle area.
4	River mile 9.9 to 5.0. From Waelderhaus Dam downstream to discharge from Kohler Company settling ponds. This section of the river runs through the Kohler Company River wildlife area and is not readily accessible from the road. This segment is similar to segment 5 and was not sampled.
5	Esslingen Park area. River mile 5.0 to 1.6. From Kohler Company settling pond discharge to Camp marina in the city of Sheboygan. This river section includes sediment contaminated with heavy metals, PAHs and PCBs. Has fast moving water with large rocks and deposition areas typical of streams this size.
6	Camp Marina area. River mile 1.6 to river mouth at Sheboygan Harbor. Surface PCB concentrations lower than upstream segments. Heavy metals present with high PAH concentrations suspected from historic coal gasification facility. Significant deposition zones with slow moving water. Historic navigation channel.

Figure 1. Sheboygan River Basin

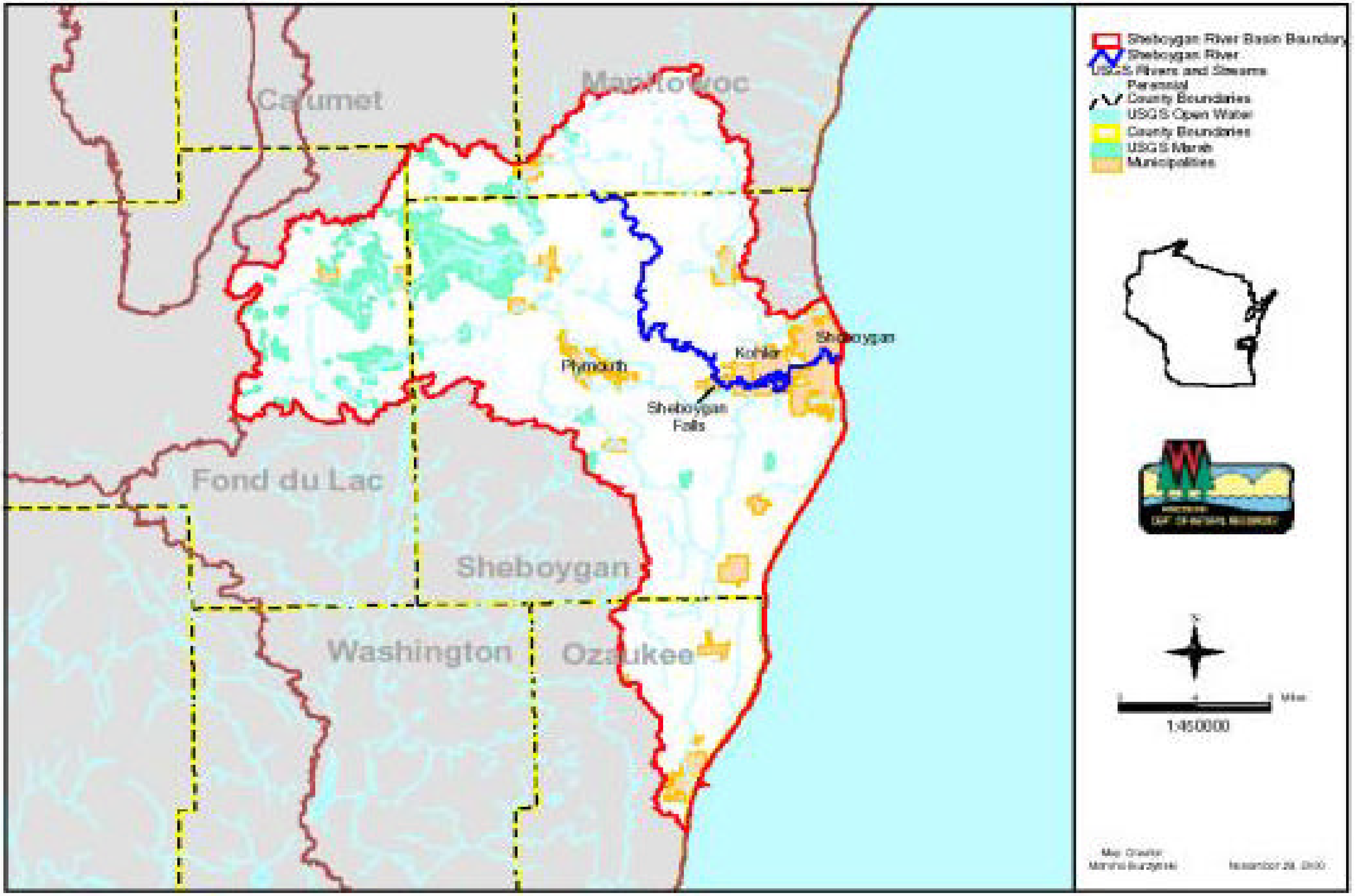
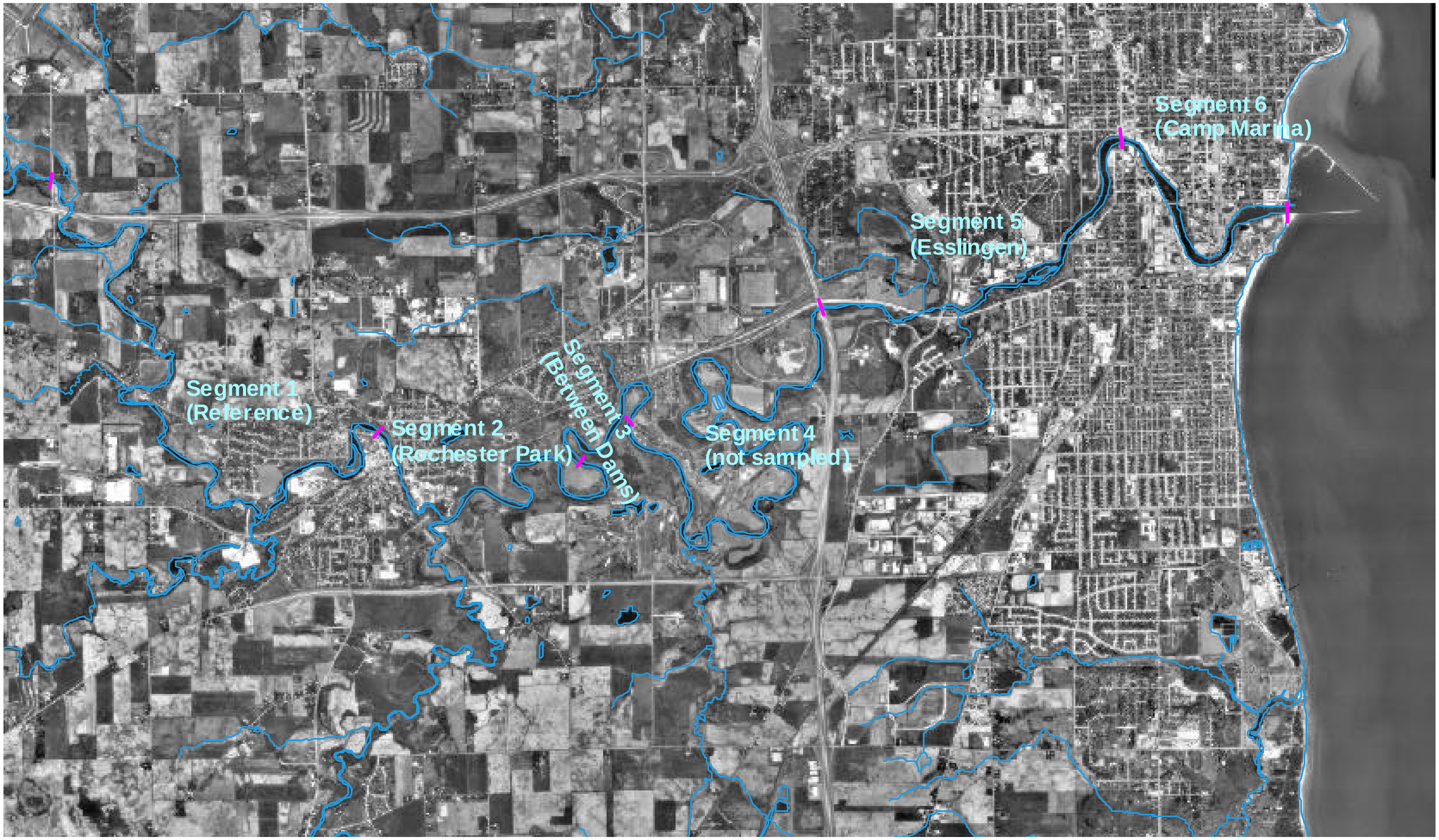


Figure 2. Food Chain Study Area



SAMPLING PROCEDURES

Schedule

Table 2 shows the sample collection schedule for the Food Chain Study. Larval and emergent aquatic macroinvertebrates were collected throughout July and August 1994. Semi-permeable polymeric membrane devices (SPMDs) to measure uptake of PCBs and PAHs from the water column were deployed twice in the study segments. Fish were collected in the fall of 1994. Most sediment samples were collected through the ice during February 1995, with the exception of the reference site cores, which were collected in April 1995.

Table 2. Sampling Dates for Food Chain Study Components

Sample Type	Segment 1	Segment 2	Segment 3	Segment 5	Segment 6
Larval inverts	01 August 1994	02 August 1994	04 August 1994	03 August 1994	No tissue samples were collected in this segment.
Larval inverts	08 August 1994	09 August 1994	11 August 1994	12 August 1994	
Larval inverts	15 August 1994	16 August 1994	18 August 1994	17 August 1994	
Larval inverts	22 August 1994	23 August 1994	25 August 1994	24 August 1994	
Emergent inverts	18 July 1994	02 August 1994	04 August 1994	20 July 1994	
Emergent inverts	01 August 1994	09 August 1994	11 August 1994	12 August 1994	
Emergent inverts	15 August 1994	16 August 1994	18 August 1994	17 August 1994	
Emergent inverts	22 August 1994	23 August 1994	25 August 1994	24 August 1994	
Crayfish	20 Sept.1994	22 Sept. 1994	22 Sept. 1994	20 Sept.1994	
Fish collections	13 Oct. 1994	24 Oct. and 01 Nov. 1994	25 Oct. and 02 Nov. 1994	19 Oct. 1994	
SPMDs	First deployment: 29 July 1994 to 12 August 1994 (14 days)				
	Second deployment: 24 August 1994 to 21 September 1994 (28 days)				
Sediment	04 April 1995	24 Feb. 1995	23 Feb. 1995	22 Feb. 1995	21 Feb. 1995

Tissue Collections

Larval Invertebrates

Larval benthic macroinvertebrates were collected from cobble sized rocks in riffle areas at segments 1, 2, 3 and 5 on four different dates (Table 2). Using latex gloves and pre-cleaned forceps, rocks were picked up, and large bodied larvae (mayfly and caddisfly) were hand picked from the rocks and deposited into pre-cleaned glass jars rinsed with site water (Figure A.1, Appendix A). The jars were kept in coolers with ice for transport to the WDNR Southeast Region Biology Laboratory. After arriving at the SER laboratory, larvae were separated from small rocks, algae and other extraneous material that may have been introduced in the field. A small sub-sample of larvae were preserved in alcohol and identified to family or genus level. A minimum of 20 g of larval invertebrates was collected and stored frozen for each sample.

Emergent Invertebrates

Emergent aquatic macroinvertebrates were collected using terrestrial light traps manufactured by Bio Quip, Inc. (Gardena, CA) at segments 1, 2, 3, and 5. The traps consist of a 3-gallon plastic bucket fitted with a funnel and fluorescent light source. The bucket was lined with aluminum foil to prevent cross contamination of the samples between sites and sampling dates. The foil also made extraction of the invertebrates from the bucket easier. The adult insects are attracted to the fluorescent light suspended above the bucket and fall through the funnel into the bucket. The traps were placed in areas representative of riffle and depositional zones for each segment on four different dates (Table 2, page 11). To ensure adequate sample, four traps were used at each site. Two of the traps were placed on rocks on the streambanks and two were suspended from overhanging tree branches (Figure A.2). The traps were placed at dusk and were left on for about two hours after dark. Traps were retrieved and placed into a large cooler containing ice for 1 to 2 hr to immobilize the insects. The traps were then opened and the aluminum foil containing the insects was removed, sealed and labeled. Emergent invertebrates were collected from the traps and stored frozen until they were sorted to exclude terrestrial invertebrates. Sub-samples of the invertebrates were taken from each sample site and identified to determine orders and families.

Crayfish

Crayfish were collected during September 1994 from riffles in segments 1, 2, 3, and 5 by disturbing cobble substrates (by kicking) upstream of a standard d-frame net. (Table 2, page 11; Figure A.3). Individuals between 38 and 44 mm long were placed in a pre-cleaned glass mason jar rinsed with site water at the collection site. After returning to the SER laboratory, the crayfish collected from each site were divided into three replicate samples, wrapped in aluminum foil and stored frozen until they were transported to the laboratories for analysis.

Fish

Longnose dace (insectivore), white suckers (omnivore) and smallmouth bass (predator) were collected from segments 1, 2, 3 and 5 by electroshocking with a direct current stream shocker in September and October 1994 (Figure A.4). PCB congeners were the only contaminants of concern analyzed in fish for this study. Fish tend to readily metabolize PAHs and do not appreciably accumulate heavy metals.

Longnose dace (*Rhinichthys cataractae)* were selected as representative of forage and insectivorous fish species for this study. The longnose dace is generally found in riffle areas in small and mid-sized fast moving streams throughout Wisconsin. These fish are primarily insectivorous, with Diptera (81%), Ephemeroptera (10%) and Trichoptera (9%) comprising their diet (Becker, 1983). Three composites of 25 similar size fish were collected, packaged in foil and frozen until they were analyzed for PCB congeners.

White suckers (*Catostomus commersonii)* were collected in two sizes to represent two distinct life stages, young (age I+) and adult. White suckers were chosen because they are omnivorous, taking whatever food may be available including insects, crustaceans, plants, fish and fish eggs. Suckers are found in streams throughout Wisconsin and are important forage for sport fish (Becker 1983). For adults, three composites of 3 to 6 similar size fish each were collected. Three composites of 6 to 8 similar sized young fish were also collected.

Smallmouth bass (*Micropterus dolomieui)* were collected in young and adult sizes. Smallmouth bass are carnivorous and begin to feed on *Daphnia* and small midge larvae 6 to 15 days from hatching. Once they reach 38 mm in length smallmouth bass feed mainly on small fishes and insects, and begin to feed on small crayfish at about 75 mm long. Fish, crayfish and adult macroinvertebrates make up the bulk of the adult smallmouth bass diet (Becker, 1983). Three composites of 6 to 8 similar sized young fish were collected, and three composites of 3 to 4 similar sized adult fish were collected.

