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Bioassessment of Mercury, Cadmium, Polychlorinated Biphenyls, and Pesticides in the Upper Mississippi River with Zebra Mussels (*Dreissena polymorpha*)

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Zebra mussels (*Dreissena polymorpha*) were sampled from artificial substrates deployed from May 30 to October 19, 1995, at 19 locks and dams from Minneapolis, MN, to Muscatine, IA. Analyses of composite tissue samples of zebra mussels (10−20-mm length) revealed accumulation of mercury (Hg), cadmium (Cd), and polychlorinated biphenyls (PCBs) during a 143-d exposure period. Concentrations of total Hg ranged from 2.6 to 6.1 ng/g wet weight and methylmercury (CH_3Hg) from 1.0 to 3.3 ng/g wet weight. About 50% (range 30−70%) of the mean total Hg in zebra mussels was CH_3Hg. Cadmium ranged from 76 to 213 ng/g wet weight. Concentrations of total PCBs (Aroclor 1254) in zebra mussels varied longitudinally (range 1000−7330 ng/g lipid weight), but the composition of PCB congeners (total of 21 measured) was similar throughout the river. Chlordane and dieldrin were the only two pesticides detected of the 15 analyzed. Zebra mussels are sentinels of contaminant bioavailability in the Upper Mississippi River and may be an important link in the trophic transfer of contaminants in the river because of their increasing importance in the diets of certain fish and waterfowl.

Introduction

The Upper Mississippi River (UMR) is contaminated by a variety of chemicals originating from point and nonpoint sources (*1*). Mercury (Hg), cadmium (Cd), and polychlorinated biphenyls (PCBs), persistent toxic substances with no known essential biological function, have been identified as the most hazardous of the many inorganic and organic contaminants released into the river (*1*−*4*). Fish and invertebrates inhabiting the river contain elevated concentrations of Hg, Cd, and PCBs (*5*−*7*), but the contribution of historically contaminated sediments to contaminant burdens in biota, relative to present inputs, is unknown.

The zebra mussel *Dreissena polymorpha*, a recent invader of the UMR (*8*), offers a new organismal model to assess the extent of present-day, dissolved-phase, and particulate contaminant influx as well as the resuspension and redistribution of historic contaminants in the Mississippi River. Due to the great filtration capacity of zebra mussels (*9*), they efficiently accumulate both organic and inorganic contaminants in their tissue and shell (*10*−*13*). Consequently, zebra mussels may prove useful as biological indicators for assessing the bioavailability and trophic transfer of contaminants to riverine biota.

The purpose of this study was to evaluate the zebra mussel as a sentinel species in the Mississippi River and to assess the bioavailability of Hg, Cd, PCBs, and persistent organochlorine (OC) pesticides (dissolved-phase and suspended particulate) in the Mississippi River over a single growing season (May to October) of the zebra mussel. Our specific objectives were to evaluate the use of zebra mussels as indicators of contaminant bioavailability in the Mississippi River; to assess the longitudinal variation in concentrations of total Hg, methylmercury (CH_3Hg), total Cd, total PCBs, selected PCB congeners, and persistent OC pesticides in zebra mussels; and to determine which areas of the UMR have the greatest potential for transfer of these contaminants to the riverine food web.

Experimental Section

Sampler Deployment. Samplers were deployed at each lock and dam (L&D) in the impounded portion of the UMR from Upper St. Anthony in Minneapolis, MN, to L&D 16 in Muscatine, IA (Figure 1). Samplers were in place from May 30 to October 19, 1995, a 143-d colonization period, allowing zebra mussels to colonize the samplers throughout their annual reproductive period in the UMR (*8*). We assumed that all zebra mussels obtained were produced during the 1995 reproductive season; therefore, zebra mussels on our samplers should have reflected the contaminant availability and accumulation for this time period. Flooding of the UMR during spring 1995 precluded the timely deployment of zebra mussel samplers downstream of L&D 16.

