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MERCURY IN FISH FROM GOLD-MINING REGIONS IN THE UPPER CUYUNI RIVER SYSTEM, VENEZUELA

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SUMMARY: To evaluate aquatic effects of gold-mining operations, we determined total Hg concentrations in nine fish species taken in November-December 1992 from the Supamo-Parapapoy rivers, upper Cuyuní River system, Venezuela. Hg levels in axial muscle tissues ranged from <0.03 to 0.86 µg/g wet weight (n=18). The highest value (0.86 ± 0.26 [±SD]) was associated with a large (63-cm long) aimara (*Hoplias macrophthalmus*), a locally important food fish. Hg contents for liver tissue were 0.11-2.57 µg/g (n=5); ovary tissue 0.09 µg/g (n=1); and gut contents (organic mud) from a loricariid catfish 0.76 µg/g (n=1).

KEY WORDS: gold mining, habitat perturbation, heavy metals, impact assessment, mercury, Neotropical fish, South America

INTRODUCTION

Many river systems in tropical South America are being contaminated with mercury (Hg) from gold-mining activities (1,2,3). In conjunction with dredging or excavating operations, miners isolate the heavy fraction of alluvial sediments with combinations of sluices, sieves, and pans. Metallic mercury (Hg^0) is added and mixed in with the resulting fraction to separate the fine gold (Au) particles by forming a Au-Hg amalgamate. After amalgamation, the Au-Hg complex is heated and Hg vapor is released to the atmosphere (3). Metallic Hg is lost directly to the ground and water during each stage of the process (2,3).

Because use of Hg in gold mining is common and widespread, large amounts of Hg are introduced to the environment. From 1979 to 1985, at least 87 t of Hg were discharged in the Madeira River region of Amazonian Brazil--45 percent lost directly to area rivers and the remainder lost to the atmosphere (eventually returning in the form of Hg^{2+}) (2). In a recent 10-year period, miners in the Pocone district in the northern Pantanal, Brazil, have released 15 to 20 t Hg into the

local environment (4). Based on a 1990 estimate, gold miners in the Guyana Shield region of Venezuela annually use 40 to 50 t of Hg (5).

Although gold-mining activities are coming under increased governmental regulation, the long-term effect of past Hg releases on complex tropical ecosystems is not understood. In attempts to quantify impacts, recent studies have documented accumulation of Hg in water, sediments, aquatic macrophytes, freshwater snails, and fish (1,4,6,7). Fish obtain Hg directly from water (via the gills) and from contaminated food (8). Bioaccumulation of Hg in fish is of particular concern because fish are important as food to miners and other local inhabitants.

In November and December 1992, we assisted the Venezuelan company Tecnica Minera (TECMIN) in assessing environmental effects of gold-mining activities in a remote area within the Supamo-Parapapoy river drainage. During the past 10 years, miners exploring the region for gold have: cut and burned virgin forest; excavated large pits throughout the floodplain with pumps and high-pressure hoses; hydraulically dredged stream channels; and used mercury--called "azogue" by Venezuelan miners--to isolate gold from sediments. In this paper, we present preliminary results of Hg analyses of fish tissue samples. Fish selected for analysis represented either important food fish or different trophic levels.

STUDY AREA

The Supamo River and its tributary the Parapapoy drain a northeastern portion of the Guyana Shield region, Bolivar State, Venezuela. The 182-km long Supamo is part of the Cuyuní River system, Essequibo River basin. The major study area, 06°34'N 62°40'W, included a 10-kilometer long reach of the lower Parapapoy and sites near and downstream of its confluence with the Supamo. These meandering rivers are characterized by long stretches with slow to moderate currents broken by intermittent cataracts and steep falls. Substrate type ranges from fine silt to huge boulders. In the study area, the Parapapoy main channel is 15 to 30 m wide, and the Supamo 25-80 m wide. Parapapoy discharge, measured on 2 Dec 1992 in a lower reach, was 15 m^3/sec. Main channel elevations in the study area are between 300 and 400 meters above mean sea level. Stream reaches heavily impacted by mining had turbid water, with pH of 6.5-7.0; reaches less affected had clearer water, the color of tea due to humic acids, and pH 4.5-6.5. Water temperatures ranged from 23 to 27.5 °C. River floodplains are surrounded by densely forested hills with scattered natural savannas at higher elevations. Miners have cleared forest along large portions of the main river courses in and around the study area. Some sites have been cleared of trees from river edge to as far as one kilometer inland. These open areas consist of actively mined pits, older pits used as collecting ponds for sludge and water, and large areas covered with mine tailings having little or no vegetation. Small mining camps are scattered throughout the region.