Sediment

Sediment samples were collected from segments 1, 2, 3, 5, and 6. Five core samples were collected from segments 1, 2, 3 and 6 and four samples were collected from segment 5 because of a lack of appropriate depositional sites. A 7.6-cm diameter push-coring device was used to collect the sediment samples (Figure A.5). The top 15 cm from each core, representing the zone where most biological activity takes place, were homogenized in the field and transferred to clean sample containers. The samples were stored at the WDNR Southeast Region laboratory at 4°C prior to delivery to the State Laboratory of Hygiene for analysis.

Semi-permeable Polymeric Membrane Devices (SPMD)

Semi-permeable polymeric membrane devices (SPMDs) were used in this study to determine water column bioavailability of PAHs and PCBs in segments 1, 2, 5 and 6. The SPMDs were purchased from CIA Laboratories (St. Joseph, MO), the laboratory holding the exclusive license. Each SPMD contained 1 ml (0.91 g) triolein, a neutral lipid similar to fish lipid, spread into a thin film inside a heat sealed 34 inch long by 1 inch wide low density polyethylene (LPDE) layflat tube twisted into a 17 inch long mobius strip. Prior to sealing, the lipid was spiked with an internal standard (d^{10} phenanthrene) for permeability evaluation. Detailed information regarding SPMD preparation methods and quality assurance are located in Appendix A of the Sheboygan River Food Chain Study Work Plan (WDNR, 1995b).

Three sets of four SPMDs were placed in segments 1, 2, 5 and 6 during two different sampling periods. The SPMDs were inserted into 3.5 inch by 24 inch tubing constructed from electrical conduit to protect them from being torn by debris washing downstream (Figure A.6). The time of SPMD exposure to the air was noted for each replicate at each site. In all cases the SPMD deployment devices were secured with cable ties attached to concrete half-blocks, and placed perpendicular to the shoreline. The tubes were oriented on the blocks parallel to stream flow. The SPMDs were left in place for 14 days for the first deployment, and 28 days for the second deployment.

After the first deployment the deployment devices were modified slightly. Several of the SPMDs at the reference site were punctured during the first deployment and appeared chewed, presumably by a turtle. We were able to retrieve adequate sample for analysis however. This is the only site that received any damage to the SPMDs. For the second deployment we fashioned end caps from galvanized hardware cloth for each deployment device to deter animals from coming in contact with the SPMDs (Figure A.7). After the second deployment no SPMDs were damaged.

Trip blanks consisting of two SPMDs were exposed to the air to correspond to the longest air exposure time of the SPMDs that were deployed. Four SPMDs were also deployed by hanging in trees at two separate locations (segment 1 and segment 5) for the entire period of aquatic deployment to measure atmospheric contribution of contaminants to the surface waters.

After the SPMDs were collected, they were stored frozen at SER in airtight containers until they were shipped to the ETF Laboratory for extraction. Following extraction the material recovered from the SPMDs was split. Half of the material was analyzed at the ETF Laboratory in Stevens Point for PAHs, while the other half was shipped to the SLOH for PCB congener analysis.

Analytical Procedures

All samples collected for this study were analyzed by the SLOH, the Environmental Task Force Trace Organics Laboratory (ETF) or the UW-Extension Soil and Plant Analysis Laboratory. The SLOH analyzed all tissue samples and SPMDs for PCB congeners, heavy metals and percent lipid, and sediment samples for PCB congeners, PAHs, heavy metals and total organic carbon (TOC). The ETF Laboratory analyzed all macroinvertebrate samples for PAHs, and SPMD samples for PAHs. The UW-Extension Soil and Plant Analysis Laboratory analyzed sediment samples for particle size. Specific analytical procedures employed for this project are described in detail in the Work Plan Appendices and the QAPP (WDNR, 1995c). Table 3 shows the analyses conducted for each sample type by segment.

Table 3. Food Chain Study Analytical Summary Table for all Samples.

Sample Type	Reference (# samples)	Rochester (#samples)	Between Dams (# samples)	Esslingen (# samples)	Camp Marina (# samples)
Larval invertebrates	Routine PCBs (4) Coplanar PCBs (3) PAHs (4) Heavy metals (4) Percent lipid (4)	Routine PCBs (4) Coplanar PCBs (3) PAHs (4) Heavy metals (4) Percent lipid (4)	Routine PCBs (4) Coplanar PCBs (3) PAHs (4) Heavy metals (4) Percent lipid (4)	Routine PCBs (4) Coplanar PCBs (3) PAHs (4) Heavy metals (4) Percent lipid (4)	
Adult invertebrates	Routine PCBs (4) Coplanar PCBs (4) PAHs (4) Heavy metals (4) Percent lipid (4)	Routine PCBs (4) Coplanar PCBs (4) PAHs (4) Heavy metals (4) Percent lipid (4)	Routine PCBs (4) Coplanar PCBs (4) PAHs (4) Heavy metals (4) Percent lipid (4)	Routine PCBs (4) Coplanar PCBs (4) PAHs (4) Heavy metals (4) Percent lipid (4)	
Crayfish	Routine PCBs (3) Coplanar PCBs (2) PAHs (3) Heavy metals (3) Percent lipid (3)	Routine PCBs (3) Coplanar PCBs (2) PAHs (3) Heavy metals (3) Percent lipid (3)	Routine PCBs (3) Coplanar PCBs (2) PAHs (3) Heavy metals (3) Percent lipid (3)	Routine PCBs (3) Coplanar PCBs (2) PAHs (3) Heavy metals (3) Percent lipid (3)	
Longnose dace	Routine PCBs (3) Coplanar PCBs (1) Percent lipid (3)	Routine PCBs (3) Coplanar PCBs (1) Percent lipid (3)	Routine PCBs (3) Coplanar PCBs (1) Percent lipid (3)	Routine PCBs (3) Coplanar PCBs (1) Percent lipid (3)	
White suckers (young and adult)	Routine PCBs (3) Coplanar PCBs (1) Percent lipid (3)	Routine PCBs (3) Coplanar PCBs (1) Percent lipid (3)	Routine PCBs (3) Coplanar PCBs (1) Percent lipid (3)	Routine PCBs (3) Coplanar PCBs (1) Percent lipid (3)	
Smallmouth bass (young and adult)	Routine PCBs (3) Coplanar PCBs (1) Percent lipid (3)	Routine PCBs (3) Coplanar PCBs (1) Percent lipid (3)	Routine PCBs (3) Coplanar PCBs (1) Percent lipid (3)	Routine PCBs (3) Coplanar PCBs (1) Percent lipid (3)	
Sediment	Routine PCBs (5) Coplanar PCBs (5) PAHs (3) Heavy metals (5) TOC (5) Particle size (5)	Routine PCBs (5) Coplanar PCBs (5) PAHs (3) Heavy metals (5) TOC (5) Particle size (5)	Routine PCBs (5) Coplanar PCBs (5) PAHs (4) Heavy metals (5) TOC (5) Particle size (4)	Routine PCBs (4) Coplanar PCBs (4) PAHs (4) Heavy metals (4) TOC (4) Particle size (4)	Routine PCBs (5) Coplanar PCBs (5) PAHs (4) Heavy metals (5) TOC (5) Particle size (5)
SPMDs	Routine PCBs (3) Coplanar PCBs (2) Percent lipid (3)	Routine PCBs (3) Coplanar PCBs (2) Percent lipid (3)	No SPMDs deployed at this site	Routine PCBs (3) Coplanar PCBs (2) Percent lipid (3)	Routine PCBs (3) Coplanar PCBs (2) Percent lipid (3)

RESULTS AND DISCUSSION

POLYCHLORINATED BIPHENYLS (PCBs)

Sixty-nine PCB congeners (62 non-coplanar, 7 coplanar) were analyzed for all food chain study components. Analyzing the PCBs by congener provides more information than reporting Aroclor or total PCB concentrations. The most bioaccumulative PCB congeners contain five (penta) to seven (hepta) chlorine molecules per atom. These isomer groups make up over half (112) of the 209 PCB congeners. The penta through hepta chlorinated congeners are also some of the most toxic PCB congeners in the environment because of their bioavailability and chronic toxicity (McFarland and Clarke, 1989). The 62 routine (non-coplanar) PCB congeners analyzed are listed in Table 4. These congeners were analyzed in every sample collected for this study. Seven coplanar congeners (77, 105, 123, 126, 156, 157, and 169) were analyzed for at least one replicate for each food chain component sampled at each site. Of all the PCB congeners in existence, the coplanar congeners are considered the most toxic. These congeners are structurally similar to 2,3,7,8-TCDD, the most potent synthetic environmental toxicant known, and display similar properties. The non-ortho substituted coplanar congeners (77, 126, 169) mostly resemble 2,3,7,8-TCDD and are considered the most toxic of all congeners produced (McFarland and Clarke, 1989; Safe, 1990). In addition, 15 of the "routine" PCB congeners (18, 44, 49, 52, 74, 87, 99, 101, 118, 128, 151, 157, 167, 177, 177, 180, 183, 194, and 201) are considered more toxicologically active to varying degrees (McFarland and Clarke, 1989).

Analyses of total PCB concentrations, PCB homolog groups, toxic PCB congeners, and biota-sediment accumulation factors are presented in the following sections.

Total PCB Concentrations

Total PCB concentrations were estimated by summing the concentrations of 62 routine (non-coplanar) congeners that were resolved as 40 individual and 22 pairs (or triplets) of co-eluting congeners (Table 4). Seven coplanar congeners were also analyzed but not added to the total since they were not analyzed for all samples. These will be discussed in a later section on toxic congeners. Only the congeners giving a positive result were summed to obtain the total. Concentrations measured at less than the level of detection (LOD) or between the LOD and level of quantitation (LOQ) were assumed to be zero.

Table 4. Non-coplanar (*routine*) PCB Congeners Analyzed for all Sheboygan River Samples

PCB Congener (IUPAC) Number	Number of Chlorines per atom	PCB Congener (IUPAC) Number	Number of Chlorines per atom
5/8	2	97	5
6	2	99	5
7	2	101	5
16/32	3	118	6
17	3	128	6
18	3	132/153	6
19	3	135/144	6
22	3	136	6
24/27	3	137/176	6/7
26	3	138/163	6
28/31	3	141	6
33	3	146	6
37/42	3/4	149	6
40	4	151	6
41/64/71	4	157	6
44	4	167	7
45	4	170/190	7/8
46	4	171/202	7/8
47/48	4	172/197	7
49	4	174	7
52	4	177	7
56/60	4	178	7
66/95	4/5	180	7
70/76	4	182/187	7
74	4	183	7
77/110	4/5	185	8
82	5	194	8/9
84/92	5	195/208	8
85	5	196/203	8
87	5	199	8
91	5	201	9
		206	

Sediments

PCB congeners and sediment particle size were measured in sediment composites taken at five locations in each study segment with the exception of the Esslingen segment. This segment has a fast-moving current with more sand and gravel than the other segments, so four composites were collected at this site

(Table 5). Composites consisted of mixing the top 15-cm of sediment taken from two different but adjacent cores. Letters A through E identified the five composites in each segment.

Table 5. Sediment Texture Characteristics for Food Chain Study Samples

Field ID	% Solids	% Sand	% Silt	% Clay	Soil Texture
1A	57	85	7	8	LOAMY SAND (B)
1B	60	55	31	14	SANDY LOAM (C)
1C	57	51	26	13	SANDY LOAM (C)
1D	44	24	56	20	SILT LOAM (E)
1E	50	42	43	15	LOAM (D)
2A	62	60	30	10	SANDY LOAM (C)
2B	48	60	23	17	SANDY LOAM (C)
2C	61	66	21	13	SANDY LOAM (C)
2D	74	82	12	6	LOAMY SAND (B)
2E	58	82	10	8	LOAMY SAND (B)
3A	66	52	36	12	LOAM (D)
3B	63	62	25	13	SANDY LOAM (C)
3C	77	85	10	5	LOAMY SAND (B)
3D	55	47	38	15	LOAM (D)
3E	47	51	35	14	LOAM (D)
5A	51	20	58	22	SILT LOAM (E)
5B	74	76	17	7	LOAM (D)
5C	73	78	14	8	LOAMY SAND (B)
5D	68	74	17	9	SANDY LOAM (C)
6A	67	52	35	13	LOAM (D)
6B	55	60	28	12	LOAM (D)
6C	46	26	56	18	SILT LOAM (E)
6D	57	31	50	19	LOAM (D)
6E	74.5	84	9	7	LOAMY SAND (B)

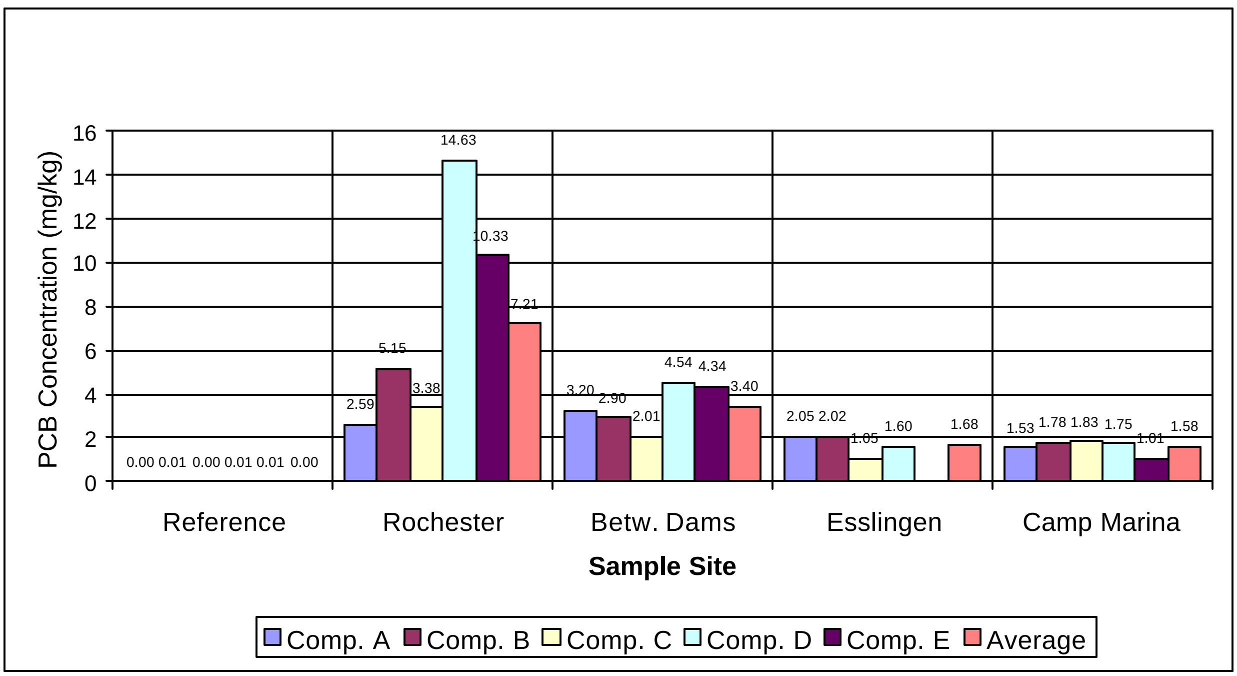
Total PCB concentrations in sediment ranged from 0.002 mg/kg at the reference site to 14.63 mg/kg at the Rochester site (Table 6, Figure 3). Total PCB concentrations in sediment generally decreased downstream from the Rochester site. PCB concentrations at the Reference site were detectable (0.002-0.007 mg/kg) but were two to three orders of magnitude lower than at the contaminated sites downstream. Average total PCB concentrations followed a similar pattern.