Concrete blocks (39.5 cm long × 19.0 cm wide × 19.5 cm high, 0.49 m^2 surface area) are useful colonization substrates for studying the population dynamics of zebra mussels (*8*, *9*) and were used in this study as samplers. The deployment and natural colonization of clean, artificial substrate samplers by zebra mussels reduces the effects of confounding variables such as differences in age, size, physiological and reproductive condition of mussels, and season of collection on contaminant uptake—all factors that have negatively influenced previous studies of contaminant accumulation and assessment when zebra mussels were sampled from preexisting populations (*10*, *13*−*15*). To minimize any potential influence of block construction materials on contaminant accumulation by zebra mussels, all of the blocks used in this study were from the same production batch and were deployed randomly at the study sites. At each site, four concrete blocks were initially deployed between May 30 and June 1, 1995, in the upper auxiliary lock chamber at each L&D. If placement of samplers in the upper auxiliary lock chamber was not feasible (Upper St. Anthony, Lower St. Anthony, L&D 3, L&D 14, and L&D 15), suitable areas within the lock structure and

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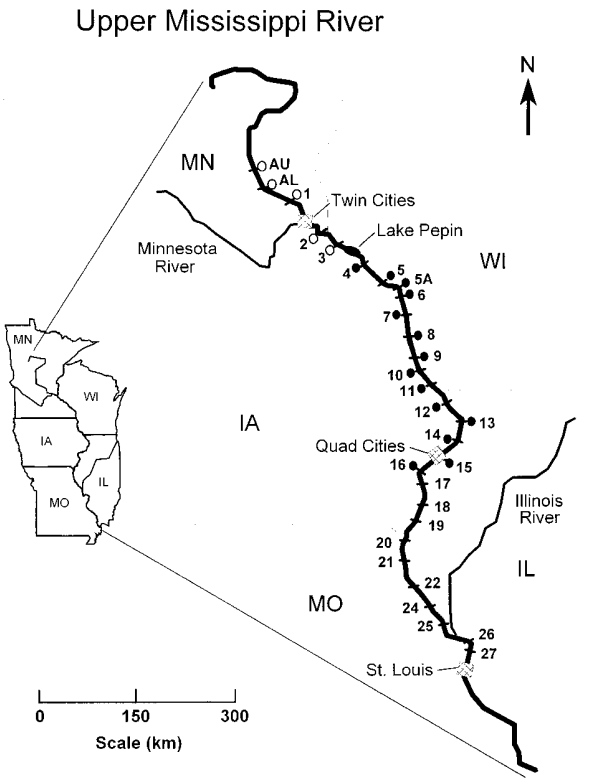

FIGURE 1. Zebra mussel sampling sites along the Upper Mississippi River, identified by lock and dam code (e.g., AU = lock and dam at Upper St. Anthony, 7 = lock and dam 7). Open circles represent sites where samplers were deployed, but zebra mussels were not collected; closed circles represent sites where samplers where deployed and zebra mussels were collected.

having similar flow characteristics to auxiliary lock chambers were used. The concrete blocks were secured to the lock structure by rope and held suspended in the water about 0.5 m above the river bottom.

Sample Collection and Processing. At the end of the deployment period (October 13−19, 1995), the concrete blocks and attached zebra mussels were placed into polyethylene bags, transported on ice to the laboratory within 24−48 h, and placed in a freezer (−20 °C). At the time of processing, one of the four concrete blocks from each site was randomly chosen, removed from the freezer, and thawed slightly; then a sample of zebra mussels was removed with a stainless steel spatula and placed on a glass plate. Identity was confirmed as *Dreissena polymorpha*, based on visual examination of shell characteristics (*16*). To minimize the influence of mussel size on the variation in contaminant burden, only organisms measuring 10−20 mm in shell length were selected for analysis. Soft tissue, excluding the byssus, was dissected from zebra mussels to produce a single composite sample per site, each consisting of a minimum tissue wet weight of 75 g. If the number of zebra mussels from a single concrete block was insufficient to obtain enough tissue mass for analysis, then zebra mussels were sampled from one of the three remaining concrete blocks (also randomly chosen) from the site. Any zebra mussels remaining on a concrete block, along with those sampled but not used in contaminant analysis, were enumerated and used to estimate population density at the site (*8*). Sufficient tissue mass could not be obtained for analysis from the five farthest upstream sites (Upper St. Anthony through L&D 3) because of the relatively low density of zebra mussels at these sites during 1995 (*8*). Therefore, zebra mussel samples analyzed in this study span the reach of river from L&D 4 at Alma, WI (river mile 752.8), through L&D 16 at Muscatine, IA (river mile 457.2). Samples of zebra mussel tissue were stored frozen at −20 °C until analysis.

