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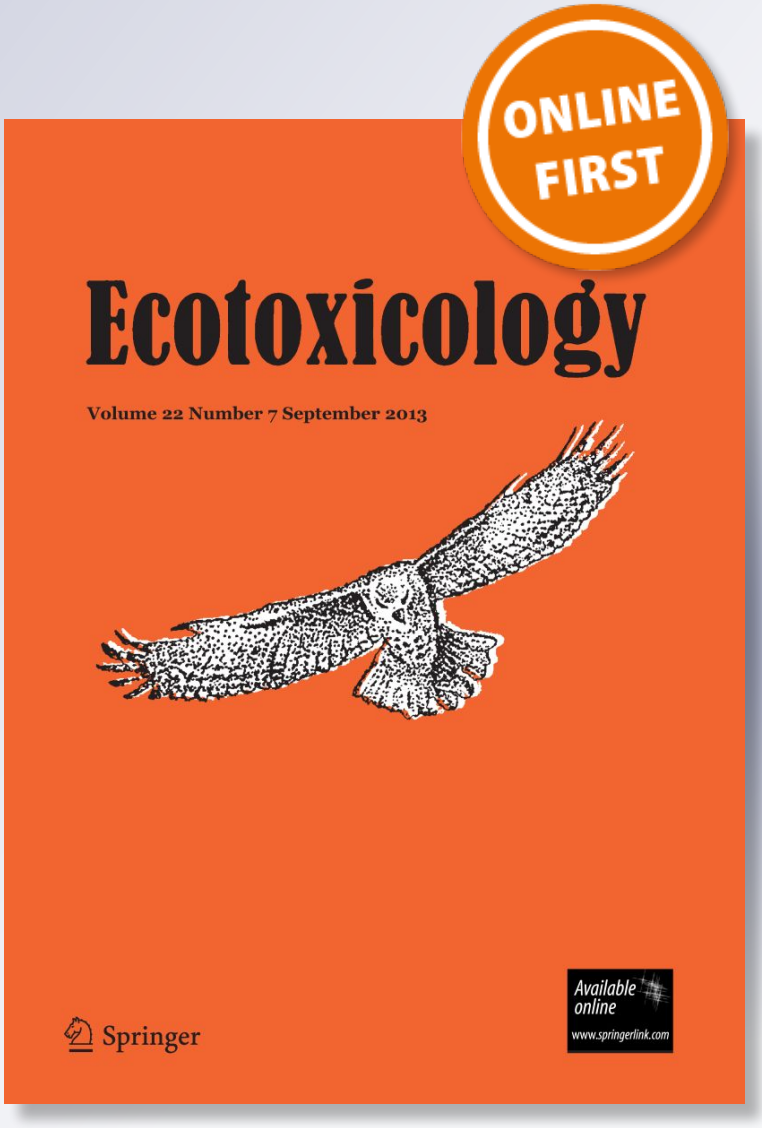

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Factors influencing fish mercury concentrations in Iowa rivers

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Abstract
Fish mercury concentrations have received considerable attention due to human health implications. Fish mercury concentrations are variable within and among systems due to a suite of biotic and abiotic influences that vary among regions and are difficult to predict. Understanding factors associated with variability in fish mercury concentrations would help guide consumption advisories. Mercury concentrations in channel catfish (*Ictalurus punctatus*, $n = 205$), flathead catfish (*Pylodictis olivaris*, $n = 123$), northern pike (*Esox lucius*, $n = 60$), smallmouth bass (*Micropterus dolomieu*, $n = 176$), and walleye (*Sander vitreus*, $n = 176$) were assessed in ten Iowa rivers and relationships with land use, water chemistry, and fish characteristics were explored. Mercury concentrations were generally low (mean among all species = 0.17 mg/kg, $n = 740$) but higher in flathead catfish, northern pike, smallmouth bass, and walleye than channel catfish and were positively related to fish length, age, trophic position, and $\delta^{13}C$ signatures. Phosphorus, sulfate, and percent open water and grassland were negatively related to fish mercury concentrations, whereas water hardness, nitrogen-ammonia, Human Threat Index, and percent wetland and forest were positively related to fish mercury concentrations. Fish collected from the Paleozoic Plateau ecoregion in northeast Iowa had higher mercury concentrations than other ecoregions in Iowa. Combined, these factors explained 70% of the variation in fish mercury concentrations. This study provides a comprehensive analysis of abiotic and biotic factors influencing fish mercury concentrations in lotic ecosystems at the individual and system scale that will help guide fish consumption advisories.

Keywords Consumption advisories · Contaminant · Trophic position · Bioaccumulation · Ecoregion · Water chemistry

Introduction

The presence of the neurotoxin methylmercury, hereafter referred to as mercury, in aquatic food webs has received much attention over the past couple decades because of its health implications for those who consume contaminated fish (Murata et al. 2006; Wentz et al. 2014). Numerous mercury monitoring programs have been developed to survey a variety of fish species and locations to develop fish consumption advisories (Wentz et al. 2014). While many factors have been suggested to influence fish mercury concentrations, they are inconsistent among studies and it is difficult to determine which abiotic and biotic factors are most important. An improved understanding of the determinants of mercury bioaccumulation and mercury cycling in the environment could help to guide mercury monitoring programs in predicting both sources and concentrations of mercury in fish.

Various abiotic and biotic factors have been related to mercury concentrations in freshwater fishes (Sackett et al. 2009; Rypel 2010; Tremain and Adams 2012). Fish mercury concentrations can vary among ecoregions (Sackett et al. 2009; Glover et al. 2010) and within ecoregion variation has been attributed to watershed land use variables, including wetland area (Rypel 2010; Wentz et al. 2014) and agricultural use (Benoit et al. 2003). In addition to watershed-scale factors, biotic factors including fish length, age, and trophic position, can also influence mercury concentrations (Rolfhus et al. 2011; Tremain and Adams 2012).

With up to 94% of mercury in fish attributed to dietary sources (Phillips and Gregory 1979; Houck and Cech Jr.