The Rochester site is closest to the original source of PCBs in the lower Sheboygan River, so the longitudinal decrease in PCBs downstream is most likely due to sediment dispersion and dilution downstream with uncontaminated sediments originating in the watershed. Since no known sources of PCBs exist above the Sheboygan Falls dam, the detectable concentrations at the Reference site are most likely caused by atmospheric deposition. Although PCBs were detected in low concentrations at the Reference site, the concentrations are far below the 0.05-0.06 mg/kg average total PCB concentrations measured as background upstream of the Sheboygan Falls Dam (Schuettpelz, 1992; David, 1990).

Table 6. Total Sediment PCB and Total Organic Carbon Concentrations at all Sites.

	Reference	Rochester	Betw. Dams	Esslingen	Camp Marina
Total PCBs (mg/kg)					
Average (n)	0.005 (5)	7.21 (5)	3.40 (5)	1.68 (4)	1.58 (5)
Minimum	0.002	2.59	2.01	1.05	1.01
Maximum	0.007	14.63	4.54	2.05	1.83
Std. Deviation	0.002	5.13	1.05	0.47	0.34
Total Organic Carbon (mg/g)					
Average	28620 (5)	21300 (5)	23000 (5)	16635 (4)	24740 (5)
Minimum	22100	14100	10200	8740	9300
Maximum	40900	33600	33100	35100	35900
Std. Deviation	8532	7695	9219	12407	10570

Figure 3. Total PCB Concentrations in Sediment



Invertebrates

PCB congeners were measured for larval macroinvertebrates and emergent macroinvertebrates collected at the Reference, Rochester, Between Dams and Esslingen sites. Collections were made weekly at each site for a total of four weeks (Table 2, page 11). Crayfish were collected in a single day at each site and separated into three similar size samples. Larval invertebrates collected were identified to genera, and are listed in Table 7). Emergent invertebrates collected were identified to family and are listed in Table 8.

Table 7. Larval Invertebrates Identified for the Sheboygan River Food Chain Study.

Order	Family	Genus	Segment Number			
			1	2	3	5
Ephemeroptera	Heptageniidae	Stenacron	X	X	X	X
		Stenonema	X	X	X	X
	Caenidae	Caenis	X			
Trichoptera	Hydropsychidae	Cheumatopsyche	X	X	X	X
		Macrostemum	X	X	X	X
		Ceratopsche	X	X	X	X
		Hydropsyche	X	X	X	X
	Polycentropodidae	Polycentropus	X		X	X
	Limnephilidae	Pycnopsyche	X	X	X	X

Table 8. Emergent Invertebrate Orders and Families Identified.

Order	Family	Segment			
		1	2	3	5
Diptera	Chironomidae	X	X	X	X
	Tipulidae		X	X	
Hemiptera	Corixidae	X	X		X
Trichoptera	Helicopsychidae	X	X	X	X
	Hydropsychidae	X	X	X	X
	Leptoceridae	X	X	X	X
	Philopotamidae	X	X	X	X
	Limnephilidae	X			
	Polycontropodidae		X		
	Hydroptilidae	X	X	X	X
	Phryganeidae		X		
Ephemeroptera	Ephemeridae	X	X	X	X
	Heptageniidae	X	X	X	X
	Polymitarcidae	X	X	X	X
	Caenidae		X	X	X
Lepidoptera	Pyralidae	X	X		
Coleoptera	Elmidae	X	X	X	X

Total PCB concentrations in larval invertebrates ranged from 0.006 µg/g at the Reference site to 8.90 µg/g at the Rochester site (Table 9). Average total PCB concentrations for larval invertebrates decreased downstream from Rochester Park. Emergent invertebrates followed the same pattern. Total PCB concentrations ranged from 0.032 µg/g at the Reference site to 20.99 µg/g at Rochester. Average total PCB concentrations decreased downstream from Rochester. Emergent invertebrate total PCB concentrations were much higher than the larval invertebrates at all sites. A couple scenarios may account for these differences. All the larval invertebrates were collected from rocks in faster flowing riffle areas. In these areas PCB exposure is primarily through the water column and food sources collected from the water column. Most of the emergent invertebrates collected were from families more closely associated with sediments and detritus. In the larval and emergent invertebrate collections, caddisflies comprised 75 to 95 percent of the invertebrates collected with mayflies comprising most of the remainder. The hydropsychid caddisflies were the dominant family of larval caddisflies collected. These caddisflies are net filter feeders, collecting their food from particles suspended in the water column. The dominant emergent caddisflies collected were from families that feed by grazing or scraping. They have direct contact with the substrate and feed on detritus, algae, very small invertebrates and fungi. The other emergent invertebrate orders collected (Diptera, Hemiptera, Lepidoptera and Coleoptera) comprised less than one percent of total invertebrates collected at any site.

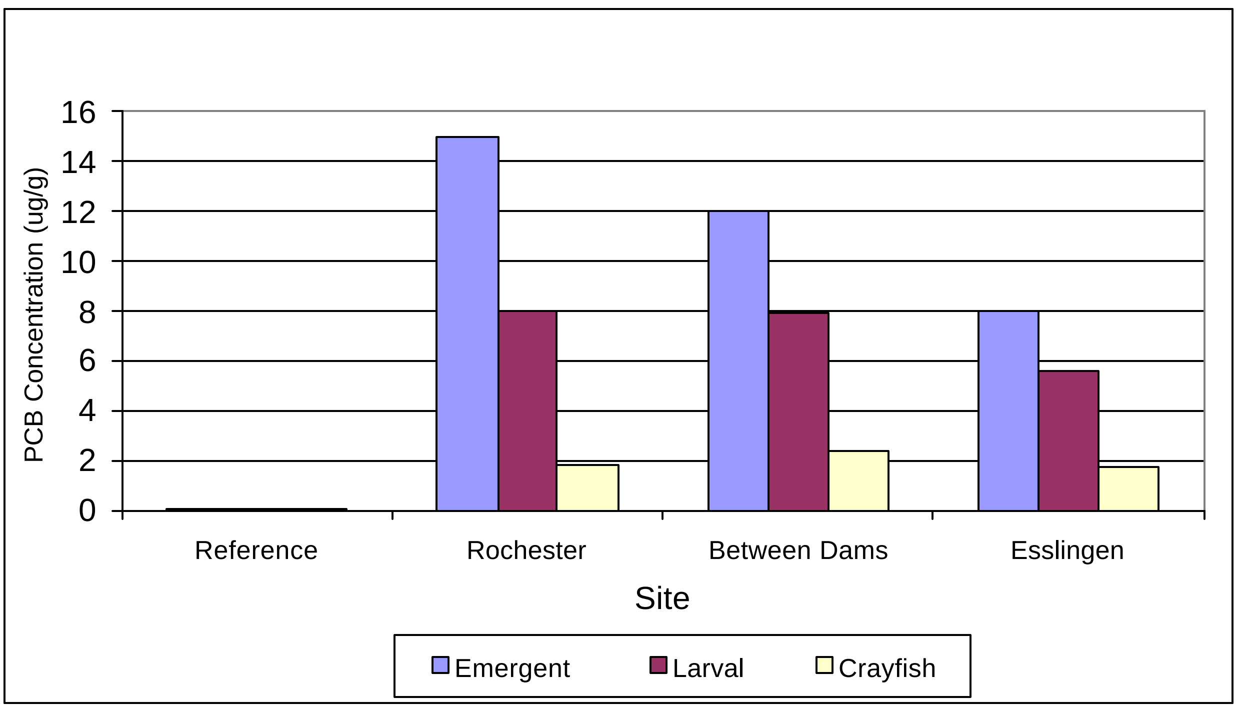
Additionally, when larval macroinvertebrates go through metamorphosis to the adult stage, PCB concentrations could increase. The mass of emergent adults is less than larvae. Larsson (1984) found that in chironomid adults, weights post metamorphosis were reduced by a factor of 3.8. The exuviae retained only 17 percent of PCBs. Therefore, weight reduction combined with PCB retention could help explain the increase in PCB concentration from larvae to adult stages.

Table 9. Total PCB Concentrations and Percent Lipid Measured at all Sites for Invertebrates.

	Reference		Rochester		Between Dams		Esslingen	
	Total PCBs*	Percent Lipid	Total PCBs*	Percent Lipid	Total PCBs*	Percent Lipid	Total PCBs*	Percent Lipid
Larval invertebrates								
Average (n)	0.016 (4)	4.53 (4)	7.99 (4)	4.58 (4)	7.89 (4)	3.53 (4)	5.54 (3)	4.40 (3)
Minimum	0.006	0.30	6.71	4.10	7.03	1.20	5.16	3.40
Maximum	0.038	8.70	8.90	5.80	8.71	5.40	5.73	5.10
Std. Dev.	0.015	3.75	1.04	0.82	0.79	1.73	0.33	0.89
Emergent invertebrates								
Average (n)	0.075 (4)	6.05 (4)	14.95 (4)	4.03 (4)	11.98 (4)	3.68 (4)	8.00 (4)	4.80 (3)
Minimum	0.032	4.80	11.85	2.90	7.31	2.00	7.09	4.20
Maximum	0.153	7.20	20.99	5.10	17.43	4.90	8.93	5.40
Std. Dev.	0.054	1.18	4.14	1.88	4.92	1.24	0.82	0.55
Crayfish								
Average (n)	0.009 (3)	0.87 (3)	1.81 (3)	0.95 (3)	2.33	1.67 (3)	1.75 (3)	1.90 (3)
Minimum	0.001	0.70	1.72	0.70	2.18	1.40	1.59	1.70
Maximum	0.026	1.00	1.90	1.20	2.48	1.80	1.88	2.10
Std. Dev.	0.015	0.15	0.09	2.25	0.15	0.23	0.15	0.20

**all concentrations are reported as μg/g wet weight.*

Figure 4. Average Total Invertebrate PCB Concentrations



Fish Species

Longnose dace (insectivores), young and adult white suckers (omnivores) and young and adult smallmouth bass (predators) were collected from the Reference, Rochester, Between Dams and Esslingen Sites (Table 2, page 11). Three composites of fish were collected and analyzed for routine PCB congeners. The numbers of fish in each composite and average length for each species collected are shown in Table 10 below.

Table 10. Fish Species Collected, Number of Fish and Average Length for Each Composite Collected by Stream Segment.

Species	Reference		Rochester		Between Dams		Esslingen	
	Comp (# fish)	Avg. length (mm)	Comp (# fish)	Avg. length (mm)	Comp (# fish)	Avg. length (mm)	Comp (# fish)	Avg. length (mm)
Longnose dace	1 (25)	108	1 (25)	58	1 (25)	53	1 (25)	116
	2 (25)	94	2 (25)	71	2 (25)	63	2 (25)	98
	3 (25)	60	3 (25)	91	3 (25)	70	3 (25)	68
Young white suckers	1 (6)	103	1 (8)	78	1 (7)	88	1 (9)	87
	2 (6)	119	2 (8)	97	2 (7)	110	2 (9)	108
	3 (6)	133	3 (8)	106	3 (7)	126	3 (9)	131
Adult white suckers	1 (4)	286	1 (3)	254	1 (6)	279	1 (3)	250
	2 (4)	254	2 (3)	278	2 (6)	299	2 (3)	289
	3 (4)	236	3 (3)	310	3 (6)	347	3 (3)	348
Young smallmouth bass	1 (7)	82	1 (8)	61	1 (6)	64	1 (8)	78
	2 (7)	88	2 (8)	73	2 (6)	74	2 (8)	90
	3 (7)	98	3 (8)	88	3 (6)	90	3 (8)	100
Adult smallmouth bass	1 (3)	216	1 (3)	243	1 (4)	292	1 (4)	192
	2 (3)	293	2 (3)	274	2 (4)	256	2 (4)	225
	3 (3)	266	3 (3)	292	3 (4)	217	3 (4)	255

PCB concentrations for all species were lowest at the Reference site (0.008-0.551 µg/g). The highest PCB concentrations measured for longnose dace (19.70 µg/g), young white suckers (15.90 µg/g) and young smallmouth bass (29.84 µg/g) were found at the Between Dams site (Table 11). Because longnose dace and young fish generally migrate less than an adult fish, a common food source that is enriched with PCBs at the Between Dams site could be responsible for the higher concentrations. Larval insects could be this common food source because the dace and young fish are primarily insectivorous or omnivorous (Becker, 1983). The highest PCB concentrations for adult white suckers (16.50 µg/g) and adult smallmouth bass (35.41 µg/g) were measured in fish taken from the Rochester site (Table 11).