Sample Preparation and Analysis. Tissue samples were thawed at room temperature (10−15 min) and homogenized for 2−3 min with a stainless steel homogenizer (Tissumizer, Tekmar, Cincinnati, OH). Subsamples of homogenate were transferred to separate containers for the analysis of total Hg, CH_3Hg, total Cd, solids, and lipid content. The remaining homogenate was retained in the original jar and used for the analysis of total PCBs, selected PCB congeners, and persistent OC pesticides. All subsamples were stored frozen (−20 °C) until analyzed.

Metals. Determinations of total Hg were made on subsamples (1.0−1.9 g wet weight) of homogenized tissue that had been digested in a 1:1 mixture of 16 N HNO_3 and 36 N H_2SO_4 (*17*). Aliquots of diluted digestate were analyzed by single-stage, gold amalgamation, cold vapor atomic fluorescence spectrophotometry (*18*). Subsamples of homogenized tissue (0.13−0.26 g wet weight) for CH_3Hg determination were digested and extracted following the method of Liang et al. (*19*). Samples were analyzed by aqueous phase ethylation with Tenax preconcentration followed by gas chromatography and atomic fluorescence detection (*20*, *21*). Subsamples of homogenized tissue (0.4−0.5 g wet weight) for total Cd determinations were digested with 16 N HNO_3 and 30% H_2O_2 at 90 °C for 2 h (*22*), followed by 30 min in an autoclave at 121 °C and 100 kPa. Aliquots of diluted digestate were analyzed by graphite furnace atomic absorption spectrophotometry with Zeeman background correction.

Organochlorines. The concentration of Aroclor 1254 was determined (*23*) and is reported here as total PCBs; a total of 21 PCB congeners was also quantified. Concentrations of total PCBs, PCB congeners (including 15 arylhydrocarbon-active [Ah-active] congeners e.g., IUPAC nos. 77, 105, 114, 118, 126, 128, 138, 156, 157, 158, 166, 167, 169, 170, and 189), and persistent OC pesticides (*p*,*p*′-DDE, *p*,*p*′-DDD, *p*,*p*′-DDT, *o*,*p*′-DDE, *o*,*p*′-DDD, *o*,*p*′-DDT, hexachlorobenzene, dieldrin, α-heptachlorepoxide, *β*-heptachlorepoxide, oxychlordane, α-chlordane, *γ*-chlordane, endrin, and mirex) were determined on 5-g subsamples (wet weight) of homogenized tissue. Samples were mixed with 40 g of sodium sulfate and extracted three times with 60 mL of 1:1 (v:v) acetone−methylene chloride under pulsed (50% full power) sonication (*24*). Extracts were vacuum filtered through glass fiber filters, partitioned with 1 L of deionized water to remove the acetone, dried on a sodium sulfate column, and concentrated to l0 mL.

Concentrated extracts were cleaned by gel permeation chromatography (GPC) with methylene chloride on a 1000 cm × 2.54 cm glass column filled with 70 g of SX-3 biobeads. The GPC was set to release to the elution of phthalate and to collect to the elution of sulfur. GPC extracts were concentrated to <10 mL on a steam table with a Kuderna-Danish (K-D) concentrator, exchanged to hexane, and further concentrated to 2−3 mL with a micro-Snyder column. The samples were cleaned further by solid-phase extraction (SPE) through florisil cartridges (*25*). Samples were eluted in two fractions: extract A, eluted with 7 mL hexane, contained the PCBs and some pesticides, and extract B, eluted with 9 mL of 1:9 (v:v) acetone−hexane, contained the remaining pesticides. Extracts A and B were individually concentrated to 1.0 mL for analysis.

