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Mercury Contamination in Fish in Midcontinent Great Rivers of the United States: Importance of Species Traits and Environmental Factors

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We measured mercury (Hg) concentrations in whole fish from the Upper Mississippi, Missouri, and Ohio Rivers to characterize the extent and magnitude of Hg contamination and to identify environmental factors influencing Hg accumulation. Concentrations were generally lower (80% of values between 20−200 ng g^{-1} wet weight) than those reported for other regions (e.g., upper Midwest and Northeast U.S.). Mercury exceeded the risk threshold for belted kingfisher (*Ceryle alcyon,* the most sensitive species considered) in 33−75% of river length and 1−7% of river length for humans. Concentrations were lower in the Missouri than in the Mississippi and Ohio Rivers, consistent with continental-scale patterns in atmospheric Hg deposition. Body size and trophic guild were the best predictors of Hg concentrations, which were highest in large-bodied top predators. Site geochemical and landscape properties were weakly related with fish Hg. Moreover, relationships often ran contrary to conventional wisdom, and the slopes of the relationships (positive or negative) were inconsistent among fish guilds and rivers. For example, sulfate is positively associated with fish Hg concentrations but was negatively correlated with Hg in five of six regression models of tissue concentrations. Variables such as pH, acid neutralizing capacity, and total phosphorus did not occur at levels associated with high fish Hg concentrations, partially explaining the relatively low Hg values we observed.

Introduction

Mercury (Hg) contamination in aquatic ecosystems poses a serious risk to human and wildlife populations (*1*). Mercury bioaccumulates in aquatic food webs and is a contaminant of concern in 80% of fish consumption advisories issued in the United States (*2*). Mercury contamination is widespread in freshwater systems, including flowing waters, and over 1.4 million river kilometers are under an advisory for Hg in the U.S. alone (*2*). Due to the prevalence of harmful levels of Hg in the environment, identifying factors driving variability in mercury concentrations among different species, regions, and ecosystems is a critical research need (*3, 4*). Large-scale studies of Hg distribution typically focus on fish because some of them are top predators in aquatic food webs, and they are a dominant pathway of Hg exposure to humans and wildlife (*3, 5*).

Spatial variability in fish Hg concentrations is generally attributed to differences in Hg loading among sites, autecology of species, or site biogeochemical processes that influence methylation (*1, 6, 7*). Atmospheric deposition of Hg from anthropogenic emissions is the primary source of Hg to aquatic systems (*1, 3, 4*) and is strongly correlated with Hg concentrations in fish and birds at continental scales (*8*). Likewise, body size (or age) and trophic position consistently account for among- and within-species variation in Hg concentrations, with higher concentration found in larger, older individuals and in top predators such as piscivores (*1, 7, 9*). Conversion of inorganic Hg to methyl mercury (MeHg, one of the most toxic and prevalent forms found in fish (*10*)) also varies with site geochemical properties. High MeHg levels, and consequently fish Hg concentrations, are positively associated with sulfate and dissolved organic carbon (DOC) concentrations and extent of wetlands in catchments and inversely related to acid neutralizing capacity (ANC), pH, and phosphorus concentrations (*1, 6, 9, 11, 12*). Investigations of spatial variation in fish Hg concentrations are less common in lotic than lentic systems, and results are mixed. Peterson et al. (*13*) found significant relationships between fish tissue and pH, ANC, sulfate, and human disturbance, but results were inconsistent among genera. Similarly, Barbosa et al. (*14*) compared fish Hg concentrations with pH and DOC and reported weak and inconsistent relationships among trophic guilds. However, Chasar et al. (*12*) reported strong relationships between fish Hg concentrations and stream Hg concentrations, DOC concentrations, fish trophic guild, and wetland density in stream catchments.

We investigated Hg concentrations in a diverse fish assemblage from the great rivers (Upper Mississippi, Missouri, and Ohio) of the U.S. Central Basin. The study area spans more than 10° of latitude and 12° of longitude and includes samples collected along 5100 river kilometers (rkm). Our objectives were to 1) characterize spatial variation in fish Hg concentrations among and within rivers; 2) determine the spatial extent of risk to humans and wildlife through fish consumption based on published risk threshold values; 3) evaluate effects of body size and trophic guild on fish Hg concentrations; and 4) examine how other environmental factors (e.g., proximity to urban areas, water chemistry) previously associated with elevated fish Hg concentrations affect fish concentrations throughout the great rivers. We expected that concentrations would be lower in the Missouri than the Ohio and Mississippi rivers because Hg deposition increases from west to east in the central U.S (*8, 15*). We also expected that body size and trophic position would be positively correlated with Hg concentrations (*1*) and that Hg would be correlated with environmental or landscape factors (e.g., ANC and proximity to wetlands) that affect Hg exposure in fish.

