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Heavy Metals in the Threeridge Mussel *Amblema plicata plicata* (Say, 1817) in the Upper Mississippi River

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Abstract

Concentrations of mercury and zinc in the threeridge mussel *Amblema plicata plicata*, sampled in 1987 from Pools 3 and 10 in the upper Mississippi River, were comparable to concentrations in mussels from moderately contaminated systems, while copper concentrations were similar to concentrations in mussels from more polluted waters. Cadmium concentrations in mussels were significantly less at a lightly contaminated site (Pool 10, range 0.53 to 0.92 µg/g dry weight) than at a site where metal abundances were strongly influenced by industrial and domestic inputs (Pool 3, range 0.80 to 1.25 µg/g dry weight). Yet, cadmium concentrations in Pool 3 were an order of magnitude less than values reported for mussels from more metal-polluted systems. In contrast, concentrations of copper, mercury, and zinc did not differ between sites. Cadmium and zinc concentrations generally increased with size of the mussel, copper concentrations decreased with size, and mercury concentrations were unrelated to size.

Introduction

Concentrations of heavy metals in aquatic ecosystems vary spatially and temporally (Luoma and Bryan 1979). Analyses of water and sediment indicate the extent of metal contamination but reveal little about the availability of metals to biota. Quantification of metal concentrations in indigenous, relatively sessile benthic organisms, such as long-lived freshwater mussels, can be used to assess the bioavailability of metals.

The upper Mississippi River is a productive ecosystem that extends from St. Anthony Falls, Minnesota, to the confluence with the Ohio River and contains a series of navigation pools divided by 29 locks and dams. Due in part to the hard water (Dawson et al. 1984) of the upper Mississippi River and the affinity of metals for fine organic and inorganic particulate matter, surficial sediments are contaminated with cadmium and mercury (Bailey and Rada 1984, Boyer 1984, Wiener et al. 1984, Rada et al. 1990). Furthermore, there is a spatial trend of decreasing metal contamination with distance downstream from the Minneapolis-St. Paul, MN, metropolitan area (Bailey and Rada 1984, Wiener et al. 1984).

Freshwater mussels are continuous filter feeders that accumulate metals from water and sediment. Consequently, mussels have been used in many contaminant monitoring programs (Bedford and Zabik 1973, Adams et al. 1981, Schmitt et al. 1987, Boryslawskyj et al. 1988). Our objectives were (1) to obtain baseline information on the concentrations of cadmium, copper, mercury, and zinc in threeridge mussels *Amblema plicata plicata* from the upper Mississippi River; (2) to compare metal concentrations in mussels from an area where metal abundances have been greatly increased

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by industrial pollution to those in mussels from a lesser contaminated site; and (3) to determine the variation in heavy metal concentrations among mussels of different ages.

Materials and Methods

Mussels were taken from Navigation Pools 3 and 10 of the upper Mississippi River (Fig. 1). Pool 3 is metal-contaminated because of its proximity to Minneapolis and St. Paul, MN--the primary overall source of industrial and municipal effluents entering the studied reach of the river (Bailey and Rada 1984, Wiener et al. 1984, Metropolitan Waste Control Commission 1989, Rada et al. 1989). The reference site, Pool 10, is 338 km downstream from Minneapolis-St. Paul, MN, and contains a dense and diverse mussel fauna. Mussels were sampled at river mile 797.3 in Pool 3 and between river miles 635 and 636 in Pool 10. Mussels were collected by hand or brailing in late July and early August 1987, placed on ice, and transported to the National Fisheries Research Center in La Crosse, Wisconsin, where they were processed. Length was measured with calipers, and age was estimated by counting external shell rings. Mussels were classified into four length groups (mm): 0-50, 51-70, 71-90, and ≥91 (Table 1), which approximated ages of 1-5, 6-10, 11-14, and ≥15 years.