MATERIALS AND METHODS

Field work was conducted during part of the low-flow season, 6 November-10 December, 1992. Fish were sampled with seines, gill nets, and hook and line and preserved on site in 10-20% formalin. The total fish sample included 44 species and 1,620 individuals. Samples representing nine fish species and seven families were selected for initial Hg analyses: *Hoplias macrophthalmus*, *H. malabaricus*, and *Hoplerythrinus unitaeniatus* (common large and medium-sized carnivores frequently eaten by miners); *Astyanax bimaculatus* (a small, widespread and abundant mid-water omnivore); *Cyphocharax spilurus* and *Hypostomus hemiurus* (bottom-dwelling detritivores); *Hemiodopsis quadrimaculatus* (a small, bottom-dwelling insectivore); and *Parauchenipterus galeatus* and *Pimelodus ornatus* (medium-sized carnivorous catfishes). Voucher specimens were deposited in the Museo de Ciencias Naturales (MCNG), UNELLEZ, Guanare, Venezuela, and in the Florida Museum of Natural History, Gainesville, Florida, USA.

In the laboratory (Guanare, Venezuela), preserved specimens were identified. Fish chosen for Hg analysis were wrapped in cloth moistened with ethanol and sealed in clean plastic bags for transport to North America. In the United States, fish were measured from tip of snout to base of caudal fin (i.e., standard length [SL]) and a 1-5 g sample of skeletal muscle was dissected from the right side of the fish, lateral and ventral to the dorsal fin, with clean stainless steel implements. Axial muscle samples were wrapped in clean (new) aluminum foil, sealed in plastic bags, and kept frozen until Hg analyses. Hg content was also determined for: liver tissues from five adult *Hoplias* (224-630 mm SL); ovary tissues (developing eggs) from a composite of two *H. hemiurus* (168 and 190 mm SL) and gut contents (organic mud) from a *H. hemiurus* (190 mm SL).

Frozen tissue samples were sent to the Animal Disease Laboratory, Illinois Department of Agriculture, Centralia, Illinois. The 23 fish were analyzed as follows: 13 individually, and 10 as five composite samples of 2 fish each. Each composite sample represented similar-sized conspecifics that came from the same collection. Hg determinations were performed on 3- to 5-g samples of tissue that were placed in a 100-mL Tuf-Tainer with 5 mL of concentrated HNO_3, heated gently on hot plate to dissolve tissue, and diluted to 100 mL. Digestate representing 1 g of sample was added to a BOD bottle half filled with water; a 5% $KMnO_4$ solution was then added until a purple color persisted. Hg-free reagents (5 mL each) were added in the following sequence: 35% HNO_3, 50% H_2SO_4, 1.5% hydroxylamine HCl, and 10% stannous chloride. Digested tissue samples were analyzed individually for total Hg with a Perkin-Elmer Model 4000 atomic absorption spectrophotometer with a cold vapor analysis. Recovery of Hg from spiked bovine liver samples ranged from 73 to 83%. Hg detection limit was 0.03 µg/g (i.e., ppm) wet weight. Moisture content of fish tissue samples ranged from 73 to 80% and were used to report Hg content on a wet weight basis. Hg was not detected in the formalin-ethanol preservative in which whole

fish were held. All Hg analyses were single runs except for duplicate analyses carried out on muscle tissue subsamples from two large specimens (*Hoplias macrophthalmus* [SL=630 mm] and *H. malabaricus* [SL=277 mm]) (results presented as the mean ± standard deviation [SD]).

