

MICHIGAN DEPARTMENT OF ENVIRONMENTAL QUALITY
WATER RESOURCES DIVISION
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STAFF REPORT

INVESTIGATION OF PCB, PAH, AND PESTICIDE CONCENTRATIONS IN THE MENOMINEE
RIVER USING SEMI-PERMEABLE MEMBRANE DEVICES
AUGUST 30-SEPTEMBER 27, 2011

The Lower Menominee River is listed as an Area of Concern (AOC) in part because of restrictions on fish consumption. Both Michigan and Wisconsin have issued advisories recommending limited consumption of certain species of fish from the Menominee River AOC, as well as selected species from the river upstream of the AOC to Kingsford, Michigan. The advisories within the AOC are due to elevated levels of polychlorinated biphenyls (PCBs), mercury, and dioxin. The number of fish samples collected from the river mouth is somewhat limited, and most of the species collected probably spend significant parts of their lives in Green Bay. It is believed that Green Bay is the primary source of the contaminants in fish collected downstream of the first dam; however, elevated concentrations of PCBs have been measured in fish from upstream of the first dam. It is not known if significant sources of PCBs exist in the Menominee River AOC.

In addition, significant concentrations of polycyclic aromatic hydrocarbons (PAHs) have been measured in sediments within the AOC. PAHs are a group of over 100 benzene-like compounds some of which are known to be toxic to humans or aquatic life, and are generally produced as a result of burning fossil fuels or other organic materials. PAHs have been found at elevated levels in sediments near the Marinette Wastewater Treatment Plant (WWTP) outfall and may contaminate sediments elsewhere within the AOC. The Wisconsin Public Service Corporation operated a coal-gasification plant at the WWTP site from 1910 to 1960 and was found to be the party responsible for the PAH contamination. Significant quantities of PAH-contaminated material were removed from the upland area during upgrades to the WWTP in 1989; in-stream remedial activities began in October 2012. Additional upland remediation by the Wisconsin Public Service Corporation will take place if ongoing monitoring determines it to be necessary.

Lastly, organochlorine pesticides have been quantified in the outfall of a facility with a permit to discharge within the Menominee River AOC. The facility is probably not a significant source of these contaminants; the facility uses the river for process water, and it is hypothesized that the intake water contamination is concentrated during filtration processes in the facility.

The objective of this project was to determine if significant sources of PCBs, PAHs, and organochlorine pesticides exist in the Menominee River watershed and to narrow the search for any such sources. The study used semi-permeable membrane devices (SPMDs) in a screening level effort to measure relative water column PCB, PAH, and chlorinated pesticide concentrations at sites within and upstream of the AOC. An SPMD is a passive transport device designed to absorb hydrophobic organic chemicals, and consists of "lay-flat" low-density polyethylene tubing containing a thin film of a pure, heavy molecular weight (HMW) lipid (triolein). The tubing allows for the selective diffusion of the target compounds, which are then sequestered in the lipid.

A set of SPMDs was deployed at each of 12 sites in the Menominee River for a period of 28 days. The SPMDs were then processed by Environmental Sampling Technologies (EST) to produce extracts of the lipid containing the contaminants absorbed by the SPMDs during deployment in the river. These extracts were analyzed for PCB, PAH, and pesticide content by the Michigan Department of Community Health, Chemistry and Toxicology Division Laboratory (MDCH Lab) and the Michigan Department of Environmental Quality, Environmental Laboratory (MDEQ Lab) in Lansing, Michigan. Results of the analyses were reported to the MDEQ, Water Resources Division, and were used to determine if concentrations of the various contaminants differ from site to site, and if any differences indicate the presence of a source or sources of contamination. The results are not used in the development of fish consumption advisories but may inform decisions regarding future sediment sampling.

SUMMARY

1. PCBs, other chlorinated hydrocarbon contaminants, and PAHs were measured in SPMDs at 12 sites in the Menominee River in 2011.
2. No net uptake of PCBs was observed upstream of the Park Mill Dam impoundment. Net uptake of PCBs downstream of the Menominee Dam varied somewhat between sites, but the maximum observed net uptake was relatively low compared to similar testing conducted in other watersheds.
3. Although the SPMD sampling indicates that there are PCB sources to the river downstream of the dam, those sources probably do not explain the concentrations measured in fish collected in the lower river.
4. Net uptake of the pesticides chlordane, DDT, dieldrin, and hexachlorobenzene (HCB) tended to be elevated downstream of the Menominee Dam relative to the upstream sites. Concentrations of those pesticides varied from site to site downstream of the Menominee Dam. Net uptake of the pesticide lindane was somewhat higher upstream of the Park Mill Dam impoundment but no spatial pattern was apparent.
5. Net uptake of PAHs was very low upstream of the Park Mill Dam impoundment and consisted primarily of 2-ring compounds. Net uptake of PAHs downstream of the Menominee Dam was highest near the river mouth, and the total PAH was dominated by HMW compounds (4 or more benzene rings). The pattern is consistent with a known coal-tar contamination site in the lower Menominee River.

METHODS

SPMD Preparation

Standard SPMDs (91 x 2.5 cm membrane containing 1 mL triolein) and stainless steel canisters and spindles to hold the membranes during deployment were obtained from EST. The SPMDs were spiked by the manufacturer with Performance Reference Compounds (PRCs) prior to shipment. These are compounds with a moderate to high tendency to dissipate from the SPMDs and can be used to estimate the differences in sampling rates between sites caused by differences in temperature, bio-fouling, and flow velocity (Huckins et al., 2002). Each SPMD was spiked prior to shipment by EST with 80 ng each of PCB congeners #14, 29, and 50 to be used as PRCs.

The SPMDs were preloaded onto the spindles by EST in a clean room and shipped in solvent-rinsed metal cans under argon gas. Four SPMDs were used in each canister, with one canister per sampling site. The SPMDs were kept frozen until deployment.

Field blanks were prepared for exposure at 2 sites and were identical to the sample SPMDs. The cans containing the sample and field blank SPMDs were kept frozen and unopened until the time of deployment/exposure in the field.

SPMD Deployment and Retrieval

SPMDs were deployed at 12 sites within and upstream of the Menominee River AOC (Figure 1). Sites were selected based on the locations of known or potential sources of surface water contamination. Table 1 describes the locations and rationale for choosing the site locations; a detailed description of the sampling sites is given in Appendix A.

Deployment and retrieval procedures for SPMDs followed guidance provided by Johnson (2007), Petty et al. (1993), and the U. S. Geological Service (Alvarez, 2010).

At each sampling site, four SPMDs, each on a separate carrier, were fitted into a stainless steel canister by field personnel using nitrile gloves (Figure 2). The canister lid was padlocked. The SPMDs were placed in flowing water but out of strong currents, situated so as to minimize the potential for vandalism, and in water deep enough to allow for water level fluctuations. The devices were attached to an existing near-shore structure and anchored to help maintain position during the deployment. Flotation was attached where needed to keep the canisters off the river bottom.

A set of 4 field blank SPMDs was exposed at each of 2 sites, both at the time of deployment and retrieval of the test SPMDs, to determine uptake of airborne contaminants. A field blank was exposed at one site downstream of the Menominee Dam (aka lower Scott Dam) (Site 4R) and at Site 6 (at US-8 near Norway). The can containing a field blank set was opened, exposed to air approximately the same amount of time as sample SPMDs, resealed, and then frozen until mobilization for retrieval of the sample SPMDs.

Sample SPMDs remained in the river for 28 days. On retrieval, the SPMDs were put back in metal cans and sealed. The appropriate field blanks were again exposed to air during sample retrieval. All SPMDs were kept chilled and shipped via overnight delivery to EST for extraction.

Analytical Procedures

The sample and field blank SPMDs were extracted and prepared for analysis by EST. The final extracts were shipped overnight from EST to the MDCH Lab.