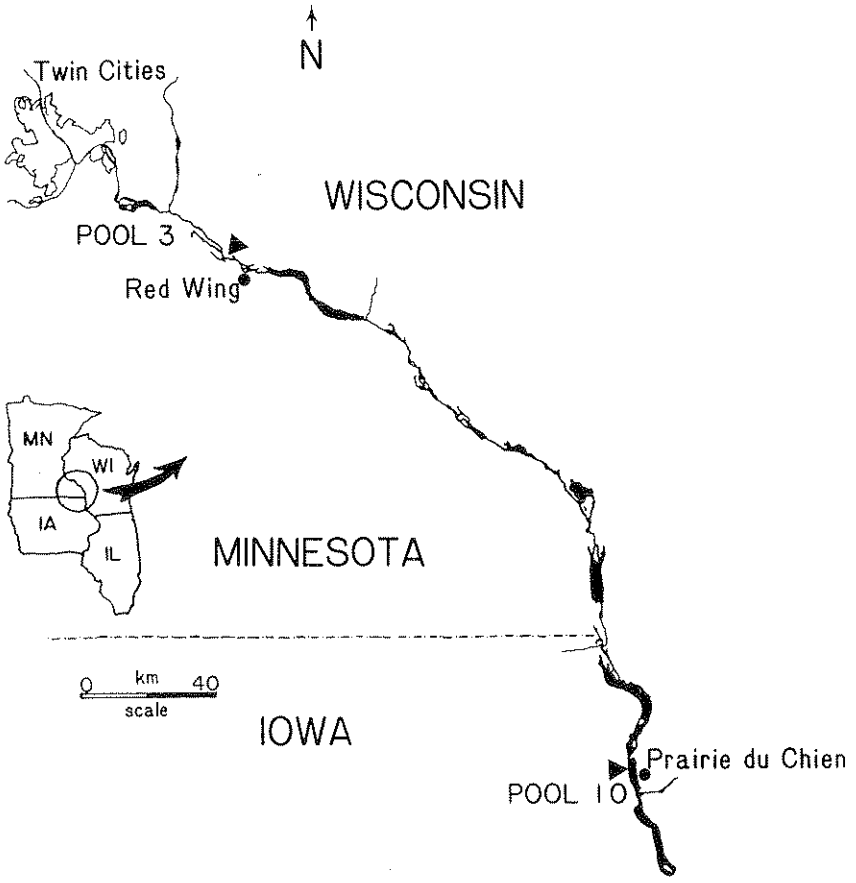

Figure 1. Map of the upper Mississippi River study area; sampling sites are denoted with triangles.

Table 1. Mean total length and age (SE in parentheses) of threeridge mussels from the upper Mississippi River that were analyzed for metals.

Pool	Length group[a] (mm)	Mean length (mm)	Mean age (years)	n
3	30-50	43.8 (5.4)	5.3 (1.1)	25
	51-70	60.0 (6.0)	7.5 (1.4)	38
	71-90	81.7 (4.9)	12.4 (1.7)	30
	91-107	96.4 (5.1)	15.4 (1.6)	20
10	22-50	34.7 (7.5)	4.3 (1.5)	120
	51-70	65.0 (5.5)	11.8 (2.2)	30
	71-90	80.9 (6.3)	16.3 (2.3)	28
	91-112	99.8 (5.2)	22.1 (2.8)	22

[a]Minimum and maximum total length of mussels within each length group.

We analyzed 10 composite samples of mussels from each length group per pool. Each sample contained a composite of total soft tissue from two or more mussels. The wet weight of all composite samples exceeded 20 g. Composite samples were stored in glass jars with Teflon lids and frozen at -20°C until analysis.

