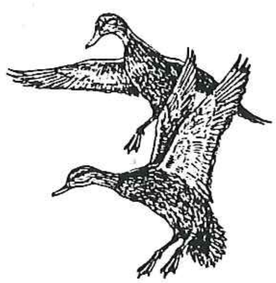
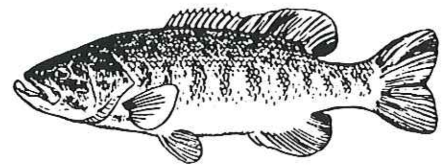
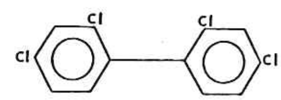
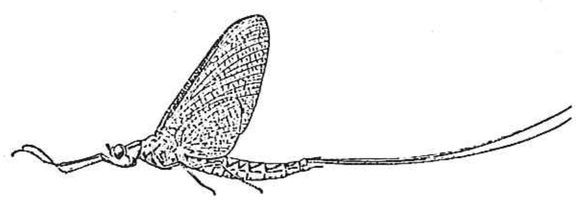
A Review of the PCB Contaminant Problem of the Upper Mississippi River System









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February 1988

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ACKNOWLEDGEMENTS

There were many individuals who provided unpublished PCB reports, data and comments on the Upper Mississippi PCB problem that greatly benefitted this review. Without this information, the scope of this report would have been severely diminished.

Dan Helwig, Minnesota Pollution Control Agency, provided a PCB summary of carp data collected during the 1980-1984 period for Pool 1 to 10 of the Upper Mississippi River, the lower Minnesota and St. Croix Rivers. Gerry Jackson, U.S. Fish and Wildlife Service, contributed PCB data on sediments and suspended sediments from throughout the UMR system, especially Lake Onalaska, Pool 2. Dennis Anderson, U.S. Corps of Engineers, provided a 10 year contaminant data base for mainly the navigation channels of the Upper Mississippi, Lower St. Croix and Minnesota rivers. Anderson's data base was provided on a Lotus 1-2-3 spreadsheet that greatly facilitated the review of the sediment data and served as the format for expanding the data base with other information. Stan Smith and C. Davis, U.S. Fish and Wildlife Service provided recent unpublished information on sediment contaminants from Pools 4-10. Bill Mauck and Ted Schwartz, Columbia National Fishery Research Laboratory (CNFRL), provided excellent information concerning previous PCB monitoring efforts in the UMR. Ted Schwartz provided additional information on analytical methods for PCB analysis. Jim Huckins, CNFRL, provided references and comments on equilibrium partitioning procedures. Paul La Liberte and Lee Liebenstein, Wisconsin DNR, provided assistance in utilizing Wisconsin's fish contaminant data base. Arthur Lubin, EPA, assisted with statistical procedures.

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SUMMARY AND CONCLUSIONS

PCBs have been monitored in the Upper Mississippi River environment over the last 17 years by Federal and State agencies, public and private institutions and by point source dischargers to the river. A majority of this monitoring has involved the analysis of fish and sediment samples. Additional PCB data have been collected on other important river ecosystem compartments including: mayflies, turtles, waterfowl, heron and egret eggs, aquatic macrophytes, bottom and suspended sediments and water.

Sediment and fish PCB data indicate the most severe contaminant problem is in Pool 2, the impoundment which extends from the Twin Cities to Hastings, Minnesota. Main channel sediments show very little PCB contamination below Pool 2. Significant PCB levels in sediments are found in the reach immediately upstream from Lock and Dam 2 and the lower Minnesota River. PCB levels in fish, mainly the larger fish with high lipid content (ie. channel catfish, carp and white bass), continue to exceed the Food and Drug Administration's standard of 2 mg/kg. The most serious fish contaminant problem is found in Pool 2, but significant PCB body burdens in fish, warranting health consumption advisories by Minnesota and Wisconsin, extend for more than 100 miles downstream.

The PCB distribution in Upper Mississippi River fish, sediments and mayflies show similar patterns with highest levels reported for the river segments adjacent to or near the Twin Cities Metropolitan Area. This information indicates the major source(s) of the PCB input to the river system is in this region.

Temporal trends in fish PCB data collected by Minnesota and Wisconsin indicate contaminant levels are declining. Wisconsin's fish contaminant data for Pool 4 (Lake Pepin) indicated significant reductions in mean PCB levels in carp (39%), white bass (41%) and drum (87%) based on fillet data collected in the late 70s (1976-79) versus the early 80s (1980-84). Mean PCB contaminant levels in channel catfish and walleye fillets from Pool 4 have also declined, 50 and 20 % respectively, but these were not statistically significant.

Sediment PCB concentrations, normalized using sediment manganese or loss on ignition, indicated higher levels in the early 80s versus the late 70s for samples collected from above Minneapolis, Pool 1 and Pool 2. This increase is not believed to be due to increased PCB loading in the 80s. This difference is probably a result of considerable contaminant variability in sediments and differences in the sampling sites between the two periods. The recent sediment data for the lower Minnesota river and Pool 2 indicate PCB concentrations exceeding 1 mg/kg are still found in some areas. As a result, PCB bioaccumulation problems in fish are expected to continue based on partitioning between sediments, water and fish.

Effluent PCB monitoring of point source discharges have not identified major PCB inputs to the Upper Mississippi River system. Municipal wastewater treatment plant effluents in the Twin Cities area account for an instream concentration of approximately 1 to 3 ng/l (ppt) at St. Paul at average river flow. Estimates of river PCB levels range from about 20 to 150 ppt based on measured values or predicted from partitioning models. The actual significance of any point or nonpoint source input is not easily established due to the uncertainty of instream PCB concentrations.

PCBs have been detected in ambient air samples and from incinerator emissions in the Twin Cities area. Atmospheric deposition from the incineration of PCB containing wastes is not believed to be an important local source input.

A preliminary sediment PCB criterion of approximately 50 to 100 ug/kg may be appropriate to prevent exceedance of FDA's 2 ppm standard for fish tissue based on partitioning models. However, the lipid content of fish, sediment organic carbon content and food chain uptake may be important factors affecting bioaccumulation and should be considered for site specific assessments. More information concerning the relationships between the sources of exposure (ie food chain, water, bottom and suspended sediments) and actual PCB body burdens in fish are needed.

Future PCB monitoring efforts should include congener or isomer-specific analysis where possible. This information provides better information on the fate of PCBs in the environment and may assist in the location of source inputs. Further, isomer-specific PCB analysis may allow for a more thorough evaluation of the more toxic PCBs.

RECOMMENDATIONS

1. Future PCB monitoring efforts should better define source inputs and instream concentrations, especially in areas exhibiting high PCB contamination in fish and sediments. For the Upper Mississippi River system, these areas include: Pool 2 of the Mississippi River and the lower Minnesota and St. Croix Rivers.

2. An inventory and analysis of past land use in areas adjacent to the above river segments should be considered to help identify potential sites of improper use or disposal of PCB containing materials. This analysis should be undertaken if future contaminant monitoring of fish and sediment fail to indicate declining trends.

2. Site specific monitoring is needed to identify sources or areas of PCB input. This could include one or more of the following activities: In situ bioaccumulation studies of caged organisms, monitoring of indigenous aquatic organisms, and the analysis of suspended and bottom sediments.

3. Congener or Isomer-specific PCB analysis should be conducted on several ecosystem compartments where substantial PCB contamination is found. This will define the types of PCB compounds present, help define the fate of PCB compounds and may help locate source inputs.

4. Minnesota and Wisconsin should continue to maintain coordinated fish contaminant monitoring programs in border waters. This should be expanded to include other environmental samples where warranted. Wisconsin should participate with Minnesota's long-term trend analysis program to assess carp PCB contamination in the Mississippi River above Pool 5. Wisconsin should conduct similar contaminant analysis of carp from Pools 5a to 9.

5. Periodic contaminant monitoring of PCB contamination in mayflies in the Upper Mississippi River System should be reestablished. The U.S. Fish and Wildlife Service reactivated this monitoring program in the summer of 1987. State environmental and resource agencies with offices bordering the river should assist in the collection efforts where possible.

6. More data is needed to better define the distribution of PCBs and other contaminants in the "fine" sediments of the Upper Mississippi River System. Future sediment monitoring programs should obtain more samples of backwater areas and boat harbors. Contaminant sampling of suspended sediments is also warranted to better assess contaminant transport and water column concentrations. Future sediment monitoring programs should include parameters to help evaluate the effect of sediment particle size and organic carbon content. Suggested normalization parameters include: total organic carbon, loss on ignition and manganese.

7. A contaminant data base of physical and biological samples from the Upper Mississippi River System should be developed. Federal and State agencies should have access to the computer system utilized. Two possible systems include: STORET, developed by EPA, or the proposed Integrated Data Management System for the Upper Mississippi River Environmental Management Program.

INTRODUCTION

This report will review the available PCB data for the Upper Mississippi River that has been collected by State, Federal and public agencies or universities since the problem was first identified in 1970. The objective of the report is to summarize the PCB data that has been obtained by monitoring various ecosystem compartments and to assess the distribution and temporal trends where possible. Particular emphasis will be placed on sediment and fish tissue data since considerable information on PCB contamination in these environmental compartments have been collected in the last 10 years. Recommendations for future PCB sampling initiatives will be made to further evaluate the fate of PCBs in the Upper Mississippi River and to better define source inputs.

PCBs

Eisler (1986) provided a review of the technical information of PCBs which was utilized to summarize the environmental chemistry, use and hazards of these compounds. Polychlorinated biphenyls (PCBs) are a class of organic compounds that are produced commercially by the chlorination of biphenyl with anhydrous chlorine. The resultant product is a complex mixture of chlorinated biphenyls with varying chlorine content. There are ten levels of chlorination of the biphenyl molecule which are refered to as congener groups. The specific location and degree of chlorination on the biphenyl molecule determines the identity of specific PCB isomers. A total of 209 PCB isomers and congeners are possible (Mullin et al. 1984). PCBs have been in wide spread use since the 1930s as heat transfer agents, lubricants, dielectric agents, flame retardants, plasticizers and water proofing materials. PCBs have entered the aquatic environment through the discharge of municipal and industrial effluents, runoff from land surfaces contaminanted with PCBs, atmospheric deposition of incinerated materials containing PCBs, spills, and illegal disposal.

Monsanto Corporation was the major manufacturer of PCBs in the United States and sold PCBs under the trade name of Aroclor. Various Aroclor formulations were developed ranging in chlorine content from 21 to 68 % by weight. Aroclor mixtures containing 21 % chlorine (ie. Aroclor 1221) were clear mobil oils. Higher chlorinated biphenyls were more viscous ranging from a yellow viscous liquid (Aroclor 1254) to a white solid (Aroclor 1268) (Safe, 1984).

Of the Aroclors produced from 1957 to 1970; 1242, 1248, 1254 and 1260 accounted for about 97 % of the sales. A well know plasticizer application of PCBs was in the production of carbonless copy paper where Aroclor 1242 was utilized (Schwartz, 1987).

Environmental contamination with PCBs is evident worldwide as a result of wide spread use and its persistence in the environment. PCBs are highly soluble in lipids and have the ability to bioaccumulate within the food chain. In aquatic environments PCBs are normally sorbed to fine sediment particles especially sediments with high organic carbon content (Karickhoff et al. 1979 and USEPA, 1986). The presence of PCBs in organisms has been shown to cause reproductive failures, birth defects, skin lesions, liver disorders tumors and death based on the summary provided by Eisler (1986).

PCB formulations may also include other toxic compounds such as polychlorinated dibenzofurans (PCDFs), (Stalling et al. 1983). Further, the burning PCB contaminated materials may also produce PCDFs and polychlorinated dibenzo-p-dioxins (PCDDs), (Thompson et al. 1986).

State and Federal regulations were enacted in the mid 70's to restrict the use, labeling and disposal requirements of PCBs and led to the ban on the manufacturing and processing of these chemicals for use in open systems. PCBs are still permitted in closed sytems of which Aroclor 1016 is predominantly used (Schwartz, 1987).

In 1984, the U.S. Food and Drug Administration (USFDA) modified their fish fillet "action level" to 2.0 ppm (formerly 5.0 ppm since 1973) for fish sold in interstate commerce. These actions were taken to reduce the risks of consuming PCB contaminated fish. The USFDA "action levels" are used by state health agencies in their development of consumption advisories for sport anglers.

PCB Measurements and Analysis

PCB compounds are extracted from environmental samples using organic solvents and analyzed using gas chromatography. The resultant chromatographic profile is compared to various Aroclor standards to establish the identity and concentration of the Aroclor mixture(s) present. Each Aroclor mixture is characterized by different PCB isomers and may contain many chromatographic peaks (Mullin et al. 1984).

More recent advances in the analysis of PCBs using capillary column gas chromatography has improved the ability to detect specific PCB isomers (Mullin et al. 1984 and Schwartz, 1987). The use of isomer-specific PCB data in combination with advanced statistical analysis (principal component analysis-PCA) has provided a new tool for assessing the fate of PCB compounds in the environment (Stalling et al. 1985 a,b and Schwartz et al. 1987). Some isomers of PCBs are approximate isostereomers of dioxin (2,3,7,8 TCDD) and may account for "dioxin like" toxicity in aquatic organisms (Smith et al. 1986). Isomer-specific PCB analysis is more definitive in determining the type of PCB mixtures present in environmental samples (Schwartz et al. 1987).

It was through the analysis of isomer-specific sediment PCB data from the UMR in the late 70s that led to the discovery of PCB contaminated soils at a U.S. Corps of Engineers (U.S. COE) boat yard located on the Mississippi River at Fountain City, Wisconsin (Schwartz, 1986). Schwartz inidcated the total PCB content of the sediments near the boat yard was not unusually high in comparison to other sites on the river. However, the chromatographic profile indicated a noticable difference in the isomers present at this site. Follow up investigations by the Wisconsin Department of Natural Resources revealed hydraulic fluids, containing PCBs, were used in the boat yard to control dust.

Upon discovery of this problem, contaminated soils were removed and taken to an approved solid waste facility.

The identification and quantification of PCBs in the same environmental samples by various laboratories may not be consistent due to differences in analytical procedures. The practice of reporting PCBs as a specific Aroclor equivalents are often subjective and may not accurately reflect the total PCB concentration or the identity of the Aroclor mixture(s) present (Schwartz et al. 1987). In addition, quality assurance records may not be available to assess the performance of the laboratory. As a result, the interpretation of PCB data from different labs has to be viewed with some caution and uncertainty.

Background on Upper Mississippi River PCB Problem

Polychlorinated Bipenyls (PCBs) were first identified in the Upper Mississippi River (UMR) system in 1970 by the Wisconsin Department of Natural Resources during the State's initial fish PCB contaminant analysis (Degurse and Ruhland, 1972 and Sheffy, 1980). The results of this initial monitoring program revealed substantial PCB contamination in fish, especially in carp, walleye, and white bass in UMR Pools 3 and 4. PCB levels in whole fish frequently exceeded 20 mg/kg with several samples exceeding 50 mg/kg.