The MDCH Lab analyzed the extracts for PCB congeners and other chlorinated organic compounds, including organochlorine pesticides (Tables 2 and 3). The extracts were first fractionated on silica gel to isolate the compounds following the MDCH Lab's Method AC.13.05, *Silica Gel-60 Fractionation of Biological Tissue Extracts for Polybrominated Biphenyls, Polychlorinated Biphenyls, and Chlorinated Pesticides*. Quantitation of PCB and chlorinated pesticide residues were performed by capillary column gas chromatography with an electron capture detector following MDCH Lab's Method AC.35.01, *Capillary Column Gas Chromatography of Silica Gel-60 Fractions from Biological Tissue Extracts for Polychlorinated Biphenyl Congeners*. MDCH Lab Methods AC.13.05 and AC.35.01 are available upon request.

PCBs were reported as individual congeners (or co-eluting congeners) and as total PCBs. Chlordane and DDT isomers were reported individually, summed, and analyzed as total chlordane and total DDT, respectively.

The MDCH Lab provided aliquots of the sample fractions to the MDEQ Lab for analysis of PAHs (Table 4) by gas chromatography/mass spectrometry following Standard Operating Procedure #500 *Semivolatile Organic Compounds By Gas Chromatography/Mass Spectrometry* (available upon request).

Data Analysis

Analytical results were received electronically and entered into an Access database. The results were reviewed for completeness and for possible outliers. Between site statistical comparisons were made using Analysis of Variance and Kruskal-Wallis statistical techniques with the Minitab software package. Differences were considered statistically significant at $\alpha=0.10$.

The Performance Reference Compound results were evaluated to determine if meaningful between site differences in uptake were apparent. PRC concentrations differed significantly between some sampling sites. A relatively low mean PRC concentration indicates a higher sampling rate relative to other sites because the SPMD is exposed to higher river flow, higher water temperature, less bio-fouling, or a combination of those factors. Conversely, a relatively high mean PRC concentration indicates a lower sampling rate. To correct for the variation in sampling rates, the concentrations of target compounds measured in the sample SPMDs were multiplied by the ratio of the mean PRC concentration at the sample site to the lowest observed mean PRC concentration (Table 5).

The concentrations measured in the sample SPMDs were also corrected for background levels (exposure to airborne contaminants) by subtracting the average concentration measured in field blanks from the concentration in each sample SPMD (field blank concentrations were corrected for relative PRC concentrations [Table 5]). The field blanks exposed at Site 4-R were used to represent the background airborne concentration for the lower river (Sites 1 through 5); field blanks exposed at Site 6 were used to represent the background concentration for the upper river (Sites 6, 7, and 8).

The concentration corrected for field blank and PRC concentrations is termed net uptake.

RESULTS AND DISCUSSION

Net uptake of PCBs, several chlorinated pesticides, and PAHs was measured in SPMDs throughout the Menominee River study area.

PCBs

PCBs are a group of chemicals produced commercially in the United States from 1929 until their manufacture was banned in 1979. PCBs were marketed for a wide variety of uses including coolants in electrical distribution transformers and capacitors, hydraulic fluids, inks, paints, and adhesives (ATSDR, 2000). High concentrations of PCBs are generally associated with industrial or urban areas, but atmospheric transport has led to elevated concentrations even in remote areas such as the Arctic.

PCBs were quantified in at least 1 SPMD at each sampling site except Site 5 (near Chappee Rapids) and in each set of field blank SPMDs; however, there was no net uptake of PCBs at any of the 4 sampling sites upstream of the Menominee Dam (Table 6; Figure 3). This indicates

that there is no significant source of PCBs upstream of the Park Mill (aka Upper Scott) Dam impoundment.

Some net uptake of PCBs occurred at Site 4-R, just downstream of the Menominee Dam nearest the right (southerly) bank, indicating that sediments in either the Menominee Dam impoundment, the Park Mill Dam impoundment, or both, are a source of PCBs to the lower river.

The maximum average net uptake of PCBs observed in this study (10 ng/g) is equivalent to the lowest average concentration observed in a similar study in and near Torch Lake (Houghton County, Michigan) in 2005. The lowest average concentration in the Torch Lake SPMD study was measured at a site near Lake Superior at the north end of the Keweenaw Waterway (Bohr, 2006). This comparison suggests that PCB levels in the lower Menominee River are near background levels and are probably not different than levels in rivers flowing through typical small cities in the region. In addition, the levels of PCBs measured in the Menominee River SPMDs were lower than levels observed in a similar study conducted in the Sheboygan River AOC, where the minimum observed concentration was over 1,500 ng/g (Burzynski, 2000). The Menominee River concentrations were also lower than SPMD concentrations observed in the St. Joseph River, Michigan; a river that is not associated with an AOC (Shim, 2004).

The levels observed in the lower Menominee River are likely due to influx from nonpoint sources throughout the watershed as well as a net release of PCBs and other contaminants from impoundment sediments. Those sediments historically acted as a sink for contaminant sources from the upper watershed; as those sources decline in significance, contributions from the contaminated sediments comprise a larger proportion of the downstream concentrations.

The sources of contamination upstream of the Menominee Dam probably do not explain the concentrations measured in fish collected in the lower river; fish with elevated PCB concentrations most likely spend significant amounts of time in Green Bay where they are exposed to PCBs and other contaminants that originated largely from the Fox River area.

Pesticides and Other Chlorinated Compounds

A total of 13 pesticides or pesticide derivatives were quantified in the Menominee River SPMDs in 2011. The pesticides toxaphene and Mirex were not quantified in any SPMDs. The pesticide heptachlor was not quantified but its metabolite heptachlor epoxide was quantified in 2 SPMDs.

Chlordane

Chlordane was used as a pesticide in the United States on home lawns and gardens, and on certain crops (e.g., corn and citrus) from 1948 to 1988. The United States Environmental Protection Agency (USEPA) banned all uses of chlordane in 1983 except to control termites. In 1988, the USEPA banned all uses (ATSDR, 2012).

Technical chlordane is not a single chemical, but a mixture of pure chlordane mixed with many related chemicals (isomers). At least 1 isomer of chlordane was quantified in at least 2 SPMDs at each sampling site, as well as in each set of field blanks. Net uptake of total chlordane was measured at all sampling sites except 2-L (left bank, downstream of the SFK discharge). The highest net uptake was measured at Site 4-R, just downstream of the Menominee Dam (Table 6; Figure 4); the concentration there was significantly higher than at all 4 sampling sites upstream of the Upper Scott Flowage. This indicates that sediments in the Menominee Dam

impoundment, the Park Mill Dam impoundment, or both, are a source of chlordane to the lower river.

The chlordane concentration at Site 4-R was significantly larger than at 2 sites further downstream: Sites 3-R (downstream of the Marinette WWTP) and 2-L (downstream of the SFK discharge). The chlordane concentration at Site 2-L was also significantly less than at the next site upstream (3-L, downstream of the Menominee WWTP). No other statistically significant differences were observed downstream of the Menominee Dam.

The site to site differences in chlordane concentration observed downstream of the Menominee Dam may be due to dynamics of the river currents rather than differences in sources. The overall picture (Figure 4) suggests impoundment sediments are the primary source of chlordane to the lower river, with the 4 upper river sites representing a background level.

DDT

DDT is a pesticide once used widely to control insects on agricultural crops, and is still used in a few countries to control malaria carrying mosquitoes. After 1972, the use of DDT was no longer permitted in the United States except in cases of a public health emergency (ATSDR, 2002a).

Technical-grade DDT is a mixture of three forms, p,p'-DDT (85%), o,p'-DDT (15%), and o,o'-DDT (trace amounts). It may also contain the isomers DDE and DDD as contaminants. Both DDE and DDD are breakdown products of DDT (ATSDR, 2002a). DDT and its breakdown products are nearly ubiquitous worldwide, and low levels can be found in water and fish samples throughout Michigan and the Great Lakes region.

At least 1 DDT isomer was quantified in at least 2 SPMDs at each sampling site, as well as in each set of field blanks. Net uptake of total DDT was measured at 6 of the 8 sampling sites downstream of the Menominee Dam, but only at the most upstream sampling site (Site 8) upstream of the AOC (Table 6; Figure 5). The net uptake of total DDT downstream of the Menominee Dam was higher than all 4 sites upstream of the AOC. This indicates that sediments in the Menominee Dam impoundment, the Park Mill Dam impoundment, or both, are a source of DDT isomers to the lower river.

