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Mercury in fish from two Nicaraguan lakes: A recommendation for increased monitoring of fish for international commerce

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Fish commonly exported into the international food supply may be contaminated with mercury.

Abstract

We measured total mercury concentrations in water and fish of Lake Managua and Lake Apoyo. Water mercury concentrations were 10-fold higher in Lake Managua than in Lake Apoyo, although differences in mercury concentration in the most common native fish were not significant. One-fourth of the commercially fished tilapia in Lake Managua exceeded maximum recommended mercury levels for consumption among pregnant women and other at-risk groups, although bioavailability to fishes was lower than in previously studied sites in Brazil and Western Maryland. The lower bioavailiability may present important information for management options to reduce mercury exposure to fishes and humans. We recommend closer mercury monitoring among freshwater fish destined for international commerce.

Keywords: Mercury; Tilapia; Cichlidae; Lakes; Fish

1. Introduction

In spite of having a low technological industrial base, Nicaragua faces diverse, poorly characterized environmental hazards. Among them are the risks of exposure to mercury due to direct releases from chemical and mining industries. A chlorine–alkali factory on the western edge of Managua released approximately 40,000 kg of mercury into Lake Managua during the 1960s and 1970s (Hassan et al., 1981; Lacayo et al., 1991). At least two gold-mining amalgamation mills continue to dump untreated mill residues directly into rivers (Rosario and Ault, 1997; Arengi and Hodgson, 2000). One mill alone accounts for 2.2–3.3 kg of elemental mercury discharged daily, and artisan gold panners contribute undetermined quantities of mercury into various watersheds (Rosario and Ault, 1997). In addition, the Pacific slope of Nicaragua, where the majority of its population resides, is bisected by a line of more than 20 recent and mostly active volcanoes, whose emissions may contain mercury and other toxic metals (Nriagu and Becker, 2003).

Former chlorine-factory employees (91.2 ± 156.9 μg Hg/g, $n = 32$) and fishermen in Lake Managua (6.22 ± 6.3 μg Hg/g, $n = 32$) showed elevated concentrations of mercury; levels were especially high among chlorine-factory workers, where 28% of the workers faced mercury poisoning (Lacayo et al., 1991). Elevated mercury levels have also been noted among artisan gold miners who handle mercury, although levels approaching mercury toxicity were not detected (Rosario and Ault, 1997).

In Lake Managua, mercury concentrations in commercially important native fish species *Amphilophus* c.f. *citrinellus*

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(0.070 ± 0.14 μg Hg/g, $n = 60$) and *Parachromis managuensis* (0.63 ± 0.22 μg Hg/g, $n = 80$) (Lacayo et al., 1991) and introduced tilapia (*Oreochromis* spp.; 0.026 μg Hg/g, $n = 29$) (Gutiérrez, 2001) have been previously measured. Although many of the native fishes contained mercury concentrations above 0.3 μg Hg/g, the levels in tilapia were much lower, with the highest concentration only 0.119 μg Hg/g. Although the mercury contamination of this lake has been recognized for some time, its fishes are captured by artisanal fishermen and marketed internationally. Mercury was also found in sediments in the lake directly in front of the release site from the chlorine/alkali factory, particularly at depths of 20–25 cm (Lacayo et al., 1991). There have not been any studies of mercury in fishes or water in Lake Apoyo, which is considered to be free of anthropogenic sources of mercury. The purpose of our work was to conduct an assessment of mercury concentrations in water and fish in both Lake Managua and Lake Apoyo, to understand mercury cycling in freshwater ecosystems better, and to determine the health risks facing local fish consumers.