In the spring of 1975, the U.S. Food and Drug Administration detected PCB levels in fish from Lake Pepin (Pool 4) above the commercial action level of 5.0 mg/kg (ppm). This resulted in the destruction of more than 60,000 lbs of carp fillets (Hora, 1984). As a result, an Interagency Task Force (IATF) was formed in 1975 to identify the source(s) of PCB discharge to the Mississippi River and to determine the extent of the problem so that PCB contamination could be controlled (IATF, 1976). Task Force members included: the Minnesota Pollution Control Agency (MPCA), Minnesota Department of Natural Resources (MDNR), Minnesota Department of Agriculture, Metropolitan Waste Control Commission (MWCC), Wisconsin Department of Natural Resources (WDNR), Wisconsin Department of Agriculture, U.S. Fish and Wildlife Service (USFWS), U.S. Food and Drug Administration (USFDA), and the U.S. Environmental Protection Agency (USEPA).

The Task Force initiated a major PCB sampling program during the summer of 1975 in the UMR reach extending from Monticello, Minnesota to Alma, Wisconsin. In addition several tributary streams were included. PCB samples were collected from municipal and industrial discharges, river water, sediments and fish fillets.

The results of the Task Force indicated highest PCB contamination in fish and sediments extending from Pool 1 to Pool 4 (IATF, 1976). The Task Force found a close relationship between fish fillet PCB levels and sediment concentrations. PCBs were detected in only a few point source discharges and were not believed to represent a significant source of PCB discharge to the river or its tributaries. PCBs resembling Aroclor mixture 1254 were believed to be the major PCB mixture present.

In 1978, consultants for the Columbia National Fishery Research Laboratory (CNFRL), Columbia, Missouri, completed a literature review of information which could help describe the transport, distribution and bioaccumulation of PCBs in the aquatic community of the UMR (Dexter et al. 1978b). A companion document specifically evaluated the hydrology, sediment and PCB transport and PCB distribution in the UMR with particular emphasis on Lake Onalaska, Pool 7 (Dexter et al. 1978a).

The results of the consultant's evaluation of existing data indicated primary sources of PCBs are in the Minneapolis-St. Paul area. Atmospheric input of PCBs was not believed to be an important source in describing the longitudinal distribution of PCBs in the river. The distribution of high levels of PCBs in aquatic habitat in the Twin Cities area to low levels downstream, was attributed to river flow, dilution by tributaries and losses to river sediments.

In 1979, the CNFRL began a more detailed study to assess the distribution of PCBs in the UMR system (Mauck, 1986). Major emphasis was directed to Lake Onalaska (Pool 7) where about 1200 environmental samples were collected and analyzed by capillary gas chromatography for 69 PCB isomers (Stalling, 1985b). PCB samples were collected from water, suspended sediments, bottom sediments, fish, benthos and aquatic plants. The results of these investigations have not been published at this time. However, some of the sediment and suspended sediment PCB data are summarized in this report.

For the last several years MPCA, MDNR and WDNR have been cooperating in the sampling and analysis of PCB contamination in fish from the river. The major purpose of this effort is to develop consumption advisories for sport fish and marketing recommendations for commercial fish species for the adjoining boundary waters. Consumption advisories issued by the two states for sport fish species from the same UMR pool have not always been consistent due to different evaluations by each State's Department of Health, the agencies primarily responsible for issuing consumption advisories. However, the Health Departments for both States have been meeting to try to establish consistent guidelines for establishing consumption advisories for PCBs in fish. Consistent marketing recommendations for commercial fish species, based on FDA's 2.0 ppm action level, have been developed jointly by the two States since 1985 (MPCA, MDNR and WDNR, 1985).

Upper Mississippi River PCB Data

A summary of PCB monitoring from the UMR over the last 15 years is presented in Table 1. This information provides an overview of the types and extent of PCB monitoring and the researchers responsible for these efforts. As stated previously, caution must be taken when comparing the results of many PCB studies since researchers may have utilized different laboratory methods which likely changed with time as newer analytical equipment and techniques became available. In addition, there was little quality assurance information from many of these studies which further complicates the interpretation of these data.

Fish

PCB levels in fish have been extensively monitored by federal and state agencies since 1970 (Table 1). The majority of the monitoring has been undertaken by the States of Minnesota and Wisconsin to assess the need for fish consumption advisories for sport and commercial fish species. The U.S. Fish & Wildlife Service has also been active at assessing the PCB contamination problem in the UMR system (Jackson et al. 1981 and Smith S. 1986). Table 1 does not include a summary of all fish species monitored for PCBs by various agencies, instead a listing of major species is provided.

The PCB contaminant data for fish indicate a definite longitudinal distribution in the Upper Mississippi River with highest levels reported for the reach extending from St. Paul (Pool 2) to Lake Pepin (Pool 4). This pattern is most evident with carp, the species most frequently monitored for PCBs by MPCA and WDNR (Fig. 2a & b). Fish below Pool 4 normally have lower PCB levels with the exception of large fish with high lipid content (eg. catfish, carp and freshwater drum). This pattern of PCB contamination in fish has been observed in several UMR studies and has been generally attributed to PCB contributions from the Twin Cities metropolitan area (Degurse & Ruhland 1972; IATF 1976; Jackson et al. 1981 and Dexter 1978).

Long term monitoring of PCB levels in carp fillets by MPCA in a river reach extending from Sartell to Wabasha, Minnesota has indicated contamination is decreasing (Hora, 1984). Mean carp fillet concentrations have declined 63 % on a tissue basis (4.01 to 1.48 mg/kg) and 72% on a lipid basis (129 to 35.9 mg/kg) for a period extending from 1975 to 1982 (MPCA, 1985). The decline in PCB levels in fish is attributed to federal and state laws which were enacted to reduce the discharge of PCBs to the environment (Hora, 1984 and MPCA, 1985).

Wisconsin's Fish PCB Data

A review of WDNR's PCB data for carp collected from Pools 4-9 also indicated a marked reduction in PCB levels when comparing data collected in the late 70s (1975-1979) versus the early 80s (1980-1984) (Fig. 3a & b). Lipid based PCB levels have decreased to a greater extent than concentrations expressed on a tissue basis. This is consistent with the results of MPCA (1985). Although PCB levels in carp have decreased over the last 10 years, concentrations are still high in comparison to samples that are not influenced by the Twin Cities metropolitan area. This is reflected in carp samples collected from Czechville Pond, which is part of Waumandee Creek tributary and enters the river at Pool 5a just north of Fountain City, Wisconsin. PCB concentrations in carp fillets from this area were less than 0.2 mg/kg (Fig. 3a).

Mean PCB levels in fish collected during the late 70s and early 80s were tested with the General Linear Models (GLM) ANOVA option using SAS (SAS Institute Inc., 1986) to determine if means differed significantly. The GLM ANOVA option was selected because sample sizes between test groups were not equal. Under such conditions, the GLM ANOVA procedure is recommended (SAS, 1986). ANOVA is a statistical technique which indicates whether differences between groups are great enough such that the probablility that the observed differences are the results of sampling errors is low. The actual probability is derived from the chosen alpha level which in this report was five percent ($p < 0.05$).

Fish PCB levels in the UMR did not appear to be normally distributed. Data were log-transformed to yield a log-normal distribution. The size of fish used in the GLM tests were restricted where possible to reduce the variability due to fish length or age. In addition, only fillet data were utilized to reduce the variation due to sampling methods.

Carp have been the fish species most extensively monitored for PCBs in the UMR and are an excellent indicator of PCB contamination because of their high lipid content and their close association with bottom sediments. Tissue based PCB levels in carp have decreased in the 80s over levels observed in the late 70s. A significant reduction in tissue based PCB concentration in carp was found in Pool 4 (Table 2). Lipid based PCB levels have decreased significantly in Pools 4, 8 and 9 (Table 3). Insufficient data are available for Pools 5A, 6 and 7 to assess temporal changes in PCB contamination in carp.

PCB levels in channel catfish, white bass, freshwater drum and walleye collected from Pool 4 were also assessed to determine if significant reductions in PCB levels have occurred in these species (Fig. 4a & b). Pool 4 was chosen because more samples were available for this pool and fish from this river segment have historically exhibited high PCB concentrations. Tissue based PCB levels were highest in channel catfish followed by carp, white bass, freshwater drum and walleye (Fig. 4). This order followed the mean lipid contents of these species which were 8.2, 7.9, 3.9, 3.9 and 1.0 %, respectively, based on all fillet data collected from the Mississippi River between 1976 and 1985.

Significant reductions in mean tissue PCB concentrations were found for carp, white bass and freshwater drum when comparing data collected in the late 70s versus the early 80s (Table 4). A similar analysis using lipid-normalized data, indicated significant PCB reductions in carp, white bass and walleye (Table 5). Although statistically significant reductions in tissue or lipid based PCB levels were not found for channel catfish, concentrations have decreased in these fish in recent years. In general, Wisconsin's fish contaminant data indicates PCB contamination in fish of the UMR is decreasing and is consistent with results reported in other studies (MPCA, 1985; Hora, 1984 and Schmitt et al. 1983).

Invertebrates

The majority of PCB monitoring in invertebrates has been directed at the mayfly, *Hexagenia bilineata* (Mauck and Olsen, 1977 and Clements and Kawatski, 1984, (Table 1). These researchers studied the longitudinal distribution of PCBs (Aroclor 1254) in adult mayflies in river Pools 3 to 10 in three different years (1977, 1980 and 1983). PCB levels in whole mayflies ranged from 2 to 3 mg/kg (wet wt) in Pools 3 & 4 and declined to concentrations less than 0.5 mg/kg in Pool 10. There was no apparent reduction in PCB levels over the six year monitoring period.

Sparks and Smith (1979) analyzed PCB content of mollusks from pool 19 during 1977 and 1978 (Table 1). They analyzed PCB contamination in snails (*Helisoma trivolvis*, *Campeloma crassula* and *Viviparus georgianus*) and fingernail clams (*Musculium transversum*). PCBs in snails ranged from less than 2 to 248 ug/kg (shells included). Levels in fingernail clams ranged from 14.5 to 927 ug/kg. PCB concentrations in mollusks were 10 to 300 times higher than sediment levels. These researchers sent mollusk samples to two laboratories for PCB analysis. The results indicated substantial differences between the two labs; therefore, the actual concentrations remain uncertain.

Mayflies and mollusks are an important component in aquatic ecosystems because these organisms are important food sources for fish and waterfowl (Henry et al. 1986 and Sparks and Smith, 1979). PCBs may be transferred to these higher organisms if invertebrates are exposed to contaminated sediments. Periodic monitoring of invertebrate PCB levels in the UMR should continue to further assess this problem. The U.S. Fish and Wildlife Service repeated contaminant monitoring of mayflies from the Mississippi River in the summer of 1987.

Birds

Nosek and Faber (1984) determined PCBs and organochlorine residues in great blue heron and great egret eggs collected from a colony located near Fountain City in Pool 5A in 1978 (Table 1). PCB concentrations in heron and egret eggs yielded a geometric mean concentration of 14.1 and 13.3 mg/kg, respectively. The PCB chromatograms resembled the Aroclor mixture 1254. These researchers indicated the PCB levels found in eggs were high in comparison to similar research conducted in other parts of the country. Several other chlorinated pesticides were also detected in eggs but at lower levels. These included: DDT, DDE, DDD, hexachlorobenzene, heptachlor epoxide, dieldrin, endrin, trans-nonachlor and mirex. The extent to which the heron and egrets were exposed to PCBs on their summer or winter feeding grounds was not determined.

Limited sampling of PCBs in mallard breast tissue (skin on) has been determined by WDNR from mallards collected from Pool 9 and 10 in 1984 and Pool 4 (Lake Pepin) in 1985. This was done as part of a statewide wildlife contaminant monitoring program (Amundson, 1985, 1987). The results for Pool 9 and 10 indicated PCB levels were below the detection limit of 0.2 mg/kg. PCBs were detected in 2 out of 3 mallard samples collected from Pool 4 at the marina at Pepin, Wisconsin (Admundson, 1987). Lipid based levels in mallard tissue from this marina exceeded 20 mg/kg. These results are consistent with fish and sediment PCB data and indicate mallard contamination is likely in areas where the aquatic envrionment is contaminated with PCBs. This relationship was noted in Amundson's waterfowl contaminant monitoring efforts in Wisconsin. Amundson recommended future waterfowl sampling efforts should be directed in those areas where fish consumption advisories are in effect. Follow up waterfowl sampling in the Lake Pepin area is planned by WDNR.

Water

PCB solubility in water is low due to the hydrophobic nature of these organic compounds. The water solubility of Aroclors 1254 and 1260, two common PCB mixtures found in fish and sediments in the UMR are 10 and 3 ug/1, respectively. The solubilities of lower chlorinated biphenyls are greater (NAS, 1979).

Information of dissolved PCB concentrations in the UMR is lacking. However, PCBs have been detected in whole water samples (ie. suspended matter included) from the UMR and some of its tributaries (IATF Task Force, 1976). PCBs in surface water samples were detected above the 0.4 ug/1 detection limit at 4 of 60 locations in the UMR system and tributaries in 1975. These sites were on the Rum River below Elk River, Minnesota (10 ug/1), on the St. Croix River at Prescott, Wisconsin (3.1 ug/1), on the Mississippi River above Minneapolis (2.7 ug/1) and at the southern end of Lake Pepin (3.0 ug/1).

MPCA (1984), using data collected by MWCC in 1981, estimated total PCB contribution from the Twin Cities Metropolitan area at approximately 0.272 kg/day of Aroclor 1016 (MPCA, 1984). This loading yields an instream concentration of 10 ng/1 (ppt) at an average river flow at St Paul of 11,000 cfs. This is a very rough estimate since it is based on limited data. It also does not include contribution from the Minnesota River or inputs to the Mississippi River above the Twin Cites. When all inputs are considered, the total Aroclor 1016 load was approximately 0.727 kg/day in the Mississippi River above the confluence with the St. Croix. This yields an instream level of about 27 ng/1 at average river flow. There is some uncertainty concerning MWCC's PCB analysis since Aroclor 1016 has not been reported in other environmental samples from the river.

An empirical estimation of PCB concentrations in water can be made using equilibrium partitioning concepts. These methods utilize the n-octanol/water partition coefficient (Kow) for selected nonpolar hydrophobic organic chemicals to predict sediment absorption, water solubility and biological uptake in aquatic organisms (EPA, 1986; Chiou et al. 1977 and Karickhoff et al. 1979).