RESULTS

Results of Hg analyses of muscle tissues are given in Table 1. Highest concentrations in muscle were associated with a large (63-cm SL) aimara (*Hoplias macrophthalmus)* ($\bar{x}$=0.86 ± 0.26 µg/g); a *Pimelodus ornatus* (0.52 µg/g); and a 277-mm long *H. malabaricus* ($\bar{x}$=0.26 ± 0.02 µg/g), all locally important food fish. Concentrations in liver tissue from five *Hoplias* in our samples ranged from 0.11 to 2.57 µg/g ($\bar{x}$=0.85). Hg in ovary tissue sample was 0.09 µg/g. Sediment found in the stomach and intestine of a 190-mm SL *Hypostomus hemiurus* had 0.76 µg Hg/g.

Table 1: Hg concentration in muscle tissue from nine fish species. (n=number of samples examined with total number of fish specimens represented in parentheses).

Family and species	Common name	n	Standard length (Range, mm)	Hg conc. µg/g ww
Erythrinidae				
Hoplias macrophthalmus	aimara	2(2)	248-630	0.11-0.86[a]
Hoplias malabaricus	guabina	5 (6)	68-277	0.12-0.26[b]
Hoplerythrinus unitaeniatus	agua dulce	2(2)	118-121	0.07-0.20
Characidae				
Astyanax bimaculatus	sardina	3(5)	58-96	0.04-0.24
Curimatidae				
Cyphocharax spilurus	coporito	1(2)	52-56	0.12
Hemiodontidae				
Hemiodopsis quadrimaculatus	saltón	1(2)	57-63	<0.03
Loricariidae				
Hypostomus hemiurus	corroncho	2(2)	168-190	0.04-0.07
Auchenipteridae				
Parauchenipterus galeatus	bagre sapo	1(1)	149	0.22
Pimelodidae				
Pimelodus ornatus	bagre guacamayo	1(1)	240	0.52

a + b: high values represent means from duplicate analyses on tissue subsamples from single fish; *a*: *H. macrophthalmus*, $\bar{x}$=0.86 ± 0.26 µg/g; *b*: *H. malabaricus*, $\bar{x}$=0.26 ± 0.02 µg/g (also see text).

DISCUSSION

Past studies of Hg-contaminated sites indicate that Hg levels in fish range widely due to such factors as rate of Hg input to the water, physical and chemical characteristics of the aquatic environment, and species and age or size of fish (10). Methyl mercury (CH_3Hg^+) is taken up much more readily than inorganic Hg, accounting for almost all (> 95%) of the Hg present in fish flesh (11). CH_3Hg^+, formed primarily by bacterial action in Hg-containing sediments, accumulates in the aquatic food web. Because of biomagnification, Hg reaches high concentrations in the muscle tissue of large predatory fish (8).

Past studies indicate that the amount of biomethylation in a given water body depends on pH, alkalinity, temperature, state of anoxia, sulfur sources, dissolved organic material, and other factors within the aquatic environment (8,10,11). For instance, soft (≤50 μeq/L), low-pH (≤6.5) waters seem to enhance methylation resulting in more rapid uptake of Hg by fish from both food and water (12). A positive correlation between water color or dissolved organic carbon and Hg levels has also been reported (13). Based on the above information, it would seem that many tropical rivers have conditions highly conducive to microbial CH_3Hg^+ production and subsequent uptake by aquatic organisms: high microbial activity, soft water, low pH, high temperatures, and tannin-stained waters. Blackwater rivers and forest streams would seem especially sensitive to Hg input (2).