Extracts were analyzed on a Hewlett-Packard model 5890, series II gas chromatograph (GC) with dual electron capture detectors (ECDs), split/splitless injection, and a double gooseneck Restek glass liner. A 15 m × 0.53 mm guard column was used with a 50 m SGE HT-8 × 0.22 mm (0.25 μm film) column on the "α" detector and a 60 m RTX-5 × 0.25 mm (0.25 μm film) column on the "β" detector. The GC conditions

TABLE 1. Characteristics of Individual Zebra Mussels Analyzed for Hg, Cd, PCBs, and OC Pesticides in Composite Samples Taken from the Upper Mississippi River from May 30 to October 19, 1995

			zebra mussels in composite sample analyzed				
lock and dam code	location	river mile	*n*	mean length (mm)	mean wet wt (mg)[a]	mean solids (%)	mean lipid (%)
4	Alma, WI	752.8	239	17.3	305.6	12.7	1.5
5	Whitman, MN	738.1	232	19.0	345.2	13.3	2.3
5A	Winona, MN	728.5	212	18.4	369.5	13.4	1.5
6	Trempealeau, WI	714.3	222	18.7	350.3	14.8	2.0
7	Dresbach, MN	702.5	197	18.9	411.2	13.5	1.5
8	Genoa, WI	679.2	227	18.7	389.8	14.2	2.0
9	Lynxville, WI	647.9	266	17.6	296.5	12.1	1.0
10	Guttenberg, IA	615.1	277	17.9	315.9	12.4	1.2
11	Dubuque, IA	583.0	225	18.6	362.7	11.5	1.6
12	Bellevue, IA	556.7	252	18.0	314.3	9.5	1.3
13	Fulton, IL	522.5	290	18.2	298.0	12.3	2.0
14	Davenport, IA	493.3	390	17.4	209.8	10.7	1.1
15	Rock Island, IL	482.9	746	14.0	104.7	9.0	0.7
16	Muscatine, IA	457.2	214	19.1	363.5	15.5	2.2

[a] Determined by dividing the total composite sample tissue mass by the number of zebra mussels (*n*) comprising the sample.

were as follows: injection port temperature, 250 °C; constant column head pressure, 40 psi; detector temperature, 300 °C; carrier gas, He; and oven temperature program (60-min run time) at −80 °C for 2 min, 30 °C/min to 170 °C, 3 °C/min to 300 °C, hold for 10.6 min.

Standards were prepared for Aroclors 1016 and 1254 (25−800 ng/mL) and pesticides and PCB congeners (1.25−100 ng/mL) at 5−7 concentrations. Dibutylchlorendate (DBCE) and PCB 30 (both at 100 ng) were used as surrogate standards. PCB 65 (100 ng) and PCB 209 (decachlorobiphenyl, 50 ng) were added as internal standards and retention time markers.

Solids and Lipid. The solids content of tissue was determined by standard methods (*26*). For determinations of lipid content, subsamples (6−8 g wet weight) of homogenized tissue were mixed with 40 g of sodium sulfate, extracted with 60 mL of 1:1 (v:v) acetone−methylene chloride, dried, and then concentrated on a steam table with a K-D flash to 10 mL. The extract was transferred to a tared glass jar, allowed to evaporate, and then dried for 30 min on a hot plate at 103 °C.

Quality Assurance. *Metals.* Measured concentrations of total Hg, CH_3Hg, and Cd in National Research Council of Canada (NRCC) standard reference materials (dogfish liver, DOLT-2, and dogfish muscle, DORM-2) were all within the certified range ($n = 16$), except for one determination of Hg in NRCC dogfish muscle, which yielded a concentration slightly (<6%) below the certified range. The recovery of total Hg, CH_3Hg, and Cd from nine spiked zebra mussel tissue samples averaged 98% (range 93−102%). Concentrations of total Hg, CH_3Hg, and Cd in all samples were 11−40-fold greater than our calculated method detection limits of 0.15 ng/g (wet weight) for total Hg, 0.08 ng/g (wet weight) for CH_3Hg, and 6.2 ng/g (wet weight) for total Cd.

Organochlorines. A U.S. National Institute of Standards and Technology (NIST) standard reference material (Organics in Mussel Tissue *Mytilus edulis*, SRM 1974a) was analyzed with each batch of samples quantified for total PCBs, selected PCB congeners, and persistent OC pesticides. Determinations yielded PCB congener concentrations within the certified range for 11 of the 20 certified congeners in SRM 1974a. Of the nine congener measurements outside of the certified range, two were <8% below the certified range and seven were <17% above the certified range. Recoveries of PCB congeners in SRM 1974a were between 80 and 120% for 17 of 20 congeners in the NIST certified sample. The recovery of surrogate standards from 18 spiked zebra mussel tissue samples averaged 94% (range 77−106%) for PCB 30 and 88% (range 68−113%) for DBCE. Mean recoveries of the 15 pesticides from the standard mix were 84% (range 72−120%) and 73% (range nondetectable-130%) from spiked zebra mussel tissue samples. Instrument detection limits were determined on seven replicate standards of Aroclors 1016 and 1254, pesticides, and the PCB congener mix. Only data exceeding the instrument detection limits are reported herein; the nominal detection limits were 6 ng/g lipid weight for PCB congeners, 88 ng/g lipid weight for total PCBs, and 19 ng/g lipid weight for OC pesticides.