Net uptake of total DDT downstream of the Menominee Dam tended to be highest at sample sites near the right (southerly) river bank. There was an apparent increase in net uptake between Sites 3-L and 2-L (downstream of SFK and downstream of the Menominee WWTP discharges, respectively), but this increase was not statistically significant.

Dieldrin

Dieldrin and the closely related pesticide aldrin were widely applied in agricultural areas worldwide. Aldrin readily changes to dieldrin in the environment. Both chemicals were used as insecticides on corn and cotton from the 1950s until 1970, when the U.S. Department of Agriculture cancelled their use. Use of aldrin and dieldrin to control termites continued until 1987 when the manufacturer voluntarily cancelled the registration for termite control (ATSDR, 2002b).

Dieldrin was quantified in at least 1 SPMD from each sampling station and in 7 of the 8 field blank SPMDs; however, net uptake was measured at only 4 sampling sites (Table 6; Figure 6). Aldrin was not quantified in any SPMD.

The concentrations of dieldrin were low compared to PCB, DDT, and chlordane. Net uptake of dieldrin was highest at the river mouth (Sites 1-L and 1-R); net uptake at Site 1-L was significantly higher than at all other sites except 1-R. No net uptake of dieldrin was measured upstream of the AOC, indicating that any sources to the lower river are likely to be in the sediments in the Park Mill or Menominee Dam impoundments.

Lindane

Lindane is a pesticide that has been used since the 1940s on a wide variety of fruit and vegetable crops, as a seed treatment, and in forestry (including Christmas tree plantations). Aerial applications are no longer permitted but it still may be used as a seed treatment for grain crops. Lindane is also still available for pharmaceutical use as a treatment of scabies and head lice (ATSDR, 2005).

Lindane was quantified in at least 2 SPMDs at each sampling site and in 7 of the 8 field blank SPMDs. Net uptake of Lindane was measured at all but 2 sampling sites (2-R and 3-R) (Table 5; Figure 7). Mean net uptake of Lindane varied from site to site, but the concentrations measured upstream of the AOC tended to be higher than concentrations measured within the AOC. At most of the sampling sites (8 of 12) only 1 SPMD had measurable net uptake; this variability within sample sets meant that the only significant differences observed were between Site 6 (US-8 at Norway) and Sites 2-R and 3-R.

No meaningful pattern in the net uptake of Lindane was observed, and concentrations were low relative to most of the other contaminants. This indicates that Lindane is widespread at low levels in the Menominee River watershed.

Hexachlorobenzene

HCB is primarily a by-product or impurity produced during the manufacture of many other chlorinated chemicals. There is evidence that HCB may be produced in chlorine-using pulp and paper mills, chlor-alkali plants, and wood-preserving plants. HCB was used until 1984 as a fungicidal seed treatment on onions as well as wheat and other grains (ATSDR, 2002c).

HCB was quantified in at least 1 SPMD at each sampling site and in all field blank SPMDs. Net uptake was measured at only 4 sampling sites, all of which were downstream of the Menominee Dam (Table 5; Figure 8). Net uptake of HCB was highest at Site 3-R (downstream of Marinette WWTP); the concentration there was significantly greater than at all other sites except 1-L and 2-L. This pattern suggests a source between the Menominee Dam and Site 3-R.

Polycyclic Aromatic Hydrocarbons

PAHs are a large group of compounds comprised of 2 or more fused benzene rings. Some PAHs are naturally occurring, but the majority are anthropogenic, entering the environment through the release of petroleum products (petrogenic sources) or by combustion of organic matter (pyrogenic sources). They are found in crude oil, petroleum products, asphalt, coal, coal tar, creosote, and roofing tar.

Twenty-one PAHs were assayed by the MDEQ Lab (Table 4). Seventeen of those PAHs were quantified in at least 1 SPMD at each sampling site and field blank set. Quantification of acenaphthylene was hindered by analytical interference in all but 2 of the 56 total SPMDs; therefore, the compound was not included in between site comparisons.

Naphthalene was the most common PAH, with net uptake measured at 10 of the 12 sites. Fluoranthene, pyrene, and phenanthrene had the highest overall average net uptake (Table 7).

PAHs can be divided into low molecular weight (LMW) compounds, having 2 or 3 benzene rings, and HMW compounds with 4 or more rings (Table 4). The ratio of HMW to LMW compounds can be used to infer sources of PAHs in the water (Stein et al., 2006). An HMW to LMW ratio can indicate a primarily pyrogenic source, while a low ratio may indicate a petrogenic source (Boehm and Farrington, 1984).

The highest net uptake of total PAHs was observed at the Menominee River mouth, with very low or no net uptake observed at the three sampling sites at the upper end of the river (Table 8; Figures 9 and 10). In addition, HMW PAHs dominated the mixture measured at the sites downstream of the Marinette WWTP; this correlates well with the known coal-tar contamination in the vicinity of that site. In contrast, the low levels observed upstream of the Marinette WWTP were dominated by LMW PAHs, which may be indicative of general runoff of automotive fluids from roadways and parking lots in the watershed.

CONCLUSIONS

Concentrations of PCBs in the water downstream of the Menominee Dam are high relative to upstream of the Park Mill Dam impoundment, but contaminated sediments in Green Bay are more likely to be causing the elevated concentrations observed in fish tissue.

The pesticides chlordane and DDT are present at measurable levels throughout the study area, but the results suggest that sediments in the Menominee and Park Mill Dam impoundments are the source for the compounds that increase in concentration downstream of the dams. Dieldrin and HCB are present at lower levels with measurable concentrations only downstream of the Menominee Dam, again suggesting the impoundments are sources. Lindane is present at low levels throughout the watershed.

The SPMD results indicate a source of HMW PAH compounds in the Menominee River downstream of the Menominee Dam; the pattern is consistent with legacy contamination near the Marinette WWTP.

Lastly, the SPMDs deployed at the sites nearest the river mouth had the potential of being affected by exposure to Green Bay water if strong northeasterly winds persisted for a significant period of time. A review of meteorological records for the area indicated that moderate northeast winds only occurred during the last 2 days of the sampling period. Even though the direct effect of water from Green Bay on the samplers cannot be completely discounted, it is unlikely the effect was significant.

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Table 1. Menominee River SPMD sampling sites, August 30-September 27, 2011.

Station	Description	Purpose
1 - L	mouth of river, left bank	Assess total discharge of target contaminants
1 - R	mouth of river, right bank	
2 - L	downstream of SFK discharge & turning basin, left bank	Assess effect of upstream discharges and sediments on concentrations of target contaminants
2 - R	downstream of SFK discharge & turning basin, right bank	
3 - L	downstream of Menominee & Marinette WWTPs, left bank	Assess effect of WWTPs on concentrations of target contaminants
3 - R	downstream of Menominee & Marinette WWTPs, right bank	
4 - L	downstream of Menominee Dam, left bank	Assess quality of water discharged from Lower Scott (Menominee) Dam
4 - R	downstream of Menominee Dam, right bank	
5	upstream of Upper Scott impoundment	Provide background levels of target contaminants entering the Upper Scott (Park Mill) impoundment
6	at US-8 near Norway	Assess effect of Niagara WWTP and Verso Paper discharges
7	downstream of Kingsford at US-141	Assess effect of Ford/Kingsford GWCU & Iron Mountain/Kingsford WWTP discharges
8	upstream of Kingsford at US-2	Provide background levels of target contaminants

Table 2. Chlorinated organic chemicals quantified in SPMD extracts by the MDCH Lab.