Samples were analyzed for metals at the U.S. Fish and Wildlife Service, Patuxent Wildlife Research Center in Laurel, Maryland. For cadmium, a 0.5-g subsample was digested in 5 ml of concentrated nitric acid to which 0.5 ml of 30% hydrogen peroxide was added. Cadmium was determined by stabilized temperature platform graphite furnace atomic absorption spectroscopy with a Perkin Elmer Zeeman 303 spectrophotometer[a]. For mercury, a 1-g subsample was digested under reflux with sulfuric and nitric acids and analyzed with cold vapor atomic absorption spectrophotometry in a Coleman MAS-50 mercury analyzer. Tissues to be analyzed for copper and zinc were ashed for 12 h at 550°C. The residues were dissolved in nitric and hydrochloric acids, and 500 μg of scandium was added as an internal standard. Digestates were analyzed for copper and zinc with a Perkin Elmer Plasma II sequential inductively coupled plasma emission spectrometer.

The following quality assurance samples were analyzed with mussel samples: procedural blanks, duplicate samples, spiked samples, and a National Bureau of Standards (NBS; now named the National Institute of Standards and Technology) reference material (bovine liver). Our estimates of concentrations in the standard reference material were within the certified concentration ranges for cadmium, copper, and zinc (Table 2).

Heavy metal concentrations were compared among all length groups within each pool by one-way analysis of variance (ANOVA). When a difference in metal concentration was observed by ANOVA, multiple comparisons of metal concentrations among length groups within each pool were made with the Student-Newman-Keuls' (S-N-K) multiple range test (SAS 1985).

[a]Reference to trade names does not constitute U.S. Government endorsement of commercial products.

Table 2. Results of quality assurance analyses done in conjunction with analyses of molluscs.

Metal	Detection limit[b] (μg/g)	Mean recovery (%)	NBS[a] bovine liver: Certified value[c] (μg/g ± 1 SD)	NBS[a] bovine liver: Our mean conc.[c] (μg/g)	NBS[a] bovine liver: RSD[d] (%)
Cadmium	0.04	97	0.44 ± 0.06	0.52	5.6
Mercury	0.02	NA[e]	NA[e]	NA[e]	NA[e]
Copper	0.5	97	158 ± 7	152	5.5
Zinc	2.9	84	123 ± 8	124	12.2

[a]National Bureau of Standards.
[b]Nominal lower limit of reportable residue, in μg/g wet weight, based on a 5.0-g (wet weight) sample.
[c]Dry-weight concentrations.
[d]Relative standard deviation.
[e]Not analyzed.

Metal concentrations are frequently correlated with mussel size (Boyden 1977, Strong and Luoma 1981, Hinch and Stephenson 1987); therefore, variations in metal concentrations among length groups within a pool could bias contrast of mean concentrations between pools. Consequently, contrasts in metal concentrations between the two pools were made by one-way analysis of covariance (ANCOVA) with metal concentrations as the dependent variables, length as the covariate, and pool as the treatment variable. Initial results indicated that one critical assumption of the ANCOVA, that there be homogeneity of slopes, was not met for cadmium and mercury. Therefore, for these two metals, metal concentrations and length were rank transformed before ANCOVA (Conover and Iman 1982). A Type I error (α) of 0.05 was used to judge the significance of all statistical tests.

Results

Cadmium concentrations in mussels were generally greater ($P = 0.007$) in Pool 3 than in Pool 10 (Fig. 2). In Pool 3, cadmium concentrations differed among size groups (ANOVA; $P = 0.005$), generally increasing with the size of the mussel, but this was not reflected by the conservative S-N-K multiple range test. In Pool 10, concentrations varied ($P = 0.0002$) among length groups and were less in the smallest (0-50 mm) and largest (≥91 mm) length groups than in mussels of intermediate size (Fig. 2).

Mean concentrations of mercury in threeridge mussels did not differ between pools ($P = 0.07$). Mercury concentrations in mussels differed among length groups in Pool 10 ($P = 0.001$), but not in Pool 3 ($P = 0.067$; Fig. 2). The high mean concentration of mercury (0.61 μg/g) in the ≥91-mm length group in Pool 10 resulted from an unusually high concentration (1.9 μg/g) in one sample; deletion of this sample from the data set yielded a mean of 0.4 μg/g.

