

DELAWARE RIVER SURVEY:
ANALYSES OF FISH SAMPLES FOR TRACE AMOUNTS OF METALS

Medical Research Project No. 1420

Haskell Laboratory Report No. 427-72

- 1 C. F. Reinhardt/J. A. Zapp, Jr.
- 2 P. E. Smith, Jr./H. J. Trochimowicz/A. Azar
- 3 J. R. Barnes/J. G. Aftosmis/R. S. Waritz
- 4 J. F. Morgan
- 5 D. B. Hood
- 6 H. Sherman
- 7 C. S. Hornberger
- 8 F. D. Griffith
- 9 Haskell Laboratory File
- 10-19 John Curry, Orchem Dept., Chambers Works
- 20 C. W. Maynard, Orchem Dept., Jackson Lab.

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Report by:

S.P. Shrivastava

Surendra P. Shrivastava
Research Biochemist

Approved by:

John A. Zepp, Jr.
John A. Zepp, Jr.
Director

SPS:dhg

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SUMMARY

Trace levels of five metals in fishes collected from three locations (above, near and below Chambers Works Plant) on the Delaware River and for twelve successive months were determined by atomic absorption spectroscopy. Although no definite conclusions can be drawn from the available data, slight differences were found among three different locations, eight types of fishes, or four quarters of the year selected for study. Average levels of chromium, copper, lead, mercury and zinc, respectively, were 0.59, 1.6, 0.42, 0.38 and 16.35 ppm of wet tissues.

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PURPOSE OF STUDY

This study was conducted to determine any contamination of fishes near Chambers Works with trace amount of metals. Monthly collections from June 1971 to May 1972 were made and metal contents determined. This report covers a period of 12 months, 8 commonly observed fish species, three locations on the river, and determinations for chromium, copper, lead, mercury and zinc metal levels.

MATERIALS AND METHODS

Three locations on the river were selected for fish sampling, one about two miles below the Chambers Works (Church's Landing), one about 12 miles up the river (Raccoon Creek), and one about 20 miles down the river (Hope Creek) from the plant. Fish samples were collected by Ichthyological Associates, Middletown, Delaware. Fishes were caught with net and trawl, on and off the shore, within one-half mile radius of the location, and were preserved in 90% alcohol and formalin prior to freezing. A variety of fishes was collected from each location and they varied in number, size, age, sex, etc.

SAMPLE PREPARATION

Frozen fish samples were warmed to room temperature, scales were removed, a small portion of flesh from one or more fish was cut finely into small bits, weighed and used as such or dried at 100°C for 16 hours, and then ground in a mortar with pestle, weighed and used for metal analysis. In studies from June 1971 - February 1972, 2 g (wet weight) flesh were used for metal analysis. Metal analyses of March - May 1972 were made with 500 mg dried fish samples in order to estimate the variation due to water content of fish samples.

Methods for digestion of samples for chromium, copper, lead and zinc were essentially the same as given in Haskell Laboratory Biochemistry Analytical Methods (1) and for mercury, the Federal Water Quality Administration, Chicago District Method (2) was used.

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METAL ANALYSES IN FISH DIGEST

Metal levels in the fish digest were determined by an atomic absorption spectrophotometer. The amount of lead was determined by chelating the lead in 25 ml fish digest with 1 ml of 2% aqueous ammonium pyrrolidinodithiocarbamate, extracting the lead complex with 5 ml methyl isobutyl ketone, and then aspirating the extract into the flame (1). The amount of chromium, copper and zinc, however, was determined by directly aspirating the fish digest. The absorption of radiation was measured at 358, 325, 283 and 214 nm, respectively, for chromium, copper, lead and zinc.

Levels of mercury in fish digest were determined by flameless atomic absorption technique (3,4). The fish digest was treated with nitric and sulfuric acids in the presence of potassium permanganate to oxidize all the mercury present to mercuric (Hg^{++}) form, the excess permanganate was reduced with hydroxylamine hydrochloride and then mercury was reduced to metallic mercury with stannous chloride. Mercury vapor was generated with an aerator and circulating pump, passed through the absorption cell, and mercury content in the vapor was determined by measuring absorption at 253.7 nm (4).

Perkin-Elmer Atomic Absorption spectrophotometer model 303, Perkin-Elmer Mercury Analysis System, a Varian recorder, and a single element hollow cathode lamp for each metal were used during the analysis. Air-acetylene flame was used for all but mercury determination.

The metal levels in fishes reported here are based on single determinations and only in certain cases they represent averages of 2 or 3 determinations. The concentration of metals was calculated from the calibration curves for each metal after correction for the background. The data are compared on wet weight basis because the amount of water content in the sample does not alter the conclusions (Table 1). No detectable levels of metals in 1 ml samples of the 90% alcohol or the formalin used as a preservative were observed when they were analyzed like a fish sample.