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Table 1 Characteristics of 16 reaches in 10 Iowa rivers examined in this study

River (U/D)	ID	Ecoregion	SO	WA	HTI	perWater	perWet	perFor	perGrass	perAg	perDev
Cedar (D)	1	IS	6	17568	52	1.0	0.5	7.2	14.9	72.9	3.1
Cedar (U)	2	IS	6	6268	68	1.2	0.6	6.2	14.8	73.9	2.9
Des Moines (D)	3	DSML	7	33223	67	1.4	1.2	12.4	20.6	61.2	2.6
Des Moines (U)	4	DSML	6	12226	50	1.0	1.7	5.3	11.3	77.8	2.5
East Nishnabotna	5	LHSRP	5	2971	54	0.8	0.2	4.8	22.2	69.5	2.0
Iowa (D)	6	SIRLP	6	12396	51	1.2	1.1	9.0	20.5	65.1	2.5
Iowa (U)	7	SIRLP	6	8044	49	1.2	1.4	8.1	17.9	68.4	2.4
Little Sioux	8	NILP	6	6492	50	1.9	0.7	5.1	17.2	72.6	2.0
Maquoketa (D)	9	SIRLP	6	4834	47	0.6	0.2	12.9	23.4	59.8	2.3
Maquoketa (U)	10	IS	5	2423	50	0.6	0.2	12.0	19.7	64.6	2.3
Rock	11	NILP	6	1998	43	0.5	0.6	1.4	11.4	82.8	2.3
Skunk	12	SIRLP	6	11228	52	0.8	0.8	11.4	21.0	62.5	2.5
Upper Iowa (D)	13	PP	5	2025	39	0.6	0.4	22.1	29.7	44.0	2.3
Upper Iowa (U)	14	IS	4	764	52	0.5	0.5	11.5	25.1	59.5	2.3
Wapsipinicon (D)	15	IS	5	6557	48	0.8	0.5	9.1	14.7	72.2	2.3
Wapsipinicon (U)	16	IS	5	4018	53	0.7	0.4	8.8	14.9	72.5	2.4

ID refers to the identification number shown in Fig. 1

Land use variables are percentages of the watershed area

U upstream sampling location, *D* downstream sampling location. Ecoregions: *DSML* Des Moines Lobe, *IS* Iowan Surface, *NILP* Northwest Iowa Loess Prairies, *PP* Paleozoic Plateau, *SIRLP* Southern Iowa Rolling Loess Prairies, *SO* stream order, *WA* watershed area (km^2), *HTI* Human Threat Index, *perWater* percent open water, *perWet* percent wetland area, *perFor* percent forested land, *perGrass* percent grassland area, *perAg* percent row crop agriculture, *perDev* percent developed land

2004; Pickhardt et al. 2006), there are distinct interspecific and intraspecific differences in mercury concentrations among fishes related to food web dynamics (Atwell et al. 1998; Sackett et al. 2009). As mercury bioaccumulates, larger and older piscivorous fishes tend to have higher mercury concentrations than smaller planktivorous or insectivorous fishes (Olsson 1976; Wiener and Spry 1996; Tremain and Adams 2012). The use of nitrogen and carbon stable isotopes ($\delta^{15}N$ and $\delta^{13}C$) provide a technique to precisely estimate trophic position and energy sources in fishes (Atwell et al. 1998), improving on previous evaluations that have only categorically assigned a general trophic position to different species (e.g., Sackett et al. 2009). Nitrogen isotope ratios ($^{15}N/^{14}N$) allow the estimation of trophic position (Cabana and Rasmussen 1994; Post 2002) while carbon isotope ratios ($^{13}C/^{12}C$) estimate the source of dietary carbon and energy flow (Overman and Parrish 2001) and have been positively related to fish mercury concentrations in some situations (e.g., Cabana and Rasmussen 1994; Atwell et al. 1998).

Although a large body of literature exists evaluating the effects of biotic and abiotic factors on mercury concentrations of fish in lakes (e.g., Larsson et al. 1992; Pickhardt et al. 2002; Rypel 2010), results on which factors are important are inconsistent among studies and few evaluations have comprehensively evaluated the influence of these factors on mercury concentrations in lotic fishes (but see Glover et al. 2010; Wentz et al. 2014). Regional, local, and individual differences in abiotic (e.g., water chemistry) and biotic (e.g., trophic position) characteristics may also explain much of the variability in mercury concentrations in lotic fishes, but have seldom been evaluated. Thus, the objective of this study was to explore the influence of a suite of abiotic and biotic factors on mercury concentrations in fishes of Iowa rivers. We hypothesized that variation in fish mercury concentrations would likely be explained by multiple abiotic and biotic factors, including water chemistry, watershed land use, and individual fish characteristics. An understanding of environmental factors related to mercury concentrations of lotic fishes would help guide consumption guidelines for these important fisheries.

Methods

Fish Collection & Processing

Our goal was to sample 10–20 individuals of each of five species of fish by 1 cm length groups (i.e., 1 individual/species/cm) at each sampling location. Substantial effort was made to collect a minimum of 10 fish of each species from each location, but fewer fish or duplicate fish within a

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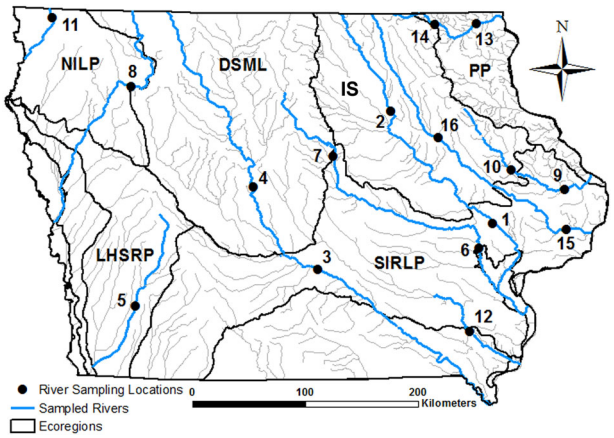

Fig. 1 Fish sampling locations (black circles) on 10 Iowa rivers. Numbers next to black dots refer to an identification number (Table 1). Ecoregions: DSML Des Moines Lobe, IS Iowan Surface, NILP Northwest Iowa Loess Prairies, LHSRP Loess Hills and Steep Rolling Prairies, PP Paleozoic Plateau, SIRLP Southern Iowa Rolling Loess Prairies

length group (i.e., two fish within a 1 cm length group) were used if 10 individuals could not be collected within a reasonable amount of sampling effort. Fishes were collected primarily with pulsed DC boat electrofishing, but angling was used to supplement electrofishing catches when needed.

Channel catfish (*Ictalurus punctatus*, $n = 205$), flathead catfish (*Pylodictis olivaris*, $n = 123$), northern pike (*Esox lucius*, $n = 60$), smallmouth bass (*Micropterus dolomieu*, $n = 176$), and walleye (*Sander vitreus*, $n = 176$) were collected between March and October in 2014 and 2015 from three rivers in the Missouri River watershed (Little Sioux River, Rock River, and East Nishnabotna River) and seven rivers in the Mississippi River watershed (Skunk River, Iowa River, Cedar River, Des Moines River, Upper Iowa River, Maquoketa River, and Wapsipinicon River; Table 1, Fig. 1) throughout Iowa. With the exception of the Skunk River, fishes sampled in the six main Mississippi tributaries were sampled from upstream and downstream locations in each river to evaluate spatial differences in mercury accumulation within river systems. Fish were collected upstream of Saylorville reservoir and downstream of Red Rock reservoir on the Des Moines River, upstream and downstream of Coralville reservoir on the Iowa River, upstream of Waterloo, Iowa and downstream of Cedar Rapids, Iowa on the Cedar River, upstream of Anamosa, Iowa and downstream of Dixon, Iowa on the Wapsipinicon River, upstream of Monticello, Iowa and downstream of Maquoketa, Iowa on the Maquoketa River, and upstream of Decorah, Iowa and downstream near Dorchester, Iowa on the Upper Iowa River (Fig. 1).

