METAL CONCENTRATIONS IN MUSCLE OF FISH FROM AQUATIC SYSTEMS IN EAST TENNESSEE, U.S.A.

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Abstract. Heavy metal residues (i.e., As, Cd, Cu, Pb, Mn, Hg, and Zn) were determined in striated muscle of 268 fish specimens harvested during a 5-yr period (1980-1984) from several aquatic systems in east Tennessee (U.S.A.). Elevated concentrations of Hg, Mn, and Cd were found in the muscle of fish from several of the aquatic systems studied; concentrations of Hg exceeded the U.S. Food and Drug Administration action level of 1.0 ppm for food intended for human consumption. In general, the concentrations of the other metals in fish muscle were low. Moreover, muscle metal content did not vary among the three fish groups (i.e., game fish, catfish, and rough fish) investigated at any one of the nine sampling stations established. The results of this study are in agreement with the 1978-1979 pilot survey of Young and Blevins (1981) conducted at the same sampling stations. It appears that, in this region of Tennessee, heavy metal contamination of fish tissues has neither improved nor deteriorated during the last 5 yr.

I. Introduction

In many regions of the United States, municipal and industrial wastewater discharges into aquatic habitats threaten aquatic life and public health. Among the myriad of organic and inorganic substances released into aquatic ecosystems, heavy metals have received considerable attention due to their toxicity and potential bioaccumulation in many aquatic species. Although numerous aquatic organisms have been used as monitors of heavy metal contamination (Anderson-Bledshoe and Scanlon, 1983; Elder and Mattraw, 1984; Nasu and Kugimoto, 1981 ; Stinson and Eaton, 1983), most studies have relied on fish as sensitive indicators of not only heavy metal pollution (Cox *et al.*, 1979; Moore and Sutherland, 1981; Ney and Van Hassel, 1984; Norris and Lake, 1984; Pagenkopf, 1983), but also radionuclide (Blevins *et aL,* 1985; Moore and Sutherland, 1981) and mutagenic chemical contamination (Osborne *et al.,* 1982). While the concentration of heavy metals in fish tissues is largely determined by the concentrations of such metals in the surrounding environment (i.e., water, sediments, and other aquatic organisms), other factors are known to influence the uptake of heavy metals by fish, namely the ability of the fish species to move into uncontaminated areas (Moore and Sutherland, 1981) and water chemistry parameters such as pH, alkalinity and hardness (Pagenkopf, 1983). The metal ions (i.e. Ca^{+2} and Mg^{+2}) have been shown to provide protection to fish from heavy metal toxicity. The protective action of these cations is due to their successful competition with heavy metal species for fish gill surface interaction sites (Pagenkopf, 1983). It should be noted that heavy metals are acutely toxic

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to fish via alteration of gill function and subsequent respiratory impairment. In addition to these factors, the size (weight and/or length) and level in the food chain of the fish have also been correlated with heavy metal residues in the fish tissues (i.e., biomagnification), especially in the case of Hg, where the highest concentrations are observed in large predatory fish (Cox *et aL,* 1979). Moreover, fish species living in the benthic region of aquatic habitats in association with the sediments displayed higher whole-body metal accumulations (Ney and Van Hassel, 1983).

The eastern region of Tennessee (U.S.A.) comprises an area that is rapidly expanding in both population and industry. As a result, surface waters and associated biota in the area have been impacted by the release of toxic organic and inorganic chemicals (Clark *et aL,* 1980). Fish harvested from aquatic habitats in this region have displayed significant levels of gamma radioactivity (Blevins *et al.,* 1985), mutagenic activity (Mohr, 1984) and heavy metals (Young and Blevins, 1981). In their 1978-1979 study of the Holston River Basin, Young and Blevins (1981) found that, based on heavy metal residues in the striated muscle of a limited number of fish, metals were in sufficient concentrations to affect the health of human consumers. Herein, we report the results of heavy metal residues (i.e., As, Cd, Cu, Pb, Mn, Hg, and Zn) in striated muscle of 268 fish specimens harvested in 1980-1984 from the same aquatic systems in east Tennessee investigated earlier by Young and Blevins (1981). The metals under investigation are known to be potentially toxic to aquatic life and to human consumers of fish muscle at some level of exposure and absorption.

