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Mercury Concentration in Fish from Streams and Rivers Throughout the Western United States

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We collected and analyzed 2,707 large fish from 626 stream/river sites in 12 western U.S. states using a probability design to assess the regional distribution of whole fish mercury (Hg) concentrations. Large (>120 mm total length) fish Hg levels were strongly related to both fish length and trophic guild. All large fish that we sampled exceeded the wet weight detection limit of 0.0024 $\mu g \cdot g^{-1}$, and the mean Hg concentration in piscivores (0.260 $\mu g \cdot g^{-1}$) was nearly three times that of nonpiscivores (0.090 $\mu g \cdot g^{-1}$). Fish tissue Hg levels were not related to local site disturbance class. After partialing out the effects of fish length, correlations between Hg and environmental variables were low ($r < 0.3$) for the most common genera (trout and suckers). Stronger partial correlations with Hg ($r > 0.5$) were observed in other genera for pH, stream size, and human population density but patterns were not consistent across genera. Salmonids, the most common family, were observed in an estimated 125,000 km of stream length, exceeded 0.1 μg $Hg \cdot g^{-1}$ (deemed protective for fish-eating mammals) in 11% of the assessed stream length, and exceeded the filet equivalent of 0.3 μg $Hg \cdot g^{-1}$ (USEPA tissue-based water quality criterion) in 2.3% of that length. Piscivores were less widespread (31,400 km), but they exceeded the 0.1 and 0.3 μg $Hg \cdot g^{-1}$ criteria in 93% and 57% of their assessed stream length, respectively. Our findings suggest that atmospheric transport is a key factor relative to Hg in fish across the western United States.

Introduction

Mercury contamination of the aquatic environment is an increasing threat to wildlife and humans (*1*). Aquatic organisms, particularly fish, bioaccumulate methylmercury from contaminated water and food (*2*), but predominately through food (*3*). Thus, predatory fishes commonly accumulate higher concentrations of mercury than do herbivorous ones, and mercury concentration increases as fish age and grow (*4*). Nearly all mercury accumulated in fish tissue (95–99%) is methymercury (*4*, *5*) and the USEPA (*6*) recommends total mercury (Hg) analysis for fish tissue surveys. Consumption of fish by mammals (including humans) and birds greatly increases their exposure to methylmercury and its potential neurological effects. Log_{10} Hg concentration in fish is proportioned predictably between the muscle (filet) and the whole body regardless of fish size, age, species, or trophic guild (*7*).

Porcella (*8*) called for better temporal data on mercury bioaccumulation. However, discovery of high mercury levels in fish and lake sediment from remote areas (*9*, *10*) implicates widespread distribution of Hg through the atmosphere (*11*). Thus, we contend that better spatial data, as well as temporal data, are important in assessments. From 2000 through 2004, we estimated the level and extent of mercury concentrations in stream/river (lotic) fishes across the states of Arizona, California, Colorado, Idaho, Montana, Nevada, North Dakota, Oregon, South Dakota, Utah, Washington, and Wyoming, (Figure 1) as part of the U.S. Environmental Protection Agency's (USEPA) Environmental Monitoring and Assessment Program (EMAP) (*12*, *13*). Sample sites were selected on a probability basis so that fish tissue Hg concentrations could be inferred to the region-wide stream network. To our knowledge, this is the first probability-based survey of stream/river fish tissue Hg covering an area of this magnitude (>3,100,000 km^2). The purpose of this paper is to (1) describe the concentration of mercury in lotic fishes throughout the western United States, (2) determine the proportion of these systems that pose a risk to piscivorous organisms, and (3) evaluate the influence of various environmental factors that might affect fish tissue Hg concentrations.

Materials and Methods

Probability Sampling Design. Inferences to a regional resource assessment requires that sample sites are representative of the resource in question (*14*). Our sites were selected through use of a systematic, randomized sample from all permanent lotic courses appearing on the 1:100,000-scale Digital Line Graph database of the U.S. Geological Survey (*15*). Site selection followed a procedure that recognized the continuous nature of lotic systems, controlled for spatial dispersion of the samples, considered their variable spatial density, and allowed for nested subsampling (*16*, *17*). The randomized, spatially distributed site selection provides an unbiased estimate of region-wide fish attributes. The assessed length of perennial streams and rivers in our 12 western state survey was 304,544 km (189,244 miles).

Sample Collection. Wadeable streams were backpack electrofished in a sample reach that was 40 times the mean wetted width, and boatable rivers were raft electrofished in a sample reach 100 times the mean wetted width (*18*, *19*). All fish captured were identified and enumerated and a subset of the fish were retained for mercury analysis. However, fish from all sites could not be analyzed for Hg for one or more of the following reasons: no fish were caught, too few fish were caught, equipment failed, or no collection permit was available. Two types of samples were collected for Hg analysis. The first was a composite sample consisting of 50–200 g of fish species whose adults are often small (<100 mm). The second type of sample consisted of up to three individual fish from up to three different species whose adults are larger. Our large fish sample type consisted only of individual fish ≥120 mm and they were purposely of various sizes so that a range of Hg concentrations might be determined and modeled by both size and taxonomy. Fish were measured, double plastic bagged, labeled, and iced for shipment to the analytical laboratory the next day. Upon receipt, samples were frozen at −20 °C and stored until prepared for analysis.