Estimates of PCB water concentrations in Pool 2 in the early 80s and Lake Onalaska (Pool 7) in the late 70s were derived from partitioning predictions between fish and water (Mackay, 1982; USEPA, 1985 and Dexter 1978) sediment and water (USEPA, 1986) and suspended sediment and water (Rice et al. 1982 and WDNR and USGS, 1988). Pool 2 and Lake Onalaska were selected for this analysis because considerable sediment and fish tissue PCB data were available for these areas. A description of the partitioning procedures is provided in Appendix A.

Partition-based PCB estimates for water concentrations in Pool 2 for the early 80s ranged from 18 to 147 ng/l (Table 6). Similar calculations for Lake Onalaska, based on data in the late 70s, yielded a range of 3 to 84 ng/l. Estimates based on fish or sediments exceed the recommended freshwater criterion of 14 ng/l (USEPA, 1980). All estimates would exceed Wisconsin's proposed warm-water PCB criteria of 0.23 ng/l listed in draft Wisconsin Admistrative Rule NR 105.

It should be stressed these partitioning calculations are rough estimates and assume equalibrium conditions are reached. It is likely the equilibrium partitioning approach overestimates PCB concentrations in water since true equilbrium is not reached due to changes in stream flow (dilution) and source inputs). It is believed the suspended solids/water partitioning model may yield a better prediction since this is a more direct measurement than methods using bed sediments or fish. Further, suspended sediment PCB analysis provides a mesurement of the particulate PCB concentration in water provided total suspended solids data are available.

Suspended Sediments

PCB levels in suspended sediments of the UMR have been determined from 16 sites between Sartell, Minnesota and L/D 11 in 1980 (Jackson, 1986), (Table 1). The mean PCB level was 479 ug/kg (dry wt) and ranged from 100 to 1440 ug/kg. The mean suspended sediment PCB concentration yields an average whole water concentration of approximately 4 ng/l using an estimated suspended solids level of 9.1 mg/l. The suspended solids level is an average of data collected during October and November 1980 at Winona, Minnesota (USGS 1982) during the time when suspended sediment PCB samples were collected. The estimated suspended solids PCB concentration of 4 ng/l does not include that portion dissolved in water.

Jackson also determined PCB levels in suspended sediments of Lake Onalaska in 1980. The average suspended sediment PCB concentration was 177 ug/kg (dry wt) and ranged from 75 to 399 ug/kg. PCB levels in the suspended sediments were more than 3 times greater than those found in Lake Onalaska bottom sediments (54 ug/kg, discussed below). The reason for this difference between suspended and bottom sediment PCB levels has not been established. It is suspected PCBs in bottom sediments in Lake Onalaska were diluted or reduced due to Black River sediment loading, bioturbation, wind mixing or biodegradation. The suspended sediment PCB levels in Lake Onalaska may have reflected "fresh" input from the Mississippi River which was found to have higher suspended sediment PCB levels.

<u>Sediments</u>

Sediment PCB analysis, in addition to other physical and chemical parameters, has been performed by several agencies over the last 12 years. A majority of this work has been conducted by the St. Paul office of the U.S. Corps of Engineers (USCOE) as part of their main channel dredging activities (Table 1), (USCOE, 1986b). The USCOE data include samples from above Pool 1 down to Pool 10. The USFWS has assessed the longitudinal distribution of PCBs in the main channel extending from Sartell, Minnesota to Pool 10 (Table 1), (Jackson et al. 1981). The Metropolitan Waste Control Commission (MWCC) has been collecting sediment data for PCB analysis in the lower Minnesota and St. Croix Rivers and the Mississippi River extending from Anoka, Minnesota to lock and dam (L/D 3), (MWCC, 1986 a & b). Limited sediment PCB analysis has been conducted by Marking et al. (1981) and Peddicord et al. (1980) at several Upper Mississippi River locations above L/D 5 as part of sediment biomonitoring studies (Table 1). Sparks and Smith (1979) conducted sediment PCB monitoring in their assessment of contaminants in Pool 19. More recent UMR sediment PCB data including metals, chlorinated pesticides, polynuclear aromatic hydrocarbons and aliphatic hydrocarbons analyses were completed by the USFWS in 1985 for Pools 4 to 10 (Smith S., 1986 and Davis 1987).

A review of these data indicates highest sediment PCB levels (1-2 mg/kg) have been found in Pool 2 and the lower Minnesota River. Sediments collected above L/D 2 (river miles 815.5 to 819.1) for the period between 1980 and 1984 had 7 samples exceeding 100 ug/kg. A few samples from Lake Pepin have also had high PCB levels (>100 ug/kg), but these were found in the mid to late 70s (Jackson et al. 1981 and IATF, 1976). Recent data collected by MWCC in 1985 continues to show high PCB levels (100-400 ug/kg) above L/D 2 (MWCC, 1987).

As part of this study, a computer data base of bulk sediment analyses was compiled from several of the sources cited above. These included data from USCOE (USCOE, 1986b), USFWS (Jackson et al. 1981 and Jackson, 1986), and the Metropolitan Waste Control Commission (MWCC 1986 a & b). A total of 665 sediment samples were obtained from these sources. This included data for the reach extending from Sartell, Minnesota to L/D 10.

Some caution must be taken when assessing the sediment data base since this information represents samples collected by different agencies and were analyzed by different laboratories. In general, the samples represent surface composite samples collected with ponar sediment samplers. There was little quality assurance information available, with the exception of MWCC's data, from which to judge the quality of the bulk sediment analyses. Most laboratories reported a 1 ug/kg (ppb) detection limit for sediment PCB concentrations. Sediment PCB levels represent total concentrations (ie. combined Aroclors). The information provided by the USFWS indicated Aroclors 1242, 1248 and 1254 were the major mixtures present (Jackson et al. 1981). In contrast, MWCC reported Aroclor 1016 was the major Aroclor found. The reason for the difference in the Aroclor mixture reported is not known and may indicate lab problems in determining relative Aroclor composition from "chromatorgraphic patterns" (Schwartz et al. 1987).

Sediment samples collected by the three agencies represented three habitat types within the river system. These included: main channel, boat harbors and backwater areas. Most samples were collected from main channel areas from Pools 1 to 10. However, considerable backwater sediment PCB sampling was conducted in Lake Onalaska by the USFWS in the late 70s (Jackson, 1986). For this report, only main channel data was selected to assess longitudinal or temporal changes in sediment PCB levels. This was done to get a better distribution of sediment PCB data from throughout the river system and helped to reduce the variability due to localized contaminant areas (harbors) and sediment particle size or carbon content.

The mean and 95 % confidence intervals for sediment PCB levels in the UMR system collected between 1980 to 1984 is presented in Figure 5. Highest mean sediment PCB levels were found in the lower Minnesota River and Pool 2, 175 and 172 ug/kg, respectively. Mean sediment PCB concentrations dropped off dramatically below Pool 2 in the Mississippi River. Sediments from the Mississippi River above Pool 1 and the St Croix indicated mean levels of 38.7 and 27.3 ug/kg, respectively. Maximum sediment PCB concentration (1800 ug/kg) was reported for the Minnesota River in 1982 at river mile 3.5. Sediments from Pool 2 exhibited the next highest levels with 4 samples exceeding 1000 ug/kg in 1982.

Mean sediment PCB levels for the 1976 to 1979 period versus the 1980 to 1984 period show distinctly higher levels for Pool 2 and the lower Minnesota River in the recent period (Fig. 6). The difference in mean PCB concentration for Pool 2 for the two periods was the only river segment where the difference was statistically significant ($P < 0.01$) using the General Linear Model, ANOVA option of log-transformed data (SAS, 1986). The reason for the apparent increase in sediment PCB levels for Pool 2 and the Minnesota River is not believed to represent an increase loading of PCBs from the Twin Cities Metropolitan area since PCB contamination in fish is declining in these waters in recent years (Hora, 1984 and Helwig, 1986). The difference is attributed to samples collected and analyzed by MWCC in the 80s at sites that were in different locations than those collected by the USCOE and the USFWS. The sediment PCB data obtained by MWCC had more samples with high PCB levels (i.e. > 1000 ug/kg) which had a strong influence on the sample means calculated for Pool 2 and the Minnesota River.

Sediment PCB concentrations, as well as other contaminants, exhibit wide variability even when sampling in discrete areas such as points across the river channel as indicated by MWCC's data (1986a,b). This variability is largely attributed to sediment grain size and organic carbon content which influence the ability of sediments to sorb contaminants. In addition, the proximity to point source inputs, current velocity and sediment disturbances may further influence sediment contaminant heterogeniety. In order to properly compare sediment contaminants at different locations and sampling times, some adjustment or normalization of the data is necessary to account for differences in the sediment adsorption potential.

In this report work, sediments PCB levels were normalized by using sediment manganese (Mn) concentrations or the percent loss on ignition (LOI). Manganese has been used to normalize sediment metals data from the UMR for grain size effects (Wiener et al. 1984). LOI or volatile solids was used since this was the best estimate of sediment organic carbon content which may be important in defining sorption of hydrophobic pollutants (Karickhoff et al. 1979). An attempt was made to adjust sediments to a specific size fraction (P200, % passing 200 sieve), but this was not successful since this information was not available from all data sources.

A plot of sediment Mn and LOI levels in the UMR system is presented in Figure 7. The need for normalizing sediment PCB data is apparent since main channel sediments from some river segments, especially Pool 2, have much higher percentages of fine materials as reflected in high levels of volatile solids and manganese. These results are consistent with sediment evaluation work conducted by Boyer (1984) who also found high levels of fine grained sediments in Pool 2.

Manganese and LOI normalized sediment PCB data in the UMR system for the late 70s and early 80s is presented in Figure 8a & b. The Mn normalization is simply the ratio of PCB to Mn levels expressed as ug/mg. The LOI normalization is the the ratio of PCBs divided by the relative sediment LOI content (% LOI/100). The normalization procedure did result in the removal of some PCB data from consideration since the ratios could not be calculated where corresponding measurements for Mn or LOI were not available. The samples that were excluded were some of MWCC's data for 1982 and 1983 where sediment composite samples were not analyzed for LOI or Mn.

The mean normalized sediment PCB levels indicate considerably higher PCB concentrations in Pools 1 and 2 relative to downstream pools or samples from the Minnesota or St. Croix Rivers (Fig. 8a & b). Mississippi River sediments (above Pool 1) also yielded high normalized sediment PCB average in the early 80s, but this was based on only 4 samples and does not adequately represent this area. Similarly, very few normalized PCB samples could be calculated for the Minnesota or St. Croix River sediments.

The normalized sediment PCB data (Fig. 8a & b) and the lipid and tissue PCB data for carp (Fig. 2a & b) indicates Pool 2 is river segment most impacted by high PCB levels. Boyer (1984) has indicated L/D 2 functions as a trap for sediments and trace metals. Boyer found highest trace metal concentrations above L/D 2 (river mile 815). Similarly, highest PCB levels were found in this area of the UMR.

<u>Backwater Sediments - Lake Onalaska</u>

There was insufficient sediment PCB data available for backwater areas to assess the spatial distribution of PCBs in the UMR (pools 3-10). This is unfortunate since backwater areas represent a major portion of these pools and contain finer sediments that would be expected to yield greater PCB concentrations than the courser main channel sediments. Further, these backwater habitats serve as important aquatic communities for the production of the diverse flora and fauna that comprise the UMR system.

An extensive sediment PCB data base (169 samples) was available for Lake Onalaska, a shallow backwater lake (about 6000 acres) located in the lower one-third of Pool 7. This information was collected by the USFWS in the late 70s as part of their detailed PCB studies of Lake Onalaska (Jackson, 1986 and Stalling et al. 1985b). This PCB analysis represents data analyzed using capillary column gas chromatography. Data was reported as total PCBs.

The sediment PCB data base for Lake Onalaska provides an excellent estimate of mean PCB levels and sample variability for a backwater area of the UMR system. There are no known point source PCB inputs into Lake Onalaska. Diffuse sources may include loadings from incoming streams or atmospheric input. It is suspected major PCB inputs are associated with suspended load contributions from the Mississippi River which comprises the greatest solids loading to Lake Onalaska (Dexter et al. 1978a).

A probability plot of sediment PCB levels in Lake Onalaska is presented in Figure 9. Mean sediment PCB concentration was 54 ug/kg (dry wt) with a coefficient of variation of 94 %. The maximum PCB level was 304 ug/kg. Approximately 17 % of the samples exceeded 100 ug/kg. No attempt was made to assess the spatial distribution of the sediment PCB levels in Lake Onalaska.

Since the Lake Onalaska sediment PCB data base was so large, the information provided an opportunity to study the effects of sample size on sample variability (ie. standard error and 95 % confidence levels). Random samples of specific sample size (ie. 3, 6, 10, 20 ect.) were selected from the 169 sediment samples using SAS. The mean standard error and 95 % confidence levels were determined after making several "runs" at a particular sample size. The results were then plotted as a function of sample size (Fig. 10a & b). This information indicated there appeared to be little improvement in reducing the standard error or 95 % confidence levels at sample sizes greater than 10. This information may be useful in determining appropriate sample sizes for assessing sediment contaminant levels in backwater habitats in the UMR system.

Tentative Sediment PCB Criterion for the UMR

There is recent interest in the development of sediment-based criteria that will offer protection of fish and aquatic life (USEPA, 1986; USCOE, 1986 and Chapman, 1986). These criteria are needed to assess contaminated sediments and to ensure dredged sediments are handled properly to prevent serious environmental pollution. Sediment-based criteria could involve a number of chemical and biological assessments. These include: bulk chemical analysis, equilibrium partitioning predictions, sediment bioassays, and in situ biomonitoring (Chapman, 1986 and USEPA, 1986).

Chapman reported sediment criteria of 100 ug/kg PCB, 50 mg/kg lead and 3.8 mg/kg polyaromatic hydrocarbons (dry wt basis) in his work in Puget Sound, Washington. Little biological effects were found below these levels. Chapman indicated it was not possible to isolate individual criterion concentrations of each of these contaminants.

The U.S. EPA (1986), utilizing a partition coefficient approach based on organic carbon normalized sediment data, estimated a "permissible sediment contaminant concentration" (PCC) for PCBs (Aroclor 1254) of 1.84 ug/g organic carbon. The PCC was based on EPA's recommended water concentration of 14 ng/l (ppt), a level established to protect wildlife (mink) from the consumption of contaminated fish. Sediment organic carbon contents of 2 to 4 %, values typical for UMR backwater sediments, would yield sediment PCC levels of 37 to 74 ug/kg dry wt., respectively, for Aroclor 1254.

Several sediment/fish partitioning models were evaluated to determine if these relationships could be used to predict observed PCB levels in fish. These models are described in Appendix A. Pool 2 and Lake Onalaska (Pool 7) were selected to test these models since considerable sediment and fish PCB data was available for these areas. The results indicated reasonable predictions of PCB levels in carp could be made using these procedures (Table 7).