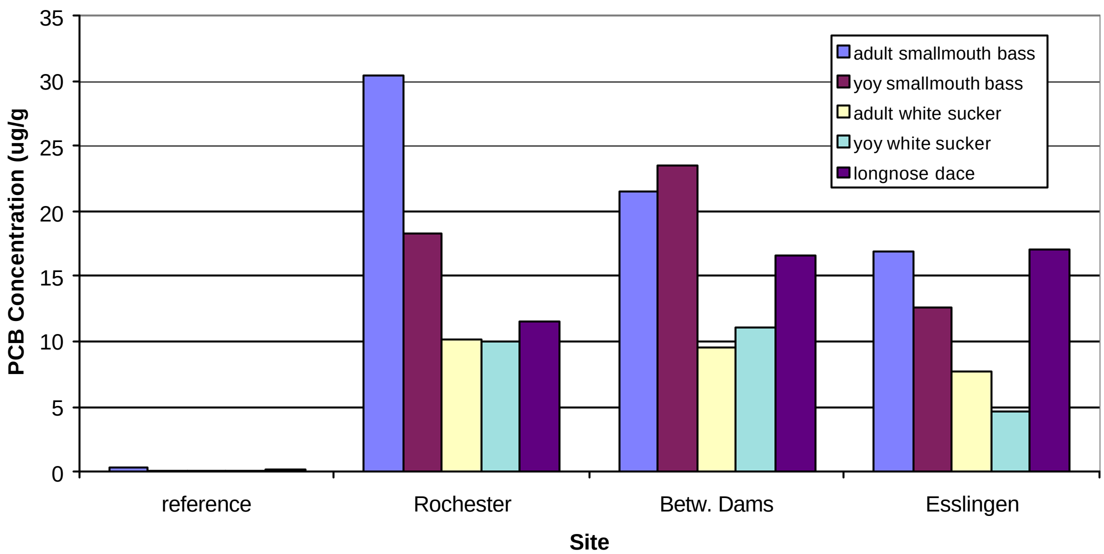
Average total PCB concentrations decreased downstream from Rochester for adult white suckers and adult smallmouth bass, while the average total PCB concentrations for young white suckers and young smallmouth bass followed the pattern: Between Dams>Rochester>Esslingen (Figure 5). Average total PCB concentrations for longnose dace increase downstream from Rochester to Esslingen.

Table 11. Total PCB Concentrations and Percent Lipid Content in Sheboygan River Fish.

	Reference		Rochester		Between Dams		Esslingen	
	Total PCBs*	Percent Lipid	Total PCBs*	Percent Lipid	Total PCBs*	Percent Lipid	Total PCBs*	Percent Lipid
Longnose dace								
Average (n)	0.175 (3)	3.00 (3)	11.46 (3)	6.87 (3)	16.67 (3)	5.53	17.06 (3)	8.83 (3)
Minimum	0.041	2.20	7.98	5.10	13.43	4.80	13.65	6.80
Maximum	0.401	3.40	17.30	10.00	19.70	6.20	19.19	10.00
Std. Dev.	0.196	0.70	5.09	2.72	3.14	0.70	2.98	1.77
Young White Suckers								
Average (n)	0.058 (3)	1.67 (3)	10.04 (3)	3.03 (3)	11.07 (3)	3.13	4.66 (3)	3.30 (3)
Minimum	0.011	1.50	9.74	2.50	8.39	2.40	4.01	2.50
Maximum	0.152	1.90	10.49	3.90	15.90	3.90	5.62	3.90
Std. Dev.	0.081	0.21	0.40	0.76	4.20	.043	0.86	0.72
Adult White Suckers								
Average (n)	0.040 (3)	0.83 (3)	10.21 (3)	0.87 (3)	9.54 (3)	1.30 (3)	7.66 (3)	1.90 (3)
Minimum	0.008	0.60	6.22	0.70	7.42	1.10	3.29	1.60
Maximum	0.096	1.20	16.50	1.00	12.29	1.60	14.43	2.50
Std. Dev.	0.049	0.32	5.52	0.15	2.50	0.26	5.95	0.52
Young Smallmouth Bass								
Average (n)	0.055 (3)	3.10 (3)	18.27 (3)	4.20 (3)	23.50	3.77 (3)	12.63 (3)	4.63 (3)
Minimum	0.028	2.60	17.17	3.90	17.96	3.40	9.81	3.80
Maximum	0.101	3.40	19.57	4.40	29.84	4.00	14.14	5.30
Std. Dev.	0.040	0.44	1.21	0.26	5.98	0.32	2.44	0.76
Adult Smallmouth Bass								
Average (n)	0.276 (3)	3.33 (3)	30.39 (3)	2.80 (3)	21.57 (3)	2.83 (3)	16.91 (3)	3.57 (3)
Minimum	0.095	2.00	21.70	2.50	15.08	2.40	16.19	3.10
Maximum	0.551	4.90	35.41	3.10	28.46	3.20	18.21	4.10
Std. Dev.	0.242	1.46	7.56	0.30	6.70	0.40	1.13	0.50

*all units for PCBs expressed as µb/g
**only one sample analyzed for coplanar PCBs

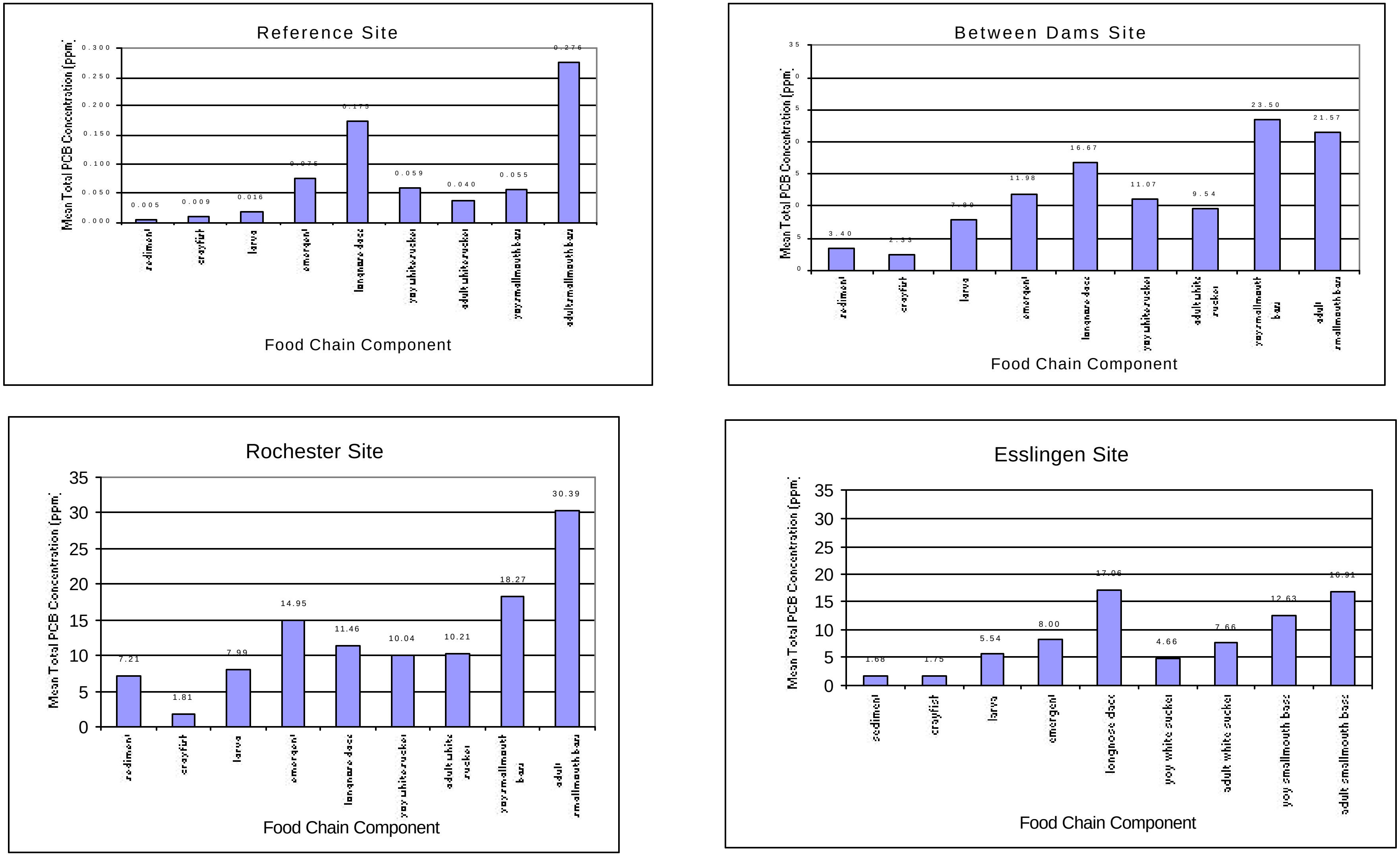
Figure 5. Average Total PCB Concentrations for Fish Species



Total PCB Accumulation

Bioaccumulation of PCBs in the Sheboygan River is evident at all sites (Figure 6). Total PCB concentrations generally increased from sediments to macroinvertebrates to fish at each site. With the exception of crayfish, mean macroinvertebrate PCB concentrations were higher than mean sediment concentrations. Crayfish have much lower mean lipid content (0.87-1.90%) compared to larval (3.53-4.58%) and emergent (3.68-6.05%) macroinvertebrates which could account for the lower PCB tissue concentrations (Table 9, page 24).

Figure 6. Total PCB Accumulation in Different Food Chain Study Components at Each Site.

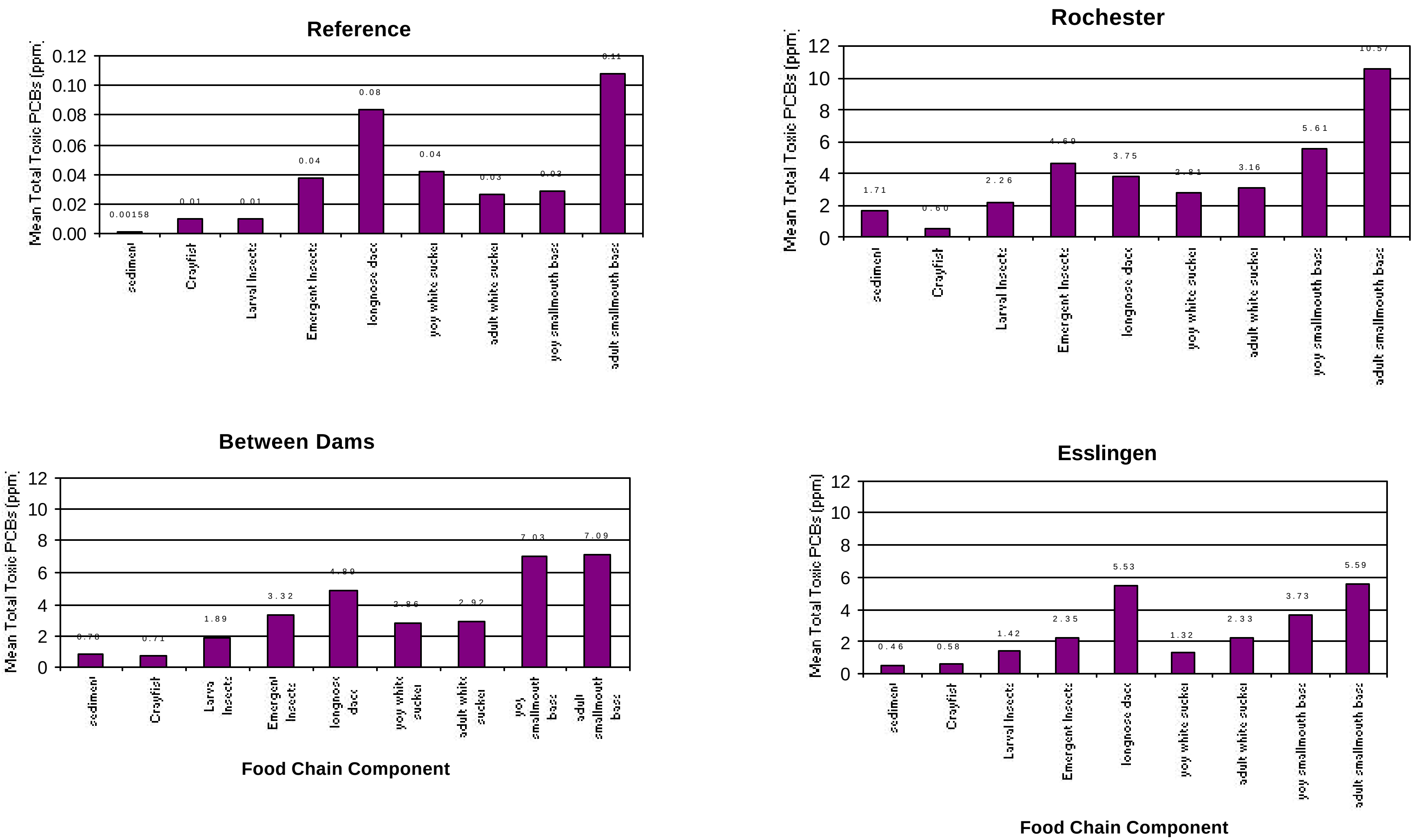


Longnose dace accumulated higher concentrations of PCBs than young and adult white suckers and young smallmouth bass. The longnose dace collected were adults, with longer exposure times to PCB contaminated materials than the young white suckers and young smallmouth bass, which were probably in the river less than one year. The longnose dace mean lipid content (3.0-8,83%) was about 3 to 8 times higher than mean lipid content of adult white suckers (0.83-1.90%) (Table 11, page 26). In addition, longnose dace on average were much smaller than the adult white suckers (60-116 mm for dace; 236-348 mm for white suckers) (Table 10, page 25); so the ratio of PCBs to body weight would be greater in longnose dace. The smallmouth bass generally accumulated higher concentrations of PCBs than the other fish species studied with the exception of young smallmouth bass at the reference and Esslingen sites. The very low average PCB concentrations at the Reference site could explain more variation in accumulation between food chain components. At the Esslingen site, longnose dace (68-116 mm average length) were of similar size to young smallmouth bass (78-116 mm average length), but mean longnose dace lipid content (8.83%) was nearly twice the mean young smallmouth bass lipid content (4.63%). The mean adult smallmouth bass lipid content (3.57%) was less than half the mean lipid content of longnose dace at the Esslingen site.

Toxic Congener Accumulation

The 22 PCB congeners considered most toxic to biota were summed for all food chain components (Figure 7). Overall, the toxic congeners represented about 23 to 34 percent of the total PCB concentration at the contaminated sites. Accumulation of these congeners followed the same general patterns as with total PCBs (sediment<macroinvertebrates<fish), with the fish species higher on the food chain generally accumulating higher concentrations of toxic PCBs than those lower on the food chain. One exception is at the Esslingen site where longnose dace and adult smallmouth bass had similar concentrations of toxic congeners. The higher average lipid content of the longnose dace (more than twice that of adult smallmouth bass) may explain this difference.

Figure 7. Toxic PCB Congener Accumulation in all Food Chain Study Components at Each Site.



PCB Homolog Distribution

PCB congeners were summed into homolog groups for all study components and averaged (Figure 8, Table 12). Average PCB homolog concentrations in all study components at the reference site were either below detection limits or at very low concentrations. Average sediment homolog concentrations were the least for all components, and above detection only for the tetra (0.58 ng/g), penta (2.19 ng/g) and hexachlorobiphenyls (2.15 ng/g). Adult smallmouth bass had the highest average homolog concentrations for most homolog groups at the reference site (with the exception of trichloropiphenyls), but still at very low concentration.

