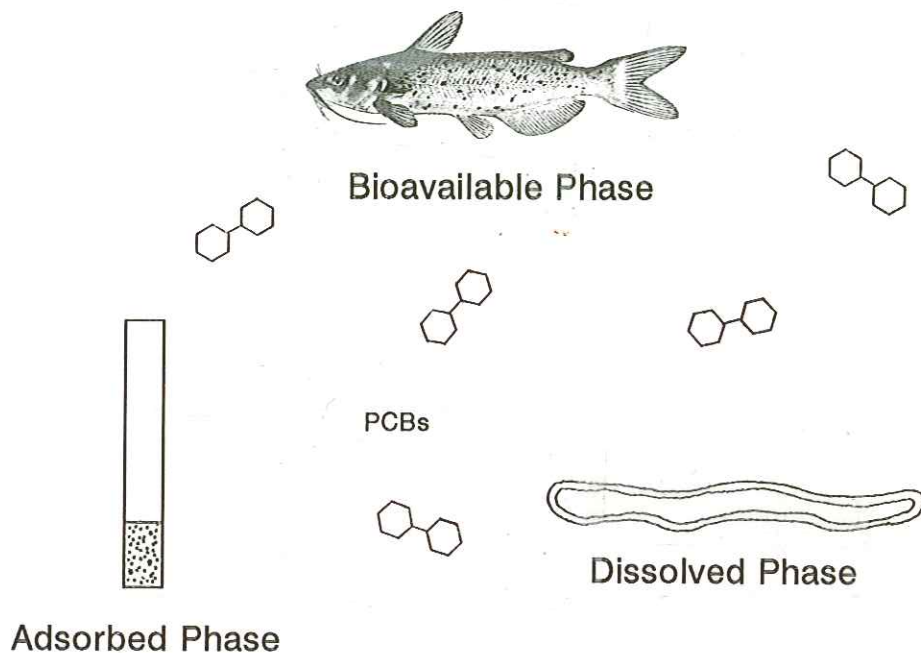


TRI-MATRIX PCB STUDY POOL 5A, UPPER MISSISSIPPI RIVER



John F. Sullivan
Mississippi River Work Unit
Wisconsin Department of Natural Resources
La Crosse, Wi.

and

Mark T. Steingraeber
Upper Mississippi Science Center
National Biological Service
La Crosse, Wi.

February, 1995

ACKNOWLEDGEMENTS

The authors would like to recognized several individuals who provided invaluable assistance in this work. Jim Huckins, National Biological Service, Columbia, Missouri provided semipermeable membrane devices (SPMDs) and substantial technical support concerning their use and deployment. John Crowther, National Biological Service, La Crosse, Wisconsin provided juvenile channel catfish. Dave Degenhardt and other chemists at the Wisconsin State Laboratory of Hygiene, Madison, Wisconsin provided laboratory services for the PCB congener analysis and associated measurements. We would also like to thank Jim Huckins, Dave Degenhardt and West Central District Water Resource Management staff of the Wisconsin Department of Natural Resources for their review of this report. Funding for this project was provided by the Office of Technical Services, Bureau of Water Resource Management, and the Mississippi River Water Resources Management program of the Wisconsin Department of Natural Resources.

INTRODUCTION

Contamination of water, sediment and biota of the Upper Mississippi River by polychlorinated biphenyls (PCBs) have presented a long term water quality problem since their first discovery in fish more than two decades ago (Degurse and Ruhland, 1972). The greatest contamination has been in the river reach extending from the Twin Cities metropolitan area to Lake Pepin (Sullivan, 1988). Recent PCB biomonitoring work utilizing emergent Hexagenia mayflies has indicated continued source inputs and a longitudinal movement of PCBs extending 175-320 km downstream of the Twin Cities area (Steingraeber et al. 1994).

Early attempts to identify specific source inputs of PCBs were largely unsuccessful. Although there was recognition that bed sediments were contaminated with PCBs, no source(s) were identified as being the primary cause(s) of this problem (Interagency Task Force, 1976). Historic PCB contamination in the river was attributed to past widespread use and numerous inputs at levels normally below analytical detection limits for water and wastewater.

Analytical methods and instrumentation for PCB analysis have improved dramatically over the last two decades. Early analytical methods relied on Aroclor-based analytical methods that provided estimates of total PCB. However, this information does not accurately characterize the complex mixture of weathered chlorinated biphenyl residues potentially present in environmental samples (Mullin and Pochini, 1984; Schwartz et al., 1987; Stalling et al., 1985). These analytical deficiencies prevented the detection of subtle differences in the PCB composition of environmental samples and assessment of their toxicological significance (Mc Farland and Clark, 1989). Improved analytical methods that are available today can quantify specific PCB congeners, including those that are most threatening to the environment.

Field methods for evaluating localized contamination have also improved, especially with the development of time-compositing sampling methods used to assess the distribution of PCBs in different environmental compartments. Techniques of this type previously used in the Upper Mississippi River include: caged fish (Huckins, 1995), sentinel mallards (Ensor et al. 1993), sediment traps (Sullivan, 1992), passive in situ concentration/extraction sampler (PICES; Helwig and King, 1995), and semipermeable membrane devices (SPMDs; Ellis et al., 1995).

We simultaneously tested three of these techniques (caged fish, sediment traps, and SPMDs) near a suspected site of PCB input to the Mississippi River. Our objective was to evaluate and compare the effectiveness of each monitoring technique at sensing the environmental distribution of PCBs that may have emanated from this site. Caged fish were chosen to provide a direct measure of PCB bioavailability. Sediment traps collect suspended sediments that can adsorb hydrophobic contaminants like PCBs. SPMDs offer a relatively new approach for evaluating the presence of dissolved

PCBs and other nonpolar organic compounds by mimicking the bioconcentration process (Huckins et al. 1990, 1993, 1994).

Study Area

The study was conducted near the U.S. Army Corps of Engineers' (USCOE) service base at Fountain City, Wisconsin. This marine facility is located at river mile 733.5 in Pool 5A of the Upper Mississippi River (Figure 1). Waste oils contaminated with PCBs were used as a dust suppressant on the grounds of the service base prior to 1980. These oils were drawn from the bilges of Corps vessels, electrical switches, transformers, and gear boxes (Wisconsin Department of Natural Resources, 1981). In 1980 and 1981, several hundred cubic yards of the more contaminated soils (10-390 ug/g) were excavated and hauled to two licensed disposal facilities as part of site remediation efforts.

Follow-up investigations by the USCOE in the summer of 1993 revealed the presence of remaining PCB contaminated soils (0.1-62 ug/g) immediately adjacent to the Mississippi River at the northern end of the boat yard (USCOE, 1994). Laboratory analysis performed by the USCOE's contract laboratory characterized these PCBs as resembling Aroclor 1260.

We installed our PCB monitoring equipment at two sites near the service base. The reference site (site 1) was located in a flowing side channel along the right descending bank, about 200 m upstream from the Corps facility and adjacent to a floodplain forest community (Figure 1). Bottom substrate at this site was primarily silt and clay. The test site (site 2) was located immediately downstream of the facility along the left descending bank. Bottom substrate at this site was sandy with some gravel and rock. No aquatic vegetation was growing at either site and water depth ranged from 0.5 to 1.5 m at both locations during the study.

METHODS

Triplicate PCB monitoring equipment consisting of caged fish, sediment traps, and SPMDs was deployed upstream (site 1) and downstream (site 2) of the suspected source in August 1993. Fish cages and SPMD holders were allowed to presoak in ambient river water at each site for one week prior to the deployment of fish and SPMDs. A special float was constructed to hold the caged fish and SPMDs at approximately mid-depth (Figure 2). The external surfaces of cages and SPMD holders were cleaned weekly using a nylon brush and ambient river water to remove sediment and aufwuchs. Care was taken to avoid exposing the SPMD membranes to air during the cleaning procedure.