The Rubenstein model was the best predictor of the models tested. This approach was used to estimate sediment PCB levels that would be expected to yield exceedances of the 2.0 mg/kg standard in carp. Based on data for Pool 2 and and Lake Onalaska, predicted sediment concentrations were 87 and 114 ug/kg, respectively. Rubenstein's sediment/fish partitioning equation indicates fish bioconcentration potential is influenced by the sediment PCB and organic carbon concentrations and the lipid content of fish. Less restrictive sediment PCB criteria, using FDA's 2.0 ppm standard as an end point, would be predicted using lower lipid content fish or sediments with high levels of organic carbon. Conversely, more restrictive sediment criteria would be predicted using a lower PCB standard for fish.

PCB Sources

The most comprehensive source survey of PCB inputs to the UMR was undertaken by the Interagency Task Force in 1975 (IATF 1976). The Task Force analyzed landfill monitoring wells, municipal and industrial effluents, municipal sludges and sediments in an industrial process and cooling water ponds at sites adjacent to the Mississippi River or major tributaries between Sartell and Winona, Minnesota. PCBs were detected in 3 of 44 municipal wastewater treatment facilities (1.1 to 2.2 ug/l) and 2 of 46 industrial effluents (4.2 and 16 ug/l). Two of 7 landfills had detectable levels in at least one monitoring well (1 to 1.4 ug/l). PCBs were most frequently encountered in municipal wastewater treatment sludges (6 of 33 facilities) and also exhibited the greatest concentrations (1000 to 26000 ug/kg). One industrial facility, was found to have PCBs in sediments from its cooling and process wastewater ponds (88 to 500 ug/kg). This same industry had one cooling water effluent PCB level of 16 ug/l. However, PCBs were not detected in follow up sampling of this industrial outfall. The Task Force concluded " no major single PCB source or group of PCB sources to the river or its tributaries could be identified". Further, the problem was attributed to past widespread use of PCBs and numerous inputs at relatively low concentrations.

Municipal Effluents - Twin Cities Area

Previous monitoring by the Interagency Task Force identified substantial PCBs in several municipal wastewater treatment plant (WWTP) sludges. Three of these facilities are located in the Twin Cities Metropolitan area (Anoka, Metro and Seneca WWTPs). Previous work in Wisconsin has indicated municipal effluents may be a significant source of PCB discharges to receiving waters (Kleinert, 1976). PCB data for municipal effluents in the Twin Cities Metropolitan area were sought to estimate the contribution from these sources.

The Metropolitan Waste Control Commission (MWCC) conducted toxicity testing at several of the metropolitan wastewater treatment plants in 1984 and 1985 (MWCC, 1986c). As part of this survey, effluents were analyzed for PCBs on 5 consecutive days based on daily grab and 24 hr composite samples. Effluent PCB concentrations ranged from 0.01 ug/l at Blue Lake WWTP to 0.11 ug/l at Seneca WWTP. When wastewater flow is considered, greatest mean PCB loadings were found at the Metro Plant and the Seneca WWTP, 0.017 and 0.007 kg/day, respectively. The remaining plants evaluated, Blue Lake, Anoka, Cottage Grove and Chaska had mean PCB loadings less than 0.001 kg/day.

At an average Mississippi River flow of 11,000 cfs at St. Paul, these WWTP PCB loadings would account for an instream PCB concentration of approximately 1.0 ng/l (ppt) below St. Paul. This is a rough approximation since it does not include losses to sediments, air, biota (ie. bioaccumulation) or losses due to degradation. Further, this estimate does not include contributions from other metropolitan WWTPs (Empire, Rosemont and Savage) or other point or nonpoint sources.

The Metro Plant, a municipal wastewater treatment plant located in St. Paul, is the largest point source discharger in the Twin Cities area. This facility has an average discharge of 230 mgd. The Metro Plant has been monitoring PCBs in its effluent for several years. This information is submitted as part of their wastewater discharge permit requirement specified by MPCA. A review of this data indicated increased PCB discharges in 1986 and part of 1987 (Fig. 11). The reason for this trend has not been determined. In 1986, the average PCB effluent concentration and loading were 0.07 ug/l and 0.058 kg/day, respectively. This PCB loading would represent an instream concentration of about 2 ng/l below the Metro Plant outfall assuming completely mixed conditions, no losses and average river flow.

The above information indicates PCB contribution from WWTPs from the Twin Cities Metropolitan area are expected to yield instream concentrations of 1 to 3 ng/l at average river flow. Measured (MPCA, 1984) or predicted (Table 6) PCB levels in Pool 2 are estimated to range from 18 to 147 ng/l. This information, if accurate, would indicate the municipal contribution from the Twin Cities area is not a major source. However, the significance of the municipal PCB input to the river can not be accurately established due to the uncertainty of the actual instream PCB levels.

Atmospheric Contribution - Twin Cities Area

PCB input from precipitation or dry fallout may be an important source in some metropolitan areas. Kleinert (1976) reported PCB levels of 0.12 to 0.24 ug/l in snow melt water in some urban areas of Wisconsin. Sources of PCB emissions could come from the accidental or intentional incineration of PCB contaminated materials such as plastics, paper, electrical equipment, contaminated oils, sludges and other materials at temperatures that do not destroy PCB compounds. In order to destroy PCBs, incineration should occur at 1200 C for at least 2 seconds (Thompson et al. 1986).

Consultants for MPCA detected PCBs in incinerator emissions and ambient air samples from the Twin Cities area in 1978 (MPCA, 1979). Ambient air PCB concentrations ranged from below detection to 0.038 ug/m^3. Maximum PCB loadings from two suspected incinerator sources, Metro WWTP and the 3M Chemolite Plant, were 0.22 and 0.16 grams/hr, respectively. These emission rates would yield a maximum daily loading of about 0.005 to 0.004 kg/day. These atmospheric loading estimates are within the same magnitude as municipal wastewater PCB loading calculations for the Twin Cities.

There is little information available to assess the significance of PCB contributions to the river from incinerator emissions. It is expected the actual contribution from incinerator emissions from the Twin Cities area would be lower than municipal wastewater discharges. A large portion of the PCBs emitted to the atmoshpere would likely be carried to areas outside the Twin Cities region.

Runoff From Contaminated Land Surfaces

Runoff or leaching of PCBs from contaminated land surfaces may be an important factor influencing the contaminant problems in riverine systems. Such a problem was identified on the Sheybogan River, Wisconsin (Sheffy, 1980). The use of PCB contaminated waste oils for dust control or dumping of PCB tainted wastes are examples where serious contamination of soils can occur. Runoff from such sites may be important source inputs, especially if these sites are adjacent to the river. These contaminant "hot spots" are difficult to find and may be discovered accidentally during other environmental investigations. Future discovery of PCB contaminated sites, followed by proper clean up actions, should help to reduce PCB loadings to the river.

Contaminated Sediments

Contaminated sediments in the Lower Minnesota River and Pool 2 of the Mississippi River, will serve as sources of PCB input due to desorption and partitioning into water and aquatic organisms. Sediment resuspension resulting from high flow events, dredging activities and tow boat operations will facilitate PCB transport downstream. The importance of this internal PCB contribution is not known and should be determined. It is expected that as external sources of PCBs are controlled, factors affecting the release of PCBs form sediments will become more important and control the rate of recovery (Brown et al. 1983).

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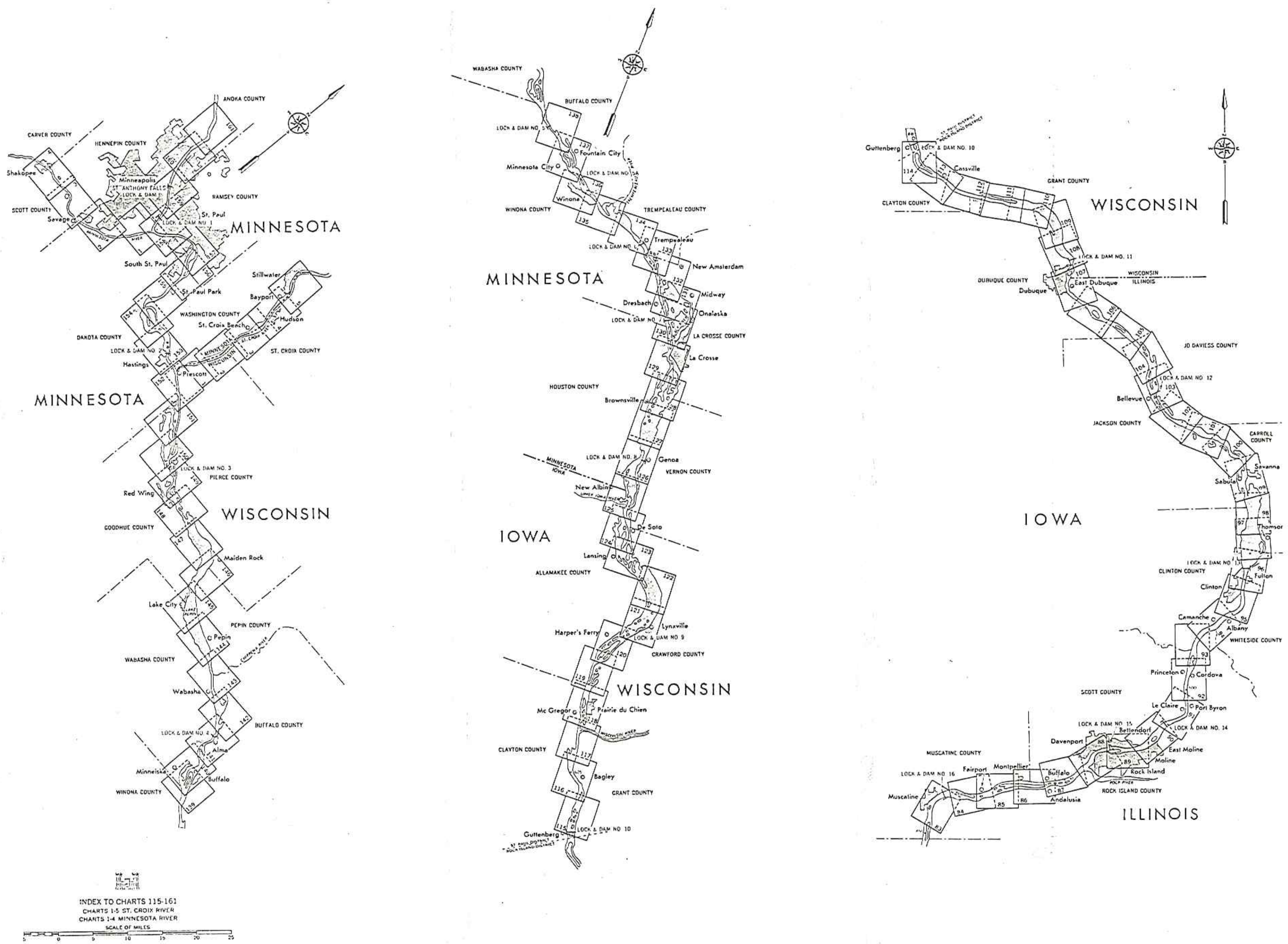


Figure 1. Upper Mississippi River System, Pool 1-16.