Average concentrations for all homologs at the downstream sites generally increased from sediment to increasingly higher biological components according to the following pattern: crayfish<sediment<larval invertebrates<emergent invertebrates<white suckers<longnose dace<smallmouth bass. Because of their low average lipid content (0.87-1.90%) crayfish probably do not accumulate lipophilic compounds as readily as other organisms with higher lipid content.

Tetra and pentachlorobiphenyls are the dominant homolog groups at the Rochester, Between Dams and Esslingen sites accounting for over 80 percent of total PCB concentrations (Figure 9). The lower chlorinated biphenyls (di and tri-chloro) generally comprise a higher percentage of PCBs in the lower trophic levels, while the fish accumulated a higher percentage of penta and hexachlorinated biphenyls. These results are consistent with other research (Oliver and Niimi, 1988; Willman et al., 1997), showing greater percentages of higher chlorinated biphenyls with increasing trophic levels. The tetra-, hepta- and octa-chlorobiphenyls are relatively uniform between food chain components.

Figure 8. PCB Homolog Concentrations for Each Food Chain Component at Each Site.

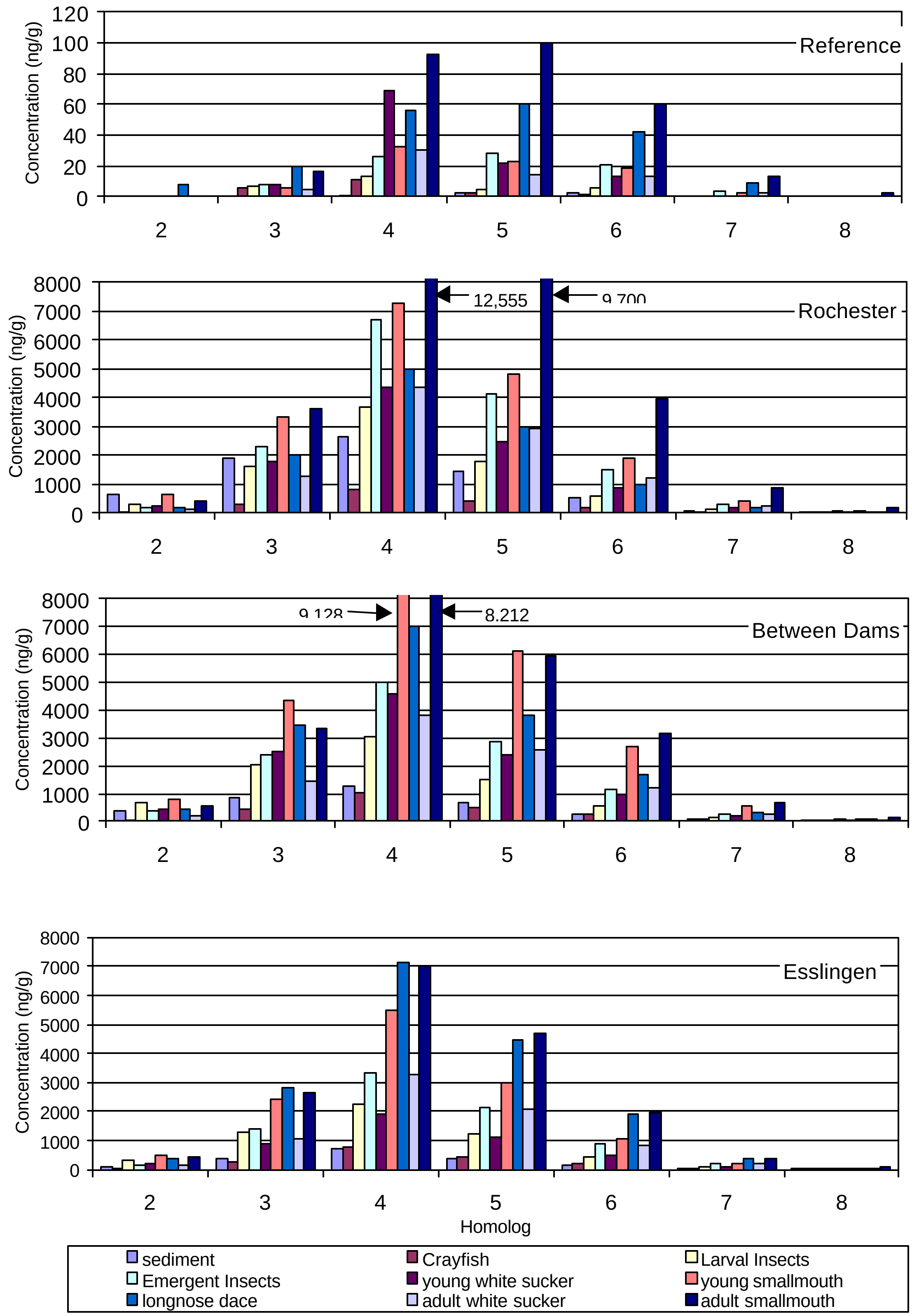
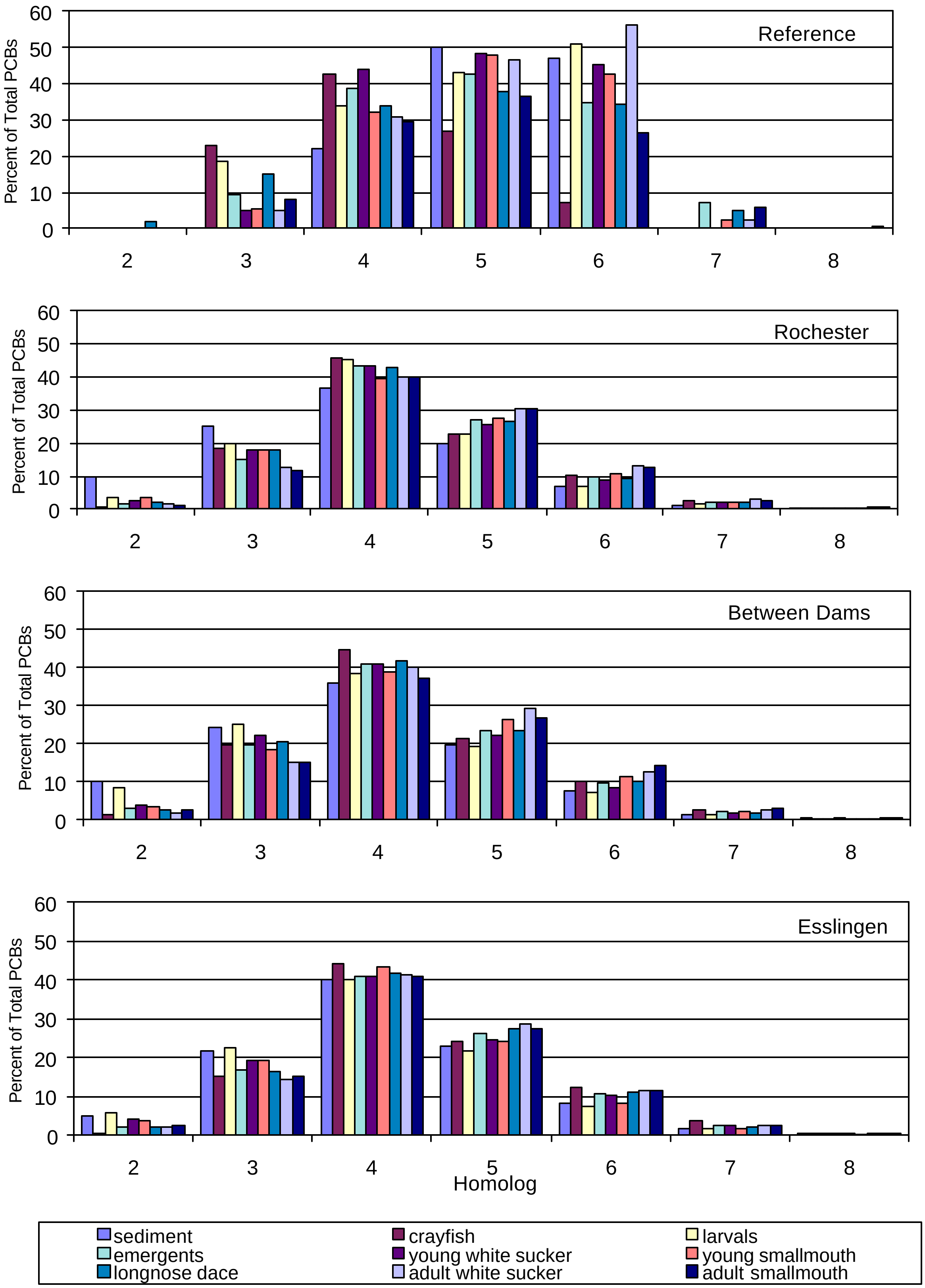


Table 12. Average PCB Homolog Concentrations by Site and Food Chain Component

Site	Type (n)	Homolog totals						
		2	3	4	5	6	7	8
Reference	Sediment (5)	0.00	0.00	0.58	2.19	2.15	0.00	0.00
Reference	Crayfish (3)	0.00	6.00	11.00	2.74	1.90	0.00	0.00
Reference	Larval Insects (4)	0.00	7.10	12.90	5.39	5.63	0.00	0.00
Reference	Emergent Insects (4)	0.00	7.80	26.00	28.25	21.03	3.90	0.00
Reference	longnose dace (3)	7.99	19.45	55.97	59.92	41.70	9.40	0.00
Reference	young white sucker (3)	0.00	7.60	68.50	21.46	12.77	0.00	0.00
Reference	adult white sucker (3)	0.00	5.10	30.50	14.91	13.00	2.50	0.00
Reference	young smallmouth (3)	0.00	5.83	32.80	22.66	18.80	2.40	0.00
Reference	adult smallmouth (3)	0.00	16.82	92.11	99.87	60.10	13.37	3.10
Rochester	Sediment (5)	634.46	1900.60	2664.20	1474.20	531.42	100.52	20.56
Rochester	Crayfish (3)	16.00	334.27	839.07	408.80	184.03	44.53	4.73
Rochester	Larval Insects (4)	294.75	1606.55	3654.03	1821.75	574.53	127.58	22.68
Rochester	Emergent Insects (4)	214.03	2342.25	6685.75	4114.75	1516.50	330.43	64.75
Rochester	longnose dace (3)	222.43	2037.67	5017.17	3020.67	1011.10	219.00	32.70
Rochester	young white sucker (3)	243.77	1819.00	4379.67	2490.00	899.67	212.37	43.33
Rochester	adult white sucker (3)	123.20	1302.67	4333.73	2919.67	1232.70	281.10	55.97
Rochester	young smallmouth (3)	642.90	3317.33	7295.00	4803.00	1887.33	398.27	67.33
Rochester	adult smallmouth (3)	404.87	3630.00	12555.00	9700.40	3995.00	907.23	179.92
Betw. Dams	Sediment (5)	367.56	841.00	1239.00	667.97	264.58	54.62	15.28
Betw. Dams	Crayfish (3)	32.67	459.30	1051.67	494.33	243.00	62.93	6.70
Betw. Dams	Larval Insects (4)	669.65	2007.50	3047.98	1522.25	561.25	120.55	21.40
Betw. Dams	Emergent Insects (4)	371.05	2378.00	5011.50	2864.50	1174.75	273.10	58.90
Betw. Dams	longnose dace (3)	420.47	3455.00	7001.53	3809.67	1656.33	342.43	58.80
Betw. Dams	young white sucker (3)	440.83	2505.67	4572.03	2420.67	944.40	194.17	29.97
Betw. Dams	adult white sucker (3)	187.04	1470.67	3847.23	2602.67	1182.00	254.33	47.67
Betw. Dams	young smallmouth (3)	810.03	4353.67	9128.00	6114.67	2662.00	543.43	85.84
Betw. Dams	adult smallmouth (3)	569.83	3348.33	8212.00	5961.27	3158.67	692.83	121.00
Esslingen	Sediment (5)	87.41	376.45	689.45	392.18	141.53	28.66	6.56
Esslingen	Crayfish (3)	11.33	270.83	785.30	418.70	217.87	59.33	7.67
Esslingen	Larval Insects (3)	332.37	1271.67	2242.87	1216.33	424.63	98.83	18.07
Esslingen	Emergent Insects (4)	164.60	1369.50	3326.85	2141.00	867.23	214.65	41.33
Esslingen	longnose dace (3)	357.80	2818.33	7165.67	4494.00	1905.00	371.87	59.60
Esslingen	young white sucker (3)	190.63	901.67	1909.47	1087.00	468.47	108.80	18.03
Esslingen	adult white sucker (3)	131.00	1062.27	3270.40	2104.00	857.30	207.03	40.23
Esslingen	young smallmouth (3)	474.93	2435.00	5519.33	2974.33	1051.03	212.47	34.27
Esslingen	adult smallmouth (3)	414.87	2650.33	7029.70	4690.00	1954.67	400.90	69.10

Figure 9. Percent PCB Homolog Composition for all Food Chain Components.



Semi-permeable Polymeric Membrane Devices (SPMDs)

Individual PCB congeners were summed for homolog mass for each study site and deployment period. Homolog group PCB concentrations were calculated by dividing homolog PCB masses by the mass of the lipid recovered from SPMDs in each deployment device. The homolog concentrations from the three deployment devices at each site were then averaged. SPMDs were not deployed at the Between Dams site but were deployed upstream and downstream of a site near the Sheboygan Harbor called Camp Marina. Habitat at the Camp Marina site was not suitable for collecting invertebrate and fish species, so SPMDs were used as a fish surrogate to determine organic pollutant bioconcentration (or bioavailability) at this site.

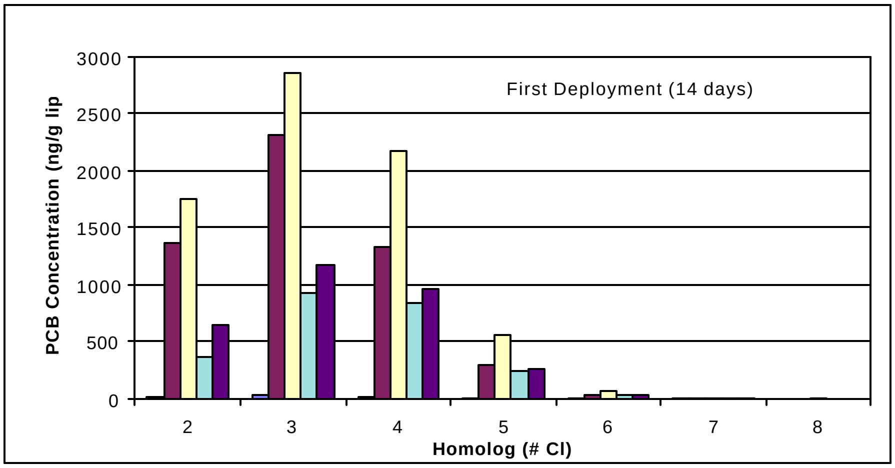
Homolog concentrations at the reference site were very low to undetectable for all groups during both deployments (Figure 10). Concentrations for the lower chlorinated homolog groups (di-tetrachlorobiphenyls) at the Rochester and Esslingen sites were nearly double during the first deployment than during the second. PCB homolog concentrations at the two Camp Marina sites were similar between both deployment periods. Hepta- and octa-chlorinated biphenyls were generally below detection at all sites during both deployment periods.