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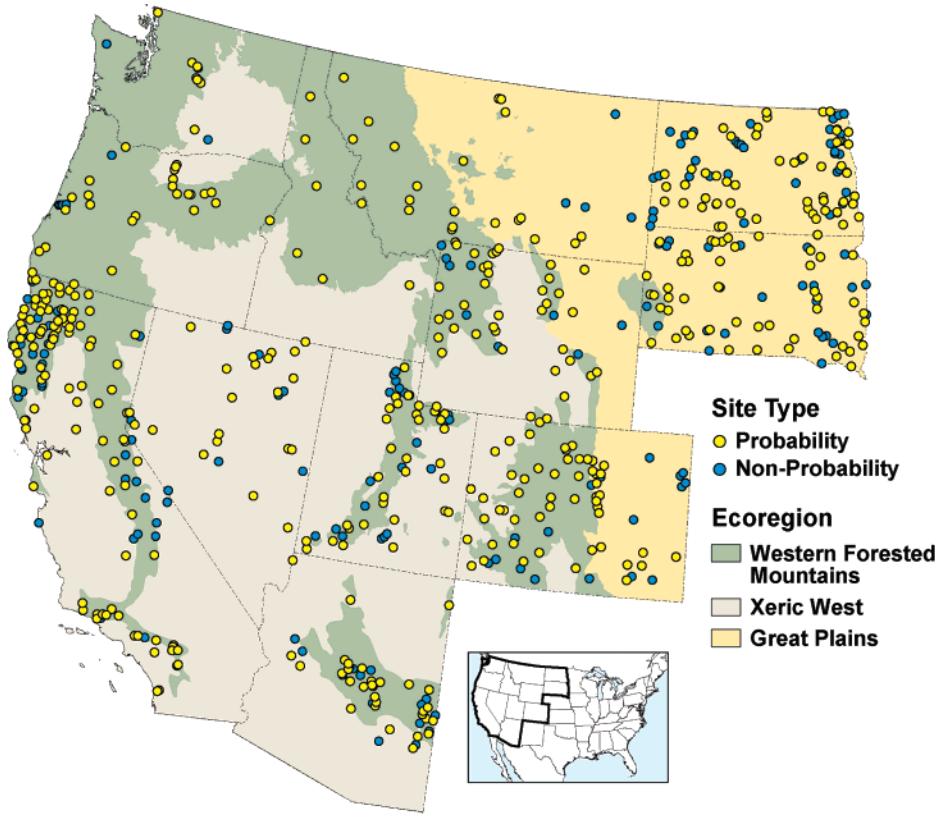

FIGURE 1. Location of sample sites for tissue Hg assessment in EMAP-Western stream survey study area (2000−2004). Ecoregions aggegrated from Omernik (*20*).

Between 2000 and 2004, a total of 699 sample visits to 626 sites (441 probability survey sites and 185 hand-picked sites) throughout aggregated Omernik ecoregions (*20*) of the western United States yielded 2707 large fish for Hg analysis (Figure 1). Small fish composite samples were collected from 241 probability sites. Chemical and physical habitat variables were measured at each site (*18*, *19*). The hand-picked sites were selected in an attempt to get information about least-disturbed site conditions in the West. Environmental characteristics at many hand-picked sites, however, differed little from the randomly selected probability sites. Therefore, to increase the statistical power of our associational model, both hand-picked and probability sites were included in our analysis of Hg concentration, fish attribute, and environmental factor relationships. Estimates of the regional distribution of Hg in fish used only the 441 probability sites.

Laboratory Procedures. All Hg analyses were performed on whole fish homogenates as described by Peterson et al. (*7*). The analyses were done by combustion atomic absorption spectrophotometry (CAAS) (Milestone DMA80 direct mercury analyzer, Milestone, Monroe, CT) according to USEPA (*21*), which produces results statistically equivalent to cold vapor atomic absorption (*22*). Results were reported as wet weight means of two or three replicate analyses.

Mercury Detection Limits and Quality Assurance. The method detection limit (MDL) for Hg in fish tissue, on a dry weight basis, was determined to be 0.02 μg Hg·g^{-1} according to the method of Taylor (*23*), using repeated analyses of freeze-dried Standard Reference Material (SRM) 2976 (0.0610 μg Hg·g^{-1}) (National Institute of Standards and Technology, Gaithersburg, MD). The dry weight MDL was converted to a wet weight MDL (0.0024 μg Hg·g^{-1}) by correcting for the water content of as-received fish and the amount of water added to each sample during homogenization. All individual large fish, and all but one small fish composite (0.0019 μg Hg·g^{-1}), exceeded the wet weight MDL. Thus, all analyzed samples were included in our data analysis.

Critical Mercury Thresholds. The whole-fish Hg level of 0.1 μg Hg·g^{-1}, from Yeardley et al. (*24*), was used to estimate environmental risk to sensitive piscivorous mustelids such as mink and otter. The current USEPA tissue-based water quality criterion relative to consumption of fish by sensitive humans, including children and women of child-bearing age, is 0.3 μg Hg·g^{-1} (*25*).

Humans consume primarily fish muscle (filet) rather than whole fish. Therefore, using the same data as Peterson et al. (*7*) we built a regression model to predict filet concentrations from our whole fish Hg concentrations. The model predicts that a fish whole body concentration of 0.185 μg Hg·g^{-1} will have a filet tissue concentration of 0.3 μg Hg·g^{-1} (Figure 2). Thus, fish with whole body concentrations exceeding 0.185 μg Hg·g^{-1} will exceed the USEPA's current human consumption criterion for fish filet (*25*).