Compound	Level of Quantification (ppm)	Number of SPMDs with Concentrations above Quantification Limit (of 48 total samples)
Hexachlorobenzene	0.001	26
gamma-BHC (Lindane)	0.001	38
Aldrin	0.001	0
Dieldrin	0.001	41
4,4'-DDE	0.001	17
4,4'-DDD	0.001	19
4,4'-DDT	0.001	35
2,4'-DDD	0.001	17
2,4'-DDT	0.001	21
Heptachlor Epoxide	0.001	2
Oxychlorane	0.001	1
gamma-Chlordane	0.001	37
trans-Nonachlor	0.001	21
alpha-Chlordane	0.001	36
cis-Nonachlor	0.001	0
Octachlorostyrene	0.001	0
Hexachlorostyrene	0.001	0
Heptachlorostyrene	0.001	0
Pentachlorostyrene	0.001	0
Heptachlor	0.001	0
Terphenyl	0.25	0
Toxaphene	0.05	0
Mirex	0.001	0
Total PCB	0.001	32

Table 3. PCB structure and corresponding identification number of congeners quantified in SPMD extracts by the MDCH Lab.

BZ#	Structure	BZ#	Structure
TRICHLOROBIPHENYLS		HEXACHLOROBIPHENYLS	
17	2,2',4	128	2,2',3,3',4,4'
18	2,2',5	130	2,2',3,3',4,5'
22	2,3,4'	132	2,2',3,3',4,6'
25	2,3',4	135	2,2',3,3',5,6'
26	2,3',5	136	2,2',3,3',6,6'
28	2,4,4'	137	2,2',3,4,4',5
31	2,4',5	138	2,2',3,4,4',5'
32	2,4',6	141	2,2',3,4,5,5'
33	2',3,4	144	2,2',3,4,5',6
37	3,4,4'	146	2,2',3,4',5,5'
TETRACHLOROBIPHENYLS		149	2,2',3,4',5',6
40	2,2',3,3'	151	2,2',3,5,5',6
42	2,2',3,4'	153	2,2',4,4',5,5'
44	2,2',3,5'	156	2,3,3',4,4',5
45	2,2',3,6	157	2,3,3',4,4',5'
47	2,2',4,4'	158	2,3,3',4,4',6
49	2,2',4,5'	163	2,3,3',4',5,6
52	2,2',5,5'	167	2,3',4,4',5,5'
56	2,3,3',4'	HEPTACHLOROBIPHENYLS	
60	2,3,4,4'	170	2,2',3,3',4,4',5
63	2,3',4',5	171	2,2',3,3',4,4',6
64	2,3,4',6	172	2,2',3,3',4,5,5'
66	2,3',4,4'	174	2,2',3,3',4,5,6'
70	2,3',4',5	175	2,2',3,3',4,5',6
71	2,3',4',6	177	2,2',3,3',4',5,6
74	2,4,4',5	178	2,2',3,3',5,5',6
77	3,3',4,4'	179	2,2',3,3',5,6,6'
PENTACHLOROBIPHENYLS		180	2,2',3,4,4',5,5'
82	2,2',3,3',4	182	2,2',3,4,4',5,6'
84	2,2',3,3',6	183	2,2',3,4,4',5',6
87	2,2',3,4,5'	185	2,2',3,4,5,5',6
90	2,2',3,4',5	187	2,2',3,4',5,5',6
91	2,2',3,4',6	190	2,3,3',4,4',5,6
92	2,2',3,5,5'	193	2,3,3',4',5,5',6
95	2,2',3,5',6	OCTACHLOROBIPHENYLS	
97	2,2',3',4,5	194	2,2',3,3',4,4',5,5'
99	2,2',4,4',5	195	2,2',3,3',4,4',5,6
100	2,2',4,4',6	196	2,2',3,3',4,4',5,6'
101	2,2',4,5,5'	198	2,2',3,3',4,5,5',6
105	2,3,3',4,4'	199	2,2',3,3',4,5,6,6'
110	2,3,3',4',6	201	2,2',3,3',4,5,5',6'
118	2,3',4,4',5	203	2,2',3,4,4',5,5',6
126	3,3',4,4',5	205	2,3,3',4,4',5,5',6
		NONACHLOROBIPHENYLS	
		206	2,2',3,3',4,4',5,5',6

Table 4. PAHs assayed in SPMD extracts by the MDEQ Lab.

Compound	Number of Rings	Reporting Limits (ng/g)
Low Molecular Weight		
1-Methylnaphthalene	2	1
1-Methylphenanthrene	3	1
2,6-Dimethylnaphthalene	2	1
2-Methylnaphthalene	2	5
Acenaphthene	2	1
Acenaphthylene	3	1
Anthracene	3	1
Fluorene	3	1
Naphthalene	2	1
Phenanthrene	3	1
Heavy Molecular Weight		
Benzo(a)anthracene	4	1
Benzo(a)pyrene	5	1
Benzo(b)fluoranthene	5	1
Benzo(e)pyrene	5	1
Benzo(g,h,i)perylene	6	1
Benzo(k)fluoranthene	5	1
Chrysene	5	1
Dibenz(a,h)anthracene	5	2
Fluoranthene	4	1
Indeno(1,2,3-cd)pyrene	6	2
Pyrene	4	1

Table 5. Mean concentrations of PRCs in SPMDs at Menominee River sampling sites and field blanks, and target compound correction factors based on those concentrations.

Station	Description	Mean PRC Concentration (ng/g)	Correction Factor
1 - L	mouth of river, left bank	29.3	1.1
1 - R	mouth of river, right bank	30.4	1.2
2 - L	downstream of SFK discharge & turning basin, left bank	28.4	1.1
2 - R	downstream of SFK discharge & turning basin, right bank	32.1	1.2
3 - L	downstream of Menominee & Marinette WWTPs, left bank	28.0	1.1
3 - R	downstream of Menominee & Marinette WWTPs, right bank	26.0	1
4 - L	downstream of Menominee Dam, left bank	30.4	1.2
4 - R	downstream of Menominee Dam, right bank	31.0	1.2
5	upstream of Upper Scott impoundment	34.2	1.3
6	downstream of Quinnebec at US-8	36.7	1.4
7	downstream of Kingsford at US-141	29.9	1.2
8	upstream of Kingsford at US-2	34.8	1.3
Field Blank 1	downstream of Menominee Dam, right bank	28.9	1.1
Field Blank 2	downstream of Quinnebec at US-8	29.1	1.1

Table 6. Mean net uptake of total PCB and chlorinated pesticides in Menominee River SPMDs, August 30-September 27, 2011.

Site	Location	PCB (ng/g)	Chlordane (ng/g)	DDT (ng/g)	Dieldrin (ng/g)	Lindane (ng/g)	HCB (ng/g)
1-L	Mouth, left bank	8.86	0.72	3.03	0.37	0.08	0.46
1-R	Mouth, right bank	6.65	0.63	0.48	0.08	0.02	0.05
2-L	d/s SFK	2.17	0.00	3.16	0.01	0.04	0.42
2-R	d/s Turning Basin	5.05	0.63	0.00	0.00	0.00	0.00
3-L	d/s Menominee WWTP	0.66	0.72	1.10	0.00	0.13	0.00
3-R	d/s Marinette WWTP	10.38	0.17	0.29	0.05	0.00	1.43
4-L	Dam, left bank	0.00	0.33	0.00	0.00	0.03	0.00
4-R	Dam, right bank	1.96	0.96	0.84	0.00	0.17	0.00
5	Chappee Rapids	0.00	0.07	0.00	0.00	0.18	0.00
6	US-8 Norway	0.00	0.02	0.00	0.00	0.15	0.00
7	US-141	0.00	0.21	0.00	0.00	0.08	0.00
8	US-2	0.00	0.29	0.13	0.00	0.17	0.00

Table 7. Number of SPMD sampling sites in the Menominee River with net uptake of PAHs in 2011, and overall average net uptake by compound.

