Methylmercury Concentrations Found in Wild and Farm-raised Paddlefish

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ABSTRACT: Paddlefish (*Polyodon spathula*) were collected from 4 sites in Kentucky: the Ohio River, Lake Cumberland, and 2 aquaculture sources (private reservoir and catfish ponds). They were tested for methylmercury concentrations in their flesh. Paddlefish from all sources had methylmercury levels below the 1 part per million Food and Drug Administration-mandated action limit for seafood. However, using the U.S. Environmental Protection Agency reference dose for methylmercury, only paddlefish from the Ohio River exceeded the reference dose for unrestricted consumption. Some Ohio River and Lake Cumberland paddlefish had higher-than-average methylmercury concentrations, whereas aquacultured paddlefish had low concentrations of methylmercury. There was a direct proportionality between fish age and methylmercury concentration; older paddlefish tended to have higher amounts of methylmercury in their meat.

Keywords: paddlefish, wild, aquaculture, methylmercury, reservoir ranching, reference dose

Introduction

Mercury, in its organic form (methylmercuric acetate or methylmercury), has been identified as a significant hazard source for the developing nervous systems of fetuses and children (Laws 1981). Dietary methylmercury is almost completely absorbed into the circulatory system and distributed to all tissues including the brain. In pregnant women, methylmercury readily passes through the placenta to the fetal brain. In addition to nerve and brain damage, methylmercury poisoning has been found to hamper reproduction by interfering with the process of cell division (Montague and Montague 1971).

Grant (1971) discovered that methylmercury is relatively ubiquitous because of the ability of methanogenic bacteria to convert elemental mercury to methylmercury. Because these bacteria occur in sediments, the high mercury levels found in benthic creatures, such as bottom-feeding catfish, are not surprising. Additionally, bioaccumulation results in high mercury levels in piscivorous fish such as tuna, shark, and swordfish. According to Bloom (1992), 99% of mercury accumulated in fish tissue is methylmercury. Santerre and others (2001) have studied heavy metals (including mercury) and other contaminants in farmed catfish, trout, and crawfish from Alabama, Florida, Georgia, Louisiana, Mississippi, North Carolina, Tennessee, and Texas. They found that none of the fish and crustaceans had methylmercury concentrations higher than the U.S. Food and Drug Administration (USFDA) action limit of 1 part per million (ppm). Bahnick and others (1994) reported that methylmercury on predatory fish ranged from 0.14 to 0.51 ppm. Test results of the Kentucky Div. of Water have placed Kentucky on a list of 44 states that have issued fish consumption advisories because of excessive mercury contamination (USEPA 2002). The Kentucky Div. of Water tested paddlefish from the Ohio River for methylmercury: average methylmercury levels ranged from 0.08 to 0.17 ppm (DEPCK 2001). Bender (2000) reported methylmercury contamination exceeding the USFDA action limit in tuna, swordfish, and shark.

Researchers in Kentucky are currently investigating the aquaculture potential of paddlefish, *Polyodon spathula*, a zooplanktivorous, cartilaginous freshwater finfish, which is native to rivers and lakes of Kentucky and the Mississippi River system. Although there are some limited aquaculture initiatives for paddlefish, currently all of the paddlefish consumed are caught in the wild. Currently there are 2 paddlefish culture technologies in existence: reservoir ranching (Onders and others 2001) and polyculture with catfish in ponds (Schardein and others 2002). Reservoir ranching is a technique of extensive aquaculture of paddlefish in large bodies of water, with no additional inputs (including no feed) until harvest. This aquaculture method might be practiced in a less controlled environment compared with pond culture. Hence, reservoir-ranched paddlefish, in addition to wild paddlefish, might be susceptible to methylmercury contamination. Paddlefish in polyculture with catfish feed primarily on zooplankton supported by the high nutrient inputs that result from intensively feeding catfish. If mercury is present in catfish-pond sediments, paddlefish might accumulate methylmercury in this environment through the food web.

This study investigated these hypotheses by sampling paddlefish from wild sources, reservoirs, and catfish ponds. The methylmercury contamination in the paddlefish samples was analyzed and this article reports the results of the analyses.

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Materials and Methods

Paddlefish meat and jawbone samples were obtained from 4 Kentucky sites: Ohio River and Lake Cumberland (30 samples per site), a private reservoir (10 samples), and 2 catfish farms (33 samples). The Ohio River paddlefish came from 2 locations, below McAlpine Dam (at mile marker 606.0 near Louisville, Ky., U.S.A.) and below Myers Dam (at mile marker 846.0 near Uniontown, Ky., U.S.A.). The different sample sizes were mainly a function of fish availability. The private reservoir was selected for reservoir-ranched fish. Of the 103 fish, 3 observations were unusable for statistical analysis because of errors in either obtaining the methylmercury content or determining the age of the fish.