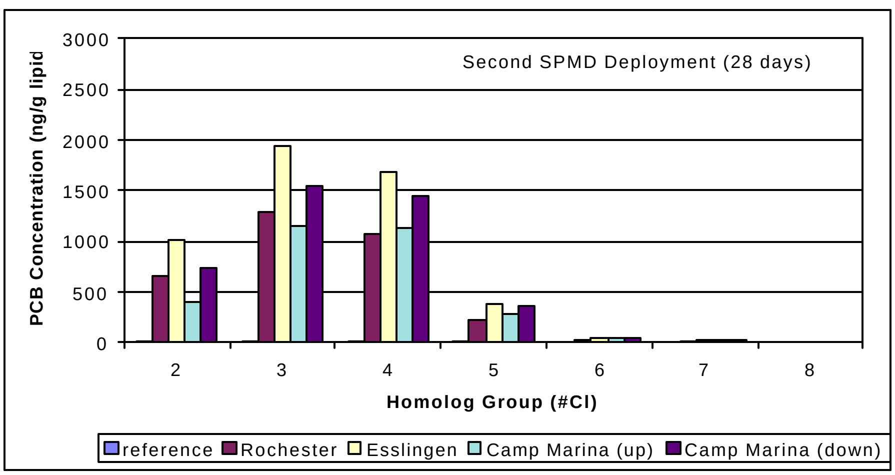
Average water temperatures during the first and second deployments were similar for each site (Table 13). Observed temperature differences were probably too small to account for any differences in PCB uptake during the two deployments. Moreover, the slightly higher average temperature combined with the longer exposure of the second deployment (28 days vs. 14 days) should have resulted in higher concentrations of PCBs detected. These marked differences between deployments were only observed at the two upstream contaminated sites, and only for the di-tetra-chlorobiphenyl homolog groups.

Table 13. Average Water Temperatures During Both SPMD Deployments

Site	First Deployment	Second Deployment
Reference	22.1	25.0
Rochester	21.5	21.3
Esslingen	20.8	24.3
Camp Marina (upstream)	19.7	21.7
Camp Marina (downstream)	21.1	22.9

Figure 10. PCB Homolog Concentrations in SPMDs





One possible explanation for the higher PCB concentrations detected during the first SPMD deployment is a decrease in the sampling rate due to biofouling. Sampling rate decreases can be calculated using the loss of a permeability reference compound (PRC). For this study, d^{10}phenanthrene was spiked into each SPMD for permeability evaluation. It is assumed net uptake of native and deuterated forms of compounds by SPMDs occur at nearly identical rates. Further, it is assumed that factors affecting phenanthrene uptake and loss affect PCB congeners similarly. Deuterated phenanthrene was spiked into all SPMDs prior to deployment. Losses of this compound relative to levels in trip blanks (exposed only during field deployment and retrieval) were used to calculate the percent decrease in sampling rate due to biofouling (Table 14).

Table 14. Average Percent Decrease in the Loss of d^{10} Phenanthrene spikes in field-deployed SPMDs vs. Trip Blank SPMDS.

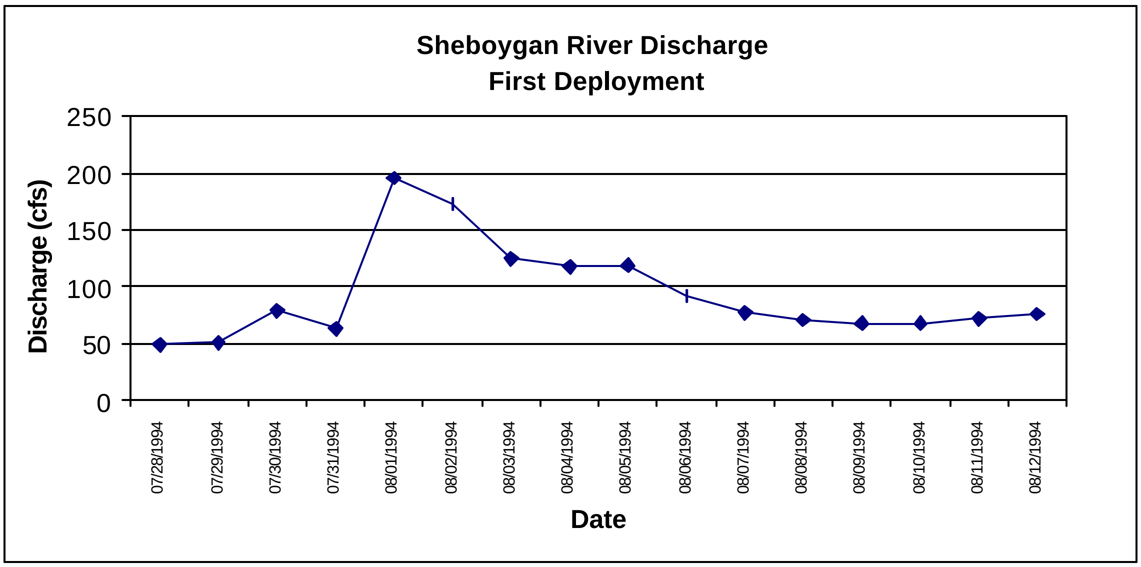
Site	First Deployment	Second Deployment
Rochester	17.8	80.7
Esslingen	25.9	67.9

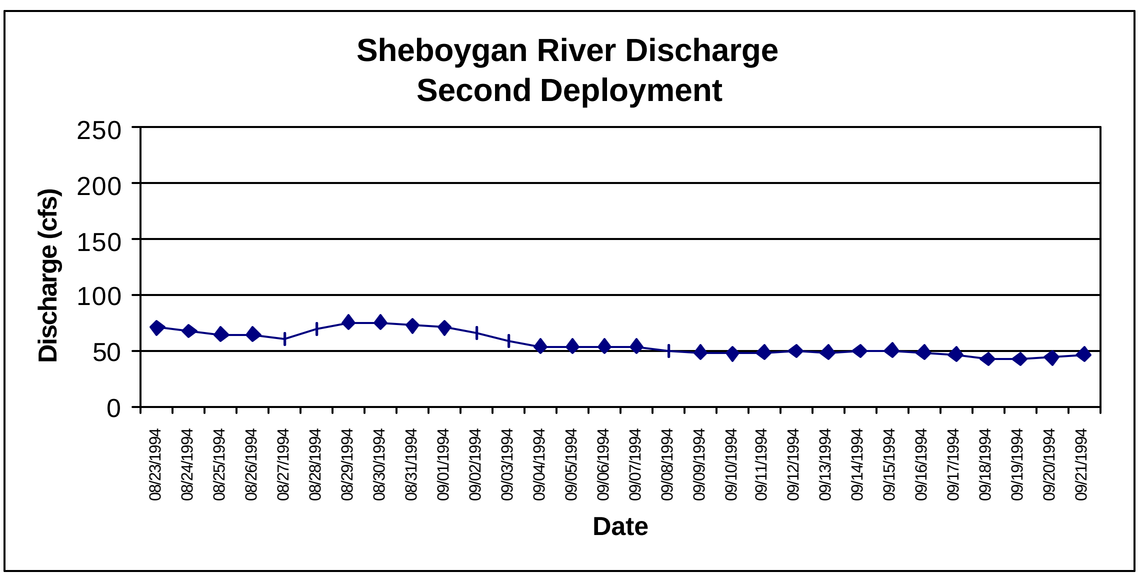
It does make sense that increased biofouling during a longer deployment period would decrease the SPMD contaminant uptake during the second deployment. Therefore, less biofouling probably accounted for the higher levels of di-tetrachlorinated biphenyls at Rochester and Esslingen during the first deployment. It is unclear however why decreased biofouling during the first deployment period did not translate into higher concentrations of the other homolog groups.

Since the SPMDs were not deployed for a long enough period to be in equilibrium with the surrounding water column, they were sampling integratively (Huckins et al., 1990). Some type of episodic event could have caused the ambient water column concentration of PCBs to increase during the first deployment period. During this time, over 3.5 inches of rain fell, with 2.7 inches falling over a three-day period (0.82” 7/30/94 and 1.87” 8/01/94). Conversely, during the second deployment period, only one inch of rain fell during the entire time. The water discharge rate of the Sheboygan River increased nearly three fold following the rainfall events during the first deployment period and remained elevated for about five days (Figure 11).

The higher flows in the river could have caused contaminated sediment or floodplain soil disturbance. Since lower chlorinated PCB congeners are more water soluble (e.g. 4 Cl congeners are 10 times more soluble than 6 Cl congeners) ambient water column concentrations of lower chlorinated PCBs could have become elevated during the first deployment period. By contrast, higher chlorinated congeners are less water-soluble and are more likely to be bound to organic particles. Since SPMDs only sample dissolved pollutants, lower chlorinated congeners would be sampled more readily.

Figure 11. Sheboygan River Discharge for Both SPMD Deployment Periods.





Biota-sediment Accumulation Factors (BSAFs) for PCB Homolog Groups

Average BSAFs for PCB homolog groups and the most toxic PCB congeners were calculated for all trophic groups by dividing the average lipid-normalized tissue PCB concentration by the average TOC normalized sediment PCB concentration.

At the reference site, BSAFs were calculated for homolog groups 4, 5 and 6 only because sediment PCB concentrations for the remaining homolog groups were below detectable levels (Table 15, Figure 12). BSAFs for PCB homologs at this site were generally 10 to 50 times greater than the other sites, probably because of the very low measured PCB concentrations in the sediment and tissue. BSAFs generally increased with increasing trophic level (with the exception of emergent invertebrates). For the highest trophic groups (adult white suckers and adult smallmouth bass), BSAFs increased with increasing chlorination (except octachlorobiphenyls). BSAFs were higher for the trichloro through heptachlorobiphenyls for all trophic groups at the Between Dams site, even though measured sediment PCB concentrations were less than half of the Rochester average (3.4 mg/kg, Between Dams; 7.21 mg/kg Rochester).

Average BSAFs were calculated for the 22 PCB congeners measured that are considered most toxicologically active (McFarland and Clarke, 1989). Only three of the congeners were detected at the Reference site (IUPAC# 87,105,118). At the downstream sites, BSAFs ranged from <1 to 16.36 (Table 16). Adult smallmouth bass and adult white suckers (the highest trophic levels) had the highest calculated BSAFs. The highest BSAFs for most congeners were found at the Between Dams site. BSAF values generally increased with increasing trophic levels at all sites. There was not a distinct relationship apparent between BSAF and extent of chlorination for individual congeners.

Table 15. BSAFs by Homolog Group for Food Chain Study Biota

Site	Tissue type (n)	PCB Homolog Group (# chlorines)						
		Dichloro	Trichloro	Tetrachloro	Pentachloro	Hexachloro	Heptachloro	Octachloro
Reference	Crayfish (3)	0.00	0.00	15.78	4.94	1.23	0.00	0.00
Reference	Larval invertebrates (4)	0.00	0.00	1.52	5.94	7.13	0.00	0.00
Reference	Emergent invertebrates (4)	0.00	0.00	110.20	6.56	4.96	0.00	0.00
Reference	Longnose dace (3)	0.00	0.00	49.81	23.74	17.73	0.00	0.00
Reference	Young white suckers (3)	0.00	0.00	36.21	15.36	9.83	0.00	0.00
Reference	Adult white suckers (3)	0.00	0.00	25.53	19.07	19.76	0.00	0.00
Reference	Young smallmouth bass (3)	0.00	0.00	12.67	10.26	8.57	0.00	0.00
Reference	Adult smallmouth bass (3)	0.00	0.00	121.48	55.06	31.03	0.00	0.00
Rochester	Crayfish (3)	0.05	0.04	0.60	0.52	0.64	0.82	0.43
Rochester	Larval invertebrates (4)	0.19	0.33	0.53	0.48	0.42	0.49	0.44
Rochester	Emergent invertebrates (4)	0.16	0.60	1.22	1.35	1.36	1.56	1.54
Rochester	Longnose dace (3)	0.10	0.28	0.47	0.50	0.47	0.57	0.43
Rochester	Young white suckers (3)	0.23	0.57	0.98	1.01	1.00	1.27	1.31
Rochester	Adult white suckers (3)	0.39	1.33	3.17	3.92	4.60	5.58	5.61
Rochester	Young smallmouth bass (3)	0.43	0.72	1.13	1.35	1.45	1.63	1.39
Rochester	Adult smallmouth bass (3)	0.41	1.21	2.99	4.17	4.71	5.72	5.72
Between Dams	Crayfish (3)	0.12	0.73	1.13	0.97	1.21	1.49	0.55
Between Dams	Larval invertebrates (4)	1.68	2.12	2.18	2.01	1.89	1.94	1.22
Between Dams	Emergent invertebrates (4)	0.70	1.99	2.80	2.88	3.00	3.25	2.44
Between Dams	Longnose dace (3)	0.46	1.63	2.22	2.23	2.46	2.43	1.48
Between Dams	Young white suckers (3)	0.84	2.06	2.54	2.49	2.48	2.43	1.32
Between Dams	Adult white suckers (3)	0.81	2.89	5.24	6.57	7.58	7.69	5.13
Between Dams	Young smallmouth bass (3)	1.29	3.02	4.27	5.25	5.79	5.61	3.15
Between Dams	Adult smallmouth bass (3)	1.21	3.10	5.10	6.80	9.15	9.52	5.91
Esslingen	Crayfish (3)	0.10	0.51	0.80	0.74	1.07	1.48	0.91
Esslingen	Larval invertebrates (4)	1.25	10.50	1.00	0.95	0.92	1.09	0.96
Esslingen	Emergent invertebrates (4)	0.56	1.02	1.34	1.50	1.68	2.10	1.94
Esslingen	Longnose dace (3)	0.68	1.19	1.64	1.80	2.13	2.09	1.62
Esslingen	Young white suckers (3)	0.95	0.99	1.14	1.13	1.36	1.61	1.28
Esslingen	Adult white suckers (3)	0.67	1.13	1.84	2.09	2.37	2.88	2.66
Esslingen	Young smallmouth bass (3)	1.67	1.87	2.28	2.15	2.10	2.15	1.68
Esslingen	Adult smallmouth bass (3)	1.91	2.66	3.83	4.45	5.13	5.30	4.38

Figure 12. BSAFs by Homolog Group for Food Chain Study Biota.