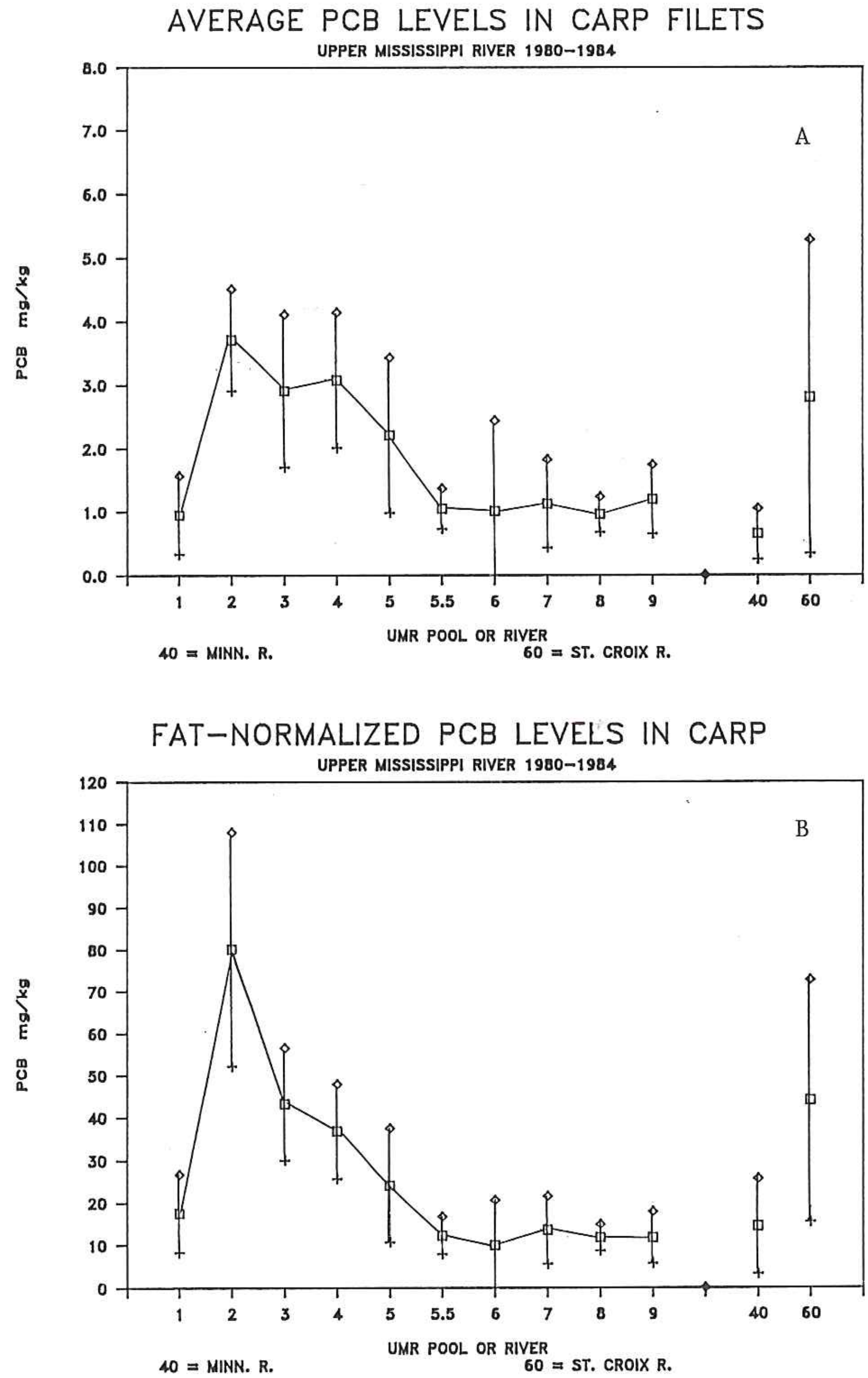
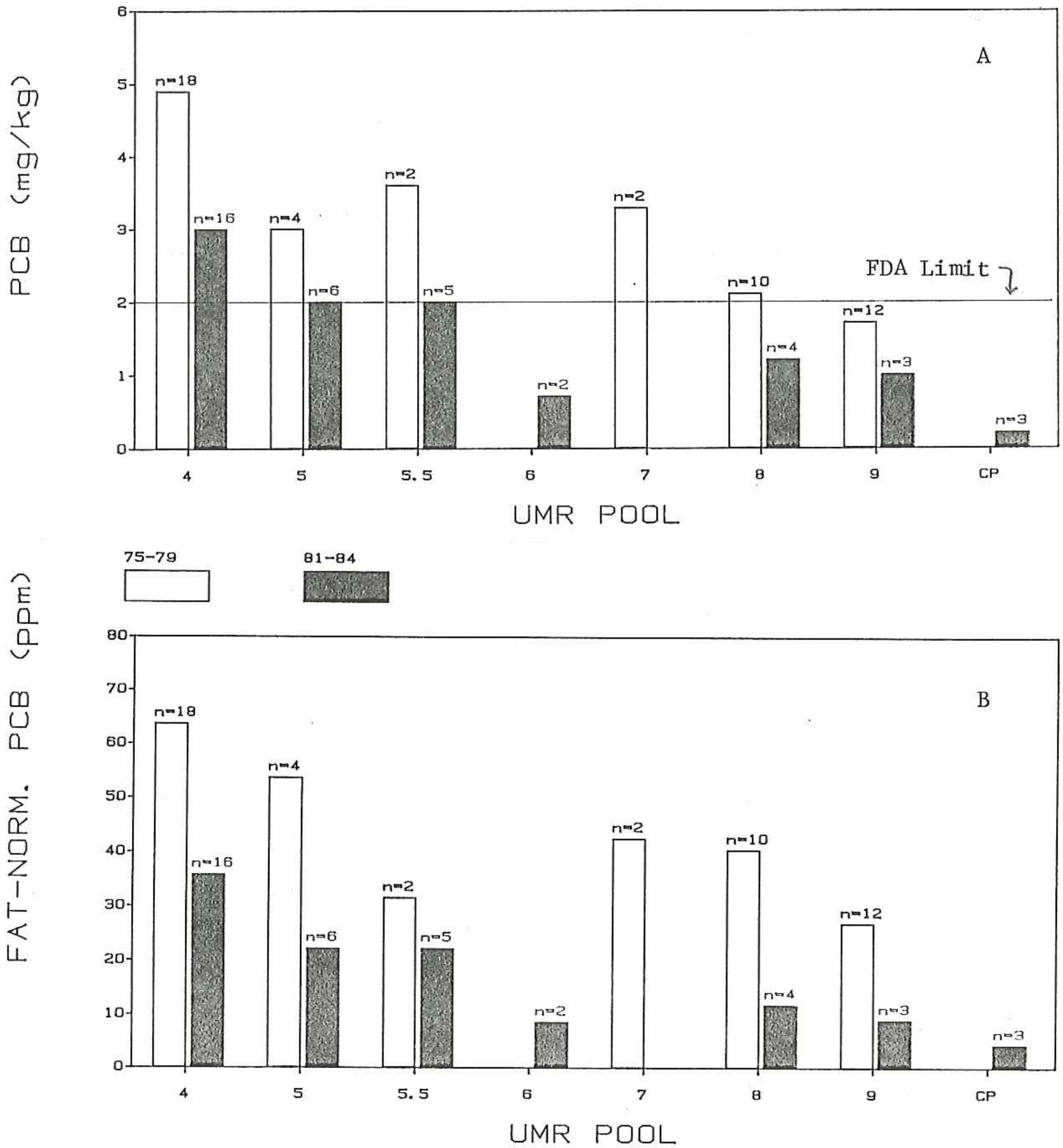


Figure 2. A. PCBs in carp fillets from Pools 2-10 of the Upper Mississippi River and lower St. Croix and Minnesota Rivers. B. Fat-normalized data. Vertical lines represent 95% confidence interval. Source: Minnesota Pollution Control Agency and Wisconsin Department of Natural Resources.



CARP SIZE: 20-26 INCHES

CP = Czechville Pond

Figure 3. A. Wisconsin's PCB data for carp fillets from Pools 4-9 of the Upper Mississippi River for two collection periods (1975-79 vs 1981-84). B. Fat-normalized data. Both plots represent 20-26 in length fish. Data represent averages and sample sizes (n). Source: Wisconsin Department of Natural Resources.

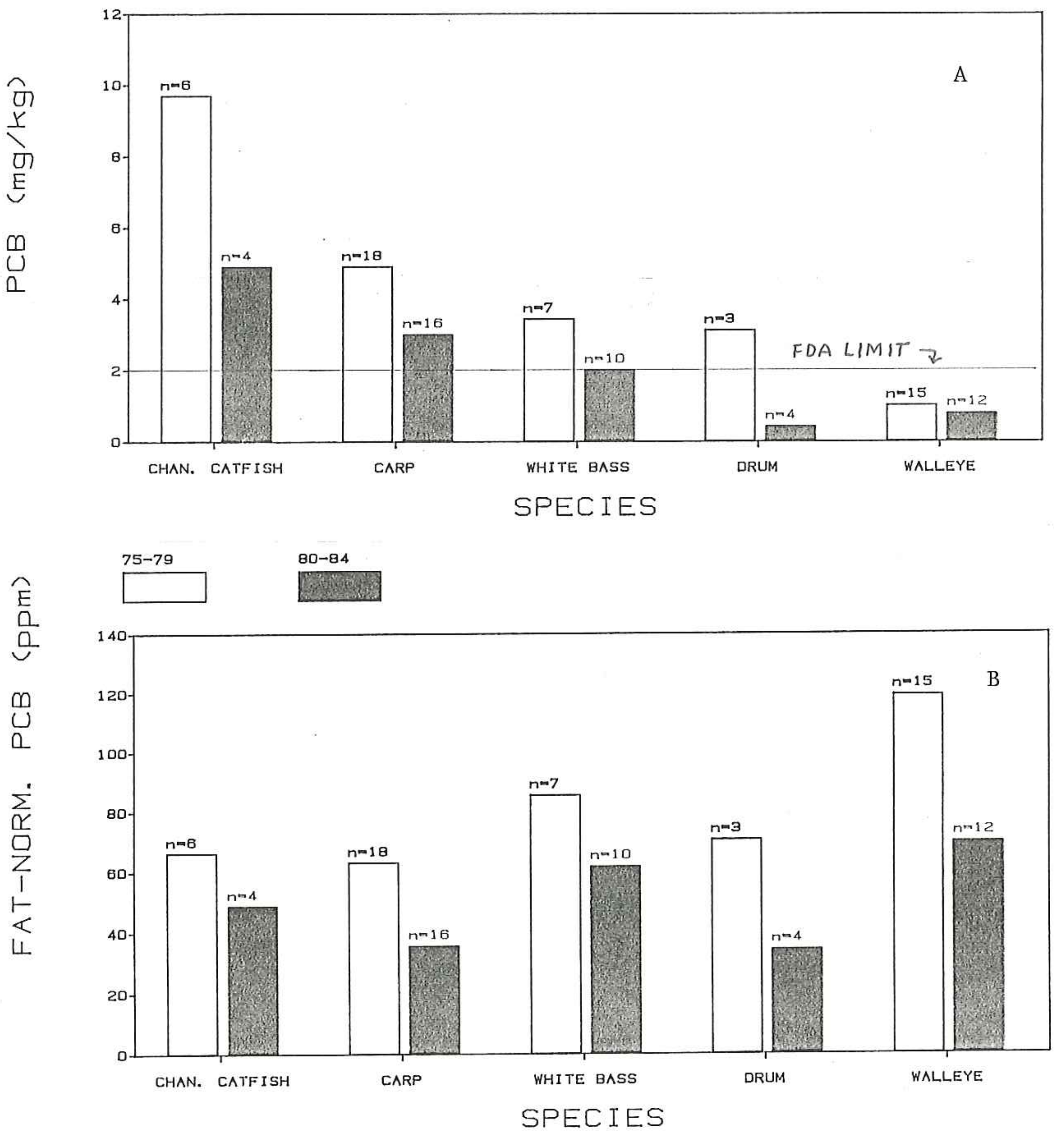
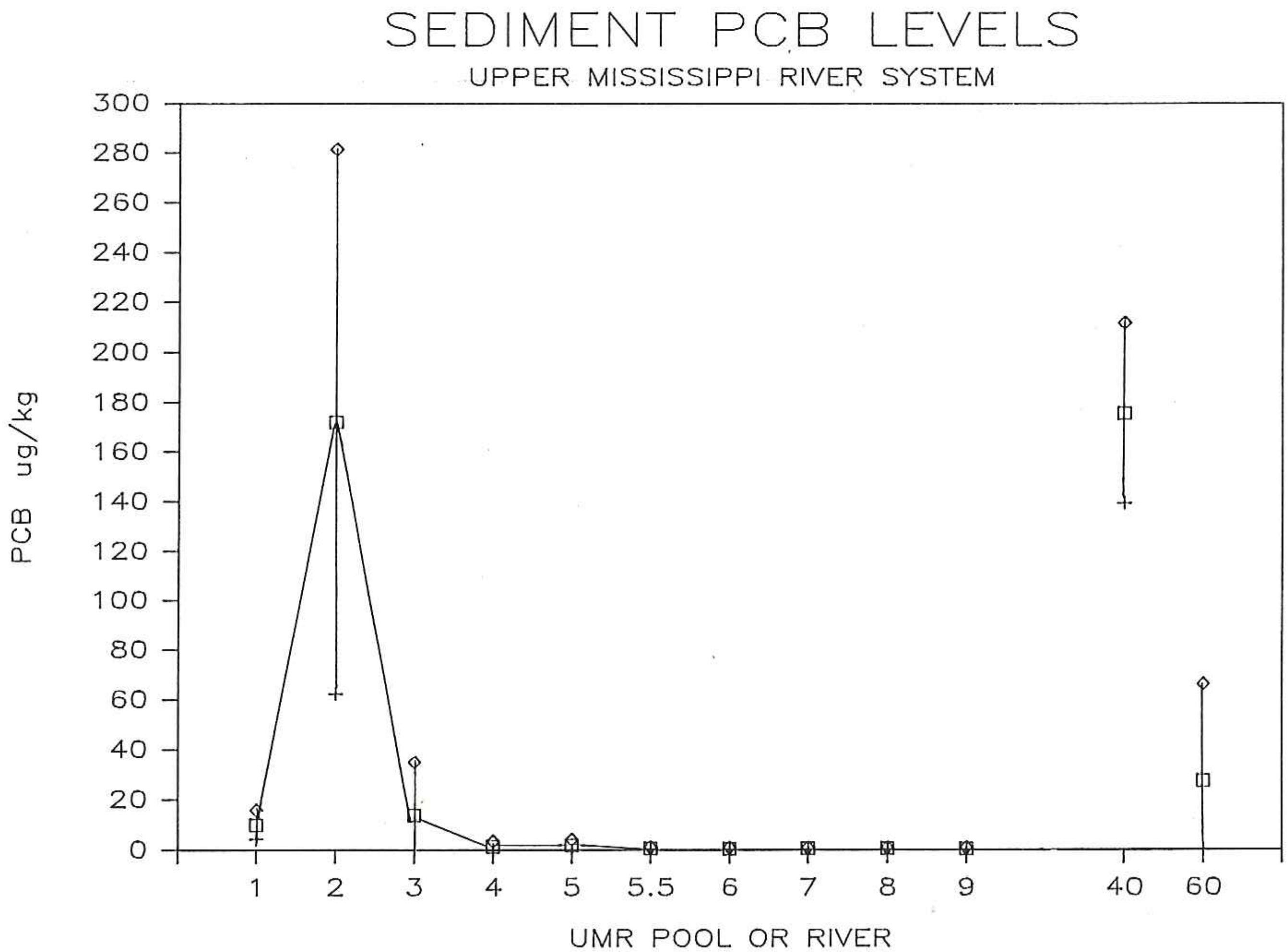


Figure 4. A. Wisconsin's PCB data for fish from Pool 4 of the Upper Mississippi River for two collection periods (1975-79 vs 1980-84). B. Fat-normalized data. Length of fish described in Table 4. Data represent averages and sample sizes (n). Source: Wisconsin Department of Natural Resources.



40 = Minn. R. 60 = St. Croix R.

Figure 5. Average sediment PCB for Pools 1-9 of the Upper Mississippi River and lower St. Croix and Minnesota Rivers. Vertical lines represent 95 % confidence interval. Data represent samples collected by the U.S. Fish and Wildlife Service, U.S. Corps of Engineers and the Metropolitan Waste Control Commission during the 1980 to 1984 period. Main channel data.

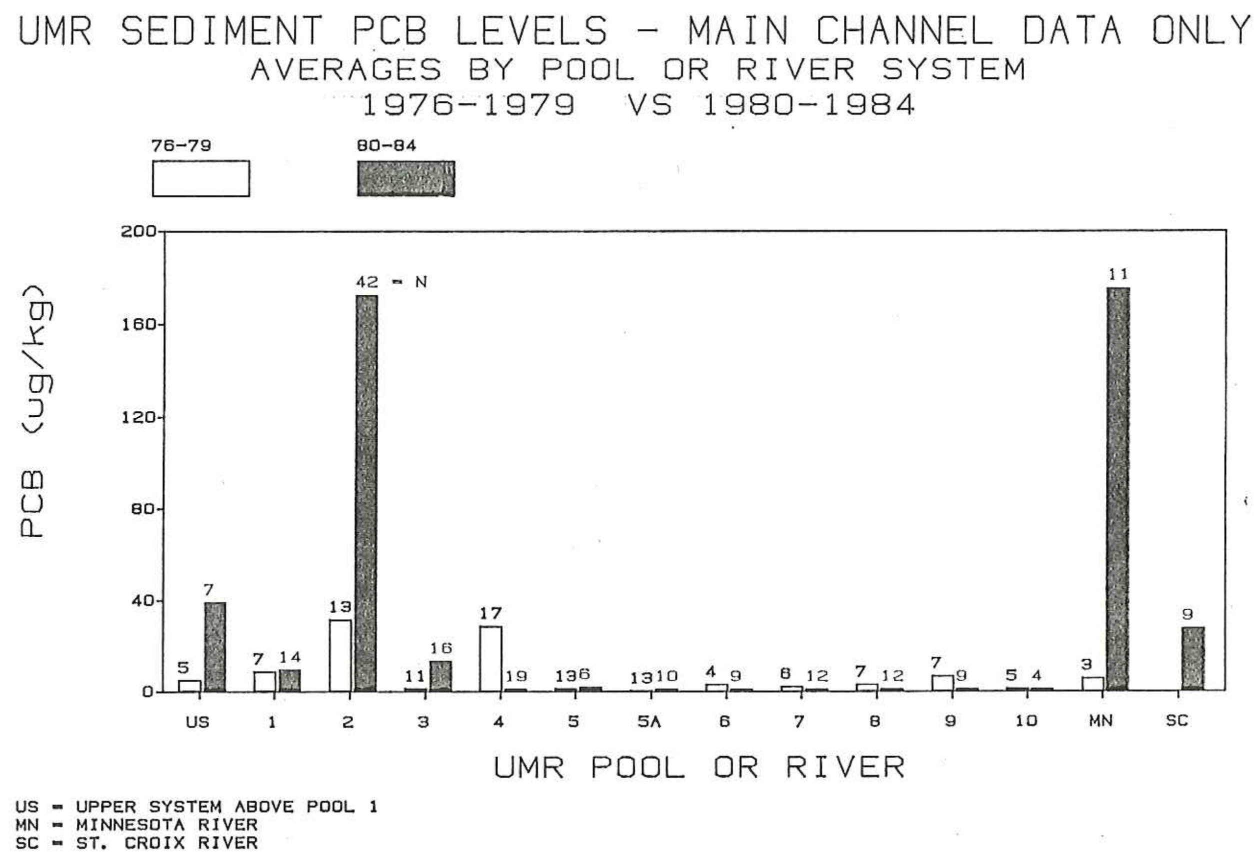


Figure 6. Average sediment PCB levels for the Upper Mississippi River and the lower St. Croix and Minnesota Rivers for two collection periods (1976-79 vs 1980-84). Numbers above bars represent sample sizes. Source: U.S. Fish and Wildlife Service, U.S. Corps of Engineers and the Metropolitan Waste Control Commission.