After collection, fishes were measured for total length (TL mm) and weight (g) and euthanized. Fish not processed immediately after capture were wrapped in aluminum foil, labeled with weight and length measurements, and frozen whole until processing. In the laboratory, sex was determined and aging structures applicable to each species were removed (e.g., sagittal otoliths for northern pike, smallmouth bass, and walleye; lapilli otoliths for channel catfish and flathead catfish). All tissue samples were collected following USEPA fish tissue extraction protocols (USEPA 2000; USEPA 2003). Two 5–10 g samples of skinless dorsal axial muscle tissue were removed from each individual, one for mercury analysis and another for stable isotope analysis of $\delta^{15}N$ and $\delta^{13}C$. To avoid cross contamination, nitrile gloves were replaced and scalpels were thoroughly rinsed and sanitized with 95% ethanol after taking tissue samples from each fish. Tissue samples were stored in a −10 °C freezer until transport for analysis.

Frozen fish tissue samples were processed at the State Hygienic Lab (SHL), Ankeny, Iowa, for mercury analysis. Mercury concentration was determined from acid-digested tissue samples using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) using USEPA Method 6020A (1998) and reported as total wet-weight mercury concentration (mg/kg). Mercury detection threshold was 0.05 mg/kg, but SHL reports detected fish mercury concentrations below 0.05 mg/kg when possible. Of the 740 observations in the dataset, only three channel catfish from separate rivers had undetected mercury concentrations (reported as <0.05 mg/kg from SHL) and were assigned a value of half the detection limit (0.025 mg/kg). An additional 13 observations had reported values less than the detection limit (three observations were reported as 0.03 mg/kg, and 10 observations were reported as 0.04 mg/kg). Quality assurance and control were done with a standard operating procedure of periodic calibrations and duplicate analyses. Duplicate samples were analyzed every 53 samples and the mean relative percent difference (RPD) was 3.81% (median = 2.00%, range = 0%–18.75%, $n = 14$). Duplicate samples were also analyzed approximately every 16 samples as part of a larger dataset where the mean RPD was 3.70% (median = 0.85%, range = 0%–50%, $n = 110$).

Otoliths were the primary structure used to estimate the age for most fish (used for 99% of individuals), but pectoral (ictalurids) or dorsal (smallmouth bass and walleye) spines (1% of individuals) were used when otoliths were destroyed or unreadable. Otoliths and spines were cross-sectioned using a slow speed saw with a diamond wafering blade and pictures were taken under a microscope. Structures were aged at least two times without prior knowledge of fish size or capture location. Additional cross-sections were taken and ages were re-estimated when there were disagreements among age estimates.

Concurrently with fish sampling, plain pocketbook mussels *Lampsilis cardium* were collected near fish

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collection sites for stable isotope analysis. These samples provide isotopic baseline data to standardize fish trophic position and energy flow estimates among systems (Overman and Parrish 2001). Between one and three mussels were collected from the upstream and downstream location on all six rivers where fish were collected, except for the downstream location on the Des Moines River where no mussels could be located despite extensive searching. We also collected mussels from the Little Sioux, Rock, and South Skunk rivers. However, no mussels were found on the East Nishnabotna River; thus, baseline values of $\delta^{15}N$ or $\delta^{13}C$ could not be directly estimated for this system. To include this river in the analysis, data from the other rivers were used to develop linear regression models between fish length and both trophic position and $\delta^{13}C$ to predict species-specific trophic position and $\delta^{13}C$ by for these fish.

Fish and mussel tissue samples were dried in an oven at 50 °C for 24–48 h. Tissue samples were crushed to a fine powder with a mortar and pestle and stored in glass scintillation vials. Approximately 1–2 µg of sample were folded in 7-mm tin capsules. Once in tin capsules, samples were transported to the Stable Isotope Laboratory at Iowa State University for stable isotope analyses of $\delta^{15}N$ and $\delta^{13}C$. Samples were analyzed using a stable isotope mass spectrometer and isotopic signatures are reported in parts per thousand using the following equation (Atwell et al. 1998):

$$\delta X = [R\,\text{sample}/R\,\text{standard}) - 1] \times 1000$$

where X is $\delta^{15}N$ or $\delta^{13}C$ and R is the ratio $^{15}N{:}^{14}N$ or $^{13}C{:}^{12}C$ (Atwell et al. 1998). Fish trophic position was calculated using the following formula developed by Cabana and Rasmussen (1996):

$$\text{Trophic position} = \left[\left(\text{fish}\,\delta^{15}\text{N} - \text{mussel}\,\delta^{15}\text{N}\right)/3.4\right] + 2$$

Watershed Land Use and Water Chemistry Data

Water quality and water chemistry data for each river were extracted from the Iowa Department of Natural Resources (IADNR) Ambient Stream Monitoring program online database (IADNR 2015). Data extracted from this database included analytes that were present for all stream monitoring sites. Analytes included in the database are hardness (CaCO3 mg/L), nitrate + nitrite (NN; mg/L), nitrogen (ammonia; N.A; mg/L), orthophosphate (ortho; mg/L), pH, phosphate-phosphorous (phos; mg/L), dissolved solids (DS; mg/L), total suspended solids (TSS; mg/L), total volatile suspended solids (TVSS; mg/L), and sulfate (mg/L). Water samples were collected by the IADNR monthly from each of 91 river monitoring sites throughout the state. Water quality variables were averaged for individual fish based upon the age of each fish. For example, a 3-year-old fish collected in 2015 had water quality metrics averaged for years 2012–2015. Upstream and downstream river monitoring sites were only available on the Iowa River, Des Moines River, Cedar River, and Wapsipinicon River. Water quality metrics were used from one sampling location for fishes collected from upstream and downstream locations on the Upper Iowa and Maquoketa rivers. River watershed area (WA, km^2) was determined using ArcGIS software. Watershed land use data were extracted from the Human Threat Index (HTI) database developed by Annis et al. (2010). Information compiled for each river sampling site included watershed land use variables such as open water (perWater, %), wetland area (perWet, %), grassland area (perGrass, %), forested land (perFor, %), row-crop agricultural (perAg, %), and developed land (perDev, %). Other variables extracted from the HTI database included stream order (SO) and three HTI values: a local HTI value, a watershed HTI value, and an overall HTI value. HTI values are on a scale of 0–100 and are assigned based on how impacted the stream segment is with higher values indicating a higher human impact on the stream segment (Annis et al. 2010). Impact assessment is based on impervious surfaces, landfills, dams, mining operations, agriculture, and other forms of anthropogenic disturbance within a watershed. In addition to these variables, Julian day (JD) based on the date of fish collection was included to account for potential seasonal influence on fish mercury concentrations in Iowa (Mills et al. 2018).