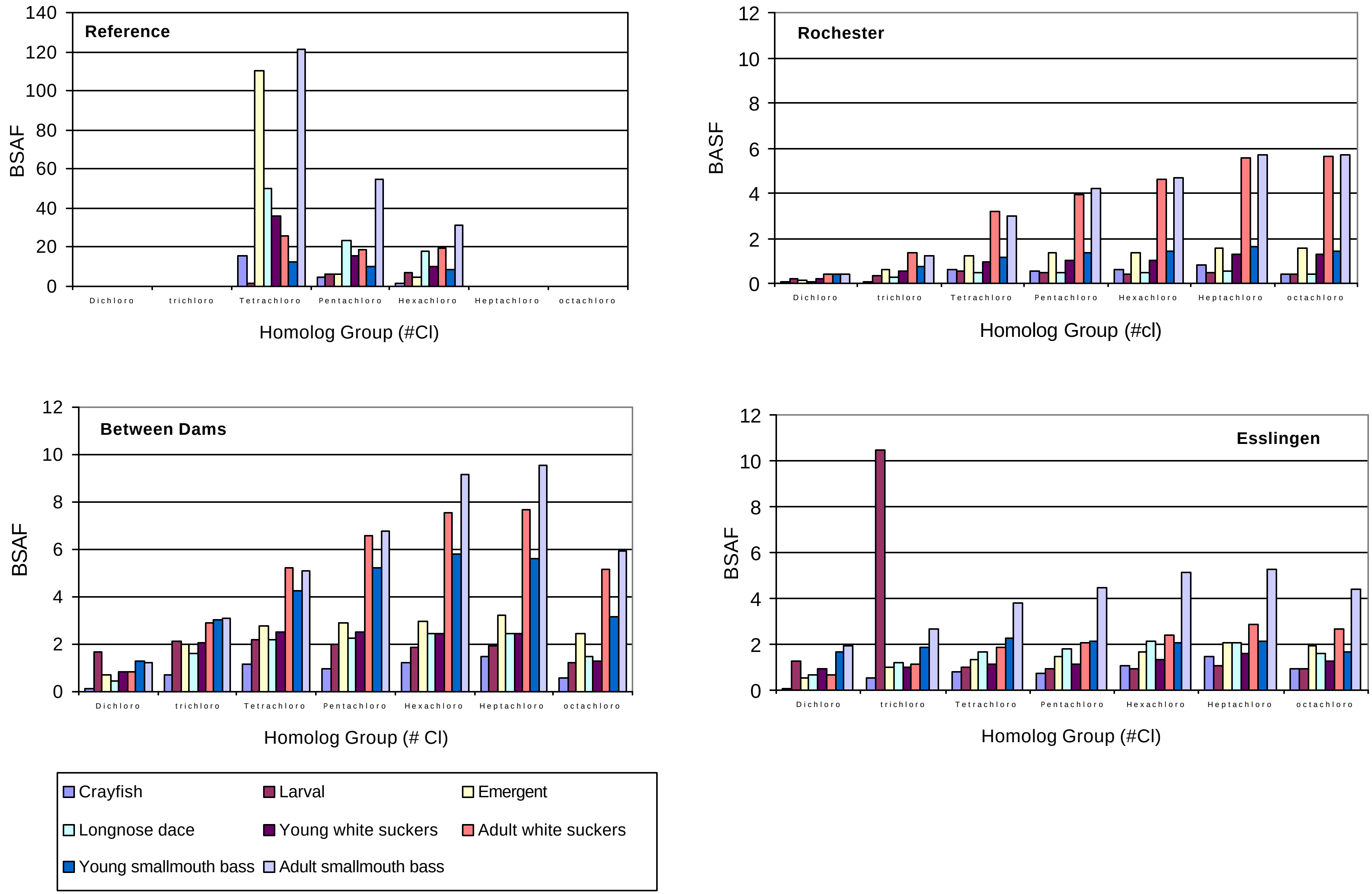


Table 16. BSAFs for the Most Toxic PCB Congeners.

Site	Tissue Type	18	44	49	52	74	77	87	99	101	105	118	126	128	151	156	157	167	177	180	183	194	201
reference	Crayfish							0.00			0.00	9.98											
reference	Larval Insects							0.00			0.00	7.80											
reference	Emergent Insects							1.53			3.79	4.85											
reference	longnose dace							5.91			31.84	16.61											
reference	yoy white sucker							8.75			18.96	11.88											
reference	yoy smallmouth bass							2.67			6.06	8.38											
reference	adult white sucker							9.35			26.26	18.18											
reference	adult smallmouth bass							14.35			23.33	38.43											
Rochester	Crayfish	0.07	0.09	0.70	0.58	1.13	0.54	0.62	1.08	0.92	0.63	0.99		0.67	0.39	0.73	0.81	1.11	0.81	1.15	0.62	0.99	1.09
Rochester	Larval Insects	0.28	0.40	0.50	0.49	0.74	0.48	0.55	0.58	0.56	0.50	0.61		0.46	0.26	0.51	0.68	0.61	0.39	0.58	0.49	0.56	0.48
Rochester	Emergent Insects	0.44	1.04	1.19	1.21	1.72	1.00	1.39	1.60	1.57	1.42	1.82		1.22	0.38	1.57	1.87	1.82	1.26	1.81	1.54	1.96	1.64
Rochester	longnose dace	0.16	0.39	0.54	0.52	0.61	0.16	0.54	0.62	0.68	0.54	0.67		0.45	0.33	0.52	0.43	0.67	0.39	0.69		0.61	0.44
Rochester	yoy white sucker	0.39	0.78	1.02	0.65	1.28	0.29	1.06	1.27	1.21	0.76	1.32		1.08	0.76	0.66	0.59	1.36	0.99	1.49	1.29	1.56	1.39
Rochester	yoy smallmouth bass	0.41	0.81	1.21	1.08	1.67	0.76	1.30	1.83	1.71	1.98	2.14		1.54	1.16	1.62	1.59	2.40	1.24	1.85	1.58	1.74	1.48
Rochester	adult white sucker	0.58	2.39	3.30	1.91	5.01	0.45	4.11	5.67	4.83	3.28	6.14		4.79	2.53	3.52	2.75	6.62	4.30	6.80	5.61	7.12	5.67
Rochester	adult smallmouth bass	0.60	1.93	3.07	2.67	4.86	2.89	4.09	5.75	5.31	5.94	6.41		5.12	3.36	6.44	6.29	7.12	4.61	6.67	5.76	7.33	5.98
Betw. Dams	Crayfish	0.14	0.16	1.25	1.01	1.87	0.00	1.26	1.97	1.87	0.81	1.86		1.39	0.75	1.10	0.85	1.98	1.40	1.79	1.07	1.04	1.37
Betw. Dams	Larval Insects	1.51	1.79	2.20	2.16	2.86	0.00	2.12	2.61	2.39	1.98	2.48		1.90	1.40	1.67	1.67	2.33	1.70	2.11	1.93	1.48	1.37
Betw. Dams	Emergent Insects	1.30	2.43	2.81	2.79	3.35	2.34	2.97	3.69	3.64	1.92	3.69		2.80	0.94	3.00	2.51	3.98	2.81	3.48	3.15	3.03	2.68
Betw. Dams	longnose dace	0.79	2.05	2.60	2.56	2.48	0.68	2.51	3.16	3.26	1.71	2.83		2.14	1.56	2.01	3.34	3.09	1.94	2.75		1.82	1.64
Betw. Dams	yoy white sucker	1.07	2.16	2.85	2.12	2.97	0.63	2.61	3.37	3.35	1.67	3.00		2.61	2.17	2.01	2.53	2.69	2.03	2.50	2.47	1.63	1.69
Betw. Dams	yoy smallmouth bass	1.79	3.59	4.55	4.18	5.56	2.62	5.76	7.29	6.72	6.87	7.19	3.82	5.97	4.12	8.31	10.05	8.62	4.24	5.95	5.73	3.86	3.75
Betw. Dams	adult white sucker	1.34	4.06	5.63	3.82	8.02	1.16	7.45	10.12	9.12	6.23	10.29		8.23	4.48	6.00	9.07	10.30	6.05	8.48	7.94	6.05	5.64
Betw. Dams	adult smallmouth bass	1.76	3.66	5.50	5.18	7.41	3.03	8.18	10.78	9.87	7.32	11.29	5.00	9.03	5.43	10.43	14.60	16.36	7.40	11.00	9.09	7.37	7.33
Esslingen	Crayfish	0.07	0.10	0.91	0.77	1.25	0.26	0.93	1.55	1.41	0.51	1.18		1.04	0.74	0.67	1.13	1.65	1.50	1.70	1.00	1.37	1.60
Esslingen	Larval Insects	0.55	0.69	1.05	1.04	1.18	0.31	0.93	1.17	1.08	0.53	1.09		0.85	0.73	0.52	0.95	1.26	1.01	1.10	0.99	1.05	0.91
Esslingen	Emergent Insects	0.52	1.02	1.35	1.37	1.50	0.45	1.33	1.87	1.92	0.94	1.83		1.42	0.83	1.22	1.33	2.11	1.97	2.15	2.01	1.96	1.80
Esslingen	longnose dace	0.58	1.72	1.97	2.01	1.81	0.60	1.85	2.27	2.53	1.80	2.06		1.57	1.54	2.47	3.94	2.27	1.77	2.19		1.66	1.50
Esslingen	yoy white sucker	0.53	1.01	1.33	0.92	1.22	0.37	1.13	1.60	1.54	0.82	1.33		1.25	1.22	1.15	1.62	1.42	1.31	1.38	1.39	1.20	1.37
Esslingen	yoy smallmouth bass	1.27	2.15	2.65	2.70	2.16	0.59	2.08	2.66	3.08	1.66	2.09		1.63	1.88	1.49	1.46	2.22	1.86	2.34	2.04	1.73	1.45
Esslingen	adult white sucker	0.94	2.59	3.24	2.89	3.76	0.29	3.55	5.05	4.84	1.17	3.87		3.33	2.41	2.14	1.67	4.67	4.02	5.01	4.45	4.73	4.19
Esslingen	adult smallmouth bass	1.45	2.99	4.37	4.40	4.90	0.89	4.69	6.74	6.42	3.09	5.96		4.36	3.68	4.22	3.11	5.91	4.60	5.48	4.95	4.34	4.29

BSAFs for PCB homolgs and congeners are generally consistent with published reports (Ankley et al., 1992; Lake et al., 1990; Ferraro et al., 1991). With the exception of the highest trophic levels at the Between Dams site, most BSAFs fell into the range of 1 to 4 as previously published.

The higher BSAFs for all organisms at the Between Dams site compared to the Rochester site is somewhat puzzling. One explanation may be that organisms at the Between Dams site had more direct contact with sediment than the other two contaminated sites. The Between Dams site is much shorter (1.3 miles) than the other contaminated sites (2.7 mi, Rochester; 3.4 mi, Esslingen). The Waelderhaus Dam may serve to hold contaminated sediments in this river segment. Instead of being transported further downstream, sediments are deposited behind the dam. The river is also less dynamic at the Between Dams site because of the ponding effect of the dam. Water moves slower and sediment has more opportunity to deposit in this area. Additionally, fish species have a more restricted range in this area of the river because the dams restrict migration.

Alternatively, water column transport of PCBs from the more contaminated Rochester site may be having an influence at the Between Dams site. Many of the larval invertebrates collected were filter and suspension feeders. The action of feeding and respiring allow these organisms to filter suspended PCB particles from the water column. The higher trophic level organisms probably accumulate PCBs through the food chain as well as the water column. The higher BSAFs for fish at the Between Dams site may be more of a function of prey concentration and respiration than to direct contact with sediments.

Another explanation may lie with the number of sediment samples collected. Only five samples were collected at each site (4 at Esslingen) and averaged for calculating BSAFs. This is relatively few samples to characterize one to 3 mile-long river segments. It is possible that we missed some areas of higher contamination. Because we sampled through the ice, we did not have the opportunity to characterize the size of each sediment deposit.

POLYCYCLIC AROMATIC HYDROCARBONS (PAHS)

Seventeen polycyclic aromatic hydrocarbon compounds (PAH) were analyzed in sediment, SPMDs and macroinvertebrates. Fish tissue was not analyzed for PAHs because they readily metabolize these compounds. The 17 compounds were summed to calculate a total PAH concentration. Eight of the 17 compounds are considered carcinogenic and were summed to estimate the most toxic fraction of the compounds analyzed.

Three sediment samples were analyzed for PAHs from segments 1, 2, 3, 5 and 6 (Table 17). One deeper sample (the lower 20 cm of a 96 cm core) was taken near the site of a former coal gasification facility adjacent to the Camp Marina overnight area in the city of Sheboygan.

All samples at the reference site were below the limit of detection for all PAH compounds. This is a primarily agricultural area with few known sources of these compounds, so very low to undetectable concentrations were expected at this site.

Sediment PAH concentrations at the Rochester site ranged from 0.28 mg/kg to 23.51 mg/kg. PAH concentrations at the Between Dams site ranged from 0.12-1.19 mg/kg, while concentrations at the Esslingen site ranged from 0.13-9.81 mg/kg. The two higher samples at Rochester (23.51 mg/kg) and Esslingen (9.81 mg/kg), while elevated, are within ranges typical of urban runoff (Table 18). These concentrations may be due to their locations near storm sewer outfalls that drain urban areas in the City of Sheboygan Falls and the City of Sheboygan respectively.

Sediment concentrations at the Camp Marina site ranged from 5.35-15.10 mg/kg. These concentrations are similar to other surface sediment samples taken in the Sheboygan River, and are far less than surface sediment samples taken in Milwaukee area streams (Table 18).

The deeper sediment sample in segment 6 (near the former coal gasification facility at Camp Marina), at 3452 mg/kg has a total PAH concentration 150 to 28,000 times higher than any of the surface samples taken from the Sheboygan River for this study. This one sample was extracted from a 96 cm long core. Upon examination of the core, the lower 20 cm appeared oil soaked and revealed a very strong odor. This portion of the core was homogenized and analyzed for PAHs. As part of an Emergency Repair Fund investigation, several cores were taken at varying depths near this site, with total PAH concentrations taken from depths of 11-119 inches ranging from 0.09 to 9294 mg/kg (NRT, 1998).