PCB congener, lipid, and total organic carbon (TOC) analyses were performed at the Wisconsin State Laboratory of Hygiene (WSLOH) following U.S. Environmental

Protection Agency (USEPA) approved methods. For PCB analysis, 85 PCB congeners, some eluting as pairs or triplets, were determined using capillary column gas chromatography with electron capture detection. A calibration standard included a mixture of Aroclors 1232, 1248, and 1262 (WSLOH, 1993). Mullin (1985) lists the concentration of each congener in this mixture. The list of congeners analyzed and typical laboratory detection limits is presented in Table 1.

Statistical procedures followed methods provided in STATISTIX, version 4.1 (Analytical Software, 1994). A two sample t-test was used to evaluate differences in sample means. In cases where there were three or more groups, one-way analysis of variance was used followed by a pairwise comparison of group means using the Bonferroni method. Significant differences were determined at a 0.05 probability level.

Caged Fish

On 25 August, 15 juvenile fathead minnows (*Pimephales promelas*) were deployed in new, Alconox[®]-washed galvanized minnow traps (20 cm o.d. x 45 cm long). However, due to unacceptable mortality during the first week of exposure, 10 juvenile channel catfish (*Ictalurus punctatus*) were substituted as the test organism on 2 September. The remaining fathead minnows still alive on this date were divided equally between the minnow cages at each site and left for the remaining exposure period. Channel catfish and fathead minnows were obtained from the National Biological Service (NBS) Upper Mississippi Science Center, La Crosse, Wisconsin. Additional unexposed fish from these lots were composited by species into a single background sample.

Channel catfish (and remaining fatheads minnows) were removed from the minnow traps on 12 October after a 40-d exposure. All fish in an experimental cage were wrapped in aluminum foil by species and sealed in plastic bags. Samples were transported in a cooler packed with ice to the Wisconsin Department of Natural Resources' (WDNR) lab in La Crosse where the total length of each fish was measured (± 1 mm). Fish were rewrapped (as described previously) and stored frozen as composite samples. Three composite samples of whole fish, consisting of 9-10 individuals each, were analyzed for PCB congener and lipid content at both sites. A single, unexposed composite sample of 10 fish comprised the background (control) sample.

Sediment Traps

Glass sediment traps were constructed using precleaned 500 mL (17 cm tall x 6 cm diameter) quality assured I-CHEM[®] (model 221-500) jars. An Alconox[®]-washed sheet of aluminum flashing (30 x 30 cm) was wrapped around each jar and secured with vinyl tape to produce an effective aspect ratio (height/diameter) of 6 to 1. A set of three traps with aluminum collars were attached to a section of metal conduit (305 cm long x 1.9 cm o.d.) using vinyl tape and deployed at three locations at each site

(Figure 2). Prior to actual trap deployment on 25 August, the traps and collars were rinsed several times with site water. Sediment traps were mounted vertically in the water column at approximately 0.2, 0.6, and 1.0 m below the water surface.

Sediment traps were removed on 12 October after a 48-d collection period, capped, placed in a cooler packed with ice, and transported to the WDNR lab in La Crosse for processing. The depth of sediment accumulation within each trap was measured (± 1 mm) after the contents of the traps were allowed to settle for several hours. Triplicate vertical composite samples, consisting of three traps each, were mixed and placed in appropriate quality assured glass laboratory containers and stored refrigerated prior to analysis.

Semi-permeable Membrane Devices (SPMDs)

SPMDs consisted of low-density polyethylene layflat tubing (0.25 cm wide x 152 cm long x 85 μ m thick) that were filled with 1.64 g of 95% pure triolein. The tubing was heat sealed to form a loop. The total weight of a single tube containing triolein was 8.41 g. A SPMD sample (controls and treatments) consisted of two such tubes with a total weight of 16.82 g containing 3.28 g (19.5%) of triolein. These passive sampling devices were constructed by and obtained from the National Biological Service, Columbia, Missouri in early August 1993. The SPMDs were shipped in argon-sealed canisters that were kept in a freezer prior to deployment in the field.

A protective shroud for the SPMDs was constructed using 0.6 cm mesh galvanized hardware cloth (10 cm o.d. x 91 cm long). Perforated PVC end caps (10 cm i.d.) were utilized at both ends of the shroud (Figure 2). The shroud and end caps were washed with Alconox[®] and sealed in aluminum foil prior to deployment on 18 August for presoaking in ambient river water. SPMDs were deployed at sites 1 and 2 on 25 August. Latex gloves were worn while two SPMDs were carefully positioned inside each shroud to prevent damage to the polyethylene tubing. Three such shrouds containing SPMDs were deployed at each site. SPMDs were similarly removed from the protective shrouds on 12 October after a 48-d exposure. SPMDs from each shroud were wiped clean of aufwuchs using latex gloves and ambient river water, folded, wrapped in aluminum foil, and sealed in separate plastic bags. Samples were transported in a cooler with ice to the WDNR lab in La Crosse where they were stored in a freezer prior to analysis.

Control SPMD samples consisted of a laboratory blank and a field blank for each study site. The laboratory blank was not removed from its canister until sample analysis. Field blanks were transported to the study sites in separate canisters on the day of deployment and retrieval. The lid of the appropriate canister was removed and the SPMDs were exposed to ambient air at each site for approximately 1.5 h during initial deployment and retrieval. Field blanks were stored in a freezer when not in use.

Prior to PCB analysis at the WSLOH, the exterior surface of the SPMDs were wiped with a clean paper towel and rinsed with hexane. SPMDs were dialyzed (Petty et al., 1993) for 24 hr in 100 mL of cyclohexane. This step was repeated with fresh cyclohexane for another 24 hr period. The dialysates were then combined, concentrated, and subjected to gel permeation chromatography clean-up and silica gel fractionation following standard laboratory procedures for PCB congener analysis (WSLOH, 1993).

Limnological Data

Measurements of dissolved oxygen (DO), water temperature, current velocity, and total suspended solids were made at near weekly intervals during the study period. Dissolved oxygen and water temperature measurements were taken at about mid-depth at sites 1 and 2 using a YSI model 57 DO meter. Mid-depth current velocity was measured using a Marsh McBirney model 201D current meter. Surface water samples were collected for total suspended solids and analyzed following USEPA approved methods at the WSLOH.

RESULTS AND DISCUSSION

River flow and stage levels fell slowly, but were substantially above normal during the study period as a result of heavy basin-wide precipitation in June and July 1993. Average river flow at the U.S. Geological Survey (USGS) gaging station at Winona, Minnesota (about 11 km downstream) was 49,460 cfs (1,400 m³/s) in September 1993. This flow is approximately 124% greater than the average September flow based on a 65-year period of record (USGS, 1994). River stage fell approximately 0.6 m over the course of the monitoring period based on field observations.

Water temperature was similar at the two sites and ranged from 25°C on 25 August to 10°C on 11 October. Dissolved oxygen concentrations were generally comparable at both sites with levels increasing as temperature decreased (Table 2). Total suspended solid concentrations averaged 14.6 mg/L at site 1 and 17 mg/L at site 2.

A unidirectional water current flowing towards the service base was measured at site 1. Current velocity at this site averaged 0.17 ft/s (5.2 cm/s) based on four grab samples collected on different days at mid-depth. In contrast, current velocity could not be determined at site 2 due to the presence of a small eddy and/or southerly winds. These conditions resulted in generally more turbulent conditions at this site making it impossible to obtain stable current velocity measurements.

