Virginia Journal of Science
Volume 41, Number 4B
Winter 1990

Mercury Concentration in Fish from Smith Mountain Lake

Aaron P. Corkum and **David M. Johnson**
Life Science Division, Ferrum College
Ferrum, Virginia 24088

ABSTRACT

Mercury levels were determined in fish taken from Smith Mountain Lake, a 20,000 acre pump-storage reservoir in southwestern Virginia. Striped bass (*Monroe saxatilis*), largemouth bass (*Mirropterus salmoides*), and channel catfish (*Ictalurus punctatus*) were collected during 1987 and 1988 by personnel from Ferrum College and the Virginia Commission of Game and Inland Fisheries. A total of 51 fish were analyzed for mercury at Ferrum College. Tissue samples were digested with nitric acid and hydrogen peroxide to convert various forms of mercury to the divalent cation. Mercury was determined by atomic absorption spectroscopy using the cold vapor technique. The overall mean mercury concentration was 50 ppb, five percent of the FDA standard of 1 ppm (1000 ppb). When grouped by species, the bass had significantly higher tissue concentrations of mercury than the catfish. Mean concentrations were 58 ppb and 29 ppb, respectively. The fish were also sorted by weight and a significant correlation between weight and tissue concentration of mercury was observed in both species of bass but not for catfish.

INTRODUCTION

The objective of this study, carried out between March, 1987 and April, 1988, was to determine the mercury concentrations in fish taken from Smith Mountain Lake. Mercury, on the U.S.Environmental Protection Agency's list of priority pollutants, is a cumulative poison producing irreversible neurological damage in humans. The recommended maximum dietary intake of mercury is 30 μg/day to avoid chronic poisoning (NAS/NAE, 1972). Because mercury is a cumulative poison, its concentration in fish tissue is indicative of mercury levels in the water. Mercury is a naturally occurring element, widely but unevenly distributed throughout the environment, and low concentrations are present in unpolluted waters. Typical concentrations in unpolluted surface waters range from 0.08 ppb to 0.12 ppb. (Horne, 1978). In a 1970 study, 93% of the U.S. streams and rivers sampled contained less than 0.5 ppb (NAS/NAE, 1972). The mercury content of unpolluted streams is less than 0.1 ppb in 31 states where natural mercury deposits are unknown (EPA, 1976). In the same reference, Hannerz reported that algae and aquatic plants accumulate mercury primarily by surface adsorption while accumulation in fish occurs by direct uptake from water and ingestion with food. Once again in this reference, McKim reported that fish tissue concentrations can exceed concentrations in the surrounding water by factors in excess of 10,000. Some researchers believe that mercury concentrations in the water column of less than

0.1 ppb can lead to fish tissue concentrations exceeding the Food and Drug Administration (FDA) action level of 1 ppm (FDER, 1984a).

METHODS

Three species of fish were examined; striped bass (*Monroe saxatilis*), largemouth bass (*Mirropterus salmoides*), and channel catfish (*Ictalurus punctatus*). Both bass species are predatory while the channel catfish is a scavenger species. Fish were sampled during the period from August, 1987 to March, 1988 by personnel from the Virginia Commission of Game and Inland Fisheries and Ferrum College. The fish were sampled at five locations; Moorman's Marina, Hales Ford Bridge, Smith Mountain Lake State Park, Penhook and Bull Run. Sampling methods included sport fishing, gill netting and the application of rotenone to coves. A total of 51 fish were analyzed. The fish were identified and the length, weight and sex recorded along with the sample number, location and any pertinent comments.

Ten grams of wet tissue were required for a single mercury determination. To provide sufficient tissue for replication, approximately 30 grams were taken from a U-shaped cut Perpendicular to the dorsal fin (FDER, 1984b). The tissue samples were washed with double glass-distilled water, wrapped in aluminum foil, placed in a polyethylene zip-lock bag with an identification tag and frozen until the time of digestion.

10.00 grams of fish tissue were placed in a 250 mL flask along with 10 mL of ultra-pure concentrated nitric acid. To avoid excessive frothing, the mixture was allowed to sit for three hours before heating. The samples were then slowly heated to 90-95 °C and held within this temperature range for three hours. The samples were allowed to cool and 2 mL of 30% hydrogen peroxide were added dropwise. The samples were again carefully heated and held at 90- 95 °C for one or two hours until the hydrogen peroxide was destroyed. The digested samples were then quantitatively transferred through glass microfiber filters into 100 mL volumetric flasks and diluted to volume with double distilled water. Because of space and equipment limitations the samples were digested in three batches.