Statistical Analyses

The initial set of 21 water chemistry and watershed land use variables was reduced by eliminating correlated variables that represent similar attributes ($r > 0.70$, $P < 0.01$). Variables eliminated during this process included orthophosphate, total volatile suspended solids, and local and watershed HTI. Phosphate-phosphorous and orthophosphate were correlated ($r = 0.86$, $P < 0.01$) and represented similar measures of nutrients; thus, orthophosphate was eliminated from the analysis. Total suspended solids and total volatile suspended solids were correlated ($r = 0.86$, $P < 0.01$) and represent similar measures of particulates in the water column; thus, the total volatile suspended solids variable was eliminated. Both local HTI ($r = 0.81$, $P < 0.01$) and watershed HTI ($r = 0.76$, $P < 0.01$) were correlated with overall HTI values. Overall HTI represents a combination of local and watershed HTI (Annis et al. 2010), and thus, the local and watershed HTI variables were removed from further analysis to reduce redundancy in the explanatory variables. All retained variables were then evaluated to ensure that the residuals were normally and independently

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distributed with a mean of 0 and equal variance. Fish mercury concentrations and percent watershed composition variables were log-transformed to normalize residuals.

Building the predictive model

A model selection procedure was used to evaluate a suite of variables for predicting fish mercury concentrations. Regression subset selection, hereon referred to as "regsubsets", under the R-package, "leaps", was used to evaluate all model combinations in two parts (Thomas Lumley using Fortran code by Alan Miller 2009): fish-level variables (biotic and water chemistry data) and river-level variables (river specific information and watershed composition data) and their appropriate interactions. First, regsubsets was conducted on fish-level variables with a fixed effect on the 'River' term. The 'River' variable is a term unique to each river sampling location was used to account for variation in fish mercury concentrations among rivers while regsubsets selects models that explain the most variation in fish mercury concentrations using fish-level variables. Models were created using the exhaustive model selection procedure (all model combinations) and sorted using Akaike's Information Criterion (AIC_c) as the model selection criterion (Burnham and Anderson 1998). Fish-level variables and interactions included in the top model were retained when evaluating river-level variables. All other fish-level variables were removed from the model for the succeeding steps in the analysis.

Next, another exhaustive regsubsets model selection procedure using AIC_c to rank models was used on river-level variables to determine if any additional variation in fish mercury concentrations could be explained by river specific characteristics. For this step, the 'River' term was omitted and the retained fish-level variables, determined in the previous step, were retained in all competing models during the model selection procedure. Using the results of the top AIC_c models from each model selection procedure, a final multiple linear regression model was created to predict fish mercury concentrations and to describe variation in fish mercury concentrations within and among Iowa river systems. Finally, analysis of variance (ANOVA) was conducted for all categorical variables identified during the AIC_c model selection procedure to identify variation in fish mercury concentrations among groups. Level of significance for the ANOVAs was determined at $\alpha = 0.05$.

Results

The 10 rivers sampled ranged widely in several characteristics (Table 1). Watershed area ranged from 764 km^2 in the upstream portion of the Upper Iowa River to more than

Table 2 Species-specific attributes including number (#) of fish collected by species, number of rivers each species was collected in, proportions of samples by sex [female (F), male (M), and unknown (Unk.)], fish mercury concentration [mean, standard deviation (SD), and maximum (Max.)], fish total length [mean, minimum (Min.)-maximum], fish age (mean, minimum-maximum), fish trophic position (mean, minimum-maximum), and fish carbon signature ($\delta^{13}C$; mean, minimum-maximum)

Species	# Fish	# Rivers	Sex (%)			Hg (mg/kg)			Length (mm)		Age (years)		Trophic position		$\delta^{13}C$					
			F	M	Unk.	Mean	SD	Max.	Mean	Min. – Max.	Mean	Min.–Max.	Mean	Min.–Max.	Mean	Min., Max.	TL R^2 (*P*-value)	Age R^2 (*P*-value)	TP R^2 (*P*-value)	$\delta^{13}C$ R^2 (*P*-value)
Channel catfish	205	8	51	33	16	0.12 [a]	0.08	0.59	460	251–721	8.3	1–17	3.03 [a]	1.49–4.29	−24.51 [a]	−28.23, −20.76	0.37 (<0.01)	0.11 (<0.01)	<0.01 (0.51)	<0.01 (0.71)
Flathead catfish	123	7	57	41	2	0.18 [b]	0.14	0.81	511	261–1,075	7.5	1–33	3.59 [b]	2.56–4.54	−25.08 [b]	−28.32, −21.98	0.62 (<0.01)	0.65 (<0.01)	0.29 (<0.01)	<0.01 (0.53)
Northern pike	60	5	57	37	6	0.15 [b]	0.06	0.35	579	303–995	3.9	1–8	3.64 [b,c]	2.69–4.42	−24.77 [a,b]	−27.78, −22.84	0.37 (<0.01)	0.39 (<0.01)	0.06 (0.07)	0.05 (0.09)
Smallmouth bass	176	7	50	49	1	0.19 [b]	0.13	0.86	302	168–461	3.1	1–10	3.53 [b]	2.58–4.63	−24.38 [a]	−28.94, −21.89	0.57 (<0.01)	0.63 (<0.01)	0.07 (<0.01)	<0.01 (0.37)
Walleye	176	7	40	29	31	0.20 [b]	0.12	0.66	401	215–695	2.8	0–9	3.75 [c]	2.83–4.71	−24.57 [a]	−28.76, −21.17	0.19 (<0.01)	0.28 (<0.01)	0.08 (<0.01)	0.18 (<0.01)
Total	740	10	50	37	13	0.17	0.12	0.86	426	168–1,075	5.3	0–33	3.47	1.49–4.71	−24.61	−28.94, −20.76	0.14 (<0.01)	0.07 (<0.01)	0.14 (<0.01)	0.02 (<0.01)

Means within fish trophic position and $\delta^{13}C$ columns sharing a common superscript are not significantly different (ANOVA; $P > 0.05$). R^2 and *P*-values refer to simple linear regressions between log-transformed mercury concentrations and total length (mm), age, trophic position, and carbon signature by species

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Table 3 Top 10 multiple regression models developed to predict fish mercury concentrations using fish-level variables (see Methods) ordered by Akaike's information criterion (AIC_c) using regression subset selection procedure