Individual PAH compound concentrations for each sample were compared to sediment quality criteria developed by the Ontario Ministry of the Environment (1993). The samples at the Rochester and Esslingen sites with elevated PAH concentrations, and the three surface samples at Camp Marina had individual compound concentrations between the lowest effects level (LEL) and the severe effects level (SEL) (Table 17). This indicates these samples are marginally to significantly polluted have the potential to affect sediment use by some benthic organisms.

The deeper core at the Camp Marina site greatly exceeded the SEL for all compounds for which there are guidelines. This indicates that the sediments are grossly polluted and are detrimental to the majority of benthic species.

Average total PAH concentrations in larval and emergent macroinvertebrate tissues increased with increasing urbanization throughout the watershed (Table 19). No PAH compounds were measured above the limit of detection in any crayfish sample at any site even though detectable levels of PAHs were found in sediments at the Rochester, Between Dams and Esslingen sites.

Average total PAH concentrations in SPMDs increased from upstream to downstream for both SPMD deployment periods (Table 20). The second deployment should have yielded higher concentrations of PAHs than the first deployment (28 days vs 14 days). Excessive biofouling may have decreased the permeability of the membrane during the second deployment (see biofouling discussion on page 37).

Table 17. PAH Compound Concentrations for Sediment.

PAH Compound	Sample Sites																	
	Reference			Rochester			Between Dams			Esslingen			Camp Marina					
	1B	1D	1E	2A	2C	2D	3A	3D	3E	5A	5B	5C	6A	6C	6D	6deep	LEL (ppm) *	SEL (ppm) *
ACENAPHTHENE	**	**	**	**	**	**	**	**	**	**	**	**	**	0.22	0.22	400.00		
ACENAPHTHYLENE	**	**	**	**	**	**	**	**	**	**	**	**	**	**	0.22	16.00		
ANTHRACENE	**	**	**	**	**	0.67	**	**	**	0.13	**	**	0.11	0.24	0.30	330.00	0.22	370
BENZO (A) ANTHRACENE	**	**	**	**	**	1.80	**	0.12	**	0.73	**	**	0.42	0.80	1.80	180.00	0.32	1480
BENZO (A) PYRENE	**	**	**	**	**	1.50	**	0.11	0.17	0.64	**	**	0.40	0.60	1.00	210.00	0.37	1440
BENZO (B) FLUORANTHENE	**	**	**	**	0.13	2.10	**	0.18	**	0.77	**	**	0.44	0.76	1.20	170.00	0.24	1340
BENZO (E) PYRENE	**	**	**	**	**	1.00	**	**	0.18	0.48	**	**	0.21	0.48	0.79	90.00		
BENZO (G H I) PERYLENE	**	**	**	**	**	0.54	**	**	**	0.19	**	**	0.16	**	0.38	43.00	0.17	320
BENZO (K) FLUORANTHENE	**	**	**	**	**	0.92	**	**	**	0.32	**	**	0.22	0.38	0.48	67.00		
CHRYSENE	**	**	**	**	**	1.60	**	0.10	0.13	0.70	**	**	0.38	0.60	1.40	130.00	0.34	460
DIBENZO (A H) ANTHRACENE	**	**	**	**	**	**	**	**	**	**	**	**	**	**	**	13.00	0.6	130
FLUORANTHENE	**	**	**	0.16	0.16	5.20	0.12	0.30	0.24	2.40	0.19	0.13	1.20	1.90	2.20	290.00	0.75	1020
FLUORENE	**	**	**	**	**	**	**	**	**	**	**	**	**	0.17	0.19	250.00	0.19	160
INDENO (1 2 3-C D) PYRENE	**	**	**	**	**	0.68	**	**	**	0.26	**	**	0.14	0.25	0.46	56.00	0.2	320
PERYLENE	**	**	**	**	**	**	**	**	0.12	0.15	**	**	0.11	0.17	0.26	27.00		
PHENANTHRENE	**	**	**	**	**	3.50	**	0.16	0.13	0.94	0.16	**	0.56	1.20	1.30	840.00	0.56	950
PYRENE	**	**	**	0.12	0.12	4.00	**	0.22	0.20	2.10	0.14	**	1.00	1.90	2.90	340.00	0.49	850
sum all PAH	**	**	**	0.28	0.41	23.51	0.12	1.19	1.17	9.81	0.49	0.13	5.35	9.67	15.10	3452.00	4	10000
sum cPAH	**	**	**	**	0.13	9.14	0.00	0.51	0.30	3.61	0.00	0.00	2.16	3.39	6.72	869.00		

**from Ontario Guidelines (1993)*

***below LOD*

Exceeds Lowest Effects Level (LEL)

Exceeds Severe Effects Level

Table 18. Comparison of Sheboygan River Camp Marina Area Total PAH Concentrations with Other Urban Streams

Streams (Reference)	Sample ID	Sample Depth	Total PAH Concentration (mg/kg)
Sheboygan River Near Camp Marina (this study)	6A	0-6"	5.35
	6C	0-6"	9.67
	6D	0-6"	15.10
Sheboygan River Near Camp Marina (NRT, 1998)	SD-701B	0-10"	0.08
	SD-702A	0-16.75"	0.16
	SD-702B	0-15.25"	0.83
	SD-704B	0-23"	443.60
	SD-706C	0-11"	1.24
Milwaukee River Basin Streams (Masterson and Bannerman, 1995)			
Beaver Creek	BV-05	0-10 cm	28.52
	BV-01	0-10 cm	79.45
Lincoln Creek	LC-09	0-10 cm	14.33
	LC-10	0-10 cm	34.04
	LC-11	0-10 cm	21.23
	LC-12	0-10 cm	42.43

Table 19. Average Total PAH Concentrations in Benthic Macroinvertebrates.

Sample Site	Larval	Emergent	Crayfish
Reference	6.50	15.05	**
Rochester	37.10	30.98	**
Between Dams	32.95	42.58	**
Esslingen	104.15	89.1	**

Table 20. Average SPMD Total PAH Concentrations for Both Deployment Periods.

Site	Total PAH Concentrations (ng/g lipid)	
	First Deployment	Second Deployment
Reference	179.13	198.85
Rochester	827.17	333.37
Esslingen	1696.90	822.10
Camp Marina up	2914.70	2313.05
Camp Marina down	2894.20	1754.13

HEAVY METALS

Heavy metal concentrations (As, Cr, Cu, Pb, Hg, Se, Cd, Ag) were analyzed for sediment at segments 1, 2, 3, 5 and 6 and for macroinvertebrates at segments 1, 2, 3 and 5 (Tables 21 and 22). Average heavy metal sediment concentrations were generally similar to sediment concentrations in urban streams studied in Milwaukee County (Masterson and Bannerman, 1995). Cadmium concentrations exceeded the Ontario Guideline's lowest effects level threshold (LEL) at the four downstream sites. Copper concentrations exceeded the LEL at the Rochester, Esslingen and Camp Marina sites, while lead exceeded the LEL at the Esslingen and Camp Marina sites. With the exception of copper (for crayfish) and lead, most of the heavy metal tissue concentrations in benthic macroinvertebrates were similar to the reference site. Emergent invertebrate tissue lead concentrations, however, were two to six times greater at the reference site than the downstream sites. The higher copper concentrations in crayfish are not surprising. Arthropods have hemocyanin for transporting oxygen through their blood (Pennak, 1978). This protein contains copper as the oxygen binding agent.

Table 21. Average Sediment Heavy Metal Concentrations.

Metal	Reference		Rochester		Between Dams		Esslingen		Camp Marina	
	Conc.	n	Conc.	n	Conc.	n	Conc.	n	Conc.	n
Arsenic	1.16	5	0.88	5	0.85	5	1.00	4	1.35	5
Cadmium	**	--	1.60	2	0.80	2	1.45	2	1.30	1
Chromium	14.60	5	13.26	5	13.08	5	18.00	4	22.40	5
Copper	13.72	5	33.44	5	14.16	5	27.50	4	32.20	5
Lead	9.60	5	19.40	5	12.20	5	40.00	4	53.20	5
Mercury	0.07	5	0.09	5	0.05	5	0.04	4	0.08	5
Selenium	0.48	5	0.26	5	0.25	5	0.31	4	0.35	5
Silver	**	5	6.00	1	**	--	**	--	**	--

Table 22. Average Macroinvertebrate Heavy Metals Concentrations.

Site	Tissue type		Metal							
		n	As	Cd	Cr	Cu	Pb	Hg	Se	Ag
Reference	Larval	4	0.18	0.018	0.68	3.38	0.46	0.03	0.49	0.01
	Emergent	4	0.10	0.01	0.13	9.30	0.76	0.06	0.86	0.02
	Crayfish	3	0.60	0.01	0.37	16.67	0.14	0.04	0.29	0.07
Rochester	Larval	4	0.18	0.02	0.75	3.90	0.74	0.02	0.45	0.01
	Emergent	4	0.15	0.01	0.10	7.83	0.13	0.05	1.05	0.02
	Crayfish	3	0.50	0.01	0.30	23.67	0.22	0.02	0.39	0.07
Betw. Dams	Larval	4	0.13	0.01	0.75	3.98	0.55	0.02	0.31	**
	Emergent	4	**	0.01	0.13	7.30	0.32	0.03	1.07	**
	Crayfish	3	0.53	0.01	0.50	22.67	0.27	0.02	0.37	0.05
Esslingen	Larval	4	0.10	0.05	0.95	4.85	1.07	0.02	0.41	**
	Emergent	4	0.10	0.02	0.15	8.88	0.31	0.04	1.11	0.01
	Crayfish	3	0.57	0.01	0.33	28.67	0.45	0.03	0.34	0.03

CONCLUSIONS

- Average total PCB concentrations in sediment, macroinvertebrates and some fish species were higher near the siource of PCB contamination ad decreasaed downstream. It is unclear why longnose dace, young smallmouth bass and young white suckers had higher PCB tissue concentrations at the Between Dams site.

- PCBs bioaccumulate significantly through the food chain in the Shebogyan River, even at the Esslingen site, with average sediment concentrations of less than 2.0 mg/kg. PCBs accumulate with increasing concentrations from sediment to macroinvertebrates to fish.

- The 22 most toxic PCB congeners accumulate through the food chain following the same pattern a the “routine” congeners. These toxic congeners account for 23-34 percent of the total at the contaminated sites.

- Average PCB concentrations for all homolog groups at the contaminated sites increased from sediment with increasing trophic levels as follows: crayfish<sediment<larval invertebrates<emergent invertebrates<white suckers<longnose dace<smallmouth bass. Crayfish were the only organisms studied that did not accumulate higher tissue PCB concentrations than sediment.

- The tetra- and pentachlorobiphenyls are the dominant homolog groups, accounting for over 80 percent of total PCB concentrations. The lower chlorinated biphenyls comprised a higher percentage of PCBs in lower trophic levels, while fish accumulated a higher percentageof penta- and hexachlorobiphenyls.

- The SPMDs accumulated lower chlorinated PCB congeners (di-tetra) in higher concentrations than higher chlorinated congeners. Concentrations for the lower chlorinated homolog groups at Rochester and Esslingen were nearly double during the first deployment, although the second deployment period was twice as long. This may be due to increased biofouling during the second deployment period, or higher ambient water column PCB concentrations during the first deployment.

- BSAFs for PCB homologs generally increased with increasaing trophic level. For the highest trophic groups, BSAFs increased with increasing chlorination. BSAFs for PCB homologs and congeners were consistent with published reports except for the highest trophic groups at the Between Dams site. The reason for the higher BSAFs at this site compared to the more contaminated Rochester site is unclear.

- Surface PAH concentrations at all downstream sites are within the ranges typical of urban runoff. PAHs were not detected at the Reference site. Individual PAH concentrations for some samples exceeded the lowest effects level, indicating marginally to significantly polluted sediments that have the potential to affect some benthic organisms. The deep core at the Camp Marina site greatly exceeded the severe effects level for all compounds, indicating the sediments at depth are grossly polluted and are detrimental to most benthic species.

- Larval and emergent macroinvertebrates had PAH tissue concentrations that increased with increasing urbanization throughout the watershed. No PAH compounds were detectred in crayfish tissue at any site.

- Average total PAH concentrations in SPMDs incrased from upstream to downstream for both deployment periods. This is consistent with the pattern of increasing PAH concentrations with increasing urbanization.

- Heavy metal concentrations in sediment were similar to sediment concentrations in Milwaukee County streams. Cadmium concentrations exceeded the lowest effects level at all downstream sites. Copper and lead exceeded the LEL at some sites.

- Heavy metal tissue concentrations for most macroinvertebrates were similar at all sites with the exception of copper (in crayfish) and lead. Since crayfish contain copper as hemocyanin (blood protein with copper as the oxygen carrier), this is not suprising.

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APPENDIX A

Photographs Depicting

Sampling Activities

for

Sheboygan River Food Chain Study

Figure A.1.
Collecting larvae from rocks in riffle areas of Sheboygan River.

Figure A.2.
Emergent light trap at streamside (above).

Right: Light trap hanging above river.

Figure A.3.
Kick net technique for collecting crayfish.

Figure A.4.
Collecting fish using stream electroshocker.

Figure A.5.
Sediment sampling device.

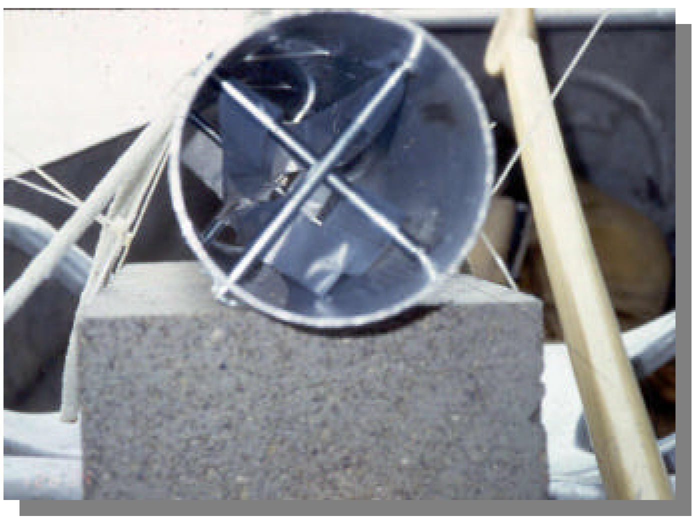

Figure A.6.
Semi-permeable polymeric membrane devices (SPMDs) in deployment device during first deployment period.

Figure A.7.
Modified SPMD deployment device to prevent damage during second deployment period.