Strong southerly winds contributed to localized sediment resuspension at the downstream site on some days. This resulted in a greater accumulation of local bed sediments (primarily silty-sands) in the sediment traps at this location. The upstream

site was not believed to have been significantly influenced by wind because it was more sheltered by shoreline and trees. New riprap and surface water drainage culverts were added at the southern end of the service base in mid-September that may have introduced additional suspended matter to site 2 during the construction period.

Caged Fish

The average total PCB concentration of exposed channel catfish was 68.3 and 64.8 ng/g (wet weight) at site 1 and 2, respectively (Table 3). However, about half of these PCBs could be attributed to previous exposure based on a moderately high background concentration of 34.5 ng/g. The average daily PCB accumulation rate (subtracting control levels) was similar at both sites and ranged from 0.84 ng/g/d at site 1 to 0.76 ng/g/d at site 2.

The lipid content of fish decreased from 7.1% at the start of the study to 4.1% at site 1 and 3.5% at site 2 by end of the 40-d exposure period. This might indicate a nutritional deficiency or some other type of physiological stress while the fish were deployed in the river. Survival rate was 90% at the upstream site and 100% below the service base. Differences in the mean lipid content and survival rate between the two sites were not statistically significant. Average lipid-normalized total PCB concentrations were 10% greater at site 2 in comparison to site 1, but this difference was not statistically significant (Table 3).

Exposed channel catfish accumulated mainly the tetra-, penta-, and hexachlorinated biphenyls (Figure 3). Hexachlorinated biphenyls showed the highest homologue concentration in control (15.8 ng/g) and exposed fish (24.2-27.3 ng/g; Table 3). Channel catfish accumulated significantly more tetra- and pentachlorinated biphenyls at site 1 than at site 2. In contrast, fish at the latter site had greater uptake of the hexa- and heptachlorinated biphenyls, but these differences were not statistically significant.

Suspended Sediments

Accumulation of sediment in the traps was about two times greater (36.5 mm) at site 2 than at site 1 (18.8 mm; Table 4). Further, the average TOC content of trapped sediments at site 2 (1.7%) was approximately one-half that at site 1 (3.3%). These differences in mean sediment accumulation and organic content between the two sites were statistically significant. This response was attributed to localized sediment resuspension of bed materials (mainly silty-sands) at site 2 on days with strong southerly winds. Therefore, suspended sediment collected at site 2 likely reflects a greater contribution of local bed materials than at site 1. Despite these physical and chemical differences, the average total PCB concentration of suspended sediments collected at site 2 (48.1 ng/g dry weight) was significantly greater than that at site 1

(31.6 ng/g; Table 4). This latter value is very similar to the average PCB concentration in autumn samples of suspended sediment collected 32 km upstream at Lock and Dam 4 (Sullivan, 1995).

The PCB composition of suspended sediments collected in traps at the two sites were markedly different from one another (Figures 3, 4). Hexa-, hepta-, and octachlorinated biphenyl concentrations were significantly greater in suspended sediments at site 2 than at site 1. In particular, heptachlorinated biphenyl concentrations were eight-fold greater at site 2 (Table 4). The average number of congeners detected at site 2 was also significantly greater than at site 1. This increase in the number of congeners detected at site 2 was associated with the hepta- and octachlorinated biphenyls. Octachlorinated biphenyls were only detected at site 2.

Mean organic carbon (OC)-normalized total PCB values were 0.97 ug/g OC at site 1 and 2.95 ng/g OC at site 2. This difference was not statistically significant and was likely due to greater variability in the TOC content of suspended sediments collected at site 2 (CV=17.6%) than at site 1 (CV=6.0%). Mean OC-normalized hexa-, hepta-, and octachlorinated biphenyl concentrations were significantly greater at site 2. These differences were most apparent for the heptachlorinated biphenyls which showed a 16-fold increase from site 1 (Table 4).

Semipermeable Membrane Devices (SPMDs)

The total PCB concentration of SPMDs averaged 71.3 and 73.0 ng/g (total SPMD weight) at sites 1 and 2, respectively (Table 5). Field and laboratory control SPMD blanks yielded generally similar concentrations (3.4-4.6 ng/g) and therefore these samples were combined for statistical evaluations and plotting. The resultant average SPMD control concentration was 4.1 ng/g and was significantly lower than exposed SPMDs. The average daily PCB accumulation rate (less average controls) was 1.68 ng/g/d at site 1 and 1.72 ng/g/d at site 2. These rates were about twice that for channel catfish measured in this study. These relatively high accumulation rates occurred in spite of continual biofouling of the membrane surface by aufwuchs and suspended matter. This fouling was particularly apparent after about four weeks of exposure. Ellis et al., (1995) reports that biofouling reduces (about 30%) but does not stop the uptake of nonpolar organic chemicals from water by SPMDs.

SPMDs at site 1 showed greater uptake of di-, tri-, tetra-, and pentachlorinated biphenyls than at site 2, but these differences were not statistically significant (Figure 3; Table 5). In contrast, SPMDs at site 2 had a significantly greater accumulation of the hexa-, hepta-, and octachlorinated biphenyls, which was similar to data from the fish and sediment matrices.

Concentrations of the lower chlorinated homologues (especially the tri- and tetrachlorinated biphenyls) were greater in SPMDs than in either channel catfish or

suspended sediments (Figure 3). In addition, two coeluting dichlorinated PCB congeners (IUPAC numbers 5 and 8) were noted in the SPMDs but were absent or present at very low levels in fish or sediments (congener ID no. 3, Figure 4).

SPMDs at both sites accumulated more PCB congeners than either channel catfish or suspended sediment (Tables 3,4,5). Further, SPMDs deployed below the service base contained a significantly greater number of detectable congeners (43) than SPMDs at the upstream reference site (36). These results reflect the broad range of PCB homologues capable of being sequestered by this passive sampling device.

SUMMARY and CONCLUSIONS

Congener analysis of caged fish, sediment trap, and SPMD samples indicated a distinct difference in the composition of PCBs accumulated at sites immediately upstream and downstream of the USCOE's service base. This difference would have gone undetected (with the possible exception of the sediment trap data) had this evaluation been done on a total PCB basis alone. These results reiterate the value of congener specific analysis in determining the environmental fate of PCBs.

PCB concentrations in all three matrices (fish, sediment, and SPMDs) at the upstream reference site were influenced to a greater degree by the lower chlorinated congeners, particularly tri-, tetra- and pentachlorinated biphenyls. Results of only the bioaccumulation test (i.e. channel catfish) revealed significantly greater tetra- and pentachlorinated biphenyl concentrations at the upstream site.

Concentrations of hexa-, hepta-, and octachlorobiphenyls were significantly greater in both suspended sediments and SPMDs at the site downstream of the service base. Moreover, the total number of congeners detected in suspended sediments and SPMDs was greater at the downstream site. The species-specific accumulation of PCBs by caged channel catfish was not sensitive enough to detect these spatial differences in environmental homologue (i.e. congener) composition that were observed in the other matrices. This may have been the result of relatively high PCB concentration in the control fish or low bioaccumulation rates for the more chlorinated biphenyls.

In the present study, SPMDs accumulated a distinctly different combination of PCB homologues and congeners from that accumulated by channel catfish and suspended sediments. Moreover, SPMDs showed the greatest net accumulation of lower chlorinated biphenyls, especially tetrachlorinated biphenyls. Prest et. al. (1992) reported similar results for SPMDs when compared to the freshwater clam, Corbicula fluminea. This response is believed to be related to differential PCB congener accumulation by organisms versus SPMDs. For example, the lower chlorinated PCBs are more likely to be metabolized and depurated in biological systems (Prest et. al.,

1992; McFarland and Clark, 1989). In contrast, little transformation of PCBs is thought to occur once they are present in the lipid phase of the SPMD (Lebo et al., 1992). Therefore, the SPMDs may provide a better indication of the presence of dissolved hydrophobic organic compounds in water than do aquatic organisms.