Statistical Analyses. Fish trophic guild and taxonomy were expected to influence the amount of Hg in fish tissue (*4*, *26*). For coarse level analyses, we grouped large fish into two trophic guilds (piscivores or nonpiscivores) (Table S1). Fish length−Hg relationships were analyzed by linear regression and local regression analysis (LOESS) at both the trophic guild and species level. Due to sample size limitations, species were also aggregated into family or genus for other data analyses.

Local, watershed-scale categories of site condition (least disturbed, moderately disturbed, or highly disturbed) were developed for each site as part of the overall EMAP-West assessment (*27*) using field comments, air photo analysis, site measurements of physical habitat (sediments and riparian condition), and water quality (nutrients, pH, turbidity, chloride, and sulfate). We tested for the effect of site condition category at the genus level on log-transformed fish Hg concentrations using ANCOVA (*28*) with fish length

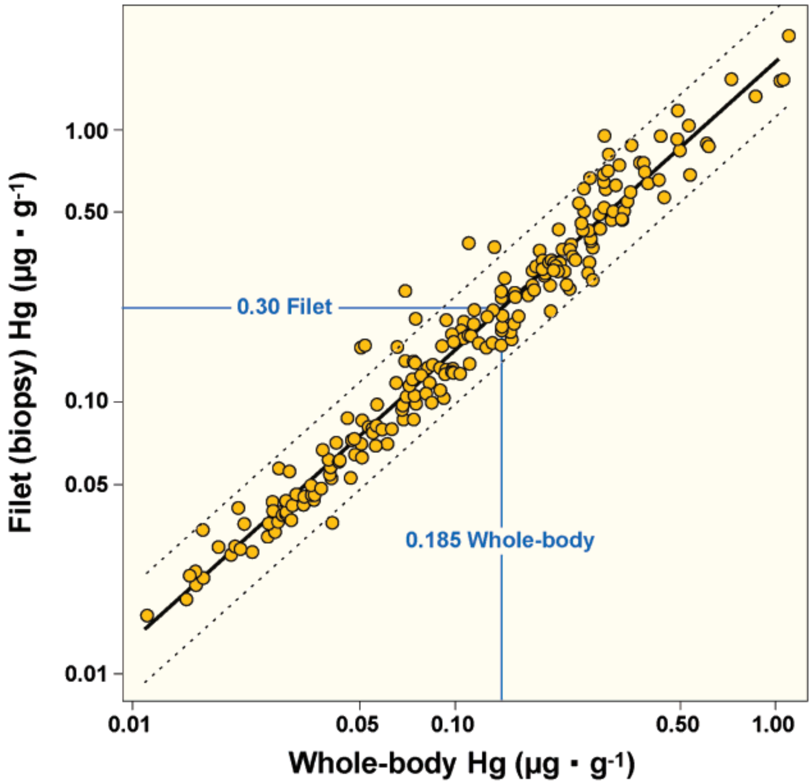

FIGURE 2. Regression of filet Hg concentration against whole-fish Hg concentration (log [filet biopsy Hg] = 0.2545 + 1.0623 log [whole-fish Hg]), r^2 = 0.957, residual SD = 0.097, *N* = 208, with 2 outliers excluded from plot and regression. Dotted lines denote 95% confidence limits on the prediction for an individual fish.

as the covariate. The length effect was tested using individual fish as sampling units, whereas the site condition effect was tested using sites as sampling units (SAS PROC MIXED, *29*).

We used partial correlation analysis to assess the effects of environmental variables on Hg concentration using fish length to partial out fish size effects (*28*, *29*). Because fish genera influence Hg levels (*10*, *30*, *31*), we analyzed fish genera separately. Genera, instead of species, were used for this analysis to obtain samples of sufficient size for statistical analysis ($n > 50$). For example, three bullhead species (yellow, brown, and black) were aggregated to their genus (*Ameiurus*) with 120 individuals for analysis. The tested environmental variables included water quality variables (pH, acid neutralizing capacity [ANC], sulfate, chloride, dissolved organic carbon [DOC], total nitrogen, total phosphorus, silica, and specific conductance), watershed variables derived from GIS data layers (% forest, % agriculture, % urban, % wetland, population density, watershed slope, watershed area, annual precipitation, and runoff), and site scale variables (elevation, latitude, longitude, mean substrate size, wetted width, and depth).

Population Estimates. Each probability sample site has a sample weight (expansion factor), calculated as the inverse of the probability of selecting that site; summing the sample weights of all sites in the data set yields an estimate of the total stream length assessed. Thus, by using the sample weights in data analysis we can infer to the entire stream length. For large fish, the Hg concentrations used in making population estimates were means of all the individual large fish analyzed in each fish class (piscivore, nonpiscivore, or fish family) at each site. When there were repeat sample visits to a site, only the first site visit, where the family, guild, or sample type was present, was used to calculate the mean site concentration. We estimated the percentage of stream/river length where Hg concentration exceeded published wildlife and human consumption thresholds. However, not all readers rely on these exact Hg thresholds. Therefore, we developed an exceedence plot to display the percentages of stream/river lengths that exceed various Hg concentrations across the whole range of their observed values.