Solids and Lipid. The percent difference for duplicate analyses of a single zebra mussel tissue sample for solids and lipids were 0.4% and 4.6%, respectively. Results from analysis of procedural blanks were always <1 mg (<0.02%) of total weight.

Results and Discussion

The overall mean length of zebra mussels analyzed in composite samples from our study was 18.0 mm and ranged from 14.0 to 19.1 mm (Table 1). The mean wet weight of a single zebra mussel in a composite sample was 317.0 mg (range 104.7−411.2 mg), and the average number of zebra mussels in a composite sample was 280 (range 197−746, Table 1). The overall mean solids content of zebra mussels in composite samples from our study was 12.5% (range 9.0−15.5%), and the average lipid content of mussels was 1.6% (range 0.7−2.3%, Table 1).

Uptake and Longitudinal Distribution of Contaminants. Metals. Zebra mussels accumulated total Hg, CH_3Hg, and Cd during the 143-d exposure period. To our knowledge, this is the first study to simultaneously measure concentrations of total Hg and CH_3Hg in zebra mussels and to assess the relative contribution of CH_3Hg to concentrations of Hg in tissue. Total Hg concentrations in zebra mussels ranged from 2.6 to 6.1 ng/g wet weight, and concentrations of CH_3Hg ranged from 1.0 to 3.3 ng/g wet weight (Figure 2). Thus, CH_3Hg comprised about 50% (range 30−70%) of the mean total Hg in zebra mussels. The relative proportion of CH_3Hg to total Hg in zebra mussels from this study is similar to that measured in other freshwater bivalves. For example, Malley et al. (*27*) found that CH_3Hg comprised 44−63% of the total Hg in a unionid mussel (*Pyganodon grandis*) caged in a lake in northwestern Ontario, Canada. The proportion of CH_3Hg to total Hg in zebra mussels (about 50%) is relatively small compared to that in fish, where 95−99% of the total Hg is in the form of CH_3Hg (*17, 28−30*). The accumulation of CH_3Hg by biota in the Mississippi River is noteworthy, however, because the physicochemical characteristics of the river water

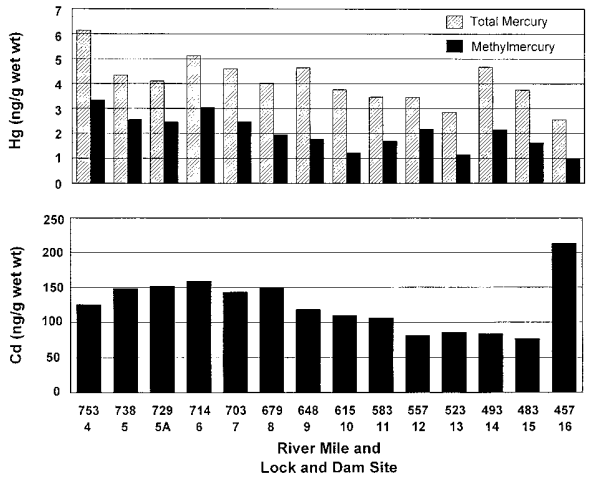

FIGURE 2. Concentrations of total Hg, CH_3Hg, and total Cd in composite samples of zebra mussels taken from the Upper Mississippi River from May 30 to October 19, 1995.

(e.g., a pH of 7.5−8.7 and alkalinity of 110−160 mg/L as $CaCO_3$ (*31*)) are generally considered unfavorable for the microbial production of CH_3Hg (*32*).

Concentrations of total Hg and CH_3Hg in zebra mussels were greatest at L&D 4 (river mile 753), about 110 km downstream of the Twin Cities (Minneapolis−St. Paul, MN) metropolitan area. Concentrations generally decreased downstream between L&D 4 to L&D 13 at river mile 523; however, additional sources of Hg were indicated upstream of L&Ds 6 and 9 and may have been reflective of the metropolitan areas of Winona, MN, and La Crosse, WI (Figure 2).