Our results indicate significantly different mixtures of PCBs occur up and downstream of the service base in Pool 5A. PCBs occurring in fish and sediments from this reach have primarily been attributed to Aroclor 1254 (Amrhein, 1994; Sullivan, 1995) and are likely associated with the longitudinal transport of PCBs from sources within the Twin Cities metropolitan area (Steingraeber et al., 1994). However, the PCBs detected in caged fish, sediment traps, and SPMDs at our downstream site reflect a distinctly higher degree of chlorination than at the upstream reference site. These results are consistent with the suspected input of higher chlorinated PCBs from the service base where high concentrations of PCBs resembling Aroclor 1260 are present in soils and sediments. The higher chlorinated PCBs emanating from the service base would likely show greater affinity to bind to organic particles and be present at low levels in the dissolved phase. This is supported by sediment trap and SPMD results for this site.

RECOMMENDATIONS

Future PCB evaluations initiated near this site should focus on identifying and quantifying the presence of toxic congeners to further evaluate the environmental significance of this contamination problem. Such information will be available for our samples once final laboratory results are completed.

The statistical results presented here should be compared to an approach using principal components analysis and classification. These techniques may provide additional insight to better characterize matrix and spatial differences in exposure to PCBs from different sources.

REFERENCES

- Amrhein, J. 1994. Personal communication. Wisconsin Department of Natural Resources, Madison, WI.
- Analytical Software. 1994. Statistix, Version 4.1. Tallahassee, FL. 329 p.
- Degurse, P., and J. Ruhland. 1972. Occurrence of chlorinated biphenyls in Mississippi River Fish. Wisconsin Department of Natural Resources, Bureau of Fish Management, Madison, WI. Report No. 52. 13 p.
- Ellis, G.S., Huckins, J.N., Rostad, C.E., Schmitt, C.J. Petty, J.D., and P. MacCarty. 1995. Evaluation of lipid-containing semipermeable membrane devices (SPMDs) and gas chromatography-negative chemical ionization-mass spectrometry for monitoring organochlorine contaminants in the Upper Mississippi River. *Environ. Toxicol. Chem.* In Press.
- Ensor, K.L., Pitt, W.C., and D.D. Helwig. 1993. Contaminants in Minnesota Wildlife 1989-1991. Minnesota Pollution Control Agency, Water Quality Division, St. Paul, MN. 75 p.
- Helwig, D.D., and P. King. 1995. Polychlorinated biphenyls (PCBs) in the St. Louis River and the Upper Mississippi River near the Twin Cities. Manuscript in preparation. Minnesota Pollution Control Agency, Division of Water Quality, St. Paul, MN.
- Huckins, J.N., Tubergen, M.W., and C.K. Manuweera. 1990. Semipermeable membrane devices containing model lipid. A new approach to monitoring the bioavailability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* 20(5):533-552.
- Huckins, J.N., Manuweera, G.K., Petty, J.D., Mackay D., and J.A. Lebo. 1993. Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ. Sci. Technol.* 27(12):2489-2496.
- Huckins, J.N., Petty, J.D., Lebo, J.A., and J.L. Zajicek. 1994. SPMD Technology, Tutorial. U.S. Department of Interior, National Biological Survey, Columbia MO. 62 p.
- Huckins, J.N. 1995. Personal communication. National Biological Service, Columbia, MO.

- Interagency Task Force. 1976. Polychlorinated biphenyls (PCBs) in the Upper Mississippi River basin. Minnesota-Wisconsin Interagency Task Force. Unpublished Report. 55 p.
- Lebo, J.A., Zajicek, J.L., Huckins, J.N., Petty, J.D., and P.H. Peterman. 1992. Use of semipermeable membrane devices for *in situ* monitoring of polycyclic aromatic compounds in aquatic environments. *Chemosphere* 25(5):697-718.
- McFarland, V.A., and J.U. Clarke. 1989. Environmental occurrence, abundance, and potential toxicity of polychlorinated biphenyl congeners: considerations for a congener-specific analysis. *Environ. Health Perspectives* (81): 225-239.
- Mullin, M.D., and C.M. Pochini. 1984. High-resolution PCB analysis: synthesis and chromatographic properties of all 209 PCB congeners. *Environ. Sci. Technol.* 18(6):468-476.
- Mullin, M.D. 1985. PCB workshop, US Environmental Protection Agency Large Lakes Research Station, Grosse Ile, MI.
- Petty, J.D., Huckins, J.N., and J.L. Zajicek. 1993. Application of semipermeable membrane devices (SPMDs) as passive air samplers. *Chemosphere* 27(9):1609-1624.
- Prest H.F., Jarman, W.M., Burns, S.A., Weismuller, T., Martin, M., and J.N. Huckins. 1992. Passive water sampling via semi-permeable membrane devices (SPMDs) in concert with bivalves in the Sacramento/San Joaquin River delta. *Chemosphere* 25(12):1811-1823.
- Schwartz, T.R., Stalling D.L., and C.L. Rice. 1987. Are polychlorinated biphenyl residues adequately described by Aroclor mixture equivalents? Isomer-specific principal component analysis of such residues in fish and turtles. *Environ. Sci. Technol.* 21(1):72-76.
- Stalling, D.L., Schwartz T.R, Dunn III, W.J., and J.D. Petty. 1985. Soft independent method of class analogy use in characterizing complex mixtures and environmental residues of polychlorinated biphenyls. ACS Symposium Series No. 292. American Chemical Society, Washington, D.C., 15p.
- Steingraeber, M.T., Schwartz, T.R., Wiener, J.G., and J. A. Lebo. 1994. Polychlorinated biphenyl congeners in emergent mayflies from the Upper Mississippi River. *Environ. Sci. Technol.* 28(4):707-714.
- Sullivan, J.F. 1988. A review of the PCB contaminant problem of the Upper Mississippi River System. Wisconsin Department of Natural Resources, La Crosse, WI, 50 p.

- Sullivan, J.F. 1992. Experiences with sediment traps as a water quality monitoring tool in the Upper Mississippi River. Proceedings of the Mississippi River Research Consortium, Inc. La Crosse, WI. Vol. 24:43-44.
- Sullivan, J.F. 1995. Contaminants in Mississippi River suspended sediments. (In prep.) Wisconsin Department of Natural Resources, La Crosse, WI.
- U.S. Army Corps of Engineers. 1994. Fountain City Service Base Remedial Investigation. Prepared by Barr Engineering Co., Minneapolis, MN.
- U.S. Geological Survey. 1994. Water Resources Data, Minnesota, Water Year 1993. Volume 2. Upper Mississippi and Missouri River Basins. U.S. Geological Survey, Mounds View, MN. pp. 196-197.
- Wisconsin Department of Natural Resources. 1981. Consent Order, Division of Enforcement, Madison, WI.
- Wisconsin State Laboratory of Hygiene. 1993. Methods manual for organic chemistry unit, Madison, WI, Method No. 1510, p. A8-3 to A8-11.

Table 1. Method detection (LOD) and quantitation (LOQ) limit for PCB congeners at the Wisconsin State Laboratory of Hygiene, Madison, Wisconsin. Listed in order as reported by the laboratory. Results are expressed as wet weight for fish, dry weight for sediments, and total sampler weight (bag plus triolein) for semipermeable membrane devices (SPMDs).