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Experimental Section

Sampling Design. The study area included the Upper Mississippi River (hereafter Mississippi River) from Minneapolis-St. Paul, Minnesota to its confluence with the Ohio River, the Missouri River from Fort Peck Dam in Montana to its confluence with the Mississippi River (excluding large, mainstem reservoirs in North and South Dakota), and the entire Ohio River from Pittsburgh, Pennsylvania to its confluence with the Mississippi River (*16*). Sample sites were selected using a probability survey design (*17*) to identify a single point on a river center line as defined by the National Hydrography Database (NHD). This point formed the basis for field sampling and collection of remotely sensed data and for calculation of population estimates. The probability survey algorithm included an explicit random element in the site selection (*17*), with spatial balance incorporated to disperse the sites and increase the representativeness of the sample (*18*). Each site was assigned a weight indicating the number of rkm represented in population estimates, based on the total number of rkm and the number of sites sampled (*19*). Weights ranged from 12.8 to 57.6 rkm (mean 31.1) among rivers.

Sample Collection. Fish were collected July through September 2004−2005 by daytime electrofishing of two separate 500 m reaches along the main-channel shoreline (*20*). Composite samples for fish tissue were collected in one or both of these reaches, and 278 sites were visited yielding 644 fish samples. At least one large and one small species were collected per site (Table S1). Large species (>150 mm total length, TL) are potentially targeted by anglers and served as indicators of human exposure to Hg in fish tissue. Small species (<150 mm TL) are potential prey for piscivorous wildlife and are more realistic indicators of wildlife exposure than large fish (*21*). Samples included similarly sized individuals (i.e., <25% variation in length) where possible, but at some locations larger individuals were included to obtain a sample (*20*). Fish were assigned into planktivore, omnivore, invertivore, generalized carnivore, and piscivore trophic guilds based on preferred food of adults as described by regional texts (e.g. refs *22* and *23*, Table S1). Omnivores are species eating multiple food types including detritus, algae, invertebrates, and fish. Generalized carnivores are predators that feed on crayfish, other invertebrates, and fish and are distinct from piscivores that feed almost exclusively on fish.

We collected environmental variables potentially affecting Hg concentrations in fish via increased Hg loading or increased MeHg production (*1, 6, 8, 9, 13, 24*). Detailed collection and sample analysis methods are provided in ref *16* and in the Supporting Information. Land use and land cover variables included the percentage of developed land (sum of National Land Cover Database (NLCD) categories 21−24), the percentage of wetlands (sum of NLCD categories 90 and 95) and number of backwater habitats adjacent to mainstem river channels, the distance from main channel dams, and total Hg deposition. Urban centers can enhance local Hg loading through increased atmospheric deposition related to fossil fuel combustion, direct discharges (e.g., industrial wastes, stormwater runoff, and landfill leachate), and other anthropogenic sources (*6*). Wetland density and connection to backwater habitats is also positively correlated with MeHg concentrations and bioaccumulation in lotic systems (*12, 25*). Dams can create more lentic-like habitats and increase deposition of fine sediments, which could favor local production of MeHg, and atmospheric Hg deposition is highly correlated with Hg concentrations in fish (*8*).

Water samples were collected concurrently with fish samples and were analyzed for pH, ANC, sulfate, total P, and total organic carbon (TOC), which have been correlated with Hg concentrations in fish (*1, 6, 8, 9, 11, 13, 26*). Sulfate concentration is generally associated with MeHg production and elevated fish Hg concentrations in lentic systems (*1, 9, 11*), and sulfate deposition along with aqueous sulfate concentration has been linked with Hg concentrations in lotic fishes (*8, 13*). We also measured total trace metals (Al, As, Cu, Fe, Ni, Se, Pb and Zn), which we viewed as a surrogate for overall metal loading into these rivers. Summary statistics for environmental variables are provided in Table S2.