Results

Large Fish. A variety of large fish species and trophic guilds and their associated mean, minimum, and maximum lengths and Hg concentrations were analyzed (Table S1) across a wide range of environmental conditions (Table S2). Overall, mean Hg concentration in large piscivores (0.26 μg Hg·g^{-1}, SE = 0.012) was nearly three times that of large nonpiscivores (0.09 μg Hg·g^{-1}, SE = 0.0021). All the large fish that we analyzed exceeded the wet weight detection limit of 0.0024 μg·g^{-1}.

Large fish tissue Hg concentration generally increased with fish size, although the relationship showed much scatter (Figure 3). LOESS analysis (*32*) suggests that the relationship is slightly nonlinear. Piscivores are represented by the upper LOESS curve and nonpiscivores are represented by the lower LOESS curve in Figure 3, showing the difference in Hg concentration between the two trophic guilds. LOESS curves suggest that, on average, Hg concentrations stopped increasing with fish length when fish exceeded 400−500 mm (Figure 3). This pattern was also seen for two of the four piscivore species (northern pikeminnow and smallmouth bass) that were abundant in our samples (Figure 4). Although Figures 3 and 4 suggest mild nonlinearities in the relationships between fish length and Hg, we assumed linear relationships when conducting ANCOVA and partial correlation analyses.

Site condition class had no significant effect on fish tissue Hg (Table 1). However, the fish length effect on Hg was highly significant for all six genera that had enough sample sites to support the ANCOVA (partial F = 19−170). Thus, site- and watershed-scale anthropogenic disturbances, which are reflected in the site condition classification, are not major

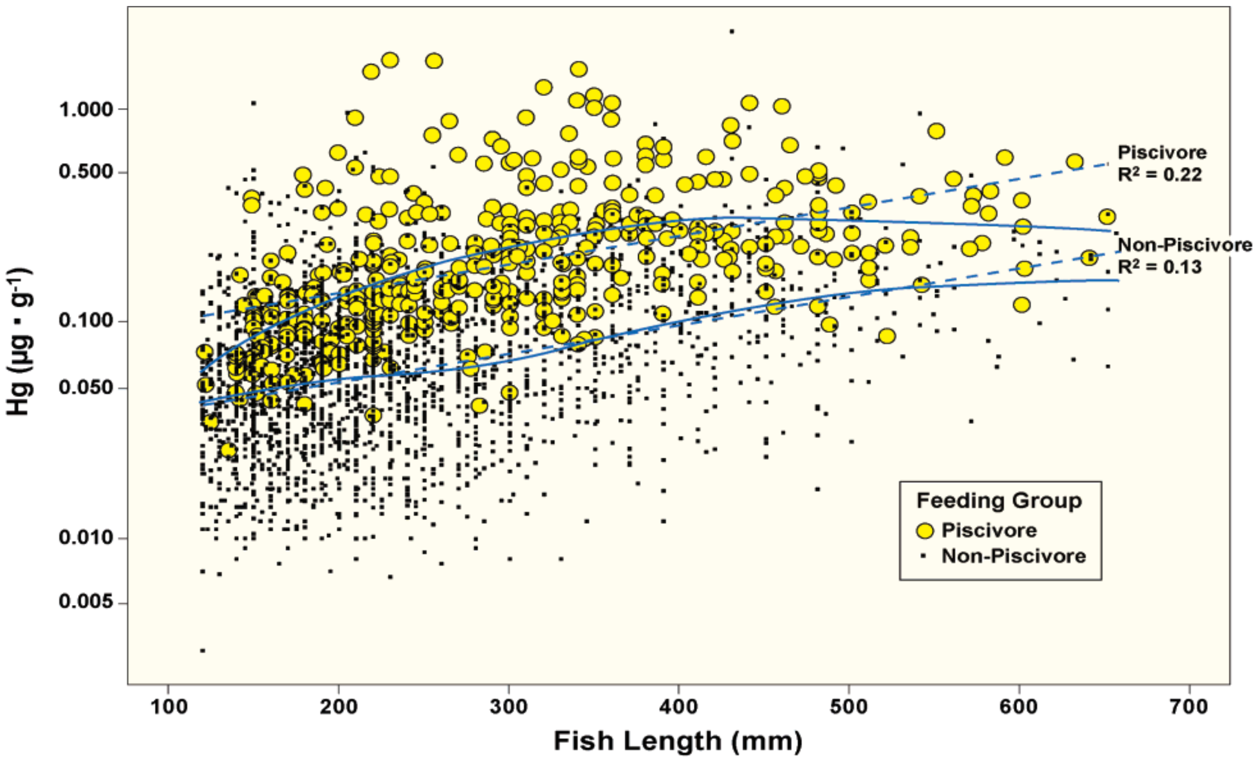

FIGURE 3. Fish length versus Hg concentration ($\mu g \cdot g^{-1}$) in large piscivores (circles) and nonpiscivores (dots). Solid lines are local (LOESS) regression curves, dashed lines are simple linear regressions, done separately for large piscivores and nonpiscivores. The r^2 values apply to the linear regression.