Congener or Peak ID	IUPAC + PCB Cong. No.	Cl Substitution Pattern	FISH		SEDIMENT		SPMD
			LOD ng/g	LOQ ng/g	LOD ng/g	LOQ ng/g	RL* ng/g
1	7	2,4	0.60	2.0	0.20	0.70	0.24
2	6	2,3'	3.0	10	0.45	1.5	0.24
3	5/8	2,3/2,4'	4.0	13	1.3	4.3	0.24
4	19	2,2',6	1.0	3.3	0.30	1.0	0.24
5	18	2,2',5	1.0	3.3	0.35	1.2	0.24
6	17	2,2',4	0.80	2.7	0.30	1.0	0.24
7	24/27	2,3,6/2,3',6	1.0	3.3	0.30	1.0	0.24
8	16/32	2,2',3/2,4',6	1.0	3.3	0.40	1.5	0.24
9	26	2,3',5	0.80	2.7	0.35	1.2	0.24
10	28/31	2,4,4'/2,4',5	2.5	8.3	1.4	4.6	0.24
11	33	2',3,4	1.0	3.3	0.45	1.5	0.24
12	22	2,3,4'	1.2	4.0	0.60	2.0	0.24
13	45	2,2',3,6	0.80	2.7	0.30	1.0	0.24
14	46	2,2',3,6'	1.0	3.3	0.35	1.2	0.24
15	52	2,2',5,5'	1.0	3.3	0.30	1.0	0.24
16	49	2,2',4,5'	0.60	2.0	0.30	1.0	0.24
17	47/48	2,2',4,4'/2,2',4,5	1.2	4.0	0.50	1.6	0.24
18	44	2,2',3,5'	1.1	3.7	0.30	1.0	0.24
19	37/42	3,4,4'/2,2',3,4'	1.1	3.7	0.40	1.3	0.24
20	41/64/71	2,2',3,4/2,3,4',6/2,3',4',6	2.0	6.6	0.50	1.6	0.24
21	40	2,2',3,3'	1.0	3.3	0.30	1.0	0.24
22	74	2,4,4',5	1.0	3.3	0.30	1.0	0.24
23	70/76	2,3',4',5/2',3,4,5	2.4	8.0	0.45	1.5	0.24
24	66/95	2,3',4,4'/2,2',3,5',6	2.8	9.2	0.60	2.0	0.24
25	91	2,2',3,4',6	1.0	3.3	0.40	1.3	0.24
26	56/60	2,3,3',4'/2,3,4,4'	1.8	5.9	0.80	2.6	0.24
27	84/92	2,2',3,3',6/2,2',3,5,5'	1.3	4.4	0.70	2.3	0.24
28	101	2,2',4,5,5'	0.60	2.0	0.30	1.0	0.24
29	99	2,2',4,4',5	0.60	2.0	0.30	1.0	0.24
30	97	2,2',3',4,5	0.80	2.6	0.30	1.0	0.24
31	87	2,2',3,4,5'	1.0	3.3	0.35	1.2	0.24
32	85	2,2',3,4,4'	1.1	3.3	0.35	1.0	0.24
33	136	2,2',3,3',6,6'	2.0	6.6	0.20	0.70	0.24
34	77/110	3,3',4,4'/2,3,3',4',6	1.3	4.3	0.40	1.3	0.24
35	82	2,2',3,3',4	1.0	3.3	0.30	1.0	0.24
36	151	2,2',3,5,5',6	1.0	3.3	0.30	1.0	0.24
37	135/144	2,2',3,3',5,6'/2,2',3,4,5',6	0.80	2.6	0.30	1.0	0.24
38	149	2,2',3,4',5',6	1.1	3.6	0.30	1.0	0.24
39	118	2,3',4,4',5	0.80	2.6	0.45	1.5	0.24
40	146	2,2',3,4',5,5'	1.1	3.3	0.35	1.2	0.24
41	132/153	2,2',3,3',4,6'/2,2',4,4',5,5'	1.8	5.9	0.45	1.5	0.24
42	141	2,2',3,4,5,5'	0.80	2.6	0.30	1.0	0.24
43	137/176	2,2',3,4,4',5/2,2',3,3',4,6,6'	1.0	3.3	0.30	1.0	0.24
44	138/163	2,2',3,4,4',5'/2,3,3',4',5,6	1.7	5.6	0.40	1.3	0.24
45	178	2,2',3,3',5,5',6	1.3	4.2	0.40	1.3	0.24
46	182/187	2,2',3,4,4',5,6'/2,2',3,4',5,5',6	1.5	5.0	0.40	1.3	0.24
47	183	2,2',3,4,4',5',6	1.8	5.9	0.40	1.3	0.24
48	185	2,2',3,4,5,5',6	1.0	3.3	0.30	1.0	0.24
49	174	2,2',3,3',4,5,6'	1.1	3.6	0.30	1.0	0.24
50	177	2,2',3,3',4',5,6	1.1	3.6	0.35	1.2	0.24
51	171/202	2,2',3,3',4,4',6/2,2',3,3',5,5',6,6'	0.80	2.6	0.30	1.0	0.24
52	172/197	2,2',3,3',4,5,5'/2,2',3,3',4,4',6,6'	1.8	5.9	0.50	1.6	0.24
53	180	2,2',3,4,4',5,5'	2.2	7.3	0.35	1.2	0.24
54	199	2,2',3,3',4,5,6,6'	0.60	2.0	0.30	1.0	0.24
55	170/190	2,2',3,3',4,4',5/2,3,3',4,4',5,6	2.5	8.2	0.70	2.3	0.24
56	201	2,2',3,3',4,5,5',6	1.8	5.9	0.50	1.6	0.24
57	196/203	2,2',3,3',4,4',5,6'/2,2',3,4,4',5,5',6	3.0	9.9	0.70	2.3	0.24
58	195/208	2,2',3,3',4,4',5,6/2,2',3,3',4,5,5',6,6'	2.0	6.6	0.70	2.3	0.24
59	194	2,2',3,3',4,4',5,5'	1.0	3.3	0.50	1.6	0.24
60	206	2,2',3,3',4,4',5,5',6	1.5	5.0	0.40	1.3	0.24
61	128	2,2',3,3',4,4'	1.4	4.7	0.50	1.6	0.24
62	167	2,3',4,4',5,5'	1.8	6.0	0.50	1.6	0.24

* Lab report limit. Actual mass limit is 4 ng.

+ International Union of Pure and Applied Chemists.

TABLE 2. General limnological data collected during the tri-matrix PCB study in Pool 5A, Upper Mississippi River in 1993.

Date	River Flow* cfs	Site 1				Site 2			
		TSS mg/L	TEMP C	DO mg/L	VEL fps	TSS mg/L	TEMP C	DO mg/L	VEL fps
AUG 25	70200	14	25.0	8.0	--	16	25.2	6.9	--
SEPT 9	54100	16	18.5	8.2	0.15	19	19.0	8.2	ND
SEPT 15	48000	16	15.0	7.8	0.13	20	15.0	7.7	ND
SEPT 21	41000	--	14.1	8.6	0.23	--	14.0	8.7	ND
SEPT 30	39000	15	11.0	11.0	0.20	18	11.0	10.9	ND
OCT 11	31200	12	9.8	12.5	--	12	10.0	13.3	--

-- = No data.

ND = Not detected.

* USGS gage at Winona, MN.

Metric conversions: 1 fps = 30.5 cm/s, 1 cfs = 0.02834 m³/s

Table 3. Summary of channel catfish PCB bioaccumulation, lipid content, and survival data after a 40-d exposure in Pool 5A, Upper Mississippi River.