Model	K	AIC_c	ΔAIC_c	w_i
Species, Sex, Age, TL, $\delta^{13}C$, TP, Hardness, N.A, Phos, TSS, Sulfate, Species*Age, Species*Sex, Age*TL	28	−794.93	0.00	0.38
Species, Sex, Age, TL, $\delta^{13}C$, TP, Hardness, N.A, Phos, Sulfate, Species*Age, Species*Sex, Age*TL	27	−794.17	0.76	0.26
Species, JD, Sex, Age, TL, $\delta^{13}C$, TP, Hardness, N.A, Phos, TSS, Sulfate, Species*Age, Species*Sex, Age*TL	30	−793.67	1.26	0.20
Species, Sex, Age, TL, $\delta^{13}C$, TP, Hardness, N.A, DS, TSS, Species*Age, Species*Sex, Age*TL	26	−792.50	2.42	0.11
Species, JD, Sex, Age, TL, $\delta^{13}C$, TP, Hardness, N.A, pH, Phos, DS, TSS, Sulfate, Species*Age, Species*Sex, Age*TL	33	−789.70	5.23	0.03
Species, Sex, Age, TL, $\delta^{13}C$, Hardness, N.A, DS, TSS, Species*Age, Species*Sex, Age*TL	25	−788.22	6.71	0.01
Species, Age, TL, $\delta^{13}C$, TP, Hardness, N.A, DS, TSS, Species*Age, Age*TL	23	−779.67	15.26	0.00
Species, JD, Sex, Age, TL, $\delta^{13}C$, TP, Hardness, NN, N.A, pH, Phos, DS, TSS, Sulfate, Species*Age, Species*Sex, Age*TL	40	−776.82	18.11	0.00
Species, Age, TL, $\delta^{13}C$, Hardness, N.A, DS, TSS, Species*Age	21	−769.01	25.92	0.00
Species, Age, TL, $\delta^{13}C$, Hardness, N.A, DS, Species*Age	20	−761.10	33.83	0.00

Each model was produced from 740 observations

K the number of parameters in the model (includes Waterbody), ΔAIC_c the distance of each model from the best AIC_c model, and w_i the model weight (a measure of relative strength)

33,000 km^2 in the downstream section of the Des Moines River. All rivers had little open water, wetlands, or developed lands within their watersheds (<4%), but had a wide range of forested and grasslands (up to 30%). Watersheds of all locations sampled were dominated by agriculture (≥44%).

Channel catfish were the most commonly collected ($n = 205$) and ubiquitous species and were collected from 8 out of 10 rivers sampled (Table 2). Smallmouth bass and walleye ($n = 176$, each) were collected from both upstream and downstream locations on the six main Mississippi River tributaries and were the only species collected from the Upper Iowa River. Flathead catfish were sampled from two of the six upstream sites and five of the six downstream sites. Northern pike ($n = 60$) were encountered less frequently but were sampled from the downstream location on the Des Moines River and the upstream locations on the Iowa, Cedar, and Wapsipinicon rivers (Table 2). Among species and rivers, fish ranged in length from 168–1,075 mm (mean = 426 mm) and from 0–33 years of age (mean = 5.3 years; Table 2). Mercury concentrations ranged from ≤ 0.05 (5.5% of samples) to 0.86 mg/kg in a smallmouth bass collected from the Upper Iowa River. Cumulatively, 10.3% (76 of 740 total samples) of fish collected had mercury concentrations ≥ 0.30 mg/kg (1 meal/week consumption advisory; USEPA 2010).

Fish-level factors

The top fish-level AIC_c model contained the main effects of fish species, sex, age, length, $\delta^{13}C$, trophic position (TP), water hardness, nitrogen-ammonia, phosphorous, total suspended solids, and sulfate along with three main effect interactions ($\Delta AIC_c = 0$, $w_i = 0.38$; Table 3). The second and third ranked models also received some support ($\Delta AIC_c < 2$, $w_i > 0.20$) and included the additional main effect of Julian Day (Table 3). Among the top ten fish-level AIC_c models evaluated, all contained biotic variables fish species, age, $\delta^{13}C$, and length, suggesting these variables are important predictors of fish mercury concentrations. Variation in the presence of water chemistry variables accounted for the majority of the differences among models (Table 3).

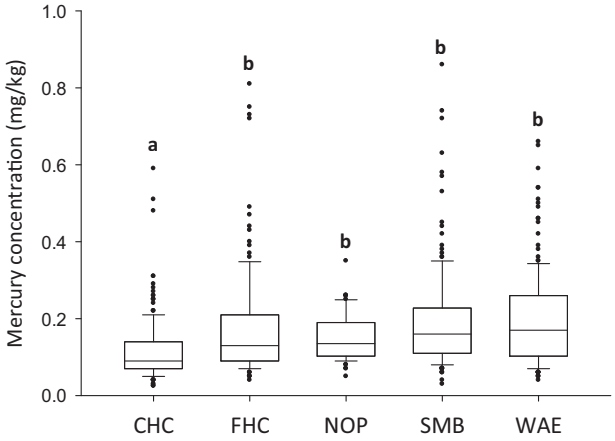

Fig. 2 Box plots of fish mercury concentrations (mg/kg) by species. The line within the box represents the median value. Dimensions of the box represent the 25th and 75th percentiles. Error bars represent the 10th and 90th percentiles. Individual points are outliers. Boxes sharing a common letter are not significantly different (ANOVA; $P > 0.05$)

Among rivers, flathead catfish, northern pike, smallmouth bass, and walleye had higher mercury concentrations than channel catfish (Fig. 2; ANOVA; $F_{4,735} = 28.26$, $P <$

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Table 4 Parameter estimates (± 95% confidence intervals; C.I.) of all variables and interactions retained in the most supported fish-level and river-level models

Variable	Parameter estimate ± 95% C.I.			Variable	Parameter estimate ± 95% C.I.		
Intercept	−0.80	−2.35	0.74	EcoregionIS	−0.31	−0.76	0.14
FHC	0.35	0.13	0.58	EcoregionLHRSP	2.29	1.19	3.39
NOP	0.50	0.19	0.81	EcoregionNILP	2.37	1.69	3.06
SMB	0.68	0.47	0.89	EcoregionPP	0.24	−0.24	0.72
WAE	0.61	0.38	0.84	EcoregionSIRLP	0.07	−0.38	0.51
SexMale	−0.16	−0.27	−0.05	Age*FHC	0.01	−0.02	0.03
SexUnk	0.04	−0.11	0.18	Age*NOP	−0.03	−0.09	0.04
Age	0.10	0.07	0.13	Age*SMB	0.07	0.04	0.11
TL	0.002	0.001	0.002	Age*WAE	0.04	−0.01	0.08
$\delta^{13}C$	0.08	0.05	0.10	SexMale*FHC	0.04	−0.13	0.21
TP	0.14	0.06	0.23	SexMale*NOP	0.28	0.07	0.50
Hardness	0.006	0.004	0.01	SexMale*SMB	0.09	−0.06	0.24
N.A	3.78	2.50	5.06	SexMale*WAE	0.35	0.18	0.53
Phos	−0.92	−1.40	−0.45	SexUnk*FHC	−0.06	−0.50	0.38
TSS	−0.001	−0.002	0.001	SexUnk*NOP	−0.26	−0.66	0.14
Sulfate	−0.02	−0.03	−0.01	SexUnk*SMB	0.04	−0.66	0.75
HTI	0.03	0.01	0.04	SexUnk*WAE	−0.02	−0.22	0.19
logperWater	−1.08	−1.44	−0.72	Age*TL	−0.0001	−0.0001	−0.00001
logperWet	0.62	0.46	0.78				
logperFor	1.49	0.96	2.01				
logperGrass	−2.32	−3.05	−1.58				

0.001) and mean mercury concentrations of all species was less than the EPA criterion of 0.30 mg/kg (Table 2). Only 5 of 205 channel catfish samples (2%) and 1 of 60 northern pike (2%) exceeded the EPA advisory limit of 0.30 mg/kg, but the proportion of individuals exceeding the advisory limit increased for flathead catfish (14 of 123 fish, 11%), smallmouth bass (26 of 176 fish, 15%), and walleye (30 of 176 fish, 17%). Mercury concentrations among fish species were similar between males and females but was lower when sex was unknown (ANOVA; $P = 0.05$). Based on the interaction between sex*species, male northern pike and walleye had higher mercury concentrations than females (Table 4; Fig. 3) but mercury concentrations were similar between sexes for the other species (95% CI overlapped with 0).