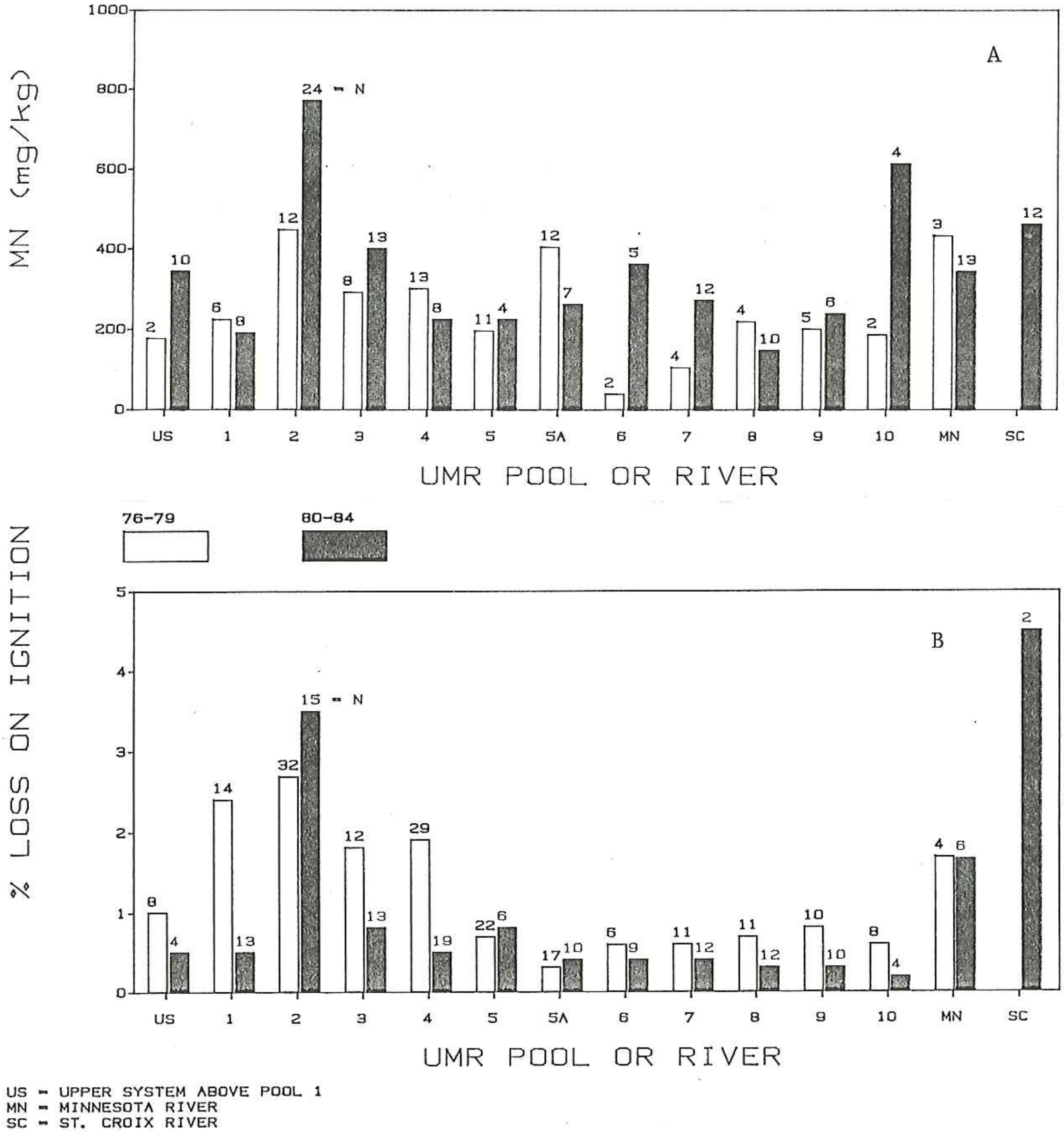


Figure 7. A. Sediment manganese levels for the Upper Mississippi River and the lower St. Croix and Minnesota Rivers for two periods (1976-79 vs 1980-84). B. Loss on ignition (LOI) data. Data represent averages. Number above bar indicates sample size (n). Source: U.S. Fish and Wildlife Service , U.S. Corps of Engineers and the Metropolitan Waste Control Commission.

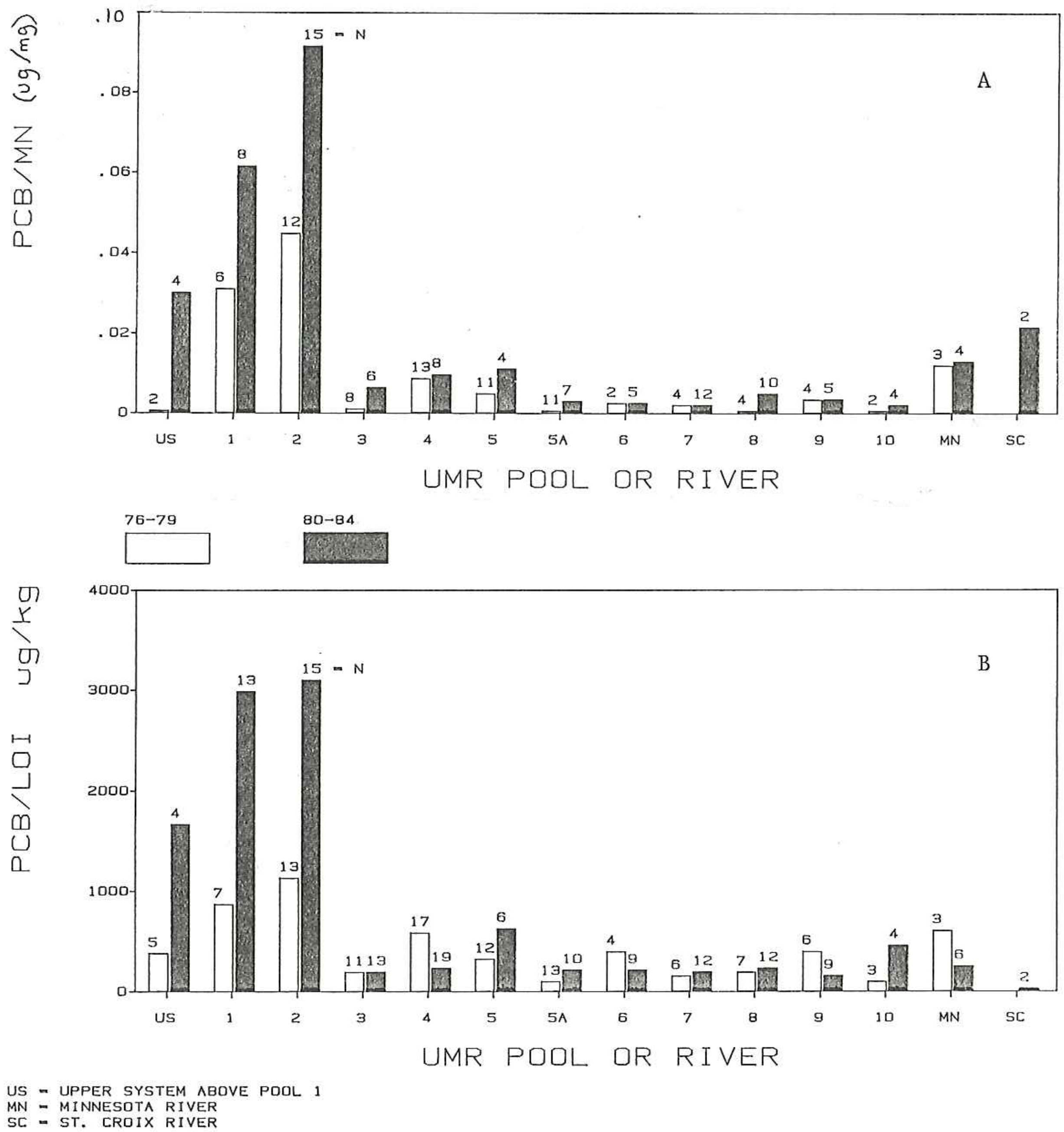


Figure 8. A. Manganese-normalized sediment PCB levels for the Upper Mississippi River and the lower St. Croix and Minnesota Rivers for two periods (1976-79 vs 1980-84). B. LOI-normalized sediment PCB data. Data represent averages. Number above bar indicates sample size (n). Source: U.S. Fish and Wildlife Service, U.S. Corps of Engineers and the Metropolitan Waste Control Commission.

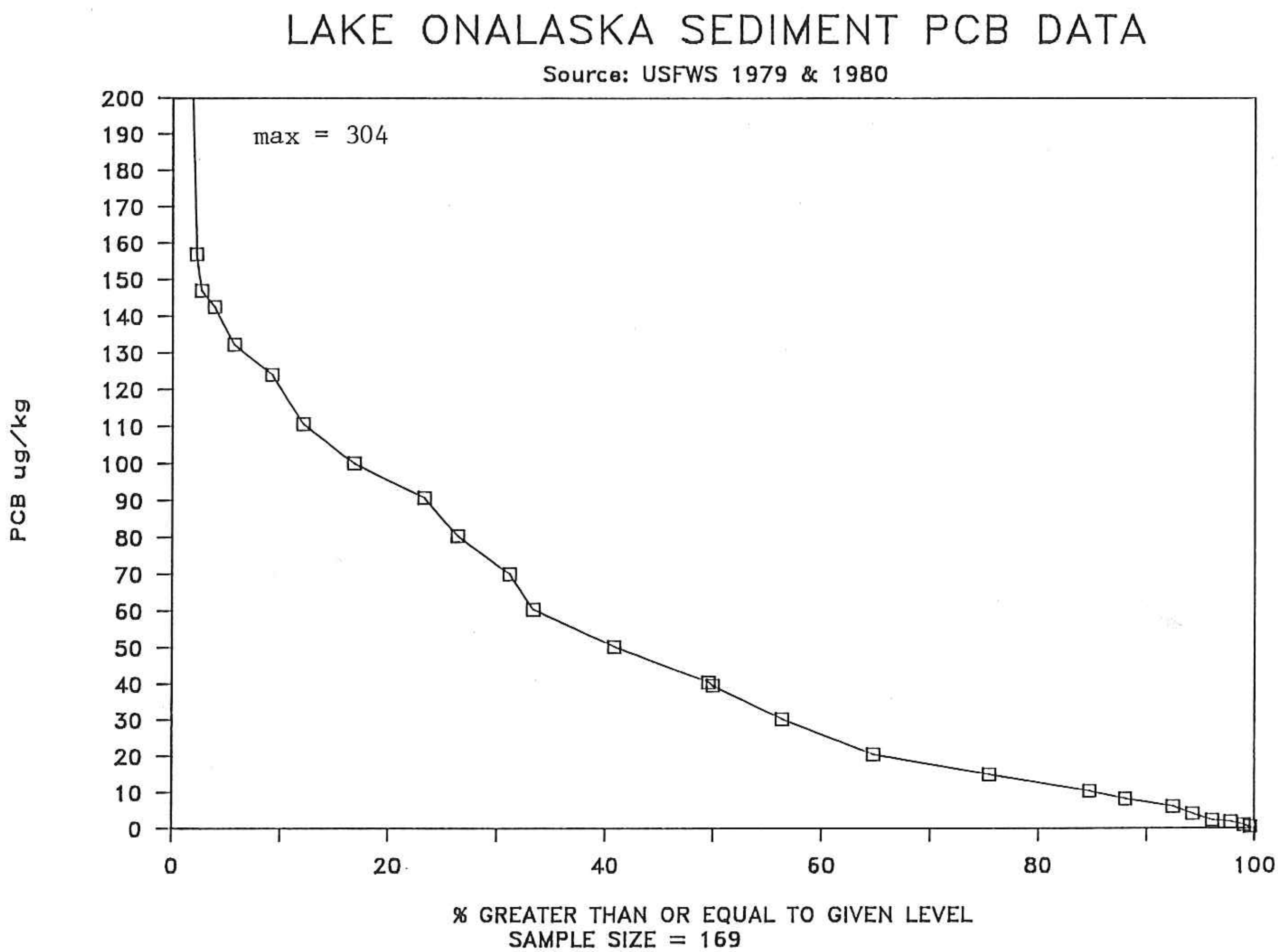
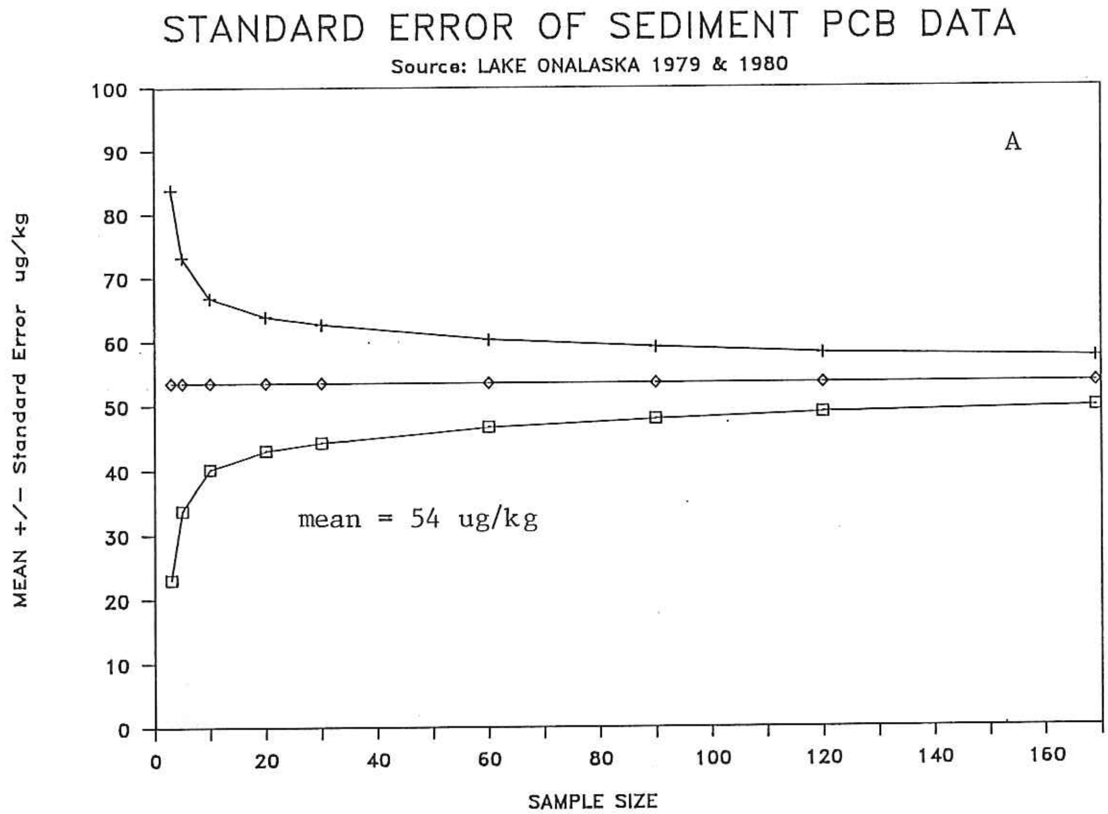