2. Site descriptions

Lake Managua is a natural impoundment with a surface area of 1016 km^2 in the Nicaraguan Graben. It drains seasonally into Lake Nicaragua, which empties into the San Juan River in the Atlantic versant. This system constitutes the largest watershed in Nicaragua (29,824 km^2). Lake Managua is relatively shallow (maximum depth 43 m, mean depth 12.4 m), with basic surface waters (pH 8.5–9.3) (Swain, 1966; Barlow et al., 1976; Montenegro-Guillén, 1991) and is unprotected from the prevailing easterly winds, resulting in low water transparency and high turnover, leading to hypertrophy (Montenegro-Guillén, 1991). Oxygen depletion does not occur even in the deepest portions of the lake (Lacayo, 1991). The mineral composition of the substrate includes quartz, feldspar, dioctahedral montmorillonite, and complexed organic matter (Swain et al., 1966) (Table 1). Twenty-six fish species are native to Lake Managua (Villa, 1982). Tilapias (*Oreochromis* spp.) have been introduced recently and have demonstrated negative impacts on native fishes in connected Lake Nicaragua (McKaye et al., 1995).

Table 1
Water conditions in Lake Apoyo and Lake Managua

Water property	Lake Managua	Lake Apoyo
pH	8.5[a], 9.3[b], 9.22[c]	8.15[a]
Conductivity (μS)	1773[c]	4095[a]
Total hardness (as ppm $CaCO_3$)	108.0[a]	268.0[a]
Total dissolved solids (ppm)	274.0[a]	2680.0[a]
Sulfate (ppm SO_4)	1.0[a]	41.0[a]
Secchi disk (m)	0.31[c]	3[d]
Phosphate (ppm PO_4)	0.14[c]	n/a
Alkalinity (mg/l)	541.75[c]	n/a

n/a – not available.
[a] Barlow et al. (1976).
[b] Swain (1966).
[c] Montenegro-Guillén (1991).
[d] Waid et al. (1999).

We sampled water and/or fishes at five sites in Lake Managua (Table 2). Water was sampled directly in front of the chlorine/alkali factory at Acahualinca. We sampled water and fishes at Isla del Amor, located directly off the southern shore of Lake Managua, several hundred meters from the shoreline and at Marina Chiltepe on the Peninsula of Chiltepe, facing directly toward the chlorine/alkali factory. We sampled water and fishes at Puerto Momotombo on the northwestern corner of the lake and shielded from the chlorine/alkali factory by the Peninsula of Chiltepe. All of our sampling sites were used by local fishermen who sell their catches locally and to exporters to El Salvador and Guatemala.

Lake Apoyo is a water-filled volcanic caldera, resulting from the most powerful volcanic explosion in Mesoamerica during the current geological epoch (Waid et al., 1999). A few small streams, which originate inside the crater, enter the lake, but no overland outflow exists. The lake sits at approximately 75 m above mean sea level (masl), some 40 m higher than Lake Nicaragua, which lies 4 km to the east. There are active thermal vents in the lake and along the shoreline. The water of Lake Apoyo is oligotrophic, hard and alkaline (Table 1).

An atherinid, a poeciliid, and the cichlids *P. managuensis* and four species of the *A. citrinellus* complex (*Amphilophus zaliosus* and three as-yet undescribed species, herein referred to as "short", "chancho", and one other not discussed here; see McKaye et al., 2002) are the fishes considered to be native to Lake Apoyo. Two species of African tilapias and an eleotrid were recently introduced into the lake (Waid et al., 1999; McCrary et al., 2001; Tate Bedarf et al., 2001). Water was sampled at five points and fishes in one location in the lake (Table 2).

3. Methods

All water samples were collected at 1-m depth by hand in 100-ml ultra-clean FEP Teflon bottles using clean techniques. Filled sample bottles were placed inside two sealed plastic bags and stored frozen until delivery to Appalachian Laboratory (AL).

Fishes were caught by monofilament gill net and the dorsal muscle was removed while fresh, using an ultra-clean stainless steel knife and clean techniques, within 3 h of capture. Disposable latex surgical gloves were changed upon completion of each fillet preparation, and the knife and work area were cleaned with distilled water afterprocessing each fish. Sample fillets were placed inside two sealed bags, stored at 0 °C, and were delivered to AL frozen on dry ice. We collected *A.* c.f. *citrinellus* at all sites; tilapias (*Oreochromis* spp.) at Puerto Momotombo in Lake Managua; and *P. managuensis* in Puerto Momotombo and in Lake Apoyo. Mercury concentrations for the fish tissues are reported on a wet-weight basis.