Fish mercury concentrations increased with fish length and age (Tables 2 and 4; Fig. 3), but based on differences in R^2 values, age explained more variation in fish mercury concentrations than length for flathead catfish, northern pike, smallmouth bass, and walleye. Trophic position and $\delta^{13}C$ were positively related to fish mercury concentrations (Table 4) but trophic position explained more variation than $\delta^{13}C$ signatures in all species except channel catfish and walleye (Table 2). Relationships between fish mercury concentrations and water chemistry variables were highly variable. Mercury concentrations were positively related to nitrogen-ammonia and water hardness and negatively related to phosphorous and sulfates (Table 4). In contrast, the slope of total suspended solids did not differ from zero.

River-level factors

The top river-level AIC_c model contained HTI, ecoregion, and percent watershed land use variables open water, wetlands, forested land, and grassland area ($\Delta AIC_c = 0$, $w_i = 0.50$; Table 5). Although not found in the top model, watershed area, stream order, and percent land in agriculture and developed lands were in the second and third ranked models that received some support ($\Delta AIC_c < 2.5$; $w_i > 0.15$; Table 5). None of the models receiving support contained the categorical upstream/downstream variable, suggesting no difference in fish mercury concentrations between upstream and downstream locations among Iowa interior rivers.

Several landscape variables helped explain variation in fish mercury concentrations among rivers. First, fish mercury concentrations were higher in the Paleozoic Plateau (PP) ecoregion than other ecoregions (ANOVA; $F_{5,734} = 14.42$, $P < 0.001$) that were similar to one another ($P > 0.05$; Fig. 4). Second, the HTI and percentage of forested and wetland area within a watershed were positively related to fish mercury concentrations, whereas percentage of

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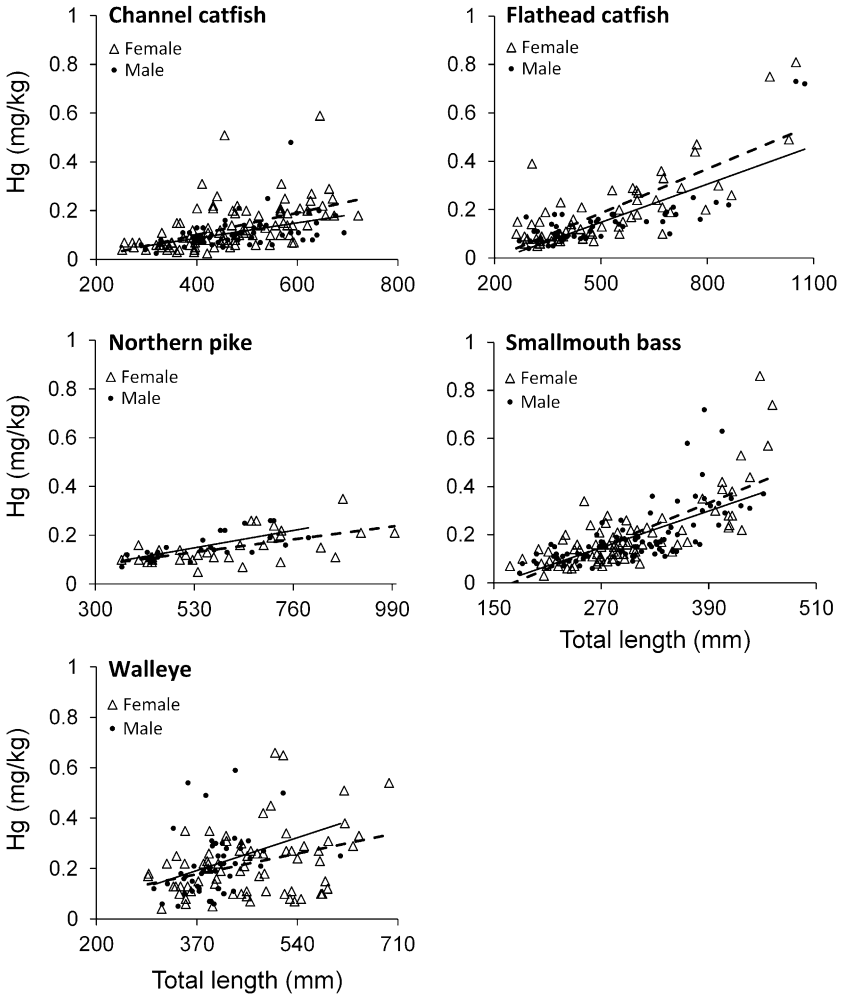

Fig. 3 Channel catfish, flathead catfish, northern pike, smallmouth bass, and walleye mercury concentrations (mg/kg) plotted by sex (female = Δ; male = •) versus total length (mm). Dashed line is the regression line for females; solid line is the regression line for males

watershed as open water and grasslands were negatively related to fish mercury concentrations (Table 4). The final combined multiple regression model based on variables included in the top fish-level and river-level AIC_c models explained 70% of the variation in fish mercury concentrations among Iowa interior rivers ($R^2 = 0.70$, $P < 0.001$; Fig. 5).

Discussion

The robust dataset collected on five common sport fishes from rivers encompassing a broad range of environmental conditions allowed us to evaluate a suite of factors influencing lotic fish mercury concentrations. Only channel catfish had lower mercury concentrations compared to other species, and across species, 10.3% (71 of 741 samples) of fish evaluated had mercury concentrations > 0.30 mg/kg (1 meal per week consumption advisory, USEPA 2000) whereas no fish had mercury concentrations > 1.0 mg/kg (no consumption advisory, USEPA 2000). Part of the reason why only a low proportion of fish collected had elevated mercury concentrations is that we collected fishes across the entire size range observed during collection, where many of the smaller individuals had low mercury concentrations; however, a larger proportion of larger fish had concentrations surpassing 0.30 mg/kg mercury. Collecting fish from such a wide size distribution was beneficial by providing insights into how mercury concentrations increase with factors related to fish size (e.g., growth, trophic position, energy acquisition, etc.). Additionally, regulated rivers may have lower mercury levels than unregulated rivers (Rypel et al. 2008) and rivers throughout the Midwest, and much of the world, are highly modified due to channelization, impoundments, and low-head dams, potentially contributing to low mercury concentrations overall. Despite relatively low overall mercury concentrations, we identified a suite of biotic and abiotic factors that explained a majority of the variation in fish mercury concentrations within and among lotic ecosystems.