Mercury Analysis. Details on analytical methods, sample homogenization, and quality control procedures are provided in the Supporting Information. Whole fish samples were analyzed for total Hg using a direct mercury analyzer (Milestone DMA-80, Milestone Inc., Shelton, CT). The detection limit (DL) was 1.6 ng g^{-1} wet weight. Recovery of Hg was assessed by analyzing one sample of certified reference material (CRM DORM-2, dogfish muscle) per batch. Percent recovery of CRM ranged from 81%−105% (mean 96.5%, ±4.9% SD). Each batch consisted of 12 samples run in duplicate, and reported values were the mean of two analyses.

Mercury Risk Thresholds and Population Estimates. Mercury wildlife values (WVs) and human screening values (SVs) estimate environmental risks of fish consumption for sensitive wildlife (e.g., mink, *Mustela vison*) and human populations (e.g., children and women of child bearing age). WVs for consumption of small species were 70 and 30 ng g^{-1} for mink and belted kingfisher, respectively (*21*). These species are found throughout the sampling area and serve as realistic mammalian and avian models of exposure. The human health screening value (SV) for large species was 300 ng g^{-1} fish tissue (*27*). This standard is based on concentration in muscle tissue (filets), the portion of fish typically consumed by humans, whereas our samples were analyzed as whole bodies. To account for sampling differences, we used a SV of 185 ng g^{-1} based on a filet/whole body regression model (*13*). The probability-based design allowed us to extrapolate our results to entire rivers and to estimate the variability around estimates of contamination extent (*18*). We used sample site weights derived from the probability design to estimate rkm having fish with Hg concentrations above WVs or the SV.

Statistical Analysis. We used analysis of variance (ANOVA) and analysis of covariance (ANCOVA) to test for effects of river, size (small and large fish), body length, and trophic guild on fish tissue Hg concentrations. Differences within sizes among rivers and differences within rivers between sizes were tested with ANOVA. These analyses identified significant differences among rivers and between sizes, so subsequent tests for the effects of body size and trophic guild were conducted separately for each river and size class. We used ANCOVA to test for trophic guild effects in large fish, with body length included as the covariate. Initial ANCOVA models included an interaction term (length*guild). Interactions were nonsignificant in all cases ($p > 0.05$), so this term was removed from final models. ANOVA was used to test for effects of trophic guild on small fish. Length was not included as a covariate in small fish models because the range of values was small (mean among species ~60−110 mm) and because the largest specimens were from a single planktivore (gizzard shad, *Dorosoma cepedianum*) that had the lowest observed Hg concentrations (Table S1). We used linear regression analysis to identify relationships between environmental variables and Hg concentrations ($\log_{10}$ transformed). Environmental variables were transformed as necessary based on normal probability plots and Shapiro-Wilk probability tests (Table S2). Mercury was modeled separately for each river and fish size class. We also included percent lipid content as a covariate in these models because lipids and trophic position (a key factor in fish Hg concentrations) are often collinear (*28*). Best subsets regression was performed based

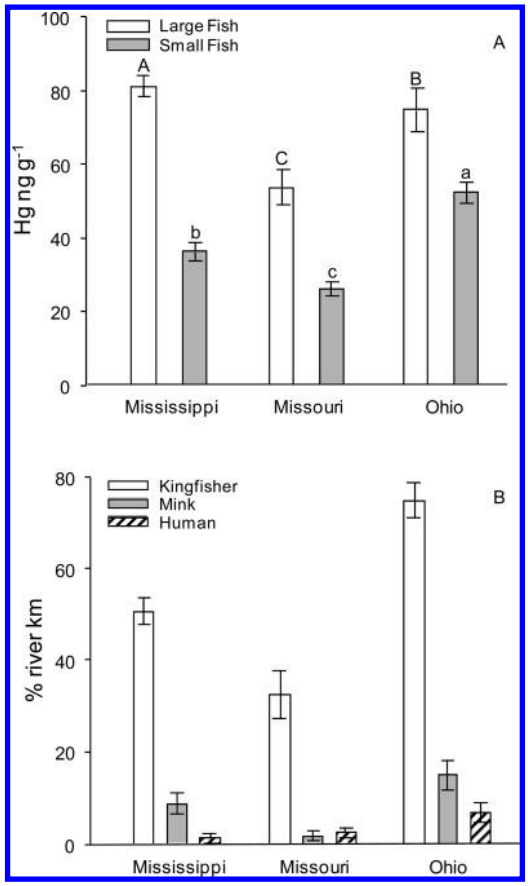

FIGURE 1. A) **Hg concentrations (mean, SE) in large and small fish in the great rivers. Bars with different letters indicate significantly different concentrations among rivers ($\alpha = 0.05$, posthoc Tukey test) for large fish (upper case letters) and small fish (lower case letters). Statistical analyses were conducted using $\log_{10}$ transformed Hg data. Results shown are for models using untransformed Hg data for illustration purposes.** B) **Extent (%, SE) of river kilometers where fish tissue Hg concentrations exceed wildlife and human health screening values.**