We digested 0.2–0.3 g of fillet in 50 ml Teflon containers with 10 ml of Ultrex nitric acid using a CEM MDS/MARS 5 microwave digester. Afterwards in our class 100 clean room, 0.2–0.5 ml of digestate was diluted with D.I. water (<0.02 ng Hg/l) and 0.25 ml of 2 N BrCl was added to produce a total volume of 50 ml (Bloom and Crecelius, 1983). The BrCl oxidation was allowed to continue for at least 24 h. Samples were then pre-reduced with NH_2OH–HCl, reduced further with 1 ml of 10% $SnCl_2$, and the Hg(0) was stripped from the sample using an argon carrier gas and a gas–liquid phase separator. The Hg(0) was pre-concentrated on gold traps and thermally desorbed and detected using a Tekran Model 2600 cold vapor atomic fluorescence spectrometric (CVAFS) system.

We also poured 50 ml subsamples of our water samples into 65 ml FEP Teflon auto-analyzer bottles. The subsamples were preserved with 0.25 ml

Table 2
Sampling locations and total mercury concentrations in epilimnion

Lake Managua sites	Coordinates	$[Hg]_T$, (ng Hg/l)	Lake Apoyo sites	Coordinates	$[Hg]_T$, (ng Hg/l)
#1 (Acahualinca)	N 12°09.722, W 86°19.590	33.7	#1	N 11°56.293, W 86°2.888	2.64
#2 (Isla del Amor)	N 12°10.546, W 86°19.020	30.7	#2	N 11°56.447, W 86°1.041	2.74
#3 (M. Chiltepe)	N 12°11.997, W 86°18.339	20.4	#3	N 11°55.900, W 86°0.543	2.49
#4 (P. Momotombo #1)	N 12°24.357, W 86°36.437	13.4	#4	N 11°54.384, W 86°1.725	3.30
#5 (P. Momotombo #2)	N 12°24.154, W 86°36.503	47.9	#5	N 11°54.508, W 86°3.073	2.53

of 2 N BrCl. All subsamples were analyzed within 2–5 days of collection using EPA Method 1631 (EPA, 1996) and a Tekran 2600 CVAFS. Triplicate samples of water and fish samples were measured over the entire range of concentrations analyzed to confirm internal variance lower than 5% of the measured concentrations. Spiked blanks were analyzed and a calibration curve was generated with $r > 0.99$. All samples were corrected for small amounts of mercury in the reagents and deionized water. The corrections were very minor. For example, correction for mercury in nitric acid used to digest our fish was smaller than 0.00005 μg Hg/g.

4. Results

Total mercury concentrations in the epilimnion of Lake Managua exceeded by 10-fold those of Lake Apoyo and were more variable (29.2 ± 13.2 vs. 2.7 ± 0.3 ng Hg/l) (Fig. 1). Statistical analysis of the geographic variation in epilimnion mercury concentrations in each lake was not possible due to the limited number of measurements (Table 2). Mercury concentrations in *A.* c.f. *citrinellus* taken from Puerto Momotombo (0.17 ± 0.24 μg Hg/g) were more than six times greater ($p < 0.05$) than in those taken from Marina Chiltepe (0.021 ± 0.010 μg Hg/g) and from Isla del Amor, nearest the industrial mercury emission site (0.028 ± 0.014 μg Hg/g; Table 3a). Lakewide averages in mercury concentrations in *A.* c.f. *citrinellus*, nonetheless, were not significantly different between the two lakes ($p > 0.10$). There was not a significant correlation between mercury concentrations in *A.* c.f. *citrinellus* and in water in the different sites in Lake Managua ($p > 0.10$).

The taxon-specific mercury concentrations in fishes of Lake Apoyo correlated strongly with body weight for *P. managuensis* ($p < 0.05$) and for all *A.* c.f. *citrinellus* forms taken together ($p < 0.001$; data not shown). This relationship was not statistically significant for fishes of Lake Managua, although fishes smaller than 100 g body weight were not sampled ($p > 0.10$ for both tilapia and for *A.* c.f. *citrinellus*). Additionally, mercury concentrations of the fishes of Lake Managua showed an apparent bimodal distribution not seen in fishes of Lake Apoyo (Fig. 2a and b).