Parameter +	Treatment				
	Control	Site 1		Site 2	
	n = 1	n = 3		n = 3	
		Mean	Std	Mean	Std
Total PCBs ng/g wet wt.	34.5	68.3	(0.9)	64.8	(6.3)
Dichlorobiphenyls	0	0		0	
Trichlorobiphenyls	0	1.0	(1.7)	0	
Tetrachlorobiphenyls	0.6	9.6 *	(0.1)	7.5 *	(0.7)
Pentachlorobiphenyls	5.6	15.5 *	(1.2)	11.2 *	(1.6)
Hexachlorobiphenyls	15.8	24.2	(1.6)	27.3	(1.3)
Heptachlorobiphenyls	9.8	10.2	(0.7)	12.3	(1.9)
Octachlorobiphenyls	0	0		0	
Total No. PCB congeners #	12	19.3	(0.6)	20.7	(1.2)
Dichlorobiphenyls	0	0		0	
Trichlorobiphenyls	0	0.3	(0.6)	0	
Tetrachlorobiphenyls	1	5 *	(0)	4 *	(0)
Pentachlorobiphenyls	3	5.3	(0.6)	4.3	(0.6)
Hexachlorobiphenyls	4	4.3	(0.6)	5	(0)
Heptachlorobiphenyls	3	3	(0)	4	(1)
Octachlorobiphenyls	0	0		0	
Total PCBs ng/g lipid	486	1714	(300)	1889	(331)
Dichlorobiphenyls	0	0.3	(0.6)	0	
Trichlorobiphenyls	0	241	(40)	0	
Tetrachlorobiphenyls	8.9	386	(51)	220	(39)
Pentachlorobiphenyls	78.9	611	(143)	324	(38)
Hexachlorobiphenyls	223	253	(27)	802	(165)
Heptachlorobiphenyls	138	0		356	(63)
Octachlorobiphenyls	0	0		0	
Mean lipid content %	7.1	4.1	(0.7)	3.5	(0.9)
Mean fish length mm	66.6	72.5	(3.1)	70.9	(1.2)

+ PCB homologue results do not include some multiple coeluting congeners where more than one homologue was possible.

* Means between sites 1 & 2 are significantly different at P = 0.95.

Coeluting congeners are treated as a single number.

Table 4. Summary of sediment trap PCB levels, total organic organic content, and sediment accumulation during a 48-d exposure period in Pool 5A, Upper Mississippi River.

Parameter +	Treatment			
	Site 1		Site 2	
	n = 3		n = 3	
	Mean	Std	Mean	Std
Total PCBs ng/g dry wt.	31.6 *	(4.2)	48.1 *	(4.0)
Dichlorobiphenyls	0.5	(0.9)	0	
Trichlorobiphenyls	2.2	(0.9)	1.3	(1.5)
Tetrachlorobiphenyls	4.5	(0.7)	3.7	(1.5)
Pentachlorobiphenyls	7.3	(0.3)	4.8	(1.8)
Hexachlorobiphenyls	9.2 *	(1.0)	14.2 *	(0.3)
Heptachlorobiphenyls	1.6 *	(0.5)	13.8 *	(1.6)
Octachlorobiphenyls	0 *		3.7 *	(0.4)
Total No. PCB congeners #	26 *	(3.6)	32.3 *	(1.5)
Dichlorobiphenyls	0.3	(0.6)	0	
Trichlorobiphenyls	2.0	(1)	0.7	(1.2)
Tetrachlorobiphenyls	5.3	(0.6)	5	(0)
Pentachlorobiphenyls	6	(0)	5.7	(1.2)
Hexachlorobiphenyls	5.7	(0.6)	5.3	(0.6)
Heptachlorobiphenyls	2.3 *	(0.6)	7 *	(0)
Octachlorobiphenyls	0 *		3 *	(0)
Total PCBs ng/g OC	965	(161)	2949	(889)
Dichlorobiphenyls	0		0	
Trichlorobiphenyls	67.3	(30.1)	91.0	(116)
Tetrachlorobiphenyls	137	(25)	240	(154)
Pentachlorobiphenyls	224	(21)	308	(191)
Hexachlorobiphenyls	280 *	(44)	857 *	(186)
Heptachlorobiphenyls	49.1 *	(16.3)	824 *	(83)
Octachlorobiphenyls	0 *		223 *	(24)
Total Organic Carbon %	3.29 *	(0.2)	1.70 *	(0.3)
Sediment Accumulation mm	18.8 *	(4.2)	36.5 *	(17.1)

+ PCB homologue results do not include some multiple coeluting congeners where more than one homologue was possible.

* Means between sites 1 & 2 are significantly different at P = 0.95.

Coeluting congeners are treated as a single number.

Table 5. Summary of semipermeable membrane device (SPMD) PCB results after a 48-d exposure period in Pool 5A, Upper Mississippi River. PCB concentration results are expressed in terms of total sampler weight (triolein plus bags).

Parameter +	Treatment					
	Control		Site 1		Site 2	
	n = 3		n = 3		n = 3	
	Mean	Std	Mean	Std	Mean	Std
Total PCBs ng/g	4.1 a	(0.6)	71.3 b	(2.6)	73.0 b	(11.3)
Dichlorobiphenyls	0.57 a	(0.04)	2.74 b	(0.16)	2.45 b	(0.56)
Trichlorobiphenyls	0.24 a	(0.21)	9.21 b	(0.50)	8.25 b	(0.97)
Tetrachlorobiphenyls	0.54 a	(0.02)	20.2 b	(1.0)	17.2 b	(2.8)
Pentachlorobiphenyls	0.77 a	(0.01)	14.9 b	(0.44)	12.6 b	(2.3)
Hexachlorobiphenyls	0.55 a	(0.05)	6.92 b	(0.48)	12.7 c	(2.1)
Heptachlorobiphenyls	0.24 a	(0.21)	1.13 a	(0.44)	4.70 b	(0.8)
Octachlorobiphenyls	0 a		0 a		0.75 b	(0.13)
Total No. PCB congeners #	11 a	(1.7)	36.3 b	(0.6)	43 c	(1.0)
Dichlorobiphenyls	1 a	(0)	1 a	(0)	1 a	(0)
Trichlorobiphenyls	0.7 a	(0.6)	5.7 b	(0.6)	6 b	(0)
Tetrachlorobiphenyls	2 a	(0)	10 b	(0)	9 b	(0)
Pentachlorobiphenyls	2.7 a	(0)	8 b	(0)	8 b	(0)
Hexachlorobiphenyls	2 a	(0)	7 b	(0)	7.3 b	(0)
Heptachlorobiphenyls	0.7 a	(0.6)	1.7 a	(0.6)	6.7 b	(1.2)
Octachlorobiphenyls	0 a		0 a		2 b	(0)

+ PCB homologue results do not include some multiple coeluting congeners where more than one homologue was possible.

* Means with different letters are significantly different at P = 0.95.

Coeluting congeners are treated as single number.

@ Lipid content extracted from SPMD.

