Bull. Environm. Contam. Toxicol. 23,779-783 (1979)

Source of Mercury in Fish in New Impoundments

J. A. Cox, J. Carnahan, J. DiNunzio, J. McCoy, and J. Meister
Department of Chemistry and Biochemistry, Southern Illinois University at Carbondale, Carbondale, Ill. 62901

That high levels of mercury are often found in fish flesh in new impoundments is well-known; however, the source(s) of the mercury is typically not identified. From the present study data are obtained which support a hypothesis that the primary source may often be natural rather than anthropogenic. A subsequent conclusion is that the problem will be short-term; within ca. 5 years the mercury levels in fish in such systems should be normal.

This study was performed on Cedar Lake, Jackson and Union Counties in Southern Illinois. The reservoir was constructed in the early 1970's, reaching normal pool level during 1974, with a surface area of 7.1×10^6 m^2 and volume of $5.1 \times 10^7 m^3$. The $1.8 \times 10^8 m^2$ watershed and lake area is unglatiated and composed primarily of Pennsylvanian sandstone stratum; some shale and limestone are present. The soil types are basically Belknap-Heymond.

In February, 1976, a joint test by the Illinois Department of Conservation, Illinois Department of Public Health and the Illinois Environmental Protection Agency found that the mercury in the largemouth bass, *micropterus saloides,* in that impoundment often exceeded the 0.5 mg/kg (ppm) level which was the upper limit for safe consumption according to the U.S. Food and Drug Administration. The results were confirmed in our laboratories. The present study was initiated to determine the source of the mercury.

MATERIALS AND METHODS

The fish for this study were obtained by netting, shocking, and angling. Soil samples were taken with a core sampler. Bottom sediments were sampled with an Eckman dredge.

Total mercury was determined by flameless atomic absorption spectrometry (HATCH and OTT 1968). The method was modified by discarding the results when the blanks had less than 90% transmittance (COX *et al.* 1975).

0007-4861/79/0023-0779 $01.00

The determinations of total mercury in fish were referenced to the weight of fillets which were dried with filter paper. Soil and sediment samples were dried at 110°C, powdered, and screened with a 500 micron sieve prior to weighing and digestion.

The soil samples after screening were divided into three parts, of which one received addition of a known quantity of mercury. All portions (1-3 gm each) were digested in 20-25 mL of concentrated sulfuric acid. During the digestion three additions of 30% hydrogen peroxide, 2 mL each, were made. The digestion was stopped when the solutions became gray. About 0.5 mL of 5% $KMnO_4$ and 20 mL of water were added. The solutions were filtered and diluted to 100 mL. Except for the filtration and standard addition, the procedure is that recommended previously (HATCH and OTT 1968). If the recovery of the added mercury exceeded 75%, the results were retained.

Methylmercury was determined by gas chromatography with a ^{63}Ni electron capture detector. Sample treatment, which involves extraction from an aqueous slurry into benzene in the presence of cysteine acetate, followed a previously reported procedure (WESTOO 1967).

Reagent Grade chemicals were used throughout except that the nitric, perchloric, and sulfuric acids were Baker Analyzed, Suitable for Mercury Determination. Distilled water was used after passing through a mixed bed ion exchange column and charcoal filter.

RESULTS AND DISCUSSION

During the course of this investigation about 200 fish samples were analyzed for mercury. As expected, species which were high in the food chain contained more mercury.

A typical set of data are summarized in Table 1. For bass the overall average, 0.48 ppm, was near the above mentioned recommended limit of 0.5 ppm Hg for safe consumption. The flesh of crappies, *pomoxis annularis,* showed a similar result, a 0.59 ppm Hg average for 15 samples taken during a comparable period. Bluegills, *lepomis macrochirus,* which are lower in the foodchain, gave an average value below 0.2 ppm.