2. Materials and Methods

2.1. COLLECTION OF FISH SPECIMENS

From 1980 to 1984, fish were harvested from the nine aquatic systems under investigation with hook and line (the locations of sampling sites are depicted in Figure 1 and described in Table I). The species of harvested fish were identified, which allowed them to be placed into one of the following three groups: (1) game fish - includes smallmouth bass *(Micropterus dolomieui),* largemouth bass *(Micropterus salmoides),* white bass *(Morone chrysops),* rockfish *(Morone saxatilis),* walleye *(Stizostedion vitreum),* crappie *(Pomoxis annularis -* white or *P. nigromaculatas -* black), and bluegill *(Lepomis macrochirus*); (2) catfish – includes channel catfish *(Ictalurus punctatus*), flathead catfish *(Pylodictus olivaris),* and yellow bullhead catfish *(Ictalurus natalis);* and (3) rough fish includes carp *(Cyprinus earpio),* drum *(Aplodinotus grunniens), gar (Lepisosteus osseus),* buffalo *(Ietiobus niger),* redchase sucker *(Moxostoma* sp.), hogsucker *(Hypentilium nigricans),* and gizzard shad *(Dorosoma cepedianum).* A minimum of six fish per group per sampling station was obtained (a total of 268 fish specimens were examined). A gross autopsy was performed (using stainless steel implements on a glass working surface) on all fresh fish specimens collected to determine the condition of the muscle, liver, kidneys, brain, adipose tissue, and gonads. The extent of pathological damage such as tumor formation was determined. In addition, the weight, length, age, and sex of each

Location and description of fish sampling sites in east Tennessee (U.S.A.)

^a These are in addition to natural sources.

fish sample were recorded (data not presented). Each fish specimen was then sealed in a sterile polyethylene bag, and frozen at -20 °C. Within 7 days of freezing, a striated muscle sample (i.e., portion of fish normally consumed by the human population) from each partially thawed fish specimen was taken from the pectoral region using stainless steel implements on a glass working surface, and analyzed immediately for the presence of heavy metals as described below.

2.2. DIGESTION OF FISH MUSCLE SAMPLES

2.2.1. *Arsenic*

Fish muscle tissue (10 g wet weight) intended for As analysis was digested with a mixture $(1:1)$ of ultrapure HCl and ultrapure H_2SO_4 (all acids used in this study were brand Ultrex, J. T. Baker Chemical Company, Phillipsburg, NJ; triple glass-distilled water was used in all analyses; all glassware used was acid washed in a 1 : 1 reagent grade $HNO₃$: glass-distilled water mixture for at least 24 hr prior to use). The digestion procedure was as previously described (Young and Blevins, 1981).

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2.2.2. *Mercury*

Fish muscle tissue (10 g wet weight) intended for Hg analysis was digested with a mixture of ultrapure H_2SO_4 , HNO_3 and perchloric acids, and sodium molybdate as previously described (Munns and Holland, 1971).

2.2.3. *Other Metals*

Fish muscle tissue (10 g wet weight) intended for Cd, Cu, Pb, Mn, and Zn analyses was digested with a mixture (5 : 1) of ultrapure $HNO₃$ and perchloric acids at 90 °C as previously described (Young and Blevins, 1981).

2.3. SPECTROPHOTOMETRIC ANALYSIS OF FISH MUSCLE DIGESTS

All metal analyses of fish muscle digests were undertaken in triplicate with a Perkin-Elmer atomic absorption spectrophotometer with deuterium arc background correction (model 550, Perkin-Elmer, Norwalk, CT). Cadmium, Cu, Pb, Mn, and Zn were determined using graphite furnace model HGA-2200 (Perkin-Elmer) as previously described (Perkin-Elmer, 1981). Arsenic was determined with the hydride vapor generation method as described by Brodie (1979). Mercury was determined with the cold vapor technique as described by Munns and Holland (1971). Random fish muscle digest samples were spiked with known amounts of heavy metals and subsequently analyzed in order to establish the effective recovery of the individual metals from this complex matrix; metal recoveries in spiked samples were greater than 95% . The method of known addition was used to quantify the metals in the fish muscle digests (Perkin-Elmer, 1981). The concentrations of metals in the original fish muscle was then calculated and expressed as μ g g⁻¹ metal per wet weight of tissue (i.e., ppm).

3. Results and Discussion

3.1. NOLICHUCKY RIVER AND LITTLE CHUCKY CREEK

The results of metal residues in fish muscle harvested from the Nolichucky River and the Little Chucky Creek are presented in Table II. As was the case at other sampling stations in this study, muscle metal content appeared to be similar among the three fish groups (i.e., game fish, catfish, and rough fish) at any one of these sampling stations. While fish metal content can be influenced by the species and size of fish, our data indicate that the metal content of the surrounding environment (e.g., water) is perhaps more important in determining the metallic content of fish muscle. Moreover, muscle metal content generally did not vary among these three sampling stations, with the exception of the markedly higher Cd (0.27 ppm mean) and Mn (0.91 ppm mean) levels observed in the fish harvested from the Little Chucky Creek. Similarly high Cd and Mn concentrations in fish muscle were reported by Young and Blevins (1981) in the Little Chucky Creek. There are natural deposits of Mn throughout this region of Tennessee resulting in high background levels of this element in most surface waters and in aquatic

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Heavy metal residues in striated muscle of fish harvested from the Nolichucky River and Little Chucky Creek during 1980 to 1984

See text for identification of fish groups.