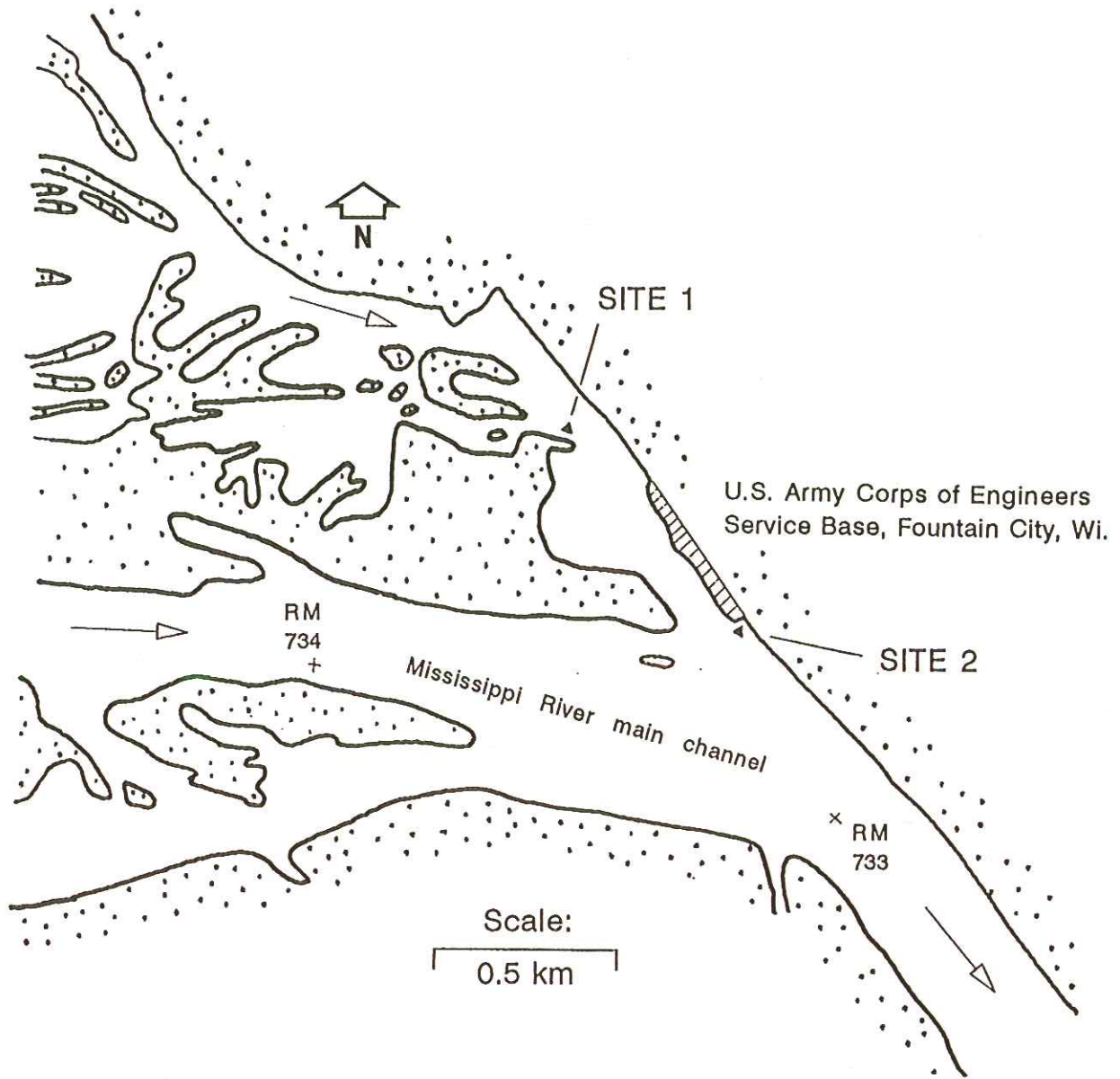


Figure 1. Map of study area. Pool 5A, Upper Mississippi River. Base map from the U.S. Corps of Engineers' navigation chart for the Upper Mississippi River (RM = river mile).

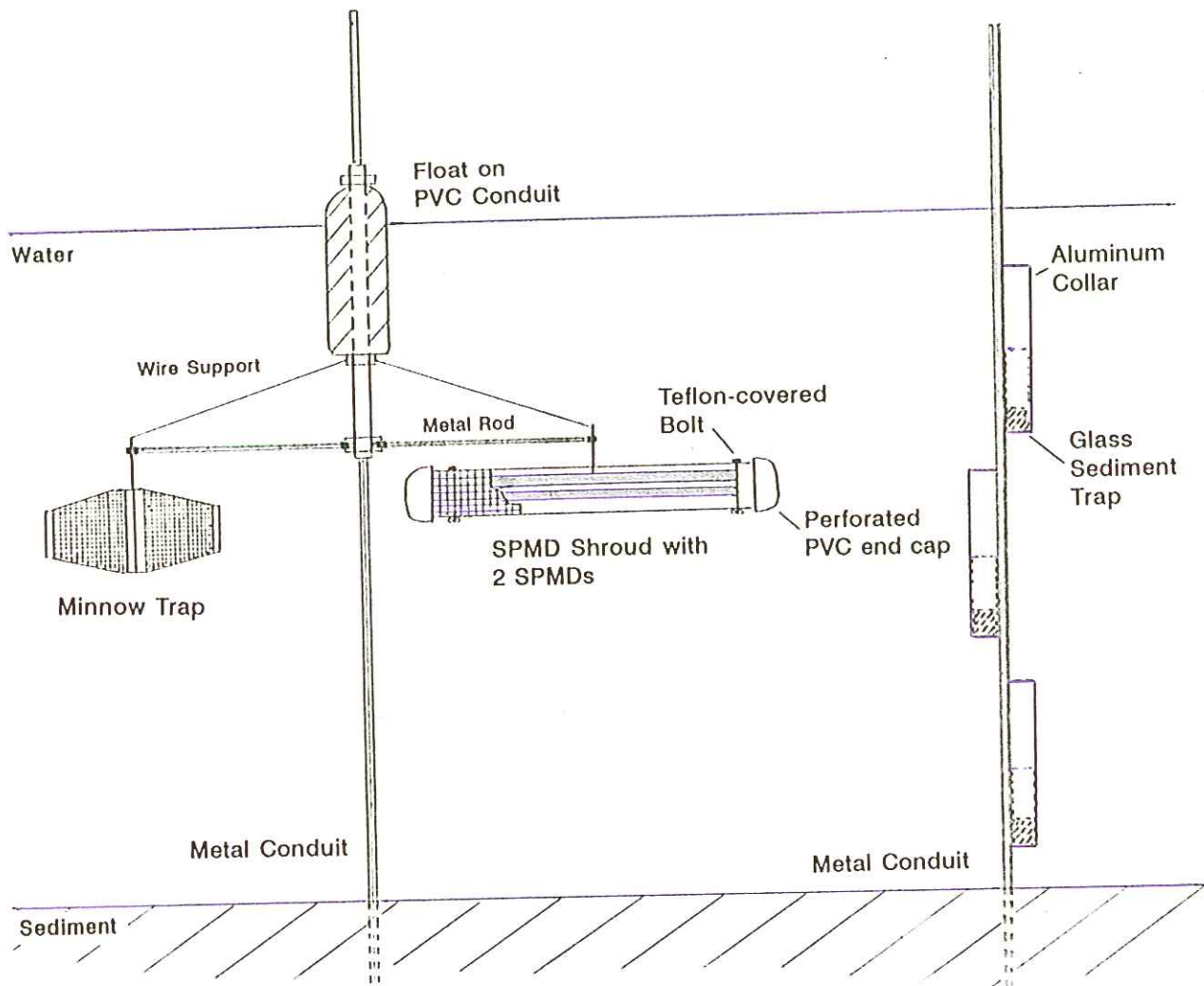


Figure 2. Field apparatus for tri-matrix PCB study in Pool 5A, Upper Mississippi River in 1993. Three such configurations of sampling equipment were deployed at each site.