Of the five species evaluated, only channel catfish had lower mercury concentrations than the other species. While

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Table 5 Top 10 multiple regression models developed to predict fish mercury concentrations using river-level variables (see Methods) ordered by Akaike's information criterion (AIC_c) using regression subset selection procedure

Model	K	AIC_c	ΔAIC_c	w_i
HTI, logperWater, logperWet, logperFor, logperGrass, Ecoregion	37	−806.10	0.00	0.50
SO, HTI, logperWater, logperWet, logperFor, logperAg, logperDev, Ecoregion	38	−804.97	1.13	0.29
WA, HTI, logperWater, logperWet, logperFor, logperAg, logperDev, Ecoregion	39	−803.98	2.13	0.17
SO, WA, HTI, logperWater, logperWet, logperFor, logperAg, logperDev, Ecoregion	41	−800.04	6.07	0.03
SO, WA, HTI, logperWater, logperWet, logperFor, logperGrass, logperAg, logperDev, Ecoregion	42	−798.06	8.05	0.01
logperWater, logperWet, logperFor, logperAg, Ecoregion	35	−794.13	11.97	0.00
logperWet, logperGrass, logperAg, logperDev, Ecoregion	34	−783.34	22.76	0.00
WA, logperWet, logperFor, logperDev, Ecoregion	33	−778.39	27.71	0.00
logperWet, logperFor, logperDev, Ecoregion	32	−775.74	30.37	0.00
logperWet, logperDev, Ecoregion	31	−772.16	33.94	0.00

Each model was produced from 740 observations

K the number of parameters in the model (includes Species, Age, $\delta^{13}C$, TP, Hardness, NN, N.A, Phos, DS), ΔAIC_c the distance of each model from the best AIC_c model, and w_i the model weight (a measure of relative strength)

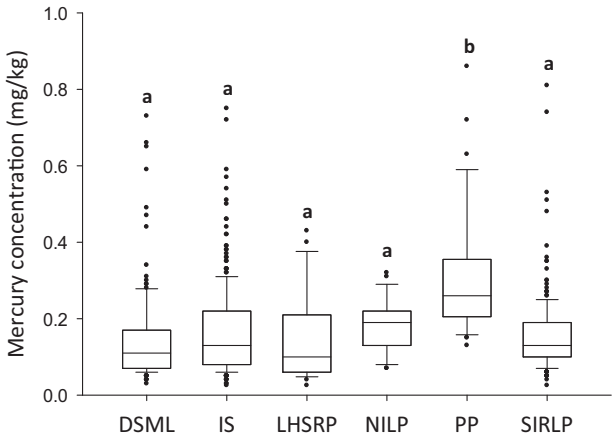

Fig. 4 Box plots of fish mercury concentrations (mg/kg) by ecoregion. DSML Des Moines Lobe, IS Iowan Surface, LHSRP Loess Hills and Steeply Rolling Prairies, NILP Northwest Iowa Loess Prairies, PP Paleozoic Plateau, SIRLP Southern Iowa Rolling Loess Prairies. The line within the box represents the median value. Dimensions of the box represent the 25th and 75th percentiles. Error bars represent the 10th and 90th percentiles. Individual points are outliers. Boxes sharing a common letter are not significantly different (ANOVA; $P > 0.05$)

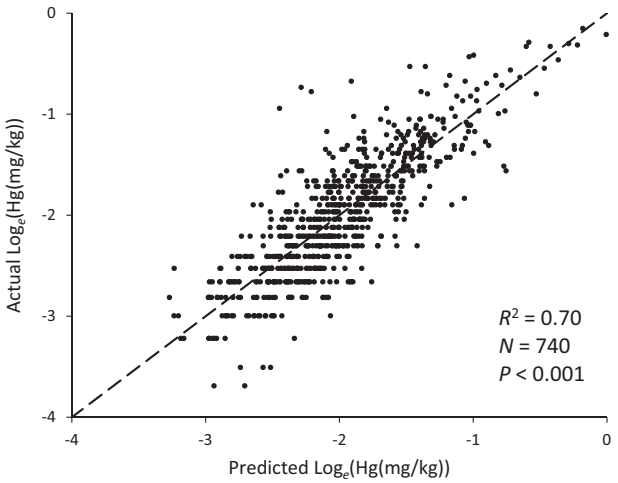

Fig. 5 Predicted versus observed log-transformed fish mercury concentrations. The long dashed line represents the 1:1 line

previous work has evaluated the effects of trophic level by assigning a categorical variable to different species (e.g., Sackett et al. 2009), we were able to directly estimate fish trophic position ($\delta^{15}N$) and resource use ($\delta^{13}C$) through the use of stable isotope analysis. Our results indicate that, in addition to lower mercury concentrations, channel catfish also had a lower mean trophic position, likely due to omnivorous feeding habits (Tyus and Nikirk 1990). Similar to previous findings (Scheuhammer et al. 2007; Sackett et al. 2009), our results indicate that mercury concentrations increase with trophic position, regardless of fish species, where individuals with higher trophic position are more reliant on fish prey and have higher mercury concentrations, likely due to bioaccumulation (Cabana and Rasmussen 1994; Atwell et al. 1998; Pickhardt et al. 2002). Thus, we anticipated that more piscivorous species, including flathead catfish, walleye, and northern pike, would have higher mercury concentrations than species such as smallmouth bass that tend to rely more on invertebrates. However, our results also indicate that mercury concentrations were similar among these species, suggesting substantial variation in diets within a species among locations. Fish mercury concentrations also increased with $\delta^{13}C$ values, suggesting mercury concentrations are higher in individuals that rely more on allochthonous than autochthonous energy sources.

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Comparatively, lake trout (*Salvelinus namaycush*) mercury concentrations were inversely related to $\delta^{13}C$ signatures, suggesting higher mercury concentrations in individuals deriving energy from pelagic versus littoral sources (Power et al. 2002).

Instead of species-specific differences, other variables were more important determinants of mercury concentrations. For example, mercury concentrations varied due to the interaction between sex and species, where male northern pike and walleye had higher mercury concentrations than females at a given length. Mercury concentrations were also positively related to fish length and age, indicating that larger and older fishes have higher mercury concentrations. Males are often older at a given length than females, and sex-specific differences in growth, body size, and age likely account for differences in mercury concentrations between male and female northern pike and walleye. Fish length is often identified as a metric that is positively related to mercury concentrations (e.g., Phillips et al. 1980; Sackett et al. 2009), as larger fish tend to be older and have a higher trophic position, providing more time to accumulate additional mercury through bioaccumulation (Cabana and Rasmussen 1994; Atwell et al. 1998; Pickhardt et al. 2002). Besides being a good predictor of mercury concentrations, fish length is easily measured by anglers. Thus, size-based consumption advisories are a commonly used tool to limit consumption risk. Regardless of fish species, only 5.5% (21 of 384 samples) of fish collected ≤ 400 mm had mercury concentrations ≥ 0.30 mg/kg. Thus, simplistic size-based consumption guidelines universally applicable to all species that are easy for anglers to understand may be useful tools to limit human consumption of mercury-contaminated fish. Additionally, understanding fish characteristics associated with elevated mercury concentrations will allow managers to develop general consumption guidelines that are broadly protective of public health while also guiding future sampling efforts to gather additional data in areas of potential concern, such as the Paleozoic Plateau.