Table 1—Summary statistics (mean ± standard deviation) of age and methylmercury concentration in the flesh of 100 paddlefish obtained from 4 sources[a]

	Source of paddlefish			
	Ohio River	Lake Cumberland	Reservoir-ranched[b]	Polycultured[c]
Sample size	29	28	10	33
Age (y)	10.74 ± 2.46	7.82 ± 3.08	4.00 ± 0[d]	2.00 ± 0[d]
Min (max) age (y)	8 (18)	4 (15)	—[d]	—[d]
Methylmercury (ppm)	0.14 ± 0.09	0.12 ± 0.09	0.02 ± 0.01	0.05 ± 0.03
Min (max) methylmercury (ppm)	0.03 (0.53)	0.01 (0.29)	0.01 (0.04)	0.03 (0.15)

[a]Average age (pooled data) = 6.37 y (stsnfstf deviation = 4.17 y). Average methylmercury concentration (pooled data) = 0.10 ppm (standard deviation = 0.08 ppm).
[b]These fish were purposefully stocked in a private reservoir for reservoir ranching.
[c]These fish were grown in polyculture with channel catfish in earthen ponds.
[d]All fish from each of these samples were found to be of the same age.

Paddlefish from the Ohio River, Lake Cumberland, and the private reservoir were collected with gill nets. A seine was used to collect polycultured paddlefish from catfish ponds. The fish were filleted and any red flesh in the fillets was trimmed and discarded. Red flesh in fish has a very strong taste, and it is common practice among processors to trim it out of paddlefish fillets. One fillet was selected from each fish and a section of flesh, weighing at least 0.1 kg, was removed from the thickest area. The samples were foil-wrapped and stored at –84 °C until sampling was complete. Frozen samples were packed in dry ice and shipped by air cargo to the laboratory site for methylmercury analysis.

Methylmercury concentrations in fish tissues were determined using head-based digestion followed by cold vapor atomic absorption. Digestion procedures of paddlefish tissues for total methylmercury were done based on the methods described by Gloss and others (1990). Analysis of digested tissues was done according to U.S. Environmental Protection Agency (USEPA) method 1631, revision B (USEPA 1999). Subsamples (about 1 g) of homogenized paddlefish tissues were digested in concentrated sulfuric acid (70 °C) for 30 min. Then, 30% hydrogen peroxide was added and digestion was continued for 2 additional hours. Potassium permanganate (5%) was added to digested samples to oxidize the tissue methylmercury, followed by dilution with distilled water (100-mL total volume). Samples were stored in capped containers at 4 °C until later analysis.

An aliquot (0.5 to 1.0 mL) of the digested samples was added to glass bubblers containing 50 mL distilled water, 5 mL of a hydroxylamine hydrochloride solution (300 g/L), and 2 mL of a 10% stannous chloride solution. Bubblers were purged with ultra-pure nitrogen for 20 min, and the elemental mercury was collected on gold-coated quartz grains. The trapped mercury was subsequently desorbed thermally and measured on a Tekran Cold Vapor Atomic Fluorescence Spectrophotometer (CVAFS, Model 2500) (Tekran, Inc., Toronto, Canada). Peak areas were recorded using a Hewlett-Packard 3396A Integrator (Hewlett-Packard Co., Palo Alto, Calif., U.S.A.). Working mercury standards were prepared from a stock mercury standard containing 1000 μg Hg/L in nitric acid (Sigma-Aldrich, St. Louis, Mo., U.S.A.). Quality assurance measures included the analysis of blanks, duplicates, and spiked samples (for each batch of 10 samples). Percent recovery of spiked samples ranged from 80% to 101%. The method detection limit was 0.017 ppm. All sample concentrations are reported on a wet weight basis.

Dentary bones were removed from individual fish and cleaned of flesh in a boiling water bath. Sections were cut 0.5 mm thick from the straight area posterior to the lateral curve of the dentary bone using a low-speed diamond wire saw (DDK Inc., Wilmington, Del., U.S.A.). The sections were floated in a drop of glycerin on a microscope slide and examined using a compound light microscope at 50×. Annuli bands were counted as described by Adams (1942) to determine age.