Suspended sediments and associated pollutants such as Hg settle out of the water column in low-velocity reaches of the river—at least partly explaining the observed longitudinal decrease in Hg concentrations in zebra mussels downstream of known and likely source areas (Figure 2). This phenomenon has been illustrated for mayflies in the reach of UMR between the Twin Cities and just upstream of L&D 4 (*5, 7*), a reach where zebra mussels were too sparse to collect in our study. Specifically, the Minnesota River, which drains a highly agricultural watershed, delivers most of the relatively large loads of suspended sediments (0.9×10^6 metric tons in 1996) and Hg (42 kg in 1996) to the UMR in the Twin Cities area (*33*). This Hg is associated almost exclusively with suspended sediments mobilized by runoff events during open-water months (*34*). A large proportion of the suspended sediment and its associated Hg is efficiently removed by settling within Lake Pepin, a natural riverine lake extending from 75 to 110 km downstream of the Twin Cities (*3, 4, 35*, S. J. Balogh, unpublished data). Thus, Lake Pepin is largely responsible for the lesser concentrations of Hg in mayflies immediately downstream of the lake compared to upstream reaches (*5, 7*). Even with the efficient trapping of suspended sediment and associated Hg in Lake Pepin, the concentrations of Hg in zebra mussels were still high at L&D 4, indicating the large load of Hg transported by the UMR.

Concentrations of total Hg and CH_3Hg in zebra mussels sharply increased between L&D 13 and L&D 14 (located just upstream of the Quad Cities metropolitan area of Rock Island-Moline, IL, and Davenport-Bettendorf, IA), suggesting an influx of Hg to the river between these two locations. Concentrations of total Hg and CH_3Hg in zebra mussels decreased between L&D 14 and L&D 16, again demonstrating the trend of decreasing concentrations of mercury with distance downstream from sources. The range of total Hg concentrations that we found in zebra mussels from the UMR (0.02−0.05 μg/g dry weight) is similar to that in zebra mussels inhabiting other North American and European rivers (0.05−0.38 μg/g dry weight), which have been contaminated by human activities (*36, 37*).

Concentrations of Cd ranged from 76 to 213 ng/g wet weight and were greatest immediately downstream of the Quad Cities at L&D 16 (Figure 2). Concentrations in the upstream reaches were relatively high and fluctuated little between L&D 5 downstream through L&D 8. Thereafter, Cd concentrations generally decreased downstream through L&D 15 near the Quad Cities. The striking 2.8-fold increase in Cd at L&D 16 (just downstream of the Quad Cities) suggests a source (influx) of Cd to the water column in this section of the river. The trends we observed for Cd in zebra mussels are similar to those of emergent mayflies in the UMR reported by Dukerschein et al. (*5*). They found that concentrations of Cd in emergent mayflies decreased significantly ($p < 0.01$) downstream from the Twin Cities (river miles 825−648) but not downstream from the Quad Cities. Concentrations of Cd in zebra mussels in this study (0.7−1.4 μg/g dry weight) are similar to those reported in zebra mussels inhabiting other anthropogenically contaminated rivers (1.0−21.0 μg/g dry weight) in North America (*36*) and Europe (*37, 38*).

Organochlorines. Observed concentrations of total PCBs in zebra mussels varied longitudinally (range 1000−7330 ng/g lipid weight) along the UMR and were greatest (≥5320 ng/g) in our samples from L&D 5A and L&D 9 (Table 2). Steingraeber et al. (*6*) similarly found elevated concentrations of total PCBs in emergent *Hexagenia* mayflies in the area of L&D 5A and attributed these greater concentrations in this reach of the river to a known point source of PCBs along the Wisconsin shore, near river mile 733.5. These observations suggest a continued influx of PCBs to this area of the river. Unexplainably, the greatest total PCB concentration (7330 ng/g lipid weight) in zebra mussels occurred at L&D 9 in Lynxville, WI, which is about 80 km downstream of La Crosse, WI. Total PCB concentrations in zebra mussels decreased substantially from L&D 9 through L&D 13 (Figure 3).