on Mallow's C_p statistic (*29*), so that some models included predictors that were not significant but led to a lower C_p value relative to the number of variables in the model. Statistical analyses were conducted using SAS v. 9.1 (SAS Institute, Cary, North Carolina). Significance level was $p < 0.05$ for all tests.

Results

Mercury was detected in all fish samples tested. Concentrations ranged from 5.0−391 ng g^{-1} wet weight of whole fish, with 80% of observations ranging from 20−200 ng g^{-1}. Concentrations were significantly different among rivers for large (ANOVA, $F = 27.9$, $p < 0.0001$) and small fish ($F = 32.2$, $p < 0.0001$, Figure 1A). Concentrations were lowest for both groups in the Missouri River. Mercury concentrations in large and small fish were highest in the Mississippi and Ohio rivers, respectively. Within rivers, Hg concentrations in large fish were significantly greater than small fish in all cases (ANOVA; Mississippi, $F = 151.3$, $p < 0.0001$; Missouri, $F = 40.3$, $p < 0.0001$; Ohio, $F = 9.3$, $p < 0.003$). The Ohio River had the highest proportion of river length exceeding WV and SV thresholds (Figure 1B). Exceedance was intermediate in the Mississippi River and lowest in the Missouri River. Kingfisher, which had the lowest risk threshold (30 ng g^{-1}) among risk end points, had the highest percentage of rkm exceeding WV (Figure 1B). Overall, 75% of the Ohio, 51% of the Mississippi, and 32% of the Missouri exceeded the WV for kingfisher. Exceedance for mink ranged from 2−15% of rkm among rivers. Concentrations above the human SV were infrequent at 1−7% of rkm across rivers.

Longitudinal patterns in fish Hg concentrations were not apparent for either large or small fishes (Figure 2). Differences in Hg concentrations between small and large fishes were more pronounced in the Mississippi and Missouri Rivers than in the Ohio River, where concentrations between these groups showed considerable overlap.

Body length and trophic guild were significant predictors of Hg concentrations in large fish in all three rivers (Table 1). Length was the dominant factor, with *F*-values ranging from around 43−97 among models. After accounting for length effects, trophic guild was also highly significant. Piscivores and carnivores consistently had the highest concentrations, whereas invertivores and omnivores had the lowest concentrations (Figure 3). Trophic effects were weakest in the Missouri River, perhaps due in part to the relationships ($r^2 = 0.52$) between fish length and Hg concentrations in this system. Trophic guild was also a factor in Hg concentrations in small fish. Concentrations in invertivores were significantly higher than those in planktivores in all cases (Figure 3). Small omnivores, which were only sampled in the Missouri River, had significantly higher Hg concentrations than planktivores but did not differ from invertivores.

As expected, length was a significant and primary covariate in Hg models for large fish (Table 2). Environmental variables were generally poor predictors of Hg concentration for large and small trophic guilds, explaining <15% of Hg concentrations in 21 of 26 cases where environmental variables were included as model parameters (Table 2). The strongest relationships were as follows: 1) Mississippi River: Hg deposition and planktivores (+), ANC and small invertivore/omnivores (+); and 2) Missouri River: sulfate and large piscivores/carnivores (−), sulfate and planktivores (−), and phosphorus and small invertivore/omnivores (−). Relationships between Hg concentration and environmental variables often ran counter to conventional wisdom or had regression slopes that were inconsistent (i.e., some slopes positive, some negative) among models. For example, SO_4 is expected to be positively related with Hg concentrations, but it was negatively correlated with Hg in 5 of 6 models. Likewise, Hg deposition was negatively correlated with fish Hg concentrations in the Missouri River but positively correlated in the Mississippi River, and TOC was negatively, rather than positively, correlated with fish Hg. Other variables with inconsistent slopes among models included fish tissue lipids, developed land, distance to dams, dissolved metals, ANC, and pH.