Mercury determinations were made on a Buck Scientific Atomic Absorption Spectrophotometer using the cold vapor technique (EPA, 1979). A 100 mL sample was placed in the cold vapor generator and the system closed. 10 mL of 1% stannous chloride was injected into the generator through a septum and the mixture was stirred and allowed to stand 1.5 minutes to ensure that the divalent mercury had been quantitatively converted to elemental mercury. An air stream was then used to purge the mercury vapor from the generator and sweep it through the quartz windowed cell of the spectrophotometer and the peak absorbance was recorded. Between samples, the vapor generator was rinsed three times with double distilled water and air flow through the system was continued until the signal returned to the baseline. This method gives a detection limit for mercury in fish ranging from 3-8 ppb (FGFC, 1987). To reduce variability, all digested samples were analyzed on the same day.

Precautions were taken at each step in the analysis to assure that the data were reliable. All glassware was washed three times under the conditions in which it would be used (*e.g.*, digestion flasks with ultra-pure nitric acid and hydrogen

peroxide were held at 90- 95 °C for 2 hours and this was repeated twice). Blanks, EPA standards and EPA reference material (freeze-dried fish tissue analyzed by EPA referee labs) were included with each of the three batches of samples before digestion. A mean value of 0.2 ppb was obtained for the undigested blanks indicating a clean analytical system. The mean value for digested blanks was 1.7 ppb, indicating that the digestion and filtration steps introduced small ($\sim 0.2\ \mu g$) but measurable amounts of mercury. This was accounted for by subtracting the mean blank value of each batch from each sample value in that batch. The EPA QA/QC standard of 4 ppb was prepared by appropriate dilution of a water pollution quality control sample obtained from the EPA Environmental Monitoring and Support Lab in Cincinnati. These standards were digested and filtered and the results were corrected against blank values. The average value obtained was 4 ppb, the same as the target value. The mean concentration of mercury in the reference material, also from the EPA Lab in Cincinnati, was 1.9 ppm. While this indicates about a 75% recovery, it is well within the 95% confidence interval of results from EPA referee labs and a valid result according to EPA criteria. Two fish samples were analyzed in duplicate and gave satisfactory results. Duplicate largemouth bass samples gave values of 152 ppb and 183 ppb, while duplicate striped bass samples gave values of 157 ppb and 179 ppb. Quality assurance data is summarized in Table 1.

RESULTS

Overall results are given in table 2. Mercury levels were well above the detection limit and the precision was higher than anticipated. The absolute deviations are very low while the relative deviations are large. This reflects the difficulty of measuring submicrogram quantities (10 g tissue x 50 ng Hg/g tissue x $1\ \mu g/1000ng = 0.5\ \mu g$ Hg), especially for samples requiring digestion. Further reduction of variability would require a clean room and dedicated equipment. Based on the last column in table 1, the relative precision of the analytical method was in the range of 10-20%. It can be seen from figures 1-3 that mercury concentrations in fish of approximately the same size vary in the range of 50-100%. Much and perhaps most of the variability found in the data reflects real differences among fish rather than the precision of the analytical methodology.

One result was rejected because of suspected contamination. This was a catfish sample in which the mercury analysis gave a tissue concentration three times as high as the next highest result and four times the mean value.

The mean mercury concentration for all fish was 50 ppb, five percent of the FDA standard of 1 ppm or 1000 ppb. At these levels, consumption of fish from Smith Mountain Lake is not a concern with respect to dietary intake of mercury. Fish tissue levels this low also indicate that there is little chance of significant mercury contamination having occurred in Smith Mountain Lake.

The mean mercury concentrations of the two bass species were nearly the same, 57 ppb and 58 ppb. However, the mean catfish concentration of 29 ppb was significantly lower, using the Student t-test at a confidence level of 99%. This was expected because bass, as predators, are higher on the food chain than catfish which are primarily scavengers. This phenomenon is a property of many cumulative poisons, known generally as bioamplification.

TABLE 1. Summary of quality assurance data. $\bar{x}$ = arithmetic mean, n = sample size, s' = sample standard deviation.

	Reagent Blanks (ppb)		EPA QA/QC	EPA fish tissue sample (ppm)		Duplicate Analysis
	undigested	digested	Std (4 ppb)	reference value	this study	(% difference)
$\bar{x}$	0.2	1.7	4.0	2.5	1.9	15.5
n	9	8	7	(large)	3	2
s'	0.1	0.7	1.0	0.6	0.1	3.5

TABLE 2. Results of mercury analysis. All values given in micrograms mercury per kilogram tissue (ppb) $\bar{x}$ = arithmetic mean, n = sample size, s' = sample standard deviation.

	All Fish	Striped Bass	Largemouth Bass	Channel Catfish
$\bar{x}$	50	57	58	29
n	50	19	17	14
s'	31	33	33	12

Scatter plots were generated to find if there was a significant correlation between fish weight and tissue mercury concentration. The plots for each species are shown in figures 1-3. Significance levels greater than 99% were obtained for both bass species. However, there was essentially no correlation between catfish weight and mercury concentration. Unfortunately, there are very few data for large fish, but the strong correlation for both bass species suggests that tissue concentrations increase with age. This is another property of cumulative poisons termed bioaccumulation. Bioamplification and bioaccumulation are both known to occur with mercury. We have reported them here primarily to indicate the reliability of the data set.