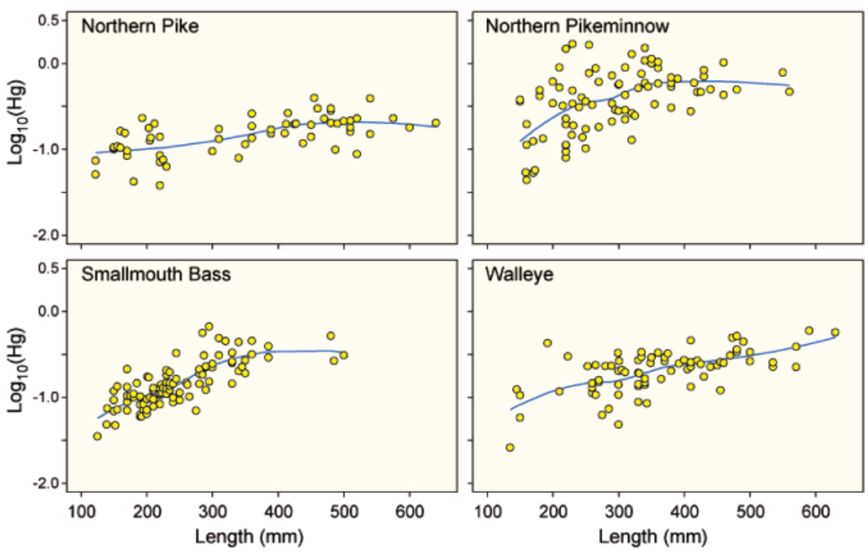

FIGURE 4. Fish length versus Hg concentrations ($\mu g \cdot g^{-1}$) for four large piscivorous species having 30 or more individuals. Solid lines are local (LOESS) regression curves.

factors in explaining regional Hg fish tissue patterns across the western U.S.

In general, Hg in piscivorous genera was more strongly related to fish length than it was in nonpiscivorous genera (Table 2). A number of nonpiscivorous genera had very weak Hg−length relationships especially *Oncorhynchus, Semotilus*, and *Salmo* ($r < 0.2$). The weakest relationships with environmental variables were exhibited by the three nonpiscivorous genera with the broadest distributions and largest sample sizes (*Oncorhynchus, Salmo*, and *Catostomus*). No partial correlation with the tested environmental variables exceeded 0.3 for any of these genera. Pikeminnow (*Ptychocheilus*) demonstrated the strongest relationship with environmental variables. The pH, watershed area, and ANC partial r values for these pikeminnow ranged from −0.56 to −0.60. The largest length-adjusted pikeminnow Hg concentrations were found in smaller watersheds with lower pH and ANC. For other piscivorous genera, partial correlations above 0.4 were observed between Hg and watershed area for *Esox*, and between Hg and mean depth and substrate size for *Sander* (Table 2). For nonpiscivores, the genera with the strongest relationship between Hg and environmental variables were *Ictalurus* (negatively with ANC and total nitrogen), and *Semotilus* (negatively with population density and % urban land cover in the watershed).

Regional Mercury Estimates. We did not analyze fish tissue Hg from all sites where fish were caught (Table 3). Thus, we compared sites where fish were caught but not

TABLE 1. Mercury Concentration ANCOVA Results for Fish Length and Site Condition Effects in Western Streams/Rivers for Large Fish Genera with Sufficient Sample Size (4 or More Sample Sites Per Class)

genus	fish length effect partial *F*	fish length effect df[b]	site condition[a] effect partial *F*	site condition[a] effect df[b]
Oncorhynchus	135[c]	1, 275	0.34[d]	2, 206
Salmo	73.8[c]	1, 157	0.22[d]	2, 102
Prosopium	117[c]	1, 83	0.56[d]	2, 36
Catostomus	137[c]	1, 259	0.29[d]	2, 179
Ameiurus	19.2[c]	1, 67	0.41[d]	2, 49
Micropterus	170[c]	1, 70	0.74[d]	2, 36

[a] Site condition = highly, moderately, least disturbed according to (*27*). [b] df = *F*-test degrees of freedom (numerator, denominator). [c] $p < 0.0001$. [d] $p > 0.4$

analyzed (CNA), with those where fish were caught and analyzed (CAA), to evaluate whether the analyzed sites were representative of all sites where fish were caught. Salmonidae tissue analyses tended to come from slightly larger, higher-elevation streams with higher chloride, pH, and total suspended solids, as compared with CNA streams for salmonids. CAA sites for Percidae tissue also tended to come from larger streams whereas Centrarchidae tended to be assessed in sites with lower turbidity, conductivity, sulfate, and larger substrate particle size relative to CNA sites. For each of the other families in Table 3 we saw no significant differences in environmental attributes between CAA and CNA sites. At the family level, differences mentioned above between CAA and CNA sites all involved environmental variables that were only weakly correlated with fish Hg. After partialing out length effects, environmental variable correlations were <0.24 with log-transformed Hg, and for 9 of the 11 families tested, the partial correlations were <0.10. In short, we saw no evidence that environmental differences between CAA and CNA sites would lead to systematic differences in Hg distributions at the CNA sites, relative to family level assessment. Therefore, we conclude that, at the family level and for piscivore/nonpiscivore groupings, our CAA sites were representative of CNA sites for the purpose of estimating region-wide Hg distribution (Table 3).