Compound	Number of Sites with Net Uptake	Average Net Uptake
Naphthalene	10	12.9
Dibenz(a,h)anthracene	9	2.0
2,6-Dimethylnaphthalene	7	8.0
1-Methylphenanthrene	6	4.5
Benzo(b)fluoranthene	6	5.6
Benzo(k)fluoranthene	6	2.1
Indeno(1,2,3-cd)pyrene	6	1.8
Phenanthrene	6	27.5
1-Methylnaphthalene	5	7.9
Benzo(e)pyrene	5	5.2
2-Methylnaphthalene	4	4.4
Benzo(a)anthracene	4	6.3
Benzo(a)pyrene	4	1.1
Benzo(g,h,i)perylene	4	1.7
Fluoranthene	4	49.1
Pyrene	4	39.5
Acenaphthene	3	4.8
Anthracene	3	1.9
Chrysene	3	4.3
Fluorene	3	1.4

Table 8. Comparison of mean concentrations of LMW and HMW PAHs in SPMDs deployed in the Menominee River in 2011.

Site		Mean PAH Concentration		Total PAH	Ratio High/Low
		Low Molecular Weight	Heavy Molecular Weight		
1-L	Mouth, left bank	194.3	629.6	823.8	3.2
1-R	Mouth, right bank	340.0	576.1	916.1	1.7
2-L	d/s SFK	90.8	109.1	199.8	1.2
2-R	d/s Turning Basin	114.7	81.3	196.0	0.7
3-L	d/s Menominee WWTP	23.1	4.7	27.8	0.2
3-R	d/s Marinette WWTP	6.0	0.3	6.3	0.0
4-L	Dam, left bank	20.4	5.0	25.3	0.2
4-R	Dam, right bank	57.7	0.9	58.6	0.0
5	Chappee Rapids	21.9	1.3	23.2	0.1
6	US-8 Norway	0.6	0.0	0.6	0.0
7	US-141	0.0	0.0	0.0	--
8	US-2	2.4	0.0	2.4	0.0

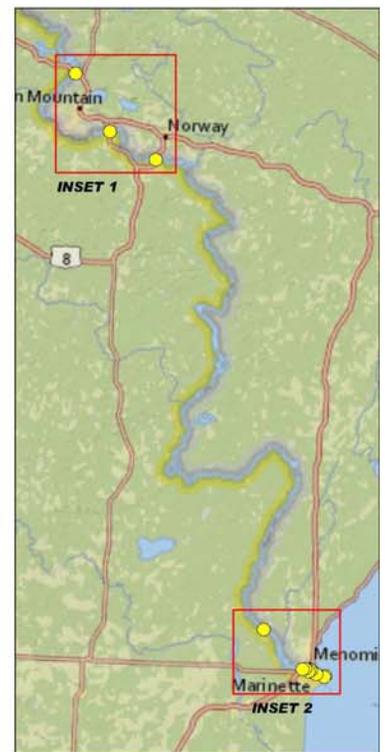
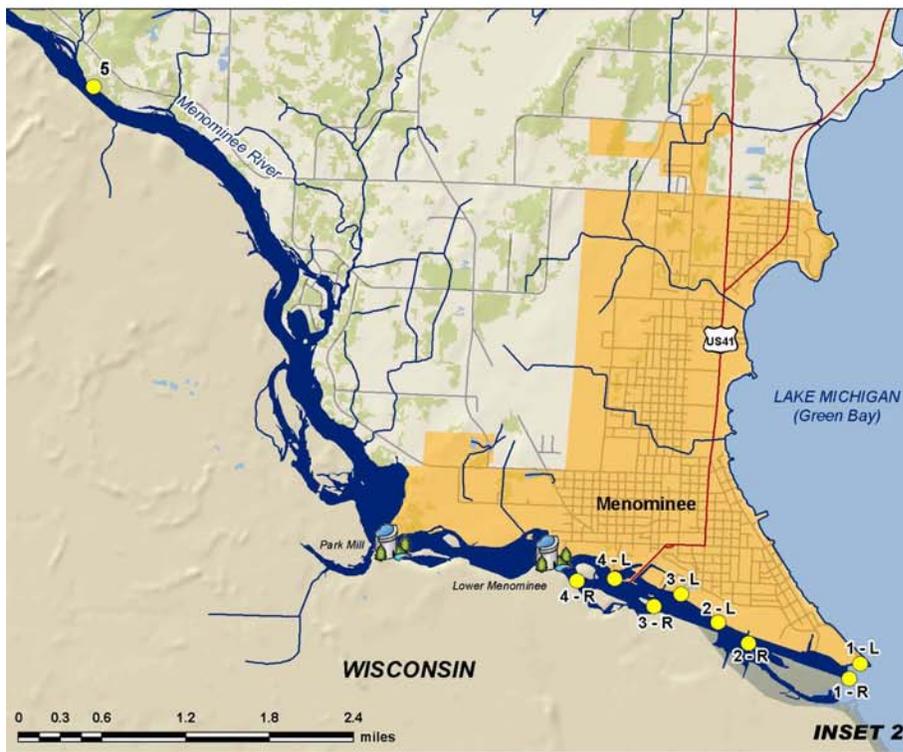
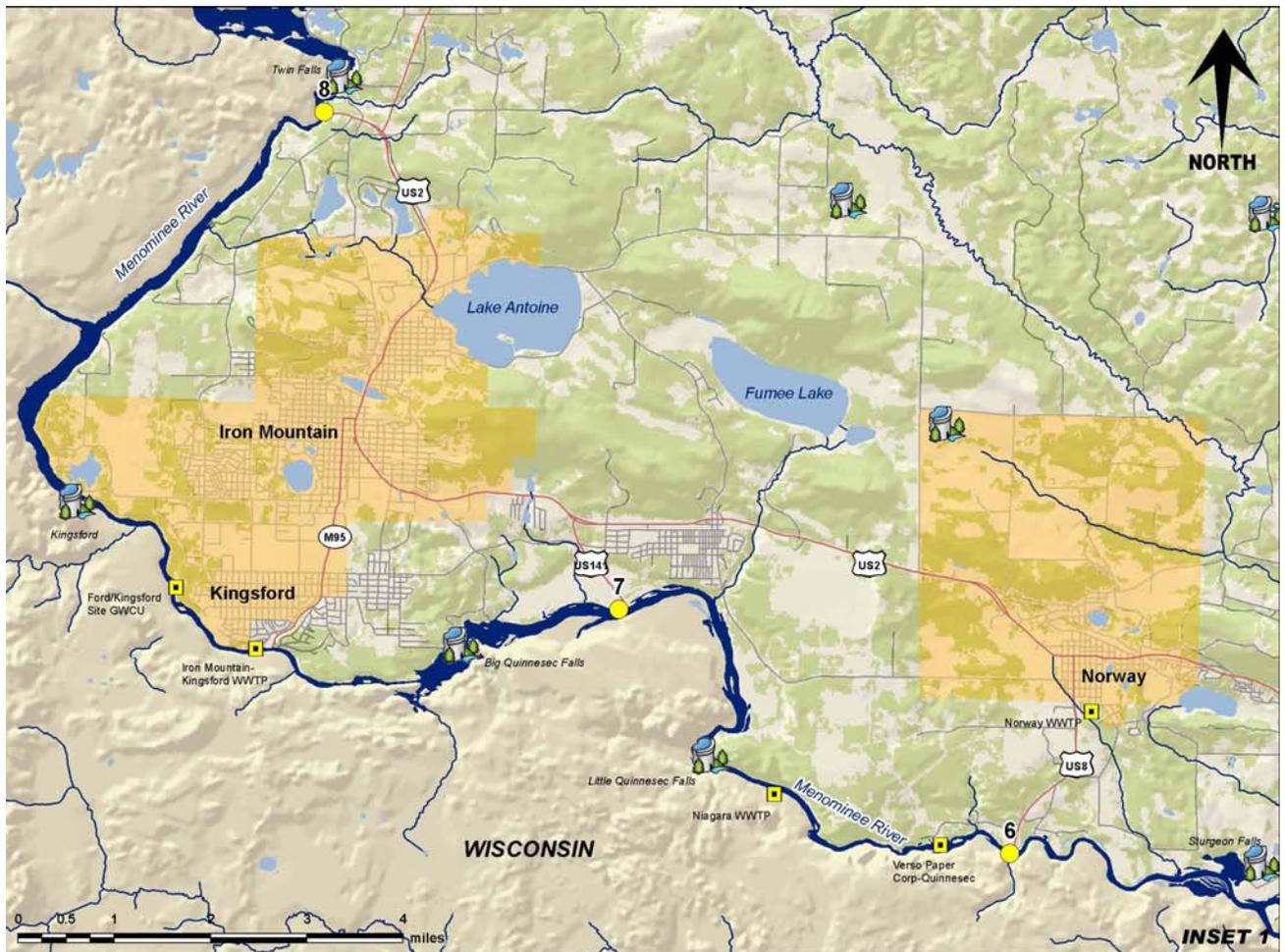


Figure 1. Map of the Menominee River showing SPMD sampling sites in the vicinity of Iron Mountain, Michigan (Inset 1) and Menominee, Michigan/Marinette, Wisconsin (Inset 2) in 2011.



a.



b.



c.