Downstream of L&D 13, concentrations of total PCBs in zebra mussels increased 4-fold to L&D 15 and then decreased sharply (*3-fold*) at L&D 16 (Figure 3). This trend is similar to that previously reported in studies with emergent mayflies. For example, Steingraeber et al. (*6*) found a 4-fold increase in total PCBs in mayflies from L&D 13 to L&D 15, which then declined 2-fold at L&D 16. They attributed the observed increase at L&D 15 to a known point source of PCBs about 10 km upstream of L&D 15. Similar to our findings, they found little transport of these PCBs downstream of the Quad Cities area. The longitudinal trends in the bioavailability of total PCBs detected by zebra mussels in this study and those of emergent mayflies in the study of Steingraeber et al. (*6*) are remarkably similar, given the differences in physical compartments that are integrated by the respective organisms. For example, burrowing mayflies reside in the upper strata of fine-grained sediments (*39, 40*) and, therefore, would primarily reflect exposure to sedimentary contaminants. In contrast, zebra mussels are epibenthic organisms that filter relatively large volumes of water (*9*); thus their contaminant burdens would primarily reflect exposure to dissolved and suspended particulate contaminants. Moreover, the trends in PCB accumulation by biota in the UMR appear to be temporally consistent because the mayfly samples analyzed by Steingraeber et al. (*6*) were collected in 1988, whereas the zebra mussels from this study were collected in 1995. The range of total PCB concentrations in zebra mussels from the UMR (0.2−0.6 μg/g dry weight) are similar to those in zebra mussels sampled from other major industrialized rivers such as the Niagara, Genesee, and Hudson Rivers (0.1−1.1 μg/g dry weight) in New York (*36*) and the River Seine (0.6−3.9 μg/g dry weight) in France (*38*).

TABLE 2. Concentrations (ng/g lipid wt) of Total PCBs, Selected PCB Congeners, and OC Pesticides in Composite Samples of Zebra Mussels Taken from the Upper Mississippi River from May 30 to October 19, 1995

	lock and dam code													
chemical	**4**	**5**	**5A**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
total PCBs	3853	3522	5320	4060	4547	3620	7330	3417	2763	2831	1000	2227	4229	1573
PCB Congeners														
44	80	57	80	70	53	50	150	75	BL[a]	BL	BL	BL	BL	BL
49	47	48	67	45	40	25	50	25	BL	BL	BL	BL	BL	BL
52	173	196	200	155	173	125	240	150	125	123	50	118	200	91
66	167	78	107	90	100	110	100	58	138	31	20	27	100	55
95	125	104	173	130	127	110	140	83	94	54	25	18	57	18
99	125	139	213	155	173	135	350	133	125	92	25	73	86	50
101	400	361	547	390	447	350	800	350	294	246	90	191	557	164
105	100	74	100	75	147	95	240	83	75	77	20	55	86	32
110	273	252	380	280	313	240	430	225	200	146	30	109	243	86
118	267	222	340	245	307	245	410	217	188	169	55	118	257	91
128	53	52	80	50	53	40	80	BL	25	46	15	BL	71	14
138	273	239	360	265	327	230	420	225	181	169	50	136	229	82
149	207	191	293	235	227	165	340	150	138	85	BL	109	143	41
151	47	48	73	50	47	40	80	33	31	31	BL	BL	43	BL
153	280	252	227	265	320	230	470	242	200	177	60	145	143	82
156	67	52	87	60	80	65	120	67	50	62	15	36	57	32
158	40	35	60	35	53	40	80	42	25	31	10	BL	BL	18
170	40	35	53	40	47	40	90	50	19	31	BL	BL	43	14
180	80	70	113	80	87	65	140	67	50	54	BL	45	71	27
183	13	17	33	25	13	10	20	BL	6	BL	BL	BL	BL	BL
187	33	48	73	30	60	30	100	42	31	BL	BL	18	43	BL
Pesticides														
α-chlordane	BL	BL	120	BL	BL	BL	190	BL	BL	BL	60	BL	BL	BL
dieldrin	47	52	60	BL	BL	BL	BL	58	BL	BL	BL	64	BL	BL

[a] BL = analyte below nominal instrument detection limit of 6 ng/g lipid wt for PCB congeners, 88 ng/g lipid wt for total PCBs, and 19 ng/g lipid wt for pesticides.