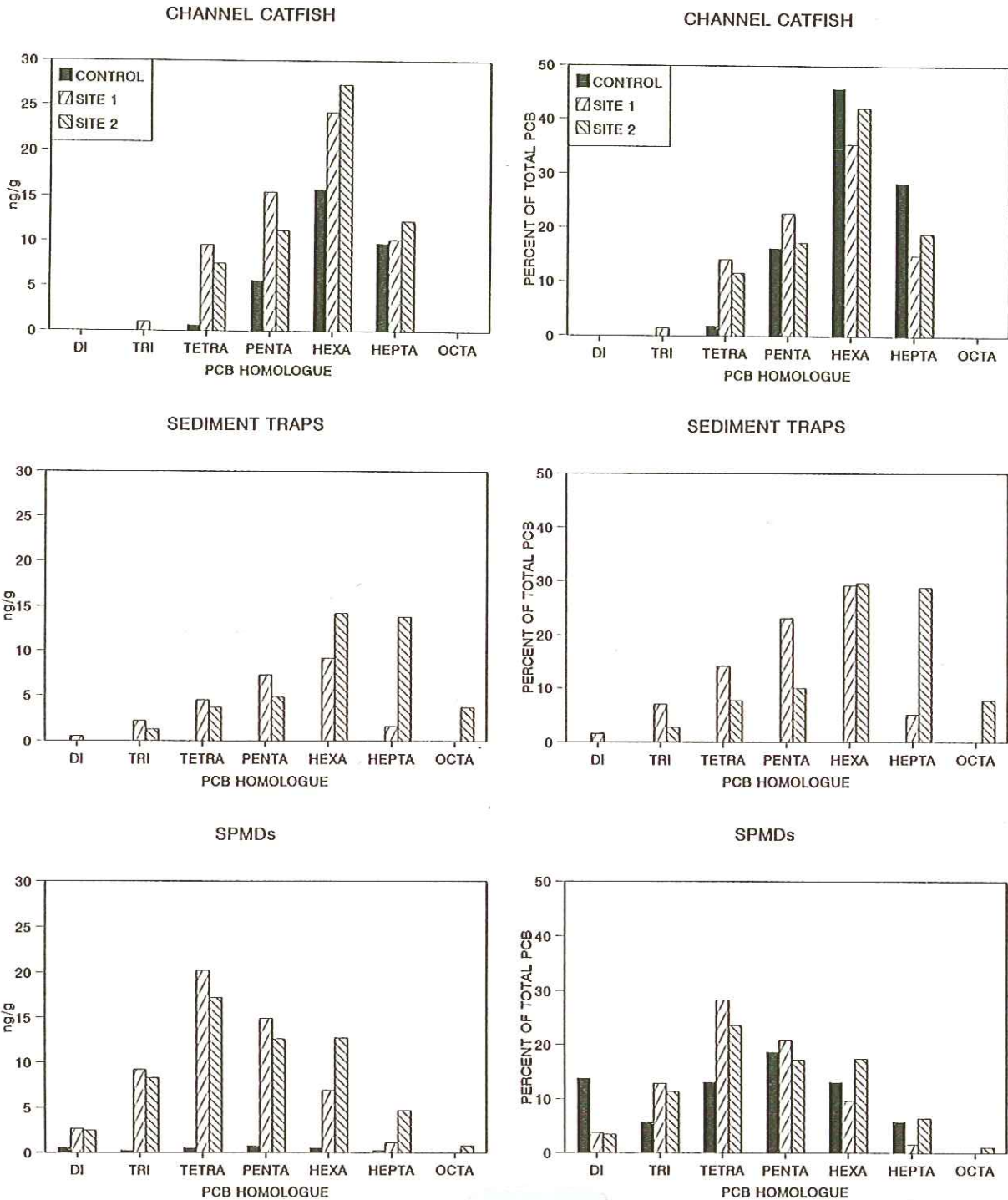


Figure 3. PCB homologue concentrations and percent composition in channel catfish, sediment traps (suspended sediments), and semipermeable membrane devices (SPMDs) exposed in Pool 5A, Upper Mississippi River in 1993.

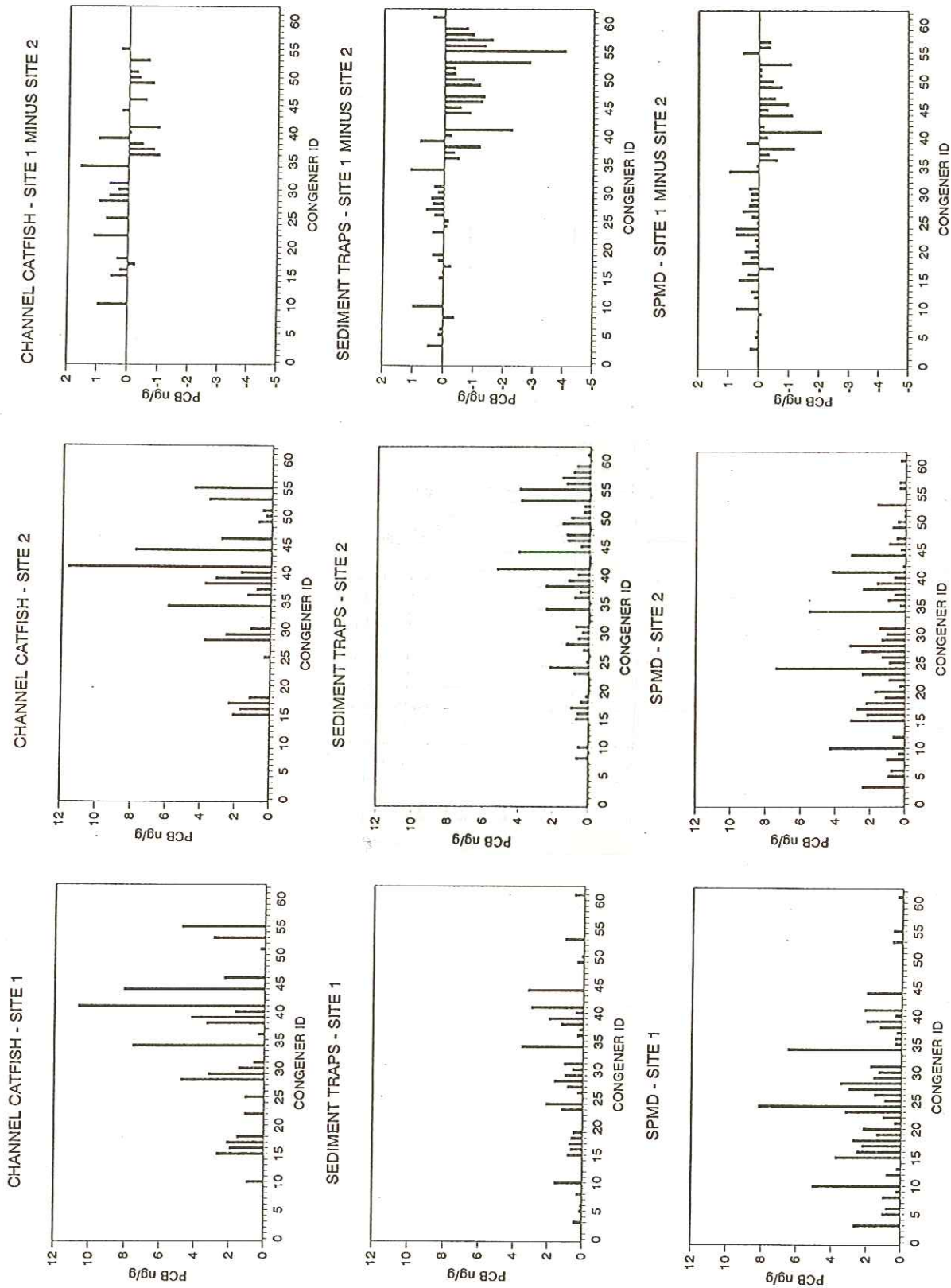


Figure 4. PCB congener concentrations in channel catfish, suspended sediments, and semipermeable membrane devices (SPMDs) deployed at two sites in Pool 5A, Upper Mississippi River in 1993. Congener identities (peak ID) are provided in Table 1.