Figure 2. SPMD (a) on spindle; (b) deployment canister; (c) canister with 4 SPMDs ready for deployment.

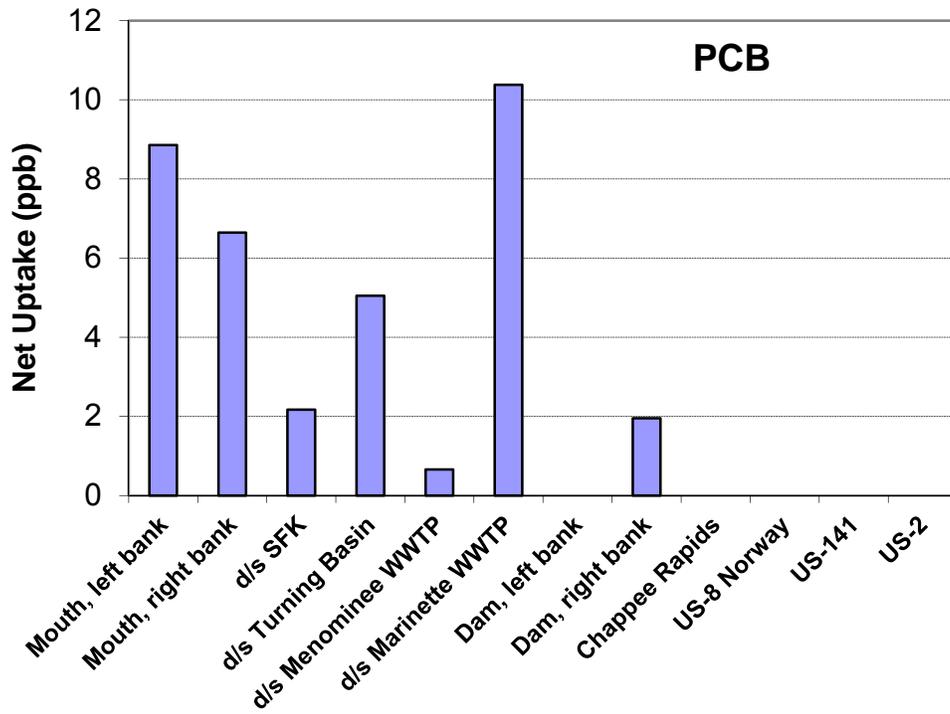


Figure 3. Mean net uptake of total PCBs in Menominee River SPMDs, August 30-September 27, 2011.

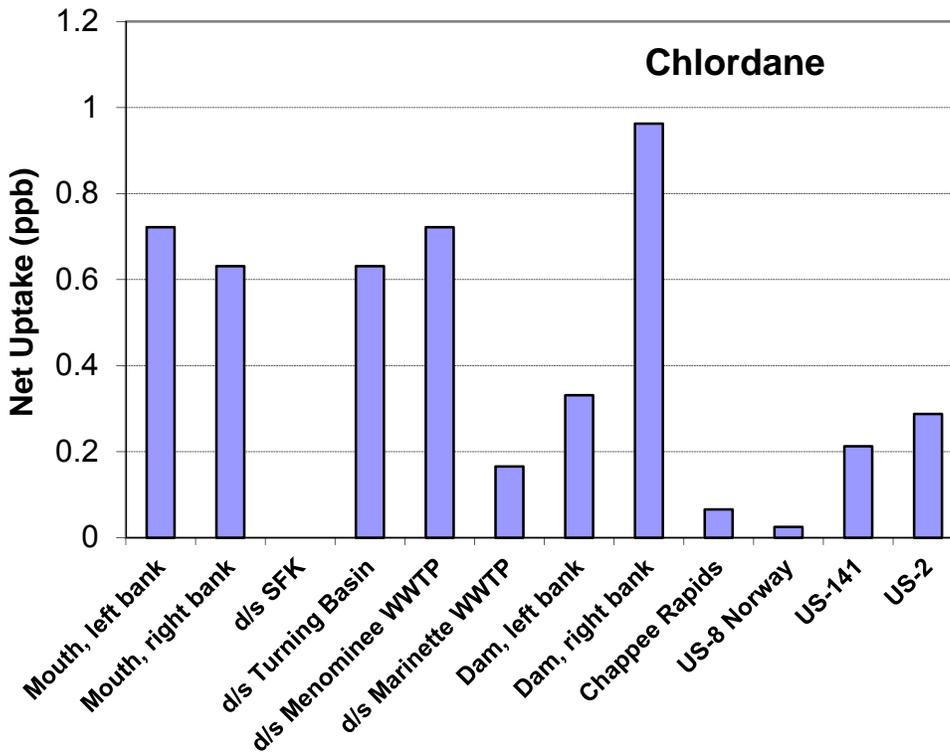


Figure 4. Mean net uptake of total chlordane in Menominee River SPMDs, August 30-September 27, 2011.

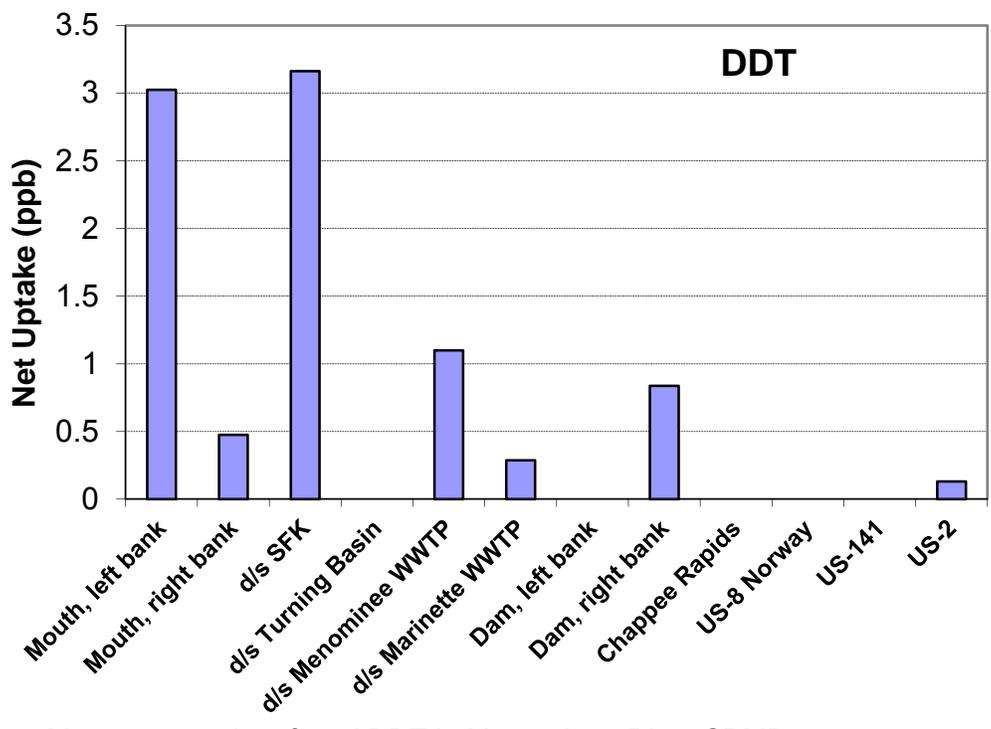


Figure 5. Mean net uptake of total DDT in Menominee River SPMDs, August 30-September 27, 2011.