Copper concentrations in mussels did not differ ($P = 0.28$) between pools and were highest in the smaller length groups. In Pool 3, copper concentrations varied significantly ($P = 0.002$) among length groups and were greatest in the 0-50 mm group (Fig. 2). In Pool 10, copper concentrations were greater ($P = 0.0003$) in mussels smaller than 71 mm (Fig. 2).

Zinc concentrations in mussels did not differ between pools ($P = 0.07$). Mean concentrations of zinc varied with size of the mussel in both pools ($P < 0.0001$) ranging from 137 to 203 μg/g dry weight in the four length groups in Pool 3 and from 117 to 204 μg/g in Pool 10 (Fig. 2). In Pool 3, mean concentrations were lowest in the <71-mm groups. In Pool 10, mean zinc concentrations were lowest in the 0-50 mm group and highest in the 71-90 mm group (Fig. 2).

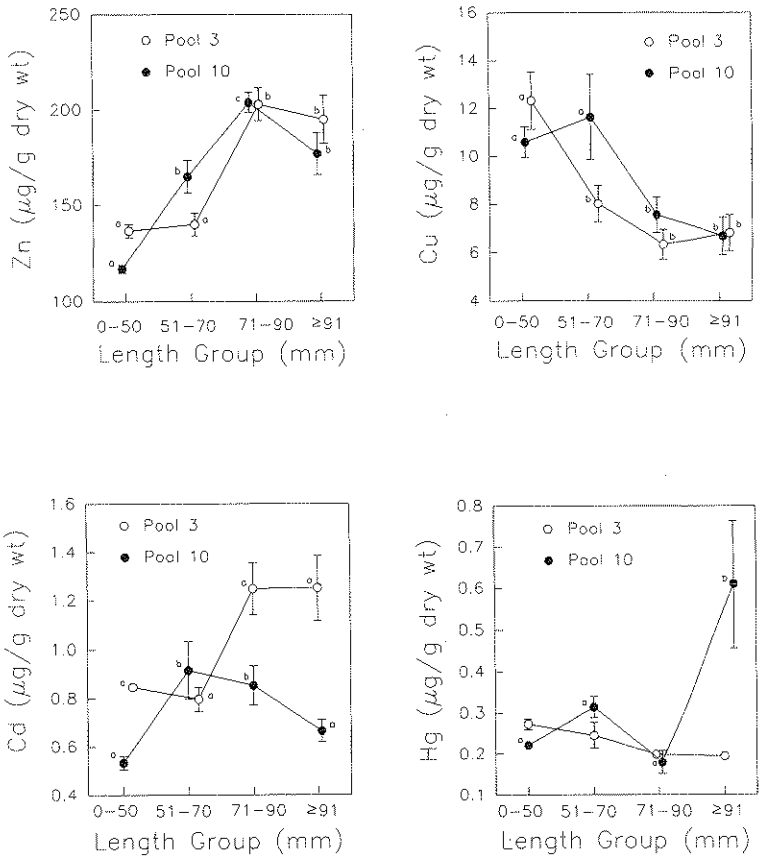

Figure 2. Mean concentrations (μg/g dry weight ± 1 SE) of zinc, copper, cadmium, and mercury in soft tissues from 10 composite samples of threeridge mussels from Pools 3 and 10, upper Mississippi River. Metal concentrations with the same letter were not significantly different from each other. Student-Newman-Keuls' multiple range test was used to determine statistical significance at $P = 0.05$.

Discussion

Mean cadmium concentrations in threeridge mussels were significantly less in Pool 10 than in Pool 3--paralleling the spatial trend in the cadmium contamination of sediments (Wiener et al. 1984) and emergent *Hexagenia* mayflies (Dukerschein et al. 1992) in the reach downstream from the Minneapolis-St. Paul metropolitan area. Although cadmium concentrations in mussels were higher in Pool 3 than in Pool 10, cadmium

concentrations reported for mussels from metal-polluted systems were up to 10-fold greater than those reported here for the upper Mississippi River (Mathis and Cummings 1973, Anderson 1977, Pugsley et al. 1988).