 μ It should be noted that ppm is synonymous with μ g g⁻¹ wet weight of fish tissue.

life such as fish (Young and Blevins, 1981). With regards to the elevated Cd concentrations in fish muscle, this is attributed to the release of this metal as a by-product during the mining of Zn in this region of Tennessee (Young and Blevins, 1981). In fact, Zn concentrations in fish muscle were also notable at all sampling stations investigated (see Tables II to IV).

3.2. WATAUGA LAKE AND BOONE LAKE

The results of metal residues in fish muscle harvested from Watauga Lake and Boone Lake are presented in Table III. As was previously noted, muscle metal content did not vary among the three fish groups at any one of these two sampling stations. Worthy of note, however, are the elevated concentrations of Cd found in fish muscle harvested from these two lakes (i.e., means of 0.23 and 0.25 ppm for Watauga Lake and Boone Lake, respectively) and the high Mn levels (mean of 0.86 ppm) observed in fish from Watauga Lake. These higher levels in fish muscle from these lakes are in agreement with the findings of Young and Blevins (1981) in their 1978-1979 survey. As described above,

TABLE III

Heavy metal residues in striated muscle of fish harvested from Watauga Lake and Boone Lake during 1980 to 1984

^a See text for identification of fish groups.

^b It should be noted that ppm is synonymous with μ g g^{-1} wet weight of fish tissue.

Zn mining and natural deposits of Mn account for the elevated levels of Cd and Mn observed in fish muscle. It appears, moreover, that municipal and industrial wastewater discharges by the Cities of Elizabethton and Johnson City have not markedly affected the metal content of fish muscle harvested from the downstream lake, Boone Lake, as compared to the upstream, pristine, mountain lake, Watauga Lake.

3.3. HOLSTON RIVER BASIN, INCLUDING CHEROKEE LAKE AND NORRIS LAKE

The results of metal residues in fish muscle harvested from several stations on the Holston River Basin, including Cherokee Lake and Norris Lake are presented in Table IV. Again, muscle metal content did not vary markedly among the three fish groups at any one of the four sampling stations. Extremely high concentrations of Hg in fish muscle were observed at the sampling station no. 6 on the North Fork of the Holston River (i.e., mean of 2.2 ppm - Table IV). Slightly lower but, nevertheless, notable concentrations of Hg (i.e., mean of 1.4 ppm) were found in fish muscle at the downstream station on the Holston River. These Hg concentrations in fish muscle exceed the FDA action level of 1.0 ppm (Sonia Delgado, FDA, Div. Regulatory Guidance, Washington, DC, personal communication). Moreover, these Hg concentrations produce osmoregulatory failure in fish (Wasserman and Koepp, 1977) and are similar to the fish muscle concentrations that produced the catastrophic Minamata disease in Minamata Bay, Japan (Harada, 1978). The Hg in the North Fork of the Holston River originates at a former Olin Corporation chlor-alkali plant located in S altville, Virginia (Clark *et al,,* **1980; Young and Blevins, 1981). Although this facility**

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Heavy metal residues in striated muscle of fish harvested from the Holston River Basin, including Cherokee Lake and Norris Lake, during 1980 to 1984

See text for identification of fish groups.

^b It should be noted that ppm is synonymous with μ g g⁻¹ wet weight of fish tissue.

has been closed since 1972, Hg-contaminated waste leached from muck ponds adjacent to the plant directly into the North Fork of the Holston River over a long period of time. In a 1978 study, the Tennessee Valley Authority (TVA) indicated that even if the Hg drainage into the river were eliminated, natural processes in this river system would continue to flush downstream the Hg-laden sediments already deposited on the river bottom (Clark *et al.,* 1980). The TVA has determined that Hg is being deposited deep in the sediments of Cherokee Lake which is 130 river miles downstream from the Olin Corporation plant at Saltville (Clark *et al.,* 1980). In spite of this deposition, the data presented in Table IV indicate that, at least through 1984, the concentration of Hg in the muscle of fish harvested from Cherokee Lake was below the FDA action level of 1.0 ppm (i.e., mean of 0.19 ppm).