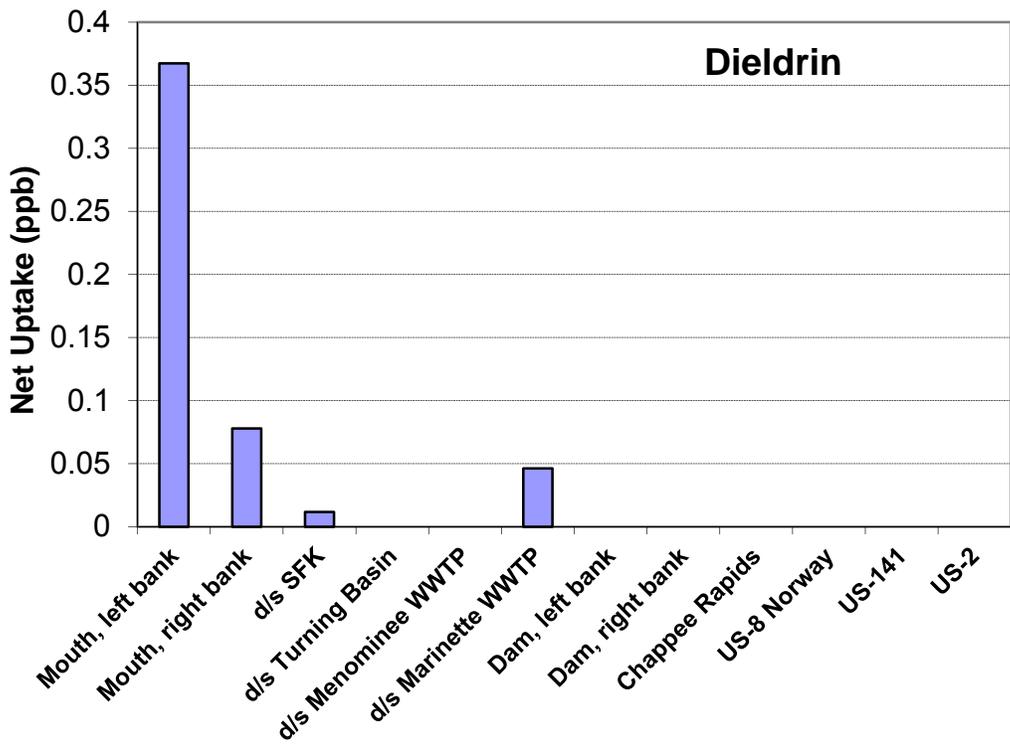


Figure 6. Mean net uptake of dieldrin in Menominee River SPMDs, August 30-September 27, 2011.

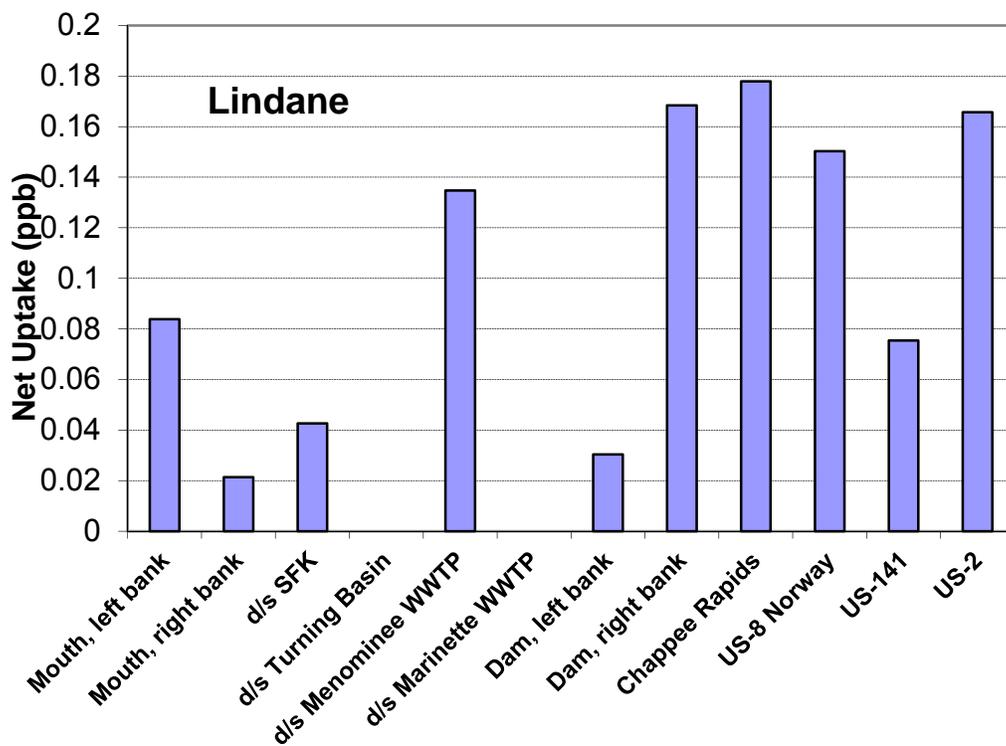


Figure 7. Mean net uptake of lindane in Menominee River SPMDs, August 30-September 27, 2011.

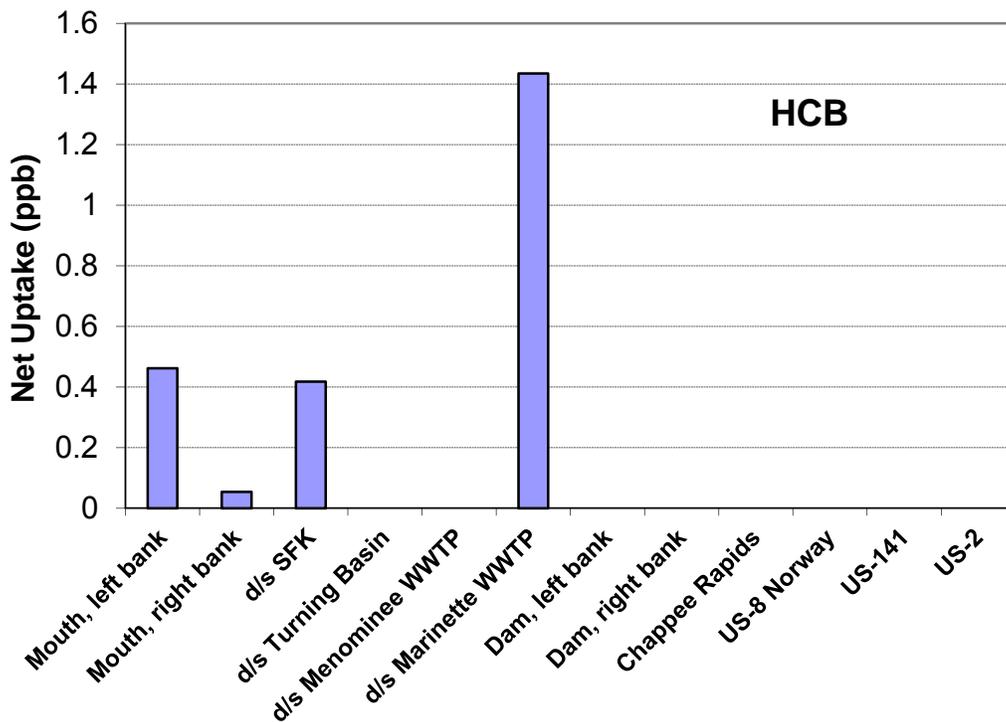


Figure 8. Mean net uptake of HCB in Menominee River SPMDs, August 30-September 27, 2011.