We will end on a whimsical note. Although presumptuous, the regression lines on the scatter plots in figures 1 and 2 do have slopes and intercepts and beg the question, "How big would a bass from Smith Mountain Lake have to be to exceed the FDA standard for mercury?". Extrapolation gives an answer of slightly over 60 pounds for striped bass and slightly under 25 pounds for largemouth bass. These are approximately world record size fish for both species and much larger than the record sizes from Smith Mountain Lake where the record for largemouth bass is about 12 pounds and for striped bass, about 45 pounds. Extrapolations for the Smith Mountain Lake record size fish give tissue mercury concentrations of 525 ppb for the largemouth bass and 740 ppb for the striped bass. It would be interesting to analyze tissue taken from record size bass caught in Smith Mountain Lake and compare the measured tissue concentrations of mercury with the values obtained by extrapolation.

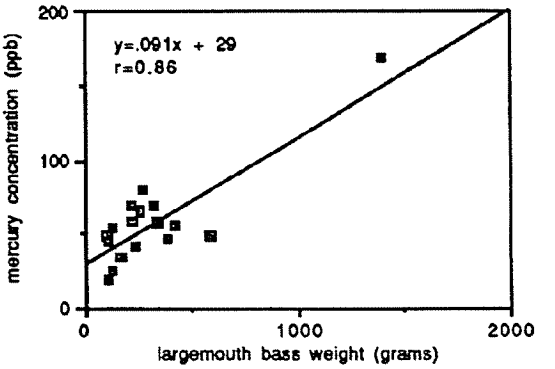

FIGURE 1. Correlation of weight with tissue concentration for largemouth bass.

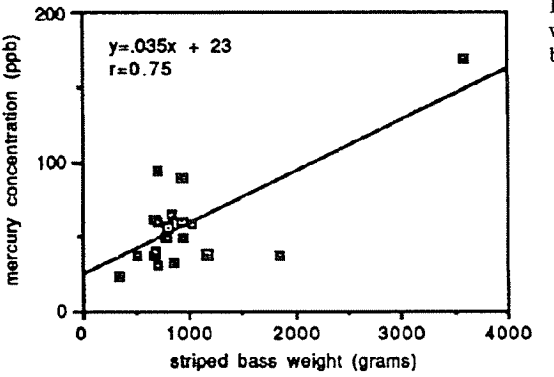

FIGURE 2. Correlation of weight with tissue concentration for striped bass.

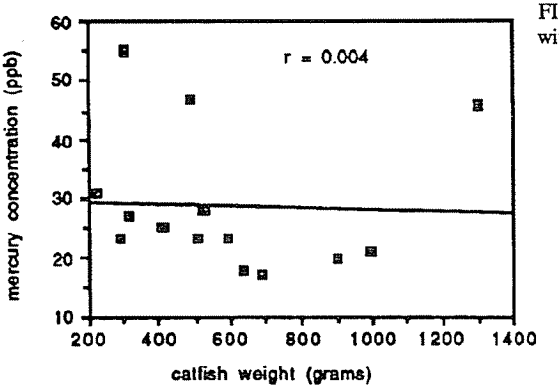

FIGURE 3. Correlation of weight with tissue concentration for catfish.

ACKNOWLEDGEMENTS

This study was supported by the Smith Mountain Lake Association and Ferrum College. The authors wish to thank Homer Royal with the Florida Game and Freshwater Fish Commission for assistance with the analytical methodology and David Whitehurst and the Virginia Game and Inland fisheries Commission for their help collecting the fish samples.

LITERATURE CITED

Environmental Protection Agency(EPA) 1976. Quality Criteria for Water (EPA-440/9-76-023). U.S. Government Printing Office, Washington, D.C. pp. 183-192

Environmental Protection Agency (EPA)1979. Methods for Chemical Analysis of Water and Wastewater (EPA-600/4--79- 020). U.S. Government Printing Office,Washington, D.C. PP- 245. 1 -24-5.5

Florida Department of Environmental Regulation (FDER) 1984a. Mercury in Florida Aquatic Systems. Florida DER, Tallahassee.

Florida Department of Environmental Regulation (FDER) 1984-b. FDER Metals Task Force Special Statewide Survey: Field Instructions and Records. FDER, Tallahassee.

Florida Game and Freshwater Fish Commission (FGFC) 1987. Heavy Metal Analysis-Mercury, in Florida GFC Quality Control Manual for Chemistry Labs. FGFC, Tallahassee, Florida.

Horne, R.A. 1978. The Chemistry of Our Environment. John Wiley and Sons, New York, p. 293.

NAS/NAE Committee on Water Quality Criteria 1972. Water Quality Criteria. U.S. Government Printing Office, Washington, D.C., p. 72