The above results suggest that the high Hg levels in the bass and crappies are a result of biomagnification through the foodchain. Supporting this interpretation is the percentage of the mercury which is organically-bound. Five largemouth bass in the range of 23-36 cm had an average methylmercury chloride

TABLE 1

Mercury in Cedar Lake Largemouth Bass, Fall, 1976

length,cm	ppm Hg,range	ppm Hg,ave.	Samples
15-25	0.14-0.31	0.27	3
25-35	0.11-0.81	0.49	11
35-60	0.49-1.20	0.67	4

content of 0.32 ppm which was 58% of the total Hg in these samples. Further, the organic mercury concentration was highly dependent upon size, ranging from 0.0 ppm in the 23 cm sample to 0.55 ppm in the 35 cm bass. Biomagnification is known to mainly occur with organic mercury; the retention of methylmercury in fish flesh is on the order of at least a few years which accounts for the effect of size (age) on concentration (LELAND *et al.* 1976, HASSELROT 1974).

The data in Table 2 indicate that the mercury entered the food chain from the soil which was inundated

TABLE 2

Effect of the Aquatic Environment on the Mercury Concentration in the Soil

	Hg,ppm			
	site 1	site 2	site 3	site 4
onshore	0.08	0.04	0.15	0.11
shoreline	0.01	0.02	0.08	0.05
lake bottom	0.00	0.02	0.00	0.02

when the impoundment was constructed. Here sites along the lake were selected on the basis of having undisturbed soil features over a wide area. Onshore samples were taken about 20m from the maximum pool shoreline. Lake bottom samples were dredged from depths of 5-10 m below the normal pool surface. The three locations at each site were on a straight line.

The Hg level on the lake bottom is clearly well-below that onshore, and the shoreline yields an intermediate value. Apparently the mercury in the soil is in an insoluble state but can enter the food chain through action of micro-organisms in the aquatic environment.

Direct solubility of the mercury species is unlikely. The Hg content of the water is 0.01 µg/L, or less, which is below the average level in water supplies (DURUM *et al.* 1971). Although this concentration is sufficient to cause high Hg levels in fish (POTTER *et al.* 1975), it would not yield the high organic mercury contents which were observed.

A consequence of the soil being the source of the mercury is that upon depletion, which has essentially occurred according to the Table 2 results, the average concentrations in the fish in the impoundment should become lower because of the influence of recent hatches. Indeed, recent data from the Illinois Department of Public Health (BUITT 1979) verify this prediction. Nine largemouth bass which were collected in September and October 1977 had an average level of 0.19 ppm Hg (range, 0.12-0.24 ppm).

Of general importance is that the source of the mercury in the soil is apparently natural rather than anthropogenic. The possibility of mercury-based fungicides being the source is discounted because of the limited area of the watershed where they could have been used and because 30 soil tests at various locations in the watershed did not show elevated Hg levels. In the latter, only one sample, 0.8 ppm, was out of the onshore range of Table 2. Repeated tests in that area did not show other samples with high concentrations. A coal-burning power plant in the area was also not considered the source since a recent study on an impoundment which is located immediately downwind of such a plant only showed 0.07 ppm Hg in largemouth bass (ANDERSON and SMITH 1977).

That the Hg source is probably natural is quite significant when it is considered that the soil type of the watershed is not associated with unusually high Hg levels. Thus predator fish in new impoundments should be anticipated to have elevated Hg concentrations. If such impoundments are to be used as fisheries, close monitoring of Hg in the predator fish during the first few years is recommended. It may sometimes be necessary to ban fish harvest during this period.

REFERENCES

ANDERSON, W. L. and K. E. SMITH: Environ. Sci. Technol. 11, 75 (1977).

BUITT, J. M.: Illinois Department of Public Health, private communication.

COX, J. A., G. L. LUNDQUIST, R. G. WEBSTER, R. A. COX, P. C. LINDAHL, and A. L. CASKEY: Bull. Environm. Contam. Toxicol. 13, 397 (1975).

DURUM, W. H., J. D. HEM, and S. G. HEIDEL: U. S. Geol. Survey Circular. 643, Washington, D. C. (1971).

HASSELROT, T. B. and A. GOTHBERG: Proc. International Conf. Transport of Persistent Chemicals in Aquatic Ecosystems, Ottawa, Canada (1974).

HATCH, W. T. and W. L. OTT: Anal. Chem. 40, 2085 (1968).

LELAND, H. V., D. J. WILKES, and E. D. COPENHAVER: Jour. WPCF. 48, 1473 (1976).

POTTER, L. D., D. KIDD, and D. STANDIFORD: Environ. Sci. Technol. 9, 43 (1975).

WESTOO, G.: Acta Chem. Scand. 21, 1790 (1967).