Discussion

Atmospheric deposition is the primary source of Hg to aquatic systems (*3, 4*), and methylation of this deposited Hg is a fundamental driver of Hg concentrations in fish (*8*). Our finding that fish Hg concentrations were lower in the Missouri River than the Mississippi and Ohio Rivers is consistent with observed continental patterns of lower deposition in western states than in midwestern and northeastern states (*8, 15*) and with mean differences in deposition among rivers (Table S2). Similar among-river differences were observed for different fish size classes, trophic guilds, and for widespread species like freshwater drum (*Aplodinotus grunniens*) and emerald shiner (*Notropis atherinoides,* Table S1). However, relationships between local Hg deposition and fish concentrations were inconsistent within rivers. Deposition was strongly correlated with Hg concentrations only for Mississippi River planktivores and was negatively correlated with some groups in the Missouri River.

As expected, body size and trophic position were key factors explaining among-species variation in fish Hg con-

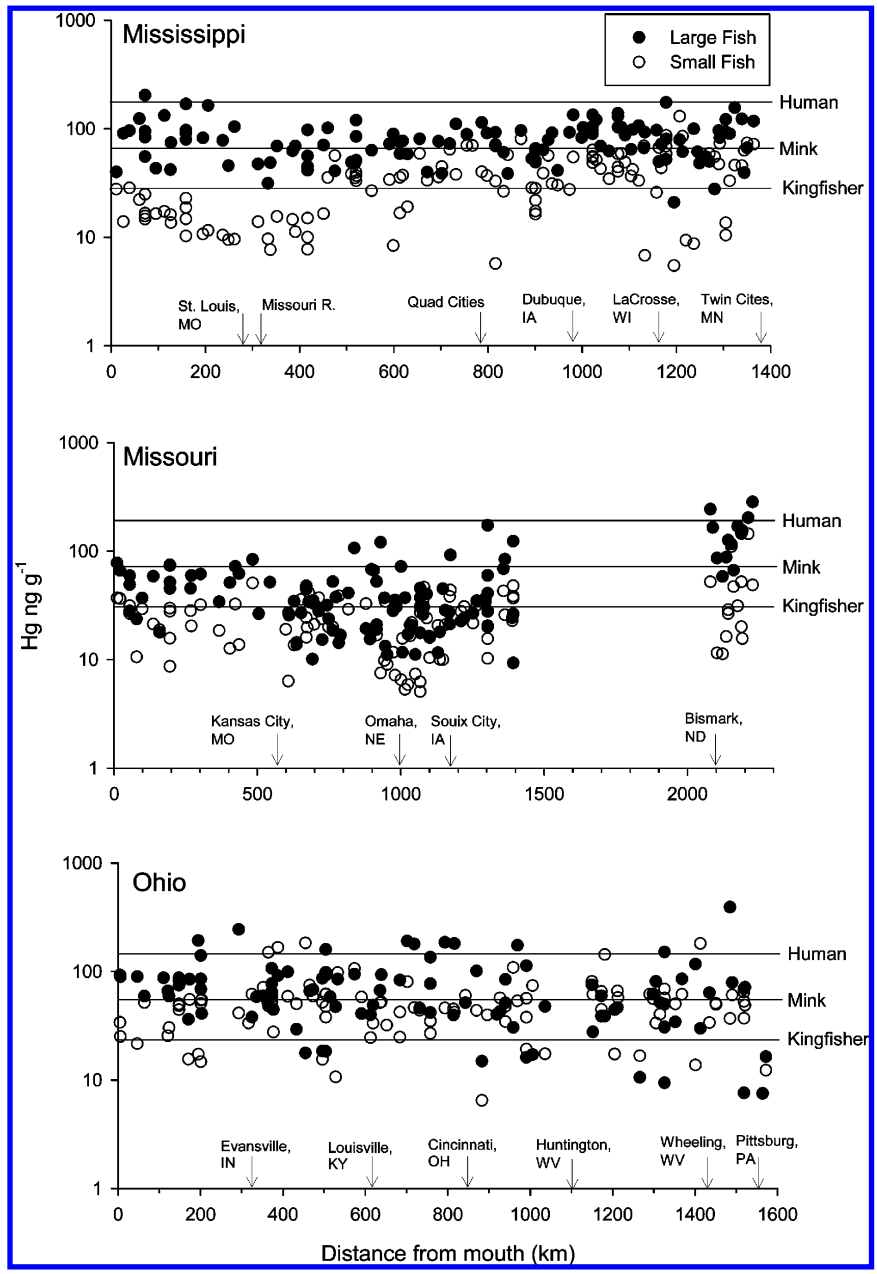

FIGURE 2. Longitudinal profiles of Hg in large and small fish within rivers. Major cities are shown for spatial context. Quad Cities refers to the towns of Davenport and Bettendorf, IA, and Moline, Rock Island, and East Moline, IL. The gap in the Missouri River plot represents six reservoirs that were excluded from the study. Horizontal lines illustrate risk thresholds for wildlife and humans.

TABLE 1. Results of ANCOVA Testing the Effect of Fish Total Length and Trophic Guild on Mercury (log_{10} Transformed) Concentrations in Large Fish in Each River

source of variation	*df*	*F*	*p*	r^2
	Mississippi			
model		17.6	<0.0001	
guild	3, 108	19.7	<0.0001	0.33