Determining the transport and fate of Hg in tropical ecosystems is difficult because these areas have very high species diversity and extremely complex food webs. Our research indicates that fish from the Parapapoy-Supamo area have accumulated low to moderate levels of Hg compared with fish from Hg-contaminated sites in other tropical and temperate regions. However, our results may be conservative because we examined mostly small-sized specimens. Hg concentrations in fish flesh generally increase with increasing age or body size (8,9). As expected, the largest fish we examined (an aimara >60 cm long) had high Hg levels (muscle 0.86 μg Hg/g). To better compare Hg levels in fish from different gold-mining sites, more intensive studies are needed.

Gold miners have invaded much of the Cuyuní River system and adjacent watersheds. Many miners work in remote areas where there is little or no regulation of their activities. Thus, Hg is being introduced to many of the region's most pristine environments. Ecosystems associated with headwater tributaries may also be the most sensitive to disturbance. Along with the threat to ecosystem health, there is the threat to human health. A primary pathway for human exposure to Hg is consumption of contaminated fish (3,10). However, miners and local residents, including indigenous peoples, depend on fish for food. Future development in the region is expected to increase Hg-related problems. For instance, impounded rivers collect Hg-

contaminated sediments coming from upstream areas. One consequence is that Hg residues typically increase in fish following river impoundment (11).

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REFERENCES

(1) Martinelli, L. A. , J. R. Ferreira, B. R. Forsberg, and R. L. Victoria. (1988) Mercury contamination in the Amazon: A gold rush consequence. Ambio 17:252-254.
(2) Lacerda, L. D., W. C. Pfeiffer, A. Teixeira-Ott, and E. G. Silveira. (1989) Mercury contamination in the Madeira River, Amazon--Hg inputs to the environment. Biotropica 21:91-93.
(3) Pfeiffer, W. C., L. D. Lacerda, W. Salomons, and O. Malm. 1993. Environmental fate of mercury from gold mining in the Brazilian Amazon. Environ. Rev. 1:26-37.
(4) Lacerda, L. D., W. C. Pfeiffer, R. V. Marins, S. Rodrigues, C. M. M Souza, and W. R. Bastos. (1991) Mercury dispersal in water, sediments and aquatic biota of a gold mining tailing deposit drainage in Pocone, Brazil. Water, Air, and Soil Pollution 55:283-294.
(5) Mendoza, V. (1990) Geología ambiental y el desarollo de recursos minerales. Boletin Geominas (Cd. Bolivar, Venezuela), no. 20: 27-60.
(6) Lacerda, L. D., W. C. Pfeiffer, and W. R. Bastos. 1991. Mercury dispersal in the Poconé region, state of Mato Grosso, central Brazil. Ciência e Cultura 43:317-320.
(7) Pfeiffer, W. C., O. Malm, C. M. Souza, L. D. Lacerda, E. G. Silveira, and W. R. Bastos. 1991. Mercury in the Madeira River ecosystem, Rondônia, Brazil. For. Ecol. Manage. 38:239-245.
(8) Spry, D. J., and J. G. Wiener. (1991) Metal bioavailability and toxicity to fish in low-alkalinity lakes: A critical review. Environ. Pollut. 71:243-304.
(9) Wiener, J. G., R. E. Martini, T. B. Sheffy, and G. E. Glass. (1990) Factors influencing mercury concentrations in walleyes in northern Wisconsin lakes. Trans. Am. Fish. Soc. 119:862-870.
(10) Fischer, J. J., and nine co-authors. (1993) Mercury in Michigan's environment: Environmental and human health concerns, April 1993. Michigan Environmental Science Board, Lansing, Michigan, USA. 144 p.
(11) Moore, J. W. (1991) Inorganic contaminants of surface waters: Research and monitoring priorities. Springer-Verlag, New York. 334 p.
(12) Wiener, J. G. (1987) Metal contamination of fish in low-pH lakes and potential implications for piscivorous wildlife. Trans. N. Am. Wildl. Nat. Res. Conf. 52:645-657.
(13) Haines, T. A., V. Komov, and C. H. Jagoe. (1992) Lake acidity and mercury content of fish in Darwin National Reserve, Russia. Environ. Pollut. 78:107-112.

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