In addition to Hg, the fish muscle harvested from the North Fork of the Holston River also contained elevated concentrations of Cd (0.33 ppm mean) and Zn (25 ppm mean) (Table IV). These higher levels of Cd and Zn in fish muscle from the North Fork of the Holston River are in agreement with the findings of Young and Blevins (1981) in their 1978-1979 survey. It should be noted that Cd is acutely toxic to fish at water concentrations as low as 1 μ g L⁻¹ (ppb), and has been reported to bioaccumulate in fish tissues (mostly in the liver and kidneys) achieving concentrations 2000 times greater than those of ambient waters (Young and Blevins, 1981). These elevated concentrations of Cd and Zn are attributable to the extensive mining of Zn undertaken in this area in past years.

At the Holston River station (i.e., station No. 7), elevated concentrations of Mn (2.4 ppm mean) and Zn (19 ppm mean), in addition to Hg, were found in fish muscle (Table IV). High concentrations of Mn (i.e., 1.1 ppm mean) were also observed in fish muscle from Cherokee Lake (station No. 8). Again, these findings are consistent with the 1978-1979 survey of Young and Blevins (1981). Clearly, the levels of Mn in the muscle of fish harvested from many of the aquatic habitats in east Tennessee exceed the world average, and are attributed to the large natural deposits of this element in this area (Young and Blevins, 1981). In contrast, the concentrations of Cu in fish muscle from this region were at or below the median values found in fish throughout the world (Young and Blevins, 1981).

At all sampling stations, except for the Norris Lake station, Pb concentrations in fish muscle were found to be low (see Tables II through IV). Fish muscle samples from Norris Lake displayed an elevated mean Pb concentration of 0.94 ppm (Table IV), which is in sharp contrast with the concentration of 0.006 ppm reported previously by Young and Blevins (1981). Nationwide, concentrations of Pb in freshwater fish have been reported to range from 0.16 to 0.24 ppm for whole-body (NAS, 1972). Clearly, the concentrations of Pb found in the muscle of fish from Norris Lake in the present investigation are high and warrant further investigation.

Finally, the concentrations of As observed in fish muscle from the aquatic systems under investigation (Tables II to IV) are low, and for the most part, are below our limit of detection (i.e., $\lt 0.03$ ppm). The major source of arsenic in aquatic environments is believed to be arsenical pesticides which have been used extensively over the years (Jelinek and Corneliussen, 1977). Lunde (1974) reported that As levels in freshwater fish ranged from 0.2 to 72.5 ppm, with inorganic As levels rarely exceeding 1 ppm in fish muscle. The latter conclusion is confirmed by the results of our study.

4. Summary

Chronic heavy metal contamination of aquatic life, in particular fish, has received little attention in the scientific literature. Although some investigators have indicated the importance of designing stream monitoring programs in a manner capable of assessing chronic heavy metal contamination (Ney and Van Hassel, 1983), most studies involving fish suffer from inadequate sample size and lack of a data-base obtained over a significant period of time. Herein, we report heavy metal residues in 268 fish harvested

over a 5-yr period from a variety of aquatic habitats in a 12-county region of eastern Tennessee. This study joins our previous pilot investigation (Young and Blevins, 1981) in representing one of the few long-term evaluations of heavy metal contamination of fish. Moreover, the waterways investigated displayed several states of pollution ranging from natural and relatively unpolluted habitats to those which are heavily polluted by industrial and domestic uses.

Throughout the region, concentrations of several metals in fish muscle were sufficiently high to affect the health of these organisms. In particular, elevated concentrations of Cd and Hg were observed in fish muscle at several sampling sites. As these metals are toxic to most organisms in trace amounts, it is reasonable that fish in these aquatic systems may be adversely affected. The elevated concentrations of Cd in fish muscle are attributed to the release of this metal as a by-product during the mining of Zn in this region of Tennessee. Notable concentrations of Zn in fish muscle were also found at all sampling stations investigated. Mercury contamination in fish muscle (i.e., exceeding the FDA action level of 1.0 ppm) in the Holston River also was attributed to an anthropogenic source, namely leaching from waste storage ponds at a former chlor-alkali plant located in Saltville, Virginia. In contrast, natural deposits of Mn throughout the region accounted for the elevated levels of this element found in fish muscle at many sampling stations. Over the last 7 yr, our research, in this region, has demonstrated that the metal concentrations in fish muscle remain fairly constant. Once introduced or perturbed in an aquatic ecosystem, heavy metals persist, and this is reflected in the tissues of aquatic organisms, such as fish.

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