length		42.8	<0.0001	
	Missouri			
model		27.1	<0.0001	
guild	4, 104	3.0	0.03	0.51
length		83.3	<0.0001	
	Ohio			
model		29.2	<0.0001	
guild	4, 93	20.0	<0.0001	0.56
length		96.9	<0.0001	

centrations within rivers, confirming results of prior studies (*1*). Concentrations were highest in large fish feeding near the top of the food web and lowest for small fish feeding near the bottom of the food web. By comparison, site-scale environmental factors were weakly related to fish Hg concentrations. Thus, differences in fish Hg concentrations were mainly attributable to ecological differences among species and to continental-scale difference in atmospheric deposition among rivers. Large-scale differences in Hg concentrations could also be due to differences in trophic structure (e.g., food chain length) or bioaccumulation factors among rivers. This alternate explanation is less likely, as fish Hg concentrations in smaller streams and rivers are more strongly related to MeHg loading at the base of the food web, rather than among-site differences in trophic structure (*12*).

Mercury concentrations in great river fish were relatively low compared to other aquatic systems and regions. Concentrations in 30−40 cm long largemouth bass (*Micropterus*

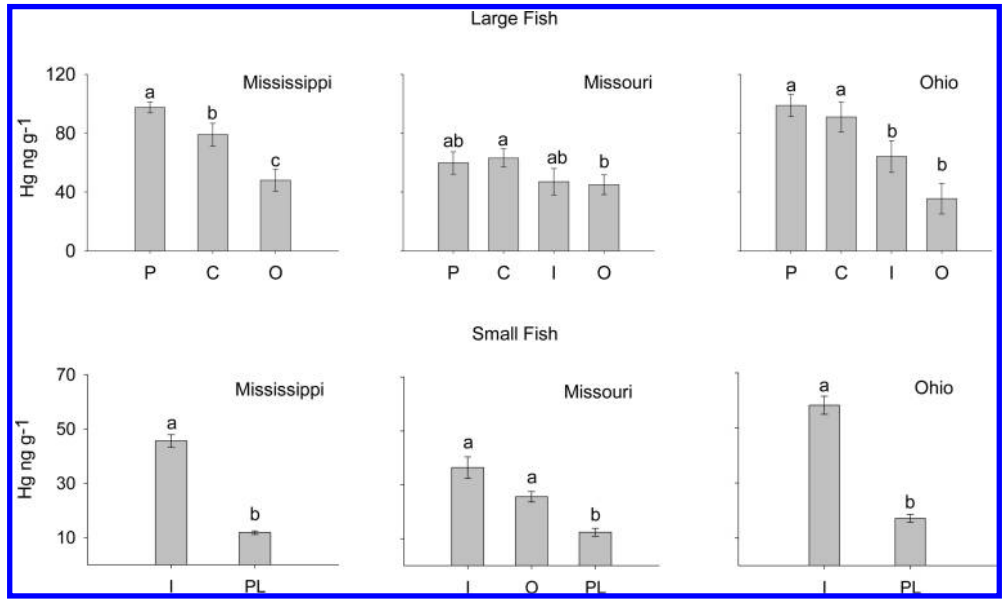

FIGURE 3. Hg concentrations (mean, SE) among trophic guilds for large (top panel) and small (bottom panel) fish. Means of large fish were length-adjusted using ANCOVA (see methods). Guilds with different letters are significantly different ($\alpha < 0.05$, posthoc Tukey test) based on analysis of log_{10} transformed Hg data. Results shown are for models using untransformed Hg data for illustration purposes. Trophic guilds: C, generalized carnivore; I, invertivore; O, omnivore; P, piscivore; PL, planktivore.