Beyond fish-specific characteristics, mercury concentrations varied among ecoregions. Fish collected from the Upper Iowa River (Paleozoic Plateau ecoregion) had higher mercury concentrations than other rivers throughout the state that were similar to one another. Specifically, average mercury concentrations were approximately twice as high in walleye and smallmouth bass collected from the Upper Iowa River than other rivers evaluated here. The soils and topography of the Paleozoic Plateau ecoregion are unique and are considered "loess with bedrock outcrops" that are defined by steeply sloped rolling hills and bluffs created from loess and abundant emergent bedrock in the form of limestone (USDA 2000). The region is also characterized by karst topography with numerous springs and water flow through limestone and dolomite bedrock that only exists in this region. The loess rich soils of this region are similar to the loess soils found in other regions of Iowa, but the heavily forested and steep terrain of the watersheds make this region unique. Combined, these unique landscape characteristics could be contributing to increased mercury levels in fish of this region, but additional work is needed to more clearly define why fish mercury concentrations of this ecoregion are higher compared to other ecoregions.

The prevalence of agricultural lands is often associated with increased mercury levels due to an increase in mercury-methylating bacteria (e.g., Sackett et al. 2009; Hayer et al. 2010). In this study, the highest mercury concentrations in fish were observed in the Upper Iowa River that is located in northeast Iowa, a region with the least agriculturally impacted watersheds in the state. Although agricultural land is inversely related to forested land ($r = -0.96$, $P < 0.01$) and grasslands ($r = -0.95$, $P < 0.01$), increases in agricultural land within a watershed does not appear to directly influence fish mercury concentrations in these systems. The lack of a positive relationship between agricultural land and fish mercury concentrations observed here may potentially be due to the prevalence of agriculture throughout Iowa that may result in low fish mercury concentrations observed throughout Iowa compared to other regions of North America (Kamman et al. 2005).

Instead of agricultural land use, we found that mercury concentrations increased with wetland and forested area and decreased with open water and grasslands. Wetland area is often positively related to mercury concentrations (Simonin et al. 2008; Hayer et al. 2010; Rypel 2010) but wetlands are uncommon in Iowa (<2% coverage) due to artificial drainage and land use conversion (McCorvie and Lant 1993). Riparian zones adjacent to streams can provide favorable conditions for enhancing the methylation of mercury (Skyllberg et al. 2003) and the organic soil layers of forested land can harbor mercury fixing bacteria (Matilainen et al. 2001). This suggests that watersheds with higher percentages of forested land, particularly riparian forests, are contributing more bio-available mercury into aquatic systems than watersheds with relatively low percentages of forested land (Driscoll et al. 2007). In contrast to forested land, the inverse relationship identified here between grasslands and mercury concentrations suggests that landscape conservation practices, such as the conservation reserve program (CRP), that add grasslands to reduce sedimentation and nutrient loading (Ribaudo 1989), may also provide an additional benefit through reducing mercury contamination in fishes.

Land use can have a pronounced effect on water chemistry and we identified several water chemistry metrics, including hardness, nitrate-ammonium, phosphorus, total suspended solids, and sulfate that were also related to

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mercury concentrations. Whereas most studies are only able to evaluate variation in water chemistry among systems, our dataset included long-term water quality monitoring and fish ages that allowed us to determine water chemistry experienced by each individual fish, providing finer resolution regarding environmental factors influencing individual mercury concentrations. These results indicate that mercury concentrations decline with increasing phosphorus, total suspended solids, and sulfate but increase with nitrate-ammonium and water hardness. In this study, sulfate was inversely related to mercury concentrations and mercury methylation in natural environments has been related to sulfate-reducing activity by bacteria in anaerobic sediment (Gilmour et al. 1992; Ekstrom et al. 2003). Additionally, mercury concentrations of fish have been inversely related to multiple metrics of productivity (Pickhardt et al. 2002; Simonin et al. 2008). Increases in nutrient availability may increase system productivity, resulting in faster growth rates of fishes and reduced mercury concentrations through biodilution (Chen and Folt 2005; Rypel 2010). However, other work has shown mercury concentrations increase with metrics of lake productivity, potentially due to an increase in mercury-methylating bacteria (Selch et al. 2007; Sackett et al. 2009) present in anaerobic zones (Garcia et al. 2013; Beutel 2016). In New York lakes, productivity was negatively related to mercury concentrations in largemouth and smallmouth bass but not yellow perch (*Perca flavescens*) or walleye (Simonin et al. 2008), suggesting that even within the same location, species-specific differences in food webs, growth rates, and life history characteristics may determine the effects of lake productivity on mercury accumulation rates.

We also identified a significant positive effect of HTI on fish mercury concentrations, suggesting that cumulative impacts of human modifications on the landscape may also contribute to increased mercury concentration in fishes. The HTI encompasses 35 individual variables reflecting different types of human impacts, including land use, impervious surfaces and development (e.g., urban areas, roads, airports), contaminant sources (e.g., mines, oils and gas wells, wastewater treatment facilities, landfills), and other indicators of human threat (Annis et al. 2010). Beyond the relationships with several specific factors identified in this study, the positive relationship with HTI suggests that unexplained variation in the current analysis could potentially be related to synergistic effects of multiple factors encompassed by HTI. Thus, locations with high HTI scores might be candidates for extra caution or confirmatory spot checks when applying spatially broad mercury consumption advisories.

Predicting fish mercury concentrations is an important component for monitoring mercury in aquatic systems and developing consumption guidelines. However, monitoring is time consuming and expensive. Thus, information related to factors influencing mercury concentrations in fishes would improve monitoring efficacy and the development of consumption guidelines. While a suite of evaluations have been conducted assessing factors responsible for mercury concentrations of fish in lentic systems, much less information is available about similar processes in lotic systems. This study provides a comprehensive analysis of factors influencing fish mercury concentrations in lotic ecosystems and serves as further evidence to suggest fish mercury concentrations are influenced by a suite of abiotic and biotic factors within and among systems. Our results provide information regarding factors influencing fish mercury concentrations that will help guide state agency mercury monitoring programs by identifying locations, species, and sizes of fish that may have elevated mercury concentrations.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest. All applicable international, national, and/or institutional guidelines for the care and use of animals were followed. This study was performed under the Iowa State University Institutional Animal Care and Use Committee (IACUC) protocol permit 4-14-7780-I and animals were collected under state permit SC1037.

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