Figure 9. Sediment PCB probability distribution for samples collected from Lake Onalaska, Pool 7, Upper Mississippi River. Note: not all samples were plotted. Source: U.S. Fish and Wildlife Service.



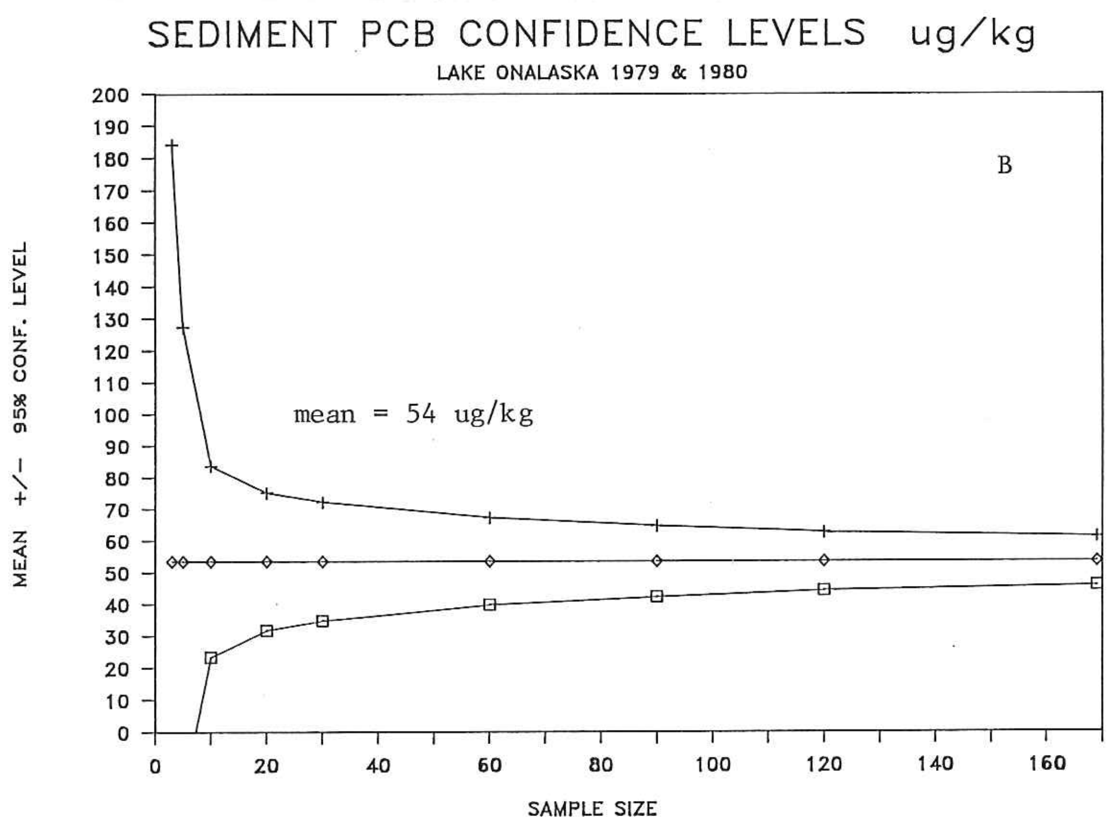
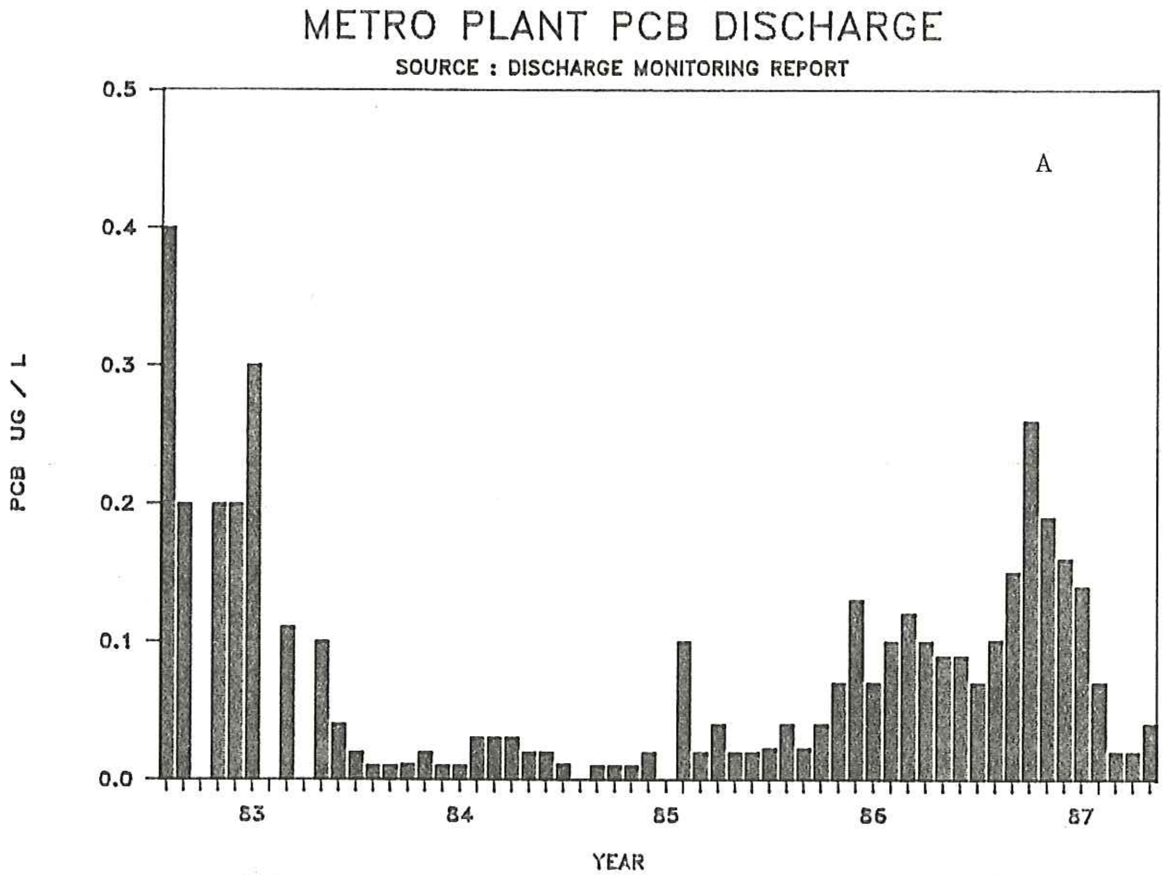


Figure 10. A. Sediment PCB standard error as a function of sample size for data collected from Lake Onalaska, Pool 7, Upper Mississippi River. B. Sediment PCB 95 % confidence levels as a function of sample size.



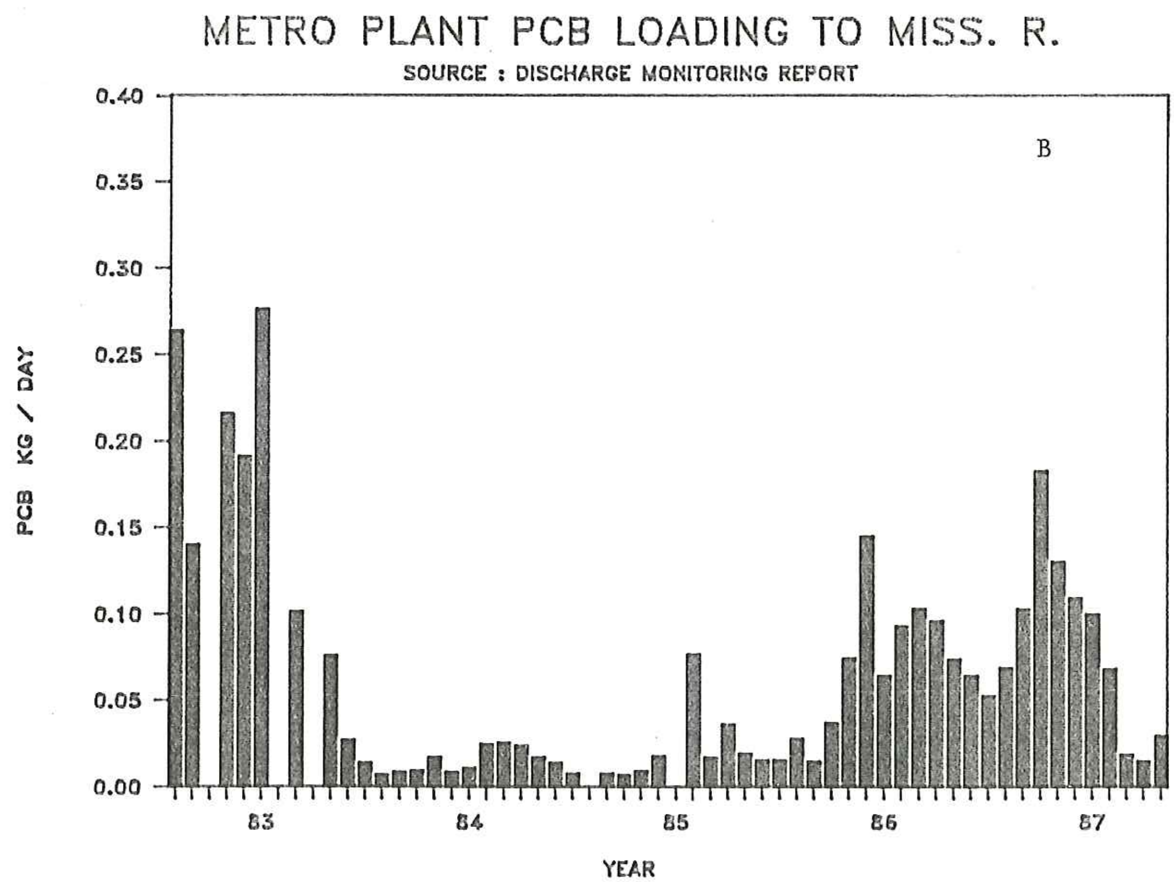


Figure 11. A. PCB concentrations in the Twin Cities Metropolitan Wastewater Treatment Plant discharge. B. PCB loading to the Mississippi River. PCB concentrations represent monthly values. Loadings based on monthly average WTP flows.

TABLE 1. UPPER MISSISSIPPI RIVER PCB DATA.

REFERENCE	MATRIX	SPECIES	YEAR	LOCATIONS	RANG./UNITS	BASIS	COMMENTS
Nosek and Faber 1984	Bird Eggs	Great Blue Heron	78	Pool 5A	0.44 - 37.2 mg/kg	Wet Wt.	Sampling site was at a heron colony located near Fountain City. Total PCBs using various Aroclor mixtures as standards. Detection limit : 0.05 mg/kg.
Nosek and Faber 1984	Bird Eggs	Great Egret	78	Pool 5A	6.51-34.9 mg/kg	Wet Wt.	Sample site was at an egret colony located near Fountain City. Total PCBs using various Arochlor mixtures as standards. Detection limit : 0.05 mg/kg.
Amundson 1985	Bird Tissue	Mallard	84	Pool 8 & 11	< 0.2 mg/kg	wet wt.	One composite sample of 3 to 5 samples. Skin on breast samples.
Amundson 1987	Bird Tissue	Mallard	86	Pool 4	< 0.2 - 1.6 mg/kg	Wet Wt.	3 skin on tissue samples. Two samples exceeded 20 mg/kg on a fat basis. Sample location at Pepin Marina.
Sparks & Smith 1980	Finger Clms.	M. transversum	77-78	Pool 19	0.014 - .930 mg/kg	Wet Wt.?	4 sites sampled in Pool 19.
Jackson et al. 1981	Fish	Bluegill	79	US - Pool 11	0.04 - 1.48 mg/kg	Wet Wt.	10 sites sampled. Highest levels found in Pool 4 and 7. Detection limit 0.05 mg/kg.
MPCA, MDNR & WDNR 1985	Fish	Carp	82-84	Pools 4-10 & SC	0.1 - 11.0 mg/kg	SOFilet	11 sites sampled. Highest levels found in Pool 4.
Degurse & Ruhland 1970	Fish	Carp	70	Pools 3 - 12	0.10 - 53.4 mg/kg	Whole F.	19 sites sampled. Highest levels found in Pool 4. Aroclors 1224, 1254 and 1260 used as standards.
Hora 1984	Fish	Carp	75-76	US - Pool 4	0.06 - 11.7 mg/kg	SOFilet	8 sites sampled. Highest levels found in Pool 2 (Spring Lake). Concentrations reported as total PCBs.
Hora 1984	Fish	Carp	79-80	US - Pool 4	0.05 - 58.0 mg/kg	SOFilet	8 sites sample. Highest levels found in Pool 2 (Spring Lake). Concentrations reported as total PCBs.
Jackson et al. 1981	Fish	Carp	79	US - Pool 11	0.83 - 11.68 mg/kg	Whole F.	15 sites sampled. Highest levels found in Pool 3 (Sturgeon Lake). Detection limit : 0.05 mg/kg.
Interagency Task Force, 1976	Fish	Carp	1975	US - Pool 4, SC, MR	0.4 - 33 mg/kg	Filets	20 sites sampled. Highest levels found in Pool 2. Several other species sampled. High levels also reported for White Bass and Channel Catfish.
Smith 1986	Fish	Carp	85	Pool 4 - 10	0.2 - 1.3 mg/kg	Whole F.	Ten sites sampled. Highest level reported for Pool 4. Conentrations reported as total PCBs.