Results and Discussion

The aggregate data indicate that the average methylmercury concentration was 0.1 ppm ($n = 100$). The distribution of methylmercury concentration indicated that 35% of the observations were at 0.05 ppm or less, 63% of observations had less than 0.1 ppm, and 99% of observations had methylmercury concentration of 0.3 ppm or less. The highest level of methylmercury in our data was 0.53 ppm from a single Ohio River fish.

Table 1 contains summary statistics for fish age and methylmercury concentrations. Table 1 shows that the Ohio River fish and Lake Cumberland fish were, on average, older than fish from the other 2 sources. Methylmercury contents of the Ohio River and Lake Cumberland fish were also higher, on average, than in the remaining fish from the private reservoir and catfish ponds.

Based on the previous observations, the following regression model was estimated on 100 observations (t-ratios appear below corresponding coefficient estimates; see Greene [1990] for details): $\text{Ln}(\hat{\text{Hg}}) = \underset{-5.73}{-4.79} - \underset{-5.73}{1.62}\,\text{Ln(Age/Mean Age)} + \underset{6.46}{2.53}\,\text{Ohio Riv.} + \underset{6.49}{2.02}\,\text{Lk. Cumb.} + \underset{3.48}{1.94}\,\text{Ohio Riv.} \times \text{Ln(Age/Mean Age)} + \underset{9.45}{3.58}\,\text{Lk. Cumb.} \times \text{Ln(Age/Mean Age)}$ (Adjusted $R^2 = 62\%$). In the model, Ln = natural logarithms, '$\hat{\text{Hg}}$' = the expected methylmercury concentration in paddlefish (in ppm), Age/Mean Age = a regressor whose value corresponds to the age of a paddlefish divided by the average age in the sample, and Ohio Riv. = a dichotomous variable (also known as a dummy variable), which is equal to 1 if the dependent variable value came from the Ohio River and 0 if the dependent variable value was from another location (Lk. Cumb. = similarly defined variable for Lake Cumberland). The results show that all estimated coefficients are significantly different from 0 ($\alpha = 5\%$).

The regression model indicated that paddlefish from the Ohio River and Lake Cumberland not only had higher levels of methylmercury than the average methylmercury concentration of the samples, but the methylmercury concentration increased with age. The rate of increase of methylmercury concentration, with respect to age, was higher in the Lake Cumberland data than in the Ohio River data. This is further illustrated in Figure 1, which plots the predicted methylmercury concentration (from the previous model) with respect to age for Lake Cumberland and Ohio River paddlefish, in addition to their corresponding raw data. Older paddlefish (approximate age 10 y) are sometimes harvested in the wild for meat and eggs. The regression results showed that the predicted methylmercury level (for meat) in a 10-y-old paddlefish from the Ohio River and Lake Cumberland would be 0.12 and 0.15 ppm, respectively. These methylmercury concentrations were less than the USFDA-mandated action limit for methylmercury content in seafood (1 ppm).

Dummy variables identifying either reservoir-ranched or polyculture paddlefish were not entered into the regression model because their presence contributed to excessive multicollinearity. Because there were no within-sample variations of age in either the reservoir-ranched or polyculture samples, their inclusion in the regression model was less interesting than the Ohio River or Lake Cumberland samples. The reservoir-ranched or polyculture samples were compared separately in an ANOVA model (age and location impacts were nonseparable). The results indicated that methylmercury concentrations in reservoir-ranched paddlefish were significantly lower than in paddlefish polycultured with catfish (*P* value < 5%).

Conclusions

This article reports results of a methylmercury detection study in paddlefish obtained from 4 sources in Kentucky (Ohio River, Lake Cumberland, private reservoir, and catfish ponds). The results show that older paddlefish from the Ohio River and Lake Cumberland tended to have higher concentrations of methylmercury than younger paddlefish. This is to be expected because methylmercury in fishes is often the result of years of bioaccumulation; hence, older fish are more likely to have higher concentrations of methylmercury than younger fish.

The USFDA has set an action level for methylmercury in fish of 1 ppm. This translates to the fact that fish sold to consumers with higher methylmercury content are adulterated under the U.S. Food, Drug, and Cosmetic Act, thus triggering regulatory action. However, the USFDA's standard has recently met criticism from environmental and consumer advocacy groups, who demand specific regulatory limits for methylmercury in fish to protect "sensitive populations" (such as pregnant women and children). These limits would be based on an exposure reference dose (RfD), which is defined as "an estimate of a daily exposure to the human population that is likely to be without a risk of adverse effects when experienced over a lifetime" (NAS 2000). In 1997, the USEPA proposed an RfD for methylmercury of 0.1 μg/kg body weight/d (USEPA 1997).