Our EMAP-West survey assessed 304,544 km of perennial flowing waters in the region. Based on the overall EMAP electrofishing catch results, 206,520 km (68%) contained small fish, 168,772 km (55%) contained one or more large non-

TABLE 2. Product−Moment Correlations between log(Hg) and 26 Environmental Variables (Table S2), after Partialing out the Effect of Fish Length for Genera with More than 50 Fish[a]

Genus (common name)[b]	r_{length}[c]	no. of fish	top three environmental correlates (partial *r*)
Piscivores			
Micropterus (Bass)	0.72	110	annual runoff (0.37), watershed slope (0.37), longitude (0.35)
Esox (Northern Pike)	0.67	57	watershed area (0.41), annual runoff (−0.37), pop. density (0.36)
Ptychocheilus (Pikeminnow)	0.52	100	pH (−0.60), watershed area (−0.59), ANC (−0.56)
Sander (Sauger, Walleye)	0.51	75	mean depth (0.43), substrate size (−0.40), DOC (0.39)
Nonpiscivores			
Moxostoma (Redhorse)	0.64	60	pH (0.48), mean depth (−0.43), ANC (0.40)
Ictalurus (Channel Catfish)	0.60	71	ANC (−0.53), total N (−0.48), longitude (0.45)
Cyprinus (Common Carp)	0.57	110	annual runoff (−0.41), substrate size (−0.36)
Prosopium (Mt. Whitefish)	0.50	123	sulfate (0.45), conductivity (0.42), ANC (0.39)
Catostomus (Suckers)	0.48	442	none[d]
Salmo (Brown Trout)	0.35	263	none[d]
Ameiurus (Bullheads)	0.33	120	total N (−0.39), annual precip. (0.38), sulfate (−0.38)
Oncorhynchus (Cutthroat, Rainbow Trout)	0.20	485	none[d]
Semotilus (Creek Chub)	0.20	52	pop. density (−0.56), % urban (−0.48), chloride (−0.40)
Salvelinus (Brook Trout)	0.17	159	DOC (0.47), watershed slope (−0.36)

[a] The top three correlates with partial *r* values >0.3 are shown. Water chemistry, population density and watershed variables were log transformed before analysis. [b] Genus common name or species common names if there were only one or two species analyzed in the genus. [c] Genus product−moment correlation for log(Hg) versus fish length. [d] No environmental correlates with partial $r > 0.3$.

TABLE 3. Estimated Total Stream/River Length with Various Fish Groups Present, Percent of Fish-Present Stream/River Length Assessed for Hg, and Percent of Steam/River Length with Mean Hg Concentrations of Large Individual Fish or Composite Small Fish Samples ≥0.1 and ≥0.185 $\mu g \cdot g^{-1}$ (Overall Assessed Stream/River Length in the Region Was 304,544 km)

fish group	total stream length with various fish groups present (km)	percent of stream length, w/fish present, that was assessed for Hg (%)	percent of assessed stream length with fish exceeding critical Hg thresholds (μg Hg·g^{-1}) (%) ≥ 0.1	percent of assessed stream length with fish exceeding critical Hg thresholds (μg Hg·g^{-1}) (%) ≥ 0.185[a]
large fish (>120 mm)				
piscivore	31,476	61	93.0	56.8
nonpiscivore	168,772	68	25.5	6.1
family				
Salmonidae	125,191	69	11.4	2.3
Percidae	5707	74	77.8	42.4
Ictaluridae	22,037	44	43.8	21.3
Hiodontidae	4483	52	84.8	41.9
Esocidae	7273	39	78.6	27.4
Cyprinidae	47,660	46	64.4	44.4
Centrarchidae	17,321	52	87.3	32.3
Catostomidae	65,625	58	47.9	14.9
small fish (<100 mm)	206,520	30	18.0	3.2

[a] ≥ 0.185 in whole fish equals or exceeds 0.3 μg Hg·g^{-1} in filet tissue, which exceeds the USEPA (1999) criterion for human consumption.

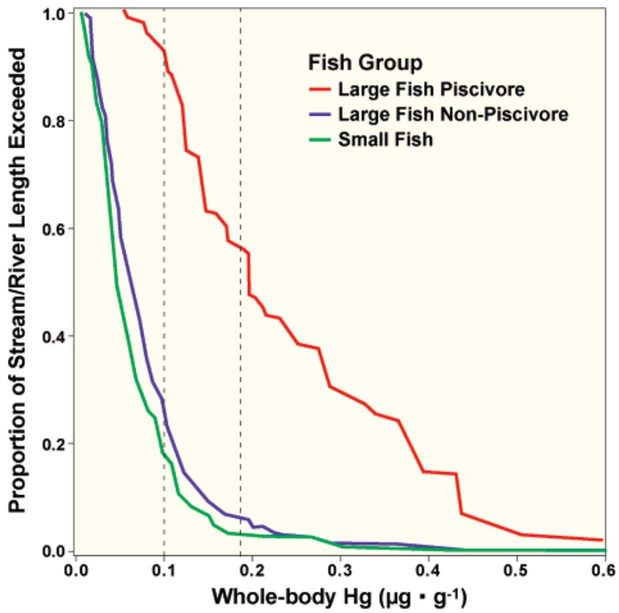

FIGURE 5. Cumulative assessed stream/river length with whole large piscivores, and nonpiscivores, and composite small fish samples exceeding various fish tissue Hg concentrations.

piscivorous fish, and only 31,476 km (10%) had large piscivorous fish (Table 3). Thus, we were able to analyze large fish for Hg from 61% (piscivores) to 68% (nonpiscivores) of the stream length where they were observed. Small fish were analyzed from 30% of the stream length where they were observed (Table 3). The exceedence estimates in Table 3 are percentages only of the amount of stream length that we assessed for Hg.