TABLE 2. Linear Regression Models Relating Environmental and Fish Variables to Hg Concentrations[a]

	large fish						small fish					
	Mississippi		Missouri		Ohio		Mississippi		Missouri		Ohio	
	P/C	I/O	P/C	I/O	P/C	I/O	PL	I/O	PL	I/O	PL	I/O
fish length (mm, +)	**0.27**+	**0.43**+	**0.25**+	**0.67**+	**0.32**+	**0.53**+						
fish tissue lipids (%, +)	**0.18**−							*0.08*+				**0.36**+
total Hg deposition (g ha^{-1}, +)	*0.03*+		*0.05*−	*0.08*−			**0.46**+					
Riparian wetlands (%, +)												<0.01+
backwaters (number, +)												
developed land (%, +)				0.01+			0.01−			<0.01+		
distance to dam (unitless[b])			*0.03*−		0.04+							
phosphorus (μg/L, −)										**0.30**−		
sulfate (mg/L, +)			**0.24**−	*0.04*−	*0.07*−			0.01−	**0.39**−			*0.07*+
total dissolved metals (μg/L, +)					0.05+			0.01−		*0.05*−		
ANC (mg l^{-1} $CaCO_3$, -)	0.02−							**0.15**+				
pH (−)	*0.03*+	0.11−										*0.04*-
TOC (mg/L, +)			*0.09*−							*0.05*−		
Cp	0.43	−6.36	1.55	−0.67	1.53	−5.39	−3.22	0.08	0.66	1.15	NA	0.64
adjusted R^2	0.50	0.50	0.61	0.76	0.44	0.52	0.43	0.20	0.37	0.45	NA	0.40
n	68	23	46	42	50	33	24	64	24	53	12	67

[a] Plus and minus signs next to predictor variables indicate the expected relationship (positive or negative) with Hg concentrations based on prior studies (*1, 6, 8, 9, 11, 31, 34*). Partial R^2 values are shown for each predictor variable with + or - indicating regression slope. Partial R^2 in bold, $p < 0.01$; italics, $p < 0.05$; plain text, $p < 0.10$. Trophic guilds: **P/C**, piscivores and carnivores; **I/O**, invertivores and omnivores; **PL**, planktivores. Piscivore and carnivore guilds and invertivore and omnivore guilds were combined because ANOVA and ANCOVA found only minor differences in Hg concentrations between them. [b] Site distance to dams was scaled to total reach length between dams (see the Supporting Information).

salmoides, mean 195 ng g^{-1} normalized to filet concentration (*13*), $n = 6$) were below statewide averages reported for 24 of 25 U.S. states (range 160−750 ng g^{-1}) (*8*). Total mean largemouth bass Hg concentrations (276 ng g^{-1}, $n = 47$, normalized to filet concentration in 400 mm fish) were 5× lower than those in southeastern U.S. rivers (1390 ng g^{-1}, $n = 80$) and substantially lower than those reported for southeastern reservoirs (390 ng g^{-1}, $n = 191$) (*30*). Thirteen species in northeastern U.S. freshwater systems had mean Hg concentrations ranging from approximately 180−780 ng g^{-1} (*9*) compared with 29−327 ng g^{-1} (normalized to filet concentrations) among great river fish. These low concentrations prevailed across rivers, despite high atmospheric deposition from long-range sources in the Ohio and Mississippi basins (*15*).