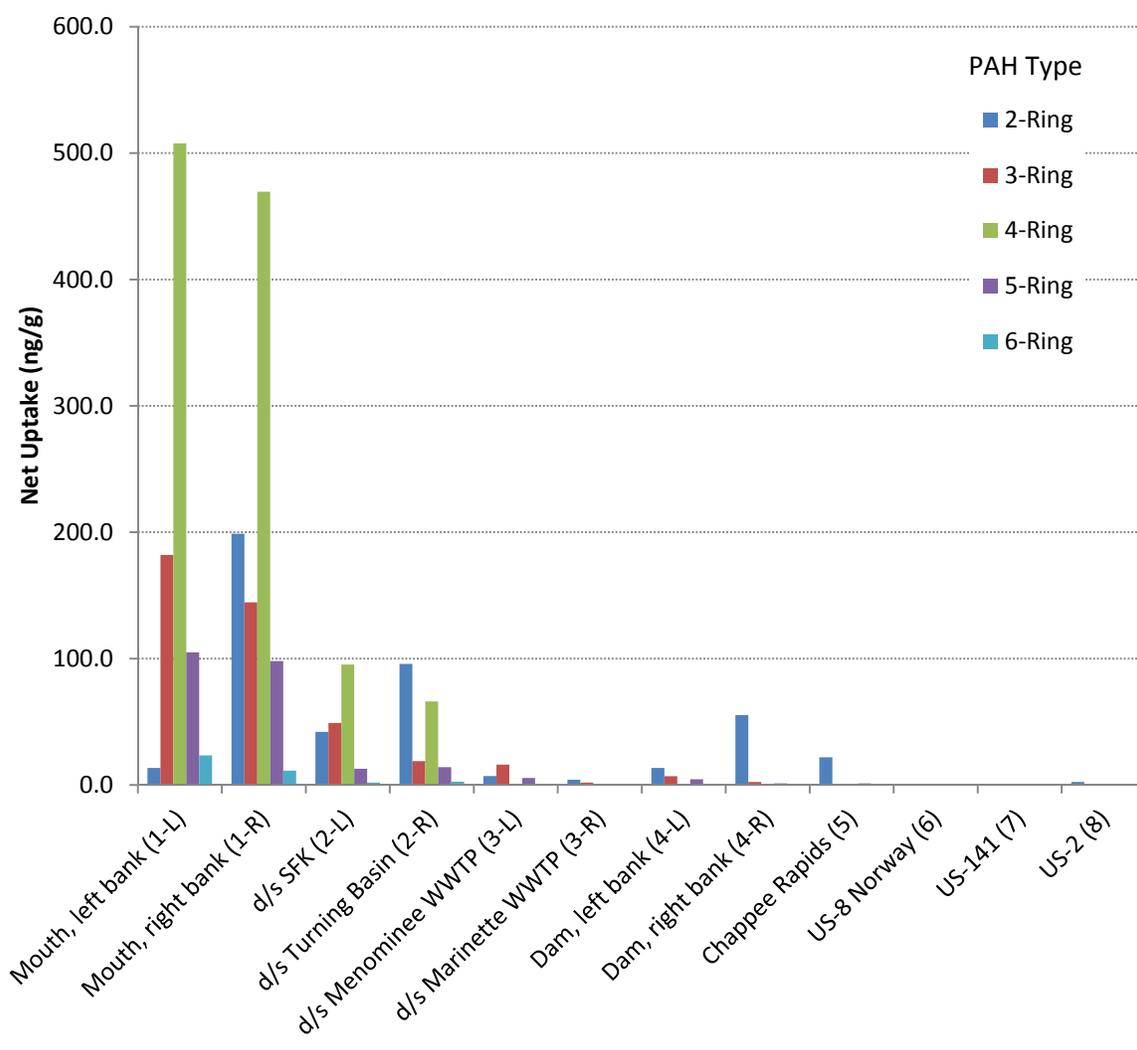


Figure 9. Net uptake of two-, three-, four-, five-, and six-ring PAHs in SPMDs deployed in the Menominee River in 2011.

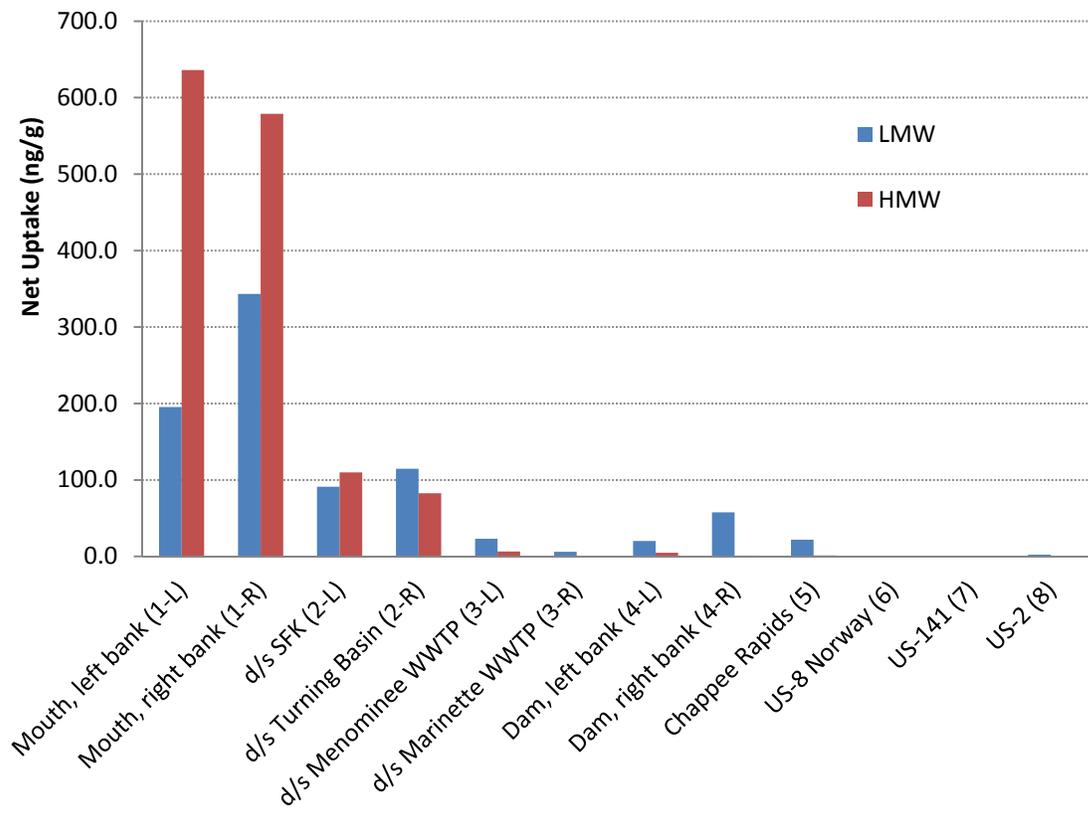


Figure 10. Net uptake of LMW and HMW PAHs in SPMDs deployed in the Menominee River in 2011.

Appendix A. Description of SPMD sampling sites, Menominee River, August 30-September 27, 2011.

SITE	Lat	Long	Description
1-L	45.09590	-87.59146	chained to post at bend near boat launch
1-R	45.09431	-87.59304	ladder u/s of flag post
2-L	45.09992	-87.61243	off point near flag on Fibrek property; d/s Fibrek outfall
2-R	45.09781	-87.60789	hanging from outermost of 3 posts near u/s end of island, d/s turning basin
3-L	45.10277	-87.61792	from shore off Menominee WWTP, d/s WWTP outfall & u/s stormwater outfall
3-R	45.10144	-87.62186	on southerly shore of Strawberry I., across from Marinette Marine; d/s of Marinette WWTP outfall
4-L	45.10424	-87.62772	from shore across from Stephenson I. launch
4-R	45.10390	-87.63320	under RR trestle, 4th pier from Wisconsin bank
5	45.15420	-87.70560	head of Chappée Rapids on Mi shore; at Chappée Historical Park
6	45.75732	-87.92250	US-8 crossing south of Norway; Mi bank u/s USGS station.
7	45.79261	-88.00787	u/s US-141 crossing (under construction) d/s Kingsford; Mi bank
8	45.86641	-88.07403	US-2 crossing u/s Iron Mountain; Mi bank u/s of bridge; access from Edgewater resort property