Kentucky's mercury advisory is based on the Great Lakes Protocol (GLP) (Anderson and others 1993), which can be summarized by the following points and assumptions: (1) to apply the USEPA RfD, fish consumed is assumed to be the sole source of exposure to methylmercury; (2) the GLP assumes that an average meal equals 227 g of uncooked fish; and (3) a representative target consumer weighs 70 kg. Individuals belonging to the following 5 advisory groups can use the GLP to identify the maximum methylmercury concentration in fish that are safe to consume: unrestricted consumption (225 meals/y), 1 meal/wk, 1 meal/mo, 6 meals/y, and no consumption. The GLP assumptions indicate that the maximum daily ingestion of methylmercury for a 70-kg person should be 7.0 μg. Hence, to be below the 7.0 μg/d ingestion level, individuals eating 225 meals/y must consume fish with methylmercury content less than 0.05 ppm. For individuals eating 1 meal/wk and 1meal/mo, fish with methylmercury content less than 0.22 ppm and 0.95 ppm, respectively, would be considered.

With respect to the previous ingestion levels, our results show that individuals eating 225 meals/y of fish or more should not consume paddlefish from the Ohio River, and can only consume young paddlefish from Lake Cumberland (less than 6 y old). However, paddlefish from private reservoirs or catfish ponds (age 2 to 4 y) were generally safe for unrestricted consumption. For individuals eating 1 meal/wk of fish, paddlefish 12 y or older might have methylmercury concentrations exceeding 0.22 ppm; such individuals should probably focus more on aquaculture paddlefish than wild caught fish.

Yess (1993) reported a range of methylmercury in canned tuna to vary from less than 0.1 ppm to 0.75 ppm, with an average of 0.17 ppm. Our data showed that, on average, paddlefish from all 4 sources had methylmercury concentrations that were lower than 0.17 ppm. Only 18% of the observations had higher than 0.17 ppm methylmercury concentrations. This suggests that the range of methylmercury concentration in both wild-caught paddlefish (Ohio River and Lake Cumberland) and aquaculture paddlefish (from private

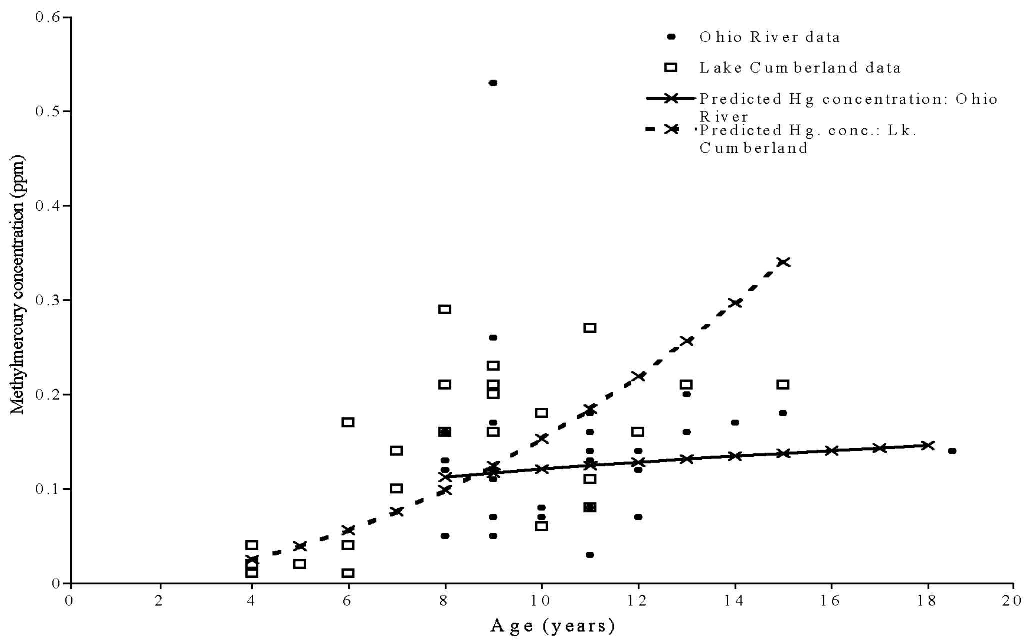

Figure 1—Ohio River and Lake Cumberland data on methylmercury concentrations and age of paddlefish meat. Predicted methylmercury concentrations in paddlefish meat, as a function of age, are also depicted for the 2 sites.

reservoir and catfish ponds) compare favorably with canned tuna, which is 1 of the most commonly consumed seafood items in the United States.

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