Where large piscivores were assessed, 94% of the stream/river length exceeded the Yeardley et al. (*24*) 0.1 μg Hg·g^{-1} wildlife threshold and 57% exceeded 0.185 μg Hg·g^{-1}. Since 0.185 μg Hg·g^{-1} in whole body corresponds to the human health consumption threshold of 0.3 μg Hg·g^{-1} in filets, fishermen, by chance, might catch large piscivorous fish exceeding the tissue-based water quality criterion in more than half the stream lengths where they catch large game fish in the western U.S. For nonpiscivores, 26% of the assessed stream/river length exceeded 0.1 μg Hg·g^{-1} and 6% exceeded 0.185 μg Hg·g^{-1}.

Among families represented by large-sized individuals, the Centrarchidae Hiodontidae, Percidae, and Esocidae exceeded 0.1 μg Hg·g^{-1} in over 75% of the assessed stream length (Table 3). However, some of these families are relatively rare in the western United States and we observed them in only a small fraction of the stream length. For example, large percids and hiodontids were each observed in <6000 km of stream or <2% of the total regional stream length. Large cyprinids had the highest proportion of assessed stream length exceeding 0.185 μg Hg·g^{-1} (44%), due mostly to high Hg levels in pikeminnow. Of the 102 individual pikeminnow analyzed in this survey, 74% exceeded 0.185 μg Hg·g^{-1}. Salmonidae, the most common fish family in the western U.S., were assessed in 69% of the 125,200 km of the stream/river length where they were observed, with large individuals, on average, exceeding 0.185 μg Hg·g^{-1} in only 2% of their assessed stream length. The Hg concentration for salmonids was <0.1 μg Hg·g^{-1} in 89% of assessed stream length. Thus, of the major game fish in our survey, large resident salmonids, as a group, represent the lowest risk to wildlife or human consumers relative to Hg ingestion.

The proportion of assessed stream length exceeding any given Hg concentration is much greater for large piscivores than for large nonpiscivores and small fish (Figure 5). Note that the plots for large nonpiscivores and small fish are very similar. The exceedence plot is useful in extracting information similar to that in Table 3 for virtually any fish tissue Hg concentration of interest. For example, Hg levels >0.6 μg Hg·g^{-1} do occur, but they are rare in western U.S. lotic systems, constituting no more than about 3% of stream length assessed for large piscivores. The chief concern for Hg in small fish is its influence on piscivorous birds and mammals when fish tissue Hg is ≥0.1 μg·g^{-1}. This occurred in 18% of the stream length assessed for small fish.

Discussion

Fish tissue sampling sites were reasonably well distributed throughout all 12 states in the conterminous western U.S. Clustered sites in northern California and the upper Missouri River Basin of the Dakotas reflect intentional intensification of sampling to improve local area estimates. However, in our west-wide Hg estimates these sites are individually down-weighted according to the unequal-probability design. The few sites in Washington, Oregon, and Idaho relate to collection permit limitations in those states. Any time endangered species were encountered electrofishing ceased.

Log-transformed fish tissue Hg concentration often is reported in the literature as having a straight line relationship to fish size and our ANCOVA and partial correlation analyses are based on the assumption of a straight line relationship. However, our results suggest a slightly curved relationship for some piscivorous species, as revealed by LOESS curves (Figures 3 and 4). The semi-straight line relationship seems to level off at piscivore lengths above 400 mm especially for northern pikeminnow and smallmouth bass although the smallmouth bass curve is driven by the three largest fish. For the other two piscivore species in Figure 4, walleye do not demonstrate a leveling effect, and while the LOESS line for northern pike shows a leveling off, the scatterplot itself is not very indicative of a leveling phenomenon. Perhaps the leveling off is characteristic of some piscivore species and not others. We saw no clear pattern of leveling-off in similar plots for nonpiscivore species (not shown). If this phenomenon does exist in some piscivorous species, the mechanism is unknown. Since fish accumulate Hg with increased size (growth), perhaps reduced Hg concentration in the largest fish is a function of reduced feeding and growth rate as implied by Luoma and Rainbow (*33*). Since Hg binds to protein in fish muscle (*5*), perhaps protein sites in large fish are saturated or the large fish contain proportionally more fat than smaller fish. We suggest that further research on larger, older, piscivorous fish Hg accumulation rates might be warranted.

The partial correlation analysis (Table 2) produced mixed signals. Four genera showed correlations of Hg with ANC or pH, however two were positively correlated and two were negatively correlated. Pikeminnow and channel catfish Hg were negatively correlated with ANC and had the highest length-adjusted Hg concentrations in sites with lower ANC. The two genera had very different ANC ranges. The lower end of the ANC range was 0.3–0.5 meq·L^{-1} for pikeminnow versus 1.5–3.0 meq·L^{-1} for catfish. On the other hand, redhorse and mountain whitefish had higher Hg in the higher ANC sites (10–17 meq·L^{-1} for redhorse, 3–5 meq·L^{-1} for whitefish). Similarly, there were four genera that showed a relationship between Hg and stream size (assuming watershed area and mean depth are surrogates for size). Hg in *Esox* and *Sander* was positively related to stream size whereas Hg in *Ptychocheilus* and *Moxostoma* was negatively related to stream size. Hg in creek chub (*Semotilus*) was negatively related to three human disturbance variables (population density, % urban watershed, and chloride). The correlation was driven by two low fish Hg level sites with six fish (out of the 52 chub analyzed) in the Denver metropolitan area.