RESULTS AND DISCUSSION

Results of metal analysis in fishes are given in Tables 2A-2E and the averages are summarized in Table 2. The range and average concentrations of metals were as follows: chromium, 0.17-2.2 and 0.59; copper, 0.25-5.0 and 1.6; lead, 0.05-2.2 and 0.42; mercury, 0.03-1.9 and 0.38; and zinc, 4.9-79.7 and 16.35 ppm wet tissues. In a similar previous study with limited number of determinations made by the Academy of Natural Sciences of Philadelphia (ANSP), the concentrations of metals in fishes were: chromium, 0.74-2.89; copper, 0.82-1.88; lead, 8.4-22.9; mercury, 0.09-1.68; and zinc, 20.1-46.5 (5). Although the results for chromium, copper, mercury and zinc are in agreement, values for lead reported by the ANSP were much higher (5).

Limited data are available in the literature on the levels of chromium, copper, lead and zinc in fishes. Although the levels of copper and zinc reported here (Tables 2B, 2E) are comparable to elemental analyses made earlier, the levels of chromium, lead and mercury (Tables 2A, 2D) respectively, are 10, 3 and 3 times reported values (6). Concentrations of

RESULTS AND DISCUSSION (Continued)

lead found in seafood, however, have ranged between 0.17-2.5 and averaged to 0.5 ppm (7).

Reports on mercury levels in fishes are numerous (8,9,10,11,12). Concentrations of mercury in fishes from Wisconsin waters, removed from any known source of mercury, ranged between 0.01-0.6 and averaged 0.19 ppm (13), which again is half the average value obtained in this present study. F.D.A. maximum permissible level of mercury in fish flesh, however, is 0.5 ppm.

Limited comparisons with respect to levels of metals in fishes and locations can be made from March and April data (Tables 2A-2E). A comparison of averages for eight fish varieties, three different locations and four quarters of the year selected for studies does not show any important differences (Table 3). Data from Academy of Natural Sciences of Philadelphia support these findings (5).

It is evident from Tables 2A-2E that there are not enough data available for any statistical analyses and meaningful conclusions. Thus, it will be observed that in no case was the same kind of fish caught at the three different locations during a month and only in three cases one kind of fish was available continuously for three months from one location. Further studies under partially controlled conditions using a number of floating fish cages at different locations on the river may be necessary to reach any definite conclusions.

SUMMARY

Trace levels of five metals in fishes collected from three locations (above, near and below Chambers Works Plant) on the Delaware River and for twelve successive months were determined by atomic absorption spectroscopy. Although no definite conclusions can be drawn from the available data, slight differences were found among three different locations, eight types of fishes, or four quarters of the year selected for studies. Average levels of chromium, copper, lead, mercury and zinc, respectively, were 0.59, 1.6, 0.42, 0.38 and 16.35 ppm of wet tissues.

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REFERENCES

1. Anonymous. Atomic Absorption Procedure for Lead Analysis. Haskell Laboratory, Clinical Laboratory Method No. 19.
2. Anonymous. 1970. Federal Water Quality Administration Method of Analysis Used by Chicago District for the Examination of Mercury in Fish by Atomic Absorption.
3. Anonymous. 1971. Perkin-Elmer Mercury Analysis System Operating Directions 303-3119.
4. Hatch, W. R. and Ott, W. L. 1968. Determination of Submicrogram Quantities of Mercury by Atomic Absorption Spectrometry. Anal. Chem. 40:2085-87.
5. Hart, B. 1970. River Survey Results of Fish Analysis by Academy of Natural Sciences of Philadelphia. Unpublished data.
6. Bowen, H. J. M. 1966. "Trace Elements in Biochemistry," p. 70, Academic Press, N. Y.
7. Schroeder, H. A., Balassa, J. J., Gibson, F. S. and Valanju, S. N. 1961. Abnormal Trace Metals in Man:Lead. J. Chron. Dis. 14:408-425.
8. Hartung, R. and Dinman, B. D., Eds. 1972. "Environmental Mercury Contamination," pp. 349. Ann Arbor Science Publishers, Inc., Mich.
9. Friberg, L. T. and Vostal, J. J. 1972. "Mercury in the Environment, a Toxicological and Epidemiological Appraisal." C. R. C. Press, Ohio.
10. Clarkson, T. W. 1972. Recent Advances in the Toxicology of Mercury with Emphasis on the Alkylmercurials. C. R. C. Crit. Rev. Environ. Control 1:203-34.
11. Katz, A. 1972. Mercury Pollution: The Making of an Environmental Crisis. C. R. C. Crit. Rev. Environ. Control. 2:517-34.
12. Turney, W. G. 1971. Mercury Pollution: Michigan's Action Program. J.W.P.C.F. 7:1427-38.
13. Kleinert, S. J. 1972. Mercury Levels in Wisconsin Fish. In "Environmental Mercury Contamination," pp. 58-70.