Mercury concentrations in mussels from the upper Mississippi River were generally 10-fold less than those in mussels from more contaminated systems (Smith et al. 1975, Renzoni and Bacci 1976, Price and Knight 1978). Freshwater mussels are poor indicators of mercury contamination because uptake rates are variable and concentrations are typically elevated only in mussels from very contaminated waters (Smith et al. 1975). Likewise, Dukerschein et al. (1992) reported no spatial trend in the concentration of mercury in female mayflies from Pool 6 to Pool 27.

Copper concentrations in threeridge mussels reported here were comparable to mean concentrations in mussels from metal-polluted waters such as the Fox River, Illinois (Anderson 1977), and the Illinois River near Peoria (Mathis and Cummings 1973). Copper concentrations varied with mussel size, perhaps because physiological requirements for this essential element vary with age.

Zinc concentrations in the threeridge mussel were comparable to those in threeridge mussels from a lightly contaminated site in the Wabash River, Indiana (Adams et al. 1981). Zinc concentrations in mussels from more heavily polluted systems are often substantially greater (ranging from 250 to 700 $\mu g/g$ dry weight; Mathis and Cummings 1973, Anderson 1977, Tessier et al. 1984, Servos et al. 1987) than those reported here. The higher concentrations of zinc in the larger mussels might be related to increased accumulation with age, and may be a result of the physiological requirement of mussels for 17 metalloenzymes that contain zinc (Manly and George 1977).

Although the concentration of each metal varied with mussel length, there was no consistent trend among the four metals studied. The literature on the size-dependency of metal concentrations is substantial for marine bivalves (e.g., Boyden 1974, Strong and Luoma 1981, Prosi 1983), but such information is scarce for freshwater bivalves (Hinch and Stephenson 1987).

Several factors may affect metal concentrations in mussels. For example, alterations in physiological requirements caused by changes in reproductive state may affect metal concentrations. Our samples were collected in late July and early August, months when most threeridge mussels in the upper Mississippi River release glochidia (Holland-Bartels and Kammer 1989). If some of the females were collected before their glochidia were released, the difference in reproductive state may have contributed to variations in metal concentrations among length groups.

Subtle differences in feeding strategies among length groups can also influence metal concentrations (Prosi 1983, Smock 1983). Food from different sources may vary in particulate metal content. We did not purge mussel intestinal contents before analysis; therefore, metal concentrations could have been influenced by ingested sediment particles.

Many investigators (Boyden 1977, Strong and Luoma 1981, Hinch and Stephenson 1987, Pip 1990) have examined the relation between metal concentration and mussel length to identify potential processes affecting metal accumulation. A negative correlation with size can occur when metal uptake is greatest in smaller individuals and declines with growth--a pattern observed for copper in the threeridge mussel in the upper Mississippi River (this study), in *Anodonta grandis* from Lake Winnipeg, Manitoba (Pip 1990), and in *Quadrula* from the Muskingum River, Ohio (Foster and Bates 1978). A positive correlation between concentration and size can occur when a metal accumulates at a faster rate than the growth of the individual; this pattern was evident for zinc in our study. A nonsignificant correlation suggests that metals are at steady-state concentrations within the tissues (Williamson 1980).

Although concentrations of cadmium and mercury are elevated in surficial sediments in the upper Mississippi River, absolute concentrations of these two metals in the threeridge mussel are lower than concentrations in mussels from more polluted waters, suggesting that cadmium and mercury are less bioavailable in the upper Mississippi River. Unlike cadmium and mercury, the essential nature of copper and zinc makes it more difficult to interpret the biological significance of these metals. Variations in concentrations of copper and zinc among length groups may simply reflect different physiological requirements.

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