In addition, the three most common genera in Table 2 had no correlations between Hg and environmental variables greater than 0.3. Overall, there was no pattern relating tissue Hg with environmental variables that is consistent across fish genera. A possible reason for this observation is that the various genera are affected differently by interacting environmental variables (synergism/antagonism) and thus bioaccumulate Hg at different rates under varying environmental conditions in a manner similar to toxicants (*34*). Alternatively, there could be an unmeasured environmental gradient correlated with some of the environmental factors specific to individual genera distributions. For example, atmospheric Hg deposition might be positively correlated with ANC for sites containing species "A" but negatively correlated with ANC for a set of mostly different sites that contain species "B".

Several factors including pH, ANC, DOC, and SO_4 have been shown to correlate more closely and consistently with midwestern and eastern U.S. fish tissue Hg concentrations than our study shows (*35*–*38*). It is possible that the density of our sampling, relative to the environmental variability across the western states, was too coarse to detect the influence of rare factors that might be detected under a more restrictive, and thus more controlled, areal coverage. Also, DOC and acidity-related variables exhibit greater ranges in midwestern and eastern regions of the U.S. than they do in the western U.S. For example, there are streams in the eastern U.S. with pH < 4.0 and color > 100 PCU (*39*, *40*). No western stream in our data had a pH < 6 and colored waters > 50 PCU were rare.

Table 3 describes stream/river lengths exceeding two critical fish tissue Hg concentrations in the western U.S. However, other factors important to understanding the behavior of Hg relative to fish tissue accumulation not revealed in Table 3 are visually evident from an exceedence plot (Figure 5). The exceedence distributions show that across the full range of Hg concentrations, a greater proportion of stream length had piscivores in exceedence of any given concentration than nonpiscivores or small fish. Kamman et al. (*38*) also found that piscivores contained greater Hg concentrations than nonpiscivores regardless of water body type (river, lake, reservoir). Figure 5 also reveals that the Hg exceedence distribution for large nonpiscivores parallels, and is almost identical to, that of small fish. This indicates that future surveys might economize by dropping analysis of one or the other of these two groups with little information loss.

Our results suggest that atmospheric deposition of Hg is an important factor in controlling regional patterns in fish tissue Hg in the western U.S. Supporting evidence for this conclusion is as follows: First, fish tissue Hg concentrations occur within a narrow concentration range with over 80% of the fish in our survey having concentrations within 1 order of magnitude (0.02–0.2 μg Hg g^{-1}). These concentration windows are narrower than those we saw for water chemistry variables that are controlled by geology (e.g., calcium and magnesium) and which ranged over 2–3 orders of magnitude. Given the vast differences in geology across the western U.S. we would have expected a wider range in fish tissue Hg if geology were a major factor controlling Hg levels. Second, there was no relationship between site condition class and fish tissue Hg levels indicating that local watershed scale disturbance factors are not major drivers of tissue Hg concentrations. Third, there was no consistent pattern relating environmental variables to Hg. Fourth, "hot spots" or sites with high tissue Hg concentrations were very rare in our data. Only 13 fish from 8 different sites out of over 600 sampled had tissue Hg > 1.0 μg Hg g^{-1}.

In addition to the above, atmospheric modeling and deposition studies by Jaffe et al. (*41*) and Berntsen and Karlsdottir (*42*) have shown that long range (Asian) air-mass transport has an influence on the western U.S. Recently, Hope (*43*) concluded that the Hg deposition in Oregon's Willamette river basin is 5 times greater from natural and anthropogenic global sources than from within-basin sources. Our findings, coupled with the above atmospheric findings, suggest that atmospheric transport and deposition are key factors relative to Hg concentrations in fish across the western U.S. Unfortunately, the current Hg deposition monitoring network in the West is too sparse to extrapolate Hg deposition estimates to our site locations and test this hypothesis.

In summary, Hg was present above detection limit in all fish tissue throughout the western U.S. Large (> 120 mm total length) fish Hg levels were strongly related to both fish length and trophic guild. Mean Hg concentration in piscivores (0.260 $\mu g \cdot g^{-1}$) was nearly three times that of nonpiscivores (0.090 $\mu g \cdot g^{-1}$). The spatial extent of Hg concentration in small fish tissue is very similar to that of nonpiscivorous large fish. Across the West, 57% of the stream length with piscivores and 6% of the stream length with nonpiscivores exceeded the filet equivalent criterion of 0.3 μg $Hg \cdot g^{-1}$. Thus, extensive proportions of western streams/rivers have large piscivores with Hg levels that present a potential risk to sensitive consumers (piscivorous mammals, children, and pregnant women). Fish tissue Hg levels were not related to local site disturbance class. After partialing out the effects of fish length, correlations between Hg and environmental variables were generally weak and not consistent across genera. Our findings suggest that atmospheric deposition is a key factor relative to fish tissue Hg concentrations across the western U.S.

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Note Added after ASAP Publication

Mentions of USEPA water quality criterion were revised after ASAP publication of this manuscript on November 22, 2006; the revised version was published ASAP on December 6, 2006.

Supporting Information Available

Table of fish tissue mercury concentrations and fish lengths, and table of 5th and 95th percentiles for 26 environmental variables. This material is available free of charge via the Internet at http://pubs.acs.org.

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