The low Hg concentrations observed throughout the study area suggest that great rivers are relatively insensitive to Hg loading. Hg-sensitive aquatic environments (i.e., where small loadings result in high MeHg concentrations in higher trophic levels) are characterized by high methylation efficiency, connection to high-efficiency systems such as wetlands, and low productivity (*1, 6, 24, 30, 31*). Reported geochemical

thresholds for Hg sensitivity are pH < 6, total $P < 30\ \mu g\ L^{-1}$, DOC > 4 mg L^{-1}, and ANC < 100 mg L^{-1} $CaCO_3$ (*6*). Great rivers would be considered Hg-insensitive systems by most of these measures. Mean pH varied from 7.5 to 8.4 and P varied from 49 to 208 $\mu g\ L^{-1}$ among rivers (Table S2), and the historic range of DOC among rivers is 3.3−4.0 mg L^{-1} (*32*). Likewise, mean total P among rivers (49−208 $\mu g\ L^{-1}$) was 1.5- to 4.5-fold greater than the threshold for Hg sensitivity. ANC was >100 in the Mississippi and Missouri rivers but was <100 in the Ohio (mean 76), where the highest Hg concentrations in small fish were observed. These rivers may also be less efficient at producing MeHg than other aquatic systems. Methylation efficiency (MeHg/total Hg) was 3.6× lower in lotic systems than lakes across northeastern North America, and efficiency declined with stream discharge (*33*). Thus, the combination of high discharge and unfavorable chemical conditions for methylation suggests that great rivers are inefficient producers of MeHg.

Human disruption of channel-floodplain linkages in great rivers may also play a role in maintaining relatively low Hg concentrations in fish. Connectivity with wetlands and floodplain habitats increases MeHg loading to streams (*1, 25, 30, 33*), resulting in elevated Hg concentrations in lotic fish (*12, 30, 34*). Human modifications of flow and riparian habitats (e.g., channel dredging, levee and lock and dam construction) have disconnected great river channels (and their food webs) from floodplains and associated wetland habitats in many reaches (*35*−*39*), potentially limiting inputs of MeHg from these productive zones of methylation and organic matter processing. Alternatively, the wetland effect may be greater in smaller lotic systems (e.g., *12, 25)* than in high-discharge systems like the great rivers due to dilution. The carbon contribution from well-connected backwater and floodplain habitats to main-channel food webs is minimal in the Upper Mississippi and Ohio Rivers (*38, 39*), and Hg dynamics may be similarly dominated by main-channel processes.

Considering this environmental setting, it was not surprising that environmental factors we measured were generally poor predictors of fish Hg concentrations. One factor driving poor predictive power was the low range of fish Hg values observed across the study area. We found that 80% of values were within 1 order of magnitude (20−200 ng g^{-1}), a range similar to that in western USA streams where relationships between Hg concentrations and environmental factors were also weak (*13*). This pattern was even more pronounced within rivers, where concentrations within a size class were fairly consistent over great distances (100s of rkm). This suggests that processes operating at the reach-scale were less important to Hg accumulation than global, larger-scale processes operating within each river system. Perhaps more importantly, the range of chemical variables seldom overlapped with thresholds associated with elevated Hg concentrations. Thus, correlations with these variables may have been weak because they did not occur at levels expected to affect Hg concentrations.

Fish Hg concentrations typically demonstrate high spatial variability, but evidence for this pattern comes from studies of small lakes, wetlands, and (more recently) streams (*1, 6, 9, 11, 12*). One implication of our findings is that widely accepted conceptual models of Hg bioaccumulation for other aquatic systems and regions lack applicability to these (and perhaps other) large river systems. This may be related to their unique hydrologic and ecological properties (e.g., high discharge systems integrating inputs received over large areas) and the high degree of connectedness among sites within a river (e.g., downstream sites are influenced by material exports from upstream sites). Water and fish tissue MeHg concentrations in lotic systems are more strongly controlled by external loading than by in situ processes such as stream bed production (*12, 40*). In that sense, large rivers may function more as conduits for Hg transport, with relatively little opportunity for biogeochemical reactions (e.g., methylation) to influence Hg accumulation in resident food webs.

Even though Hg concentrations were generally lower than those in other systems, fish consumption remains a risk to wildlife and humans. Exposure risk varied among the end points we considered, being greatest for kingfishers and lowest for humans, which had the highest risk threshold. Large sections of these rivers exceeded the risk factor for kingfisher (33%−75% of rkm among rivers), suggesting that large-scale reductions in atmospheric deposition of Hg will be needed to protect those species most sensitive to Hg exposure. Compared with kingfishers, the spatial extent of risk to humans was much more limited (1%−7% of rkm among rivers). Human risks can be further reduced by educating consumers to avoid or to limit intake of large-bodied, upper trophic-level species.

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Supporting Information Available

Mercury analytical methods and QA/QC procedures; collection of environmental variables; fish guild, length, and Hg data; and environmental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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