TABLE 1. UPPER MISSISSIPPI RIVER PCB DATA. continued.

REFERENCE	MATRIX	SPECIES	YEAR	LOCATIONS	RANG./UNITS	BASIS	COMMENTS
MPCA, MDNR & WDNR 1985	Fish	Channel Catfish	83-84	Pools 2-10 & SC	0.3 - 7.10 mg/kg	Filet	11 sites sampled. Highest levels found in Pool 3.
MPCA, MDNR & WDNR 1985	Fish	Drum	83	Pools 4 - 8	0.2 - 1.7 mg/kg	SOFilet	5 sites sampled. Highest levels found in Pool 5.
MPCA, MDNR & WDNR 1985	Fish	Flathead Catfish	83	Pools 2 - 5A	0.2 - 7.0 mg/kg	Filet	4 sites sampled. Highest levels found in pool 4.
Degurse & Ruhland 1970	Fish	Walleye	70	Pools 3 - 12	12.5 - 72.0 mg/kg	Whole F.	Ten sites sampled. Highest levels found in Pool 4. Aroclors 1224, 1254 and 1260 used as standards.
Degurse & Ruhland 1970	Fish	White Bass	70	Pools 3 - 12	1.87 - 69.8 mg/kg	Whole F.	15 sites sampled. Highest levels found in Pool 4. Aroclors 1224, 1254 and 1260 used as standards.
Clements & Kawatski 1984	Mayflies	Hexagenia bilineata	80	Pools 3 - 10	0.17 - 2.1 mg/kg	Wet Wt.	24 sites sampled. Highest levels found in Pool 3 (near Prescott). Aroclor 1254 used as standard.
Mauck & Olsen 1977	Mayflies	Hexagenia bilineata	77	Pools 3 - 9	0.3 - 2.7 mg/kg	Wet Wt.	14 sites sampled. Highest levels found in Pool 4. Reported as Aroclor 1254.
Clements & Kawatski 1984	Mayflies	Hexagenia bilineata	83	Pools 3 - 10	0.21 - 3.10 mg/kg	Wet Wt.	21 sites sampled. Highest levels found Pool 4. Aroclor 1254 used as standard.
Sparks & Smith 1979	Plants	Four Species	77-78	Pool 19	ND - 0.062 mg/kg	Wet Wt.	3 sites in Pool 19. Species: Vallisneria americana, Ceratophyllum demersum and Heteranthia dubia. Highest levels found in H. dubia.
Marking et al. 1981	Sediments		80	Pools 2- 5A	< 0.001 - 0.60 mg/kg	Dry Wt.?	10 sites sampled. Highest levels found in Red Wing Commercial Harbor. Reported as Aroclor 1254.
Peddicord et al. 1980	Sediments		78	Pools 2, 4 & MR	0.009 - 0.090 mg/kg	Wet Wt.	4 sites sampled. Highest levels found in Pool 2. Reported as total PCBs.
Sparks & Smith 1979	Sediments		77-78	Pool 19	0.002 - 0.003 mg/kg	Dry Wt.	Five sites in Pool 19.
Jackson et al. 1981	Sediments		79	US - Pool 10	< 0.001 - 0.22 mg/kg	Dry Wt.	32 sites sampled. Highest levels found in Pool 4 (Lake Pepin). Total of Aroclors 1242, 1248 and 1254.
U.S. Army COE 1986	Sediments		78-84	US - Pool 10, SC, MR	<0.001 - 1.46 mg/kg	Dry Wt.	236 samples. Highest levels found in Pool 2. Reported as total PCBs (Aroclors 1248 + 1254 & 1260).

TABLE 1. UPPER MISSISSIPPI RIVER PCB DATA. continued.

REFERENCE	MATRIX	SPECIES	YEAR	LOCATIONS	RANG./UNITS	BASIS	COMMENTS
Metro. Waste Cont. Comm. 1984	Sediments		82-84	US-Pools 1-3, SC, MR	0.002 - 1.80 mg/kg	Dry Wt.	44 samples. Pool 2 had the greatest mean PCB levels. Highest PCB level reported for the Minnesota River.
Interagency Task Force 1976	Sediments		75	US - Pool 4, SC, MR	< 0.3 - 1.0 mg/kg	Dry Wt.	32 sites sampled. Highest level found in south end of Lake Pepin. Total PCBs. Detection limit : 0.03 ug/l.
Smith 1986	Sediments		85	Pool 4 - 10	< 0.05 mg/kg	Dry Wt.	39 samples. No PCBs detected. Detection limit: 0.05 mg/kg
Davis 1987	Sediments		85	Pool 10 East Channel	< 0.05 mg/kg	Dry Wt.	14 samples. No PCBs Detected. Detection limit: 0.05 mg/kg.
Jackson 1986	Sediments	Suspended		US - Pool 11	0.100 - 1.440 mg/kg	Dry Wt.	16 sites sampled. Highest level found in Pool 6. Reported as total PCBs using capilary column technique.
Jackson 1986	Sediments	Suspended	80	Pool 7 Lake Onalaska	0.075 - 0.40 mg/kg	Dry Wt.	11 Samples from the fall of 1980. Reported as total PCBs using capillary column technique.
Sparks & Smith 1979	Snails	Three species	77-78	Pool 19	ND - 0.248 mg/kg	Wet Wt.?	5 sites in Pool 19. Species: Helisoma trivolvis, Campeloma crassula and Viviparus georgianus.
Hewlig & Hora 1983	Turtle Fat	Snapping Turtle	81	Pools 2 - 4	1.4 - 60.5 mg/kg	Wet Wt.	3 sites sampled. Highest levels found in Pool 3 near Praire Island. Reported as Aroclor 1260.
Interagency Task Force 1976	Wastewater		75	UMR point sources	< 0.4 - 16 ug/l		44 municipal and 46 industrial discharges sampled. Point sources were located on the Mississippi, Minnesota, St. Croix Rivers and several small tributary streams. PCBs were detected in 3 municipal discharges (< 0.4 - 2.2 ug/l) and 2 industrial discharges (4.2 - 16 ug/l). Detect. limit: 0.4 ppm
Interagency Task Force 1976	Wastewater	Sludges	75	UMR point sources	< 1 - 26 mg/kg	Dry Wt.	33 municipal wastewater treatment plant sludges sampled. PCBs detected at 6 facilities. Greatest concentration reported for the Metro Plant in St. Paul. Aroclor 1254 major PCB found.
Interagency Task Force 1976	Water		75	US - Pool 4, SC, MR	< 0.4 - 10 ug/l		37 sites sampled which included several small tribuatry streams. Highest level reported for Rum River (10 ug/l) Anoka Co. Minnesota. High levels also found in Mississippi River at Lake Pepin (3.0 ug/l) and in the St. Croix River at Prescott (3.1 ug/l). Detection limit : 0.4 ug/kg.

Table 2. Comparison of mean PCB levels (mg/kg fresh wt.) in carp filets from several Upper Mississippi River Pools for two periods. General Linear Model of log-transformed data was used to test for differences in sample means (SAS, 1986). Data from Wisconsin Department of Natural Resources.

Pool	Period 1 1975-1979 n	Mean	SD	Period 2 1980-1984 n	Mean	SD	PR>F
4	18	4.9	2.8	16	3.0	2.2	0.010
5	4	3.0	3.3	6	2.0	1.6	0.658
5A	2	3.6	0.3	5	2.0	1.9	0.207
8	10	2.1	1.0	4	1.2	0.2	0.057
9	12	1.7	0.7	3	1.0	0.4	0.054

Carp length: 20-26 inches

Table 3. Comparison of mean lipid-normalized PCB levels (mg/kg lipid) in carp filets from several Upper Mississippi River Pools for two periods. General Linear Model of log-transformed data was used to test for differences in sample means (SAS, 1986). Data from Wisconsin Department of Natural Resources.

Pool	Period 1 1975-1979 n	Mean	SD	Period 2 1980-1984 n	Mean	SD	PR>F
4	18	63.4	39.3	16	35.7	27.4	0.003
5	4	53.6	48.2	6	22.2	19.2	0.140
5A	2	31.6	5.6	5	22.2	19.7	0.340
8	10	40.5	22.0	4	11.7	3.9	<0.001
9	12	26.7	8.8	3	9.0	4.6	<0.001

Carp length: 20-26 inches.

Table 4. Comparison of mean PCB levels (mg/kg fresh wt.) in fish fillets from Pool 4 of the Upper Mississippi River for two periods. General Linear Model of log-transformed data was used to test for differences in sample means (SAS, 1986). Data from Wisconsin Department of Natural Resources.

Species	Length Inches	Period 1 1975-1979 n	Mean	SD	Period 2 1980-1984 n	Mean	SD	PR>F
Channel catfish	16-23	6	9.7	3.2	4	4.9	0.5	0.348
Carp	20-26	18	4.9	2.8	16	3.0	2.2	0.010
White bass	11-14	7	3.4	1.3	10	2.0	0.9	0.047
Drum	15-19	3	3.1	1.4	4	0.4	0.3	0.005
Walleye	12-23	15	1.0	0.4	12	0.8	0.3	0.286

Table 5. Comparison of mean lipid-normalized PCB levels (mg/kg lipid) in fish fillets from Pool 4 of the Upper Mississippi River Pools for two periods. General Linear Model of log-transformed data was used to test for differences in sample means (SAS, 1986). Data from Wisconsin Department of Natural Resources.

Pool	Length Inches	Period 1 1975-1979 n	Mean	SD	Period 2 1980-1984 n	Mean	SD	PR>F
Channel catfish	16-23	6	66.0	30.2	4	48.9	21.5	0.329
Carp	20-26	18	63.4	39.3	16	35.7	27.4	0.003
White bass	11-14	7	85.6	26.8	10	61.7	45.7	0.057
Drum	15-19	3	70.9	8.0	4	34.4	20.2	0.047
Walleye	12-23	15	119.6	55.6	12	69.8	17.1	0.003

Table 6. Estimated water PCB concentrations for Pool 2 and Lake Onalaska (Pool 7) of the Upper Mississippi River from fish/water (F/W), sediment/water (S/W) and suspended sediment/water (SUS/W) partitioning predictions. Methods described in Appendix A.

Reference	Basis +	Lake Onalaska 1979-1980 (ng/l)	Pool 2 1980- 1984 (ng/l)
USEPA, 1985	F/W	84	147
Mackay, 1982	F/W	44	77
Dexter et al. 1978a	F/W	26	46
USEPA, 1986	S/W	20	129
Rice et al. 1982	SUS/W	3*	18*
WDNR and USGS, 1988	SUS/W	4*	19*

* Includes particulate and dissolved fractions.

+Assumptions:

Lake Onalaska- PCB in carp= 2.1 mg/kg wet wt (1979), sediment organic carbon content = 2%, log Kow= 6.0 (Aroclor 1254) sediment PCB level = 54 ug/kg dry wt (1978-1980), suspended sediment PCB level = 177 ug/kg, TSS = 9.1 mg/l.

Pool 2- PCB in carp = 3.7 mg/kg wet wt (1980-1984), sediment organic carbon content = 1.2%, log Kow = 6.0 (Aroclor 1254), sediment PCB level = 172 ug/kg dry wt (1980-1984), suspended sediment PCB level = 476 ug/kg, TSS = 30 mg/l.

Table 7. Prediction of PCB residues in fish using sediment / fish partitioning procedures. Described in Appendix A.

System	Avg. Sediment PCB ug/kg	Est. Sediment TOC % dry wt.	Avg. Carp Lipid % wet wt.	PCB Partitioning Method: McFarland 1984	Connor 1985 & Huckins 1987	USEPA 1984 & USEPA 1986	Rubenstein from Anderson 1987	Actual PCB level Carp mg/kg Wet Wt.
<u>Pool 2</u>								
(1980-1984)	172	1	5.5	1.5	1.1	3.2	3.6	3.7
<u>Lake Onalaska</u>								
(1979-1980)	54	2	7.0	0.4	0.2	0.5	0.9	2.1
Partitioning Basis				Sed./Fish	Sed./Fish	Sed./Water/Fish	Sed./Fish	

Appendix A. Equilibrium Partitioning Models

I. Fish / Water Partitioning

USEPA, 1985

$$\log BCF = (0.85 \log P) - 0.7$$

where: BCB = bioconcentration factor (fish/water)
P = n-octanol/water partition coefficient

Mackay, 1982

$$Kb = 0.048\ Kow$$

where: Kb = bioconcentration factor (fish/water)
Kow= n-octanol/water partition coefficient

Dexter, 1978a

$$F/W = 80{,}000$$

where: F = fish tissue PCB conentration mg/kg wet wt.
W = water concentration mg/l

II. Sediment / Water Partitioning

USEPA, 1986

$$Koc = S/W$$

where: Koc = sediment/water partition coefficient, for Aroclor 1254, Koc = 131,000
S = sediment PCB ug/gram organic carbon level
W = water concentration mg/l

III. Sediment / Fish Partitioning Equations

McFarland, 1984

$$Ct = (L * Cs) / (K * Foc)$$

where: Ct = tissue concentration mg/kg wet wt.
L = lipid fraction
Cs = sediment concentraton mg/kg dry wt.
K = constant = 0.52
Foc = sediment organic carbon content fraction dry wt basis

Rubenstein, from Anderson, 1987

$$Cd = (L * Cs) / (K * TOC)$$

where: Cd = tissue concentration mg/kg <u>dry</u> wt.
L = % lipid dry wt basis
Cs = sediment concentration mg/kg dry wt.
K = constant = 0.2
TOC = sediment total organic cargon, % dry wt.

Connor, 1985 modified by Huckins, 1987

$$Cf = Cs * 0.077 / Foc$$

where: Cf = tissue concentration mg/kg wet wt.
Cs = sediment concentration mg/kg dry wt.
Foc = sediment organic carbon fraction dry wt. basis

IV. Suspended Sediment / Water Partitioning

Rice et al. 1982

$$SS/W = 133{,}000$$

where: SS = suspended sediment PCB concentration mg/kg dry wt.
W = water concentration mg/l

WDNR and USGS, 1988

$$SS/W = 93{,}800$$

where: SS = suspended sediment PCB concentration mg/kg dry wt.
W = water concentration mg/l