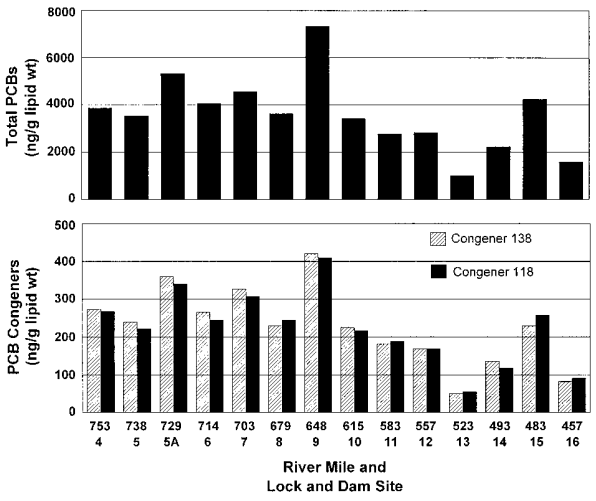

FIGURE 3. Concentrations of total PCBs, PCB congener 118, and PCB congener 138 in composite samples of zebra mussels taken from the Upper Mississippi River from May 30 to October 19, 1995.

The composition of PCB congeners in zebra mussels was similar throughout the UMR (Table 2). None of the three nonortho coplanar congeners (PCB 77, 126, 169) were detected in zebra mussel samples from the UMR. Seven of the remaining 12 Ah-active congeners, however, were detected and quantified; these included four of the highly toxic mono-ortho coplanar congeners, PCB 66, 105, 118, and 156 (41). The longitudinal trends for PCB congeners in zebra mussels from the UMR were similar to those we have described for total PCBs (Figure 3).

Persistent OC pesticides were not readily accumulated by zebra mussels in our study. The uptake of pesticides by zebra mussels varied widely in the UMR, with chlordane and dieldrin being the only two pesticides (total of 15 analyzed) that were accumulated to measurable concentrations (Table 2). There was no discernible trend in OC pesticide accumulation by zebra mussels except for dieldrin, which was quantified at three consecutive sites from Alma, WI (L&D 4), to Winona, MN (L&D 5A).

Contaminant Bioavailability and Implications for Trophic Transfer. We found that zebra mussels accumulated measurable quantities of Hg, Cd, and PCBs after only a 143-d exposure period in the UMR. Because of their importance in the diets of fish (42) and certain waterfowl (43, 44), zebra mussels are a potentially important link in the trophic transfer of contaminants. For example, the freshwater drum Aplodinotus grunniens and common carp Cyprinus carpio are both important commercial fish species harvested from the UMR and used for human consumption. The combined total commercial catch for these two species from pools 4 through 16 during 1995 (the time period and reach of river sampled by zebra mussels in this study) was 1 971 932 kg (M. Marin, Wisconsin Department of Natural Resources, Alma, WI, personal communication). Both of these species have been shown to prey on zebra mussels (42, 45, 46) and, therefore, may directly serve as an additional source of contaminants to these predators and ultimately to the human consumers. The regulatory and scientific focus on Hg, Cd, PCBs, and other OC compounds in the UMR has been motivated largely by the human health risks of consuming contaminated fish, because human exposure to these substances is largely due to consumption of fish (47, 48). However, migrating waterfowl will also consume zebra mussels from the UMR (e.g., ref 44), and the consumption of waterfowl may also represent an additional route of exposure to humans. Therefore, zebra mussels represent an alternative route for contaminant movement (e.g., ref 49) in the UMR and may be a highly efficient route for contaminant exposure to higher trophic levels. The gut contents of zebra mussels from this study

were not depurated prior to analysis; therefore, the contaminant concentrations in zebra mussels reflect the toxicological dose of contaminant that would be ingested by a predator and, thus, available for any subsequent trophic transfer.

Contaminant Bioassessment with Zebra Mussels. Our results show that zebra mussels are sentinels of contaminant bioavailability in the UMR. They accumulated contaminants to measurable concentrations within a relatively short exposure period (143 d), and they accurately reflected the longitudinal trends in both historic and present-day inputs of contaminants to the river. Analysis of zebra mussels should provide resource managers with an additional biomonitoring tool for assessing dissolved and suspended particulate contaminants and for assessing their potential entry into the aquatic food web supporting fish, wildlife, and higher trophic levels, including humans.

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