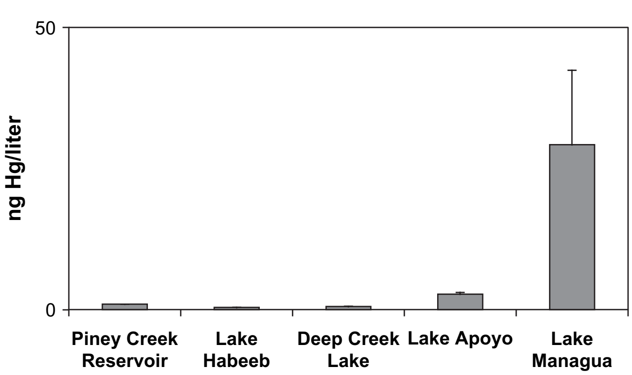

Fig. 1. Comparison of total water mercury levels in epilimnion layer, Western Maryland (see Castro et al., 2002) and Nicaragua (this paper).

The *A.* c.f. *citrinellus* species complex exhibits "normal" and amelanic "gold" color morphs in some parts of its habitat (Webber et al., 1973; Barlow, 1976), and both morphs are abundant in Lake Managua. Mercury concentrations did not vary among gold and normal morphs in Lake Managua ($p > 0.05$; Table 3a). Mercury concentrations in the strictly piscivorous *P. managuensis* were significantly greater than in two of the analyzed forms of this species complex ($p < 0.05$), but not "chancho", a third, predatory form (Table 3b).

5. Discussion

Tilapias are widely marketed in the US as a safe, inexpensive fish. They are inveterate diggers for both feeding and reproduction, and may be ingesting directly and/or liberating into the water column mercury trapped in the substrate. This report of high levels of mercury in tilapia raises concern regarding food security in the international marketing of tilapias from Nicaragua, as they have generally been listed as safe for human consumption with regard to mercury levels. Prior reports of mercury concentrations in tilapias in their native range in Africa (Campbell et al., 2003) and in Lake Managua (Gutiérrez, 2001) have been within recommended levels (0.3 mg Hg/g; EPA, 2001). This study constitutes the first such report of mercury concentrations in tilapia in excess of recommended levels for human consumption, and suggests that species alone may not be a sufficient indicator of mercury contamination risk. Additional attention to the health risks to humans from these widely marketed fishes is warranted.

With the exception of the piscivorous predator *P. managuensis* the trophic positions of the fish species analyzed in this study have not been determined. As mentioned above, tilapias are considered to maintain a relatively low position on the food web. Previous studies of members of the *A.* c.f. *citrinellus* species in another lake showed trophic specialization among individual species (Vivas and McKaye, 2001; McKaye et al., 2002), and trophic specialization may well occur among them in Lake Managua. Furthermore, marked seasonality of rainfall and winds likely makes trophic positions of some of these fishes shift. We recommend further study in the relations between trophic positions, life histories and mercury concentrations in the fishes in this study.

Table 3
Mercury concentrations in water and fishes of (a) Lake Managua (b) Lake Apoyo

Material analyzed	Location, description	Concentration Hg ± std. dev.	# Samples analyzed
Water	Lakewide average, epilimnion	29.2 ± 13.2 ng/L	5
Fishes	Lakewide average, *A.* c.f. *citrinellus*	0.068 ± 0.14 μg/g	33
	M. Chiltepe, *A.* c.f. *citrinellus*	0.021 ± 0.010 μg/g	13
	M. Chiltepe, *A.* c.f. *citrinellus* gold morph	0.022 μg/g	1
	M. Chiltepe, *A.* c.f. *citrinellus* normal morphs	0.021 ± 0.010 μg/g	12
	Isla del Amor, *A.* c.f. *citrinellus*	0.028 ± 0.014 μg/g	11
	Isla del Amor, *A.* c.f. *citrinellus* gold morphs	0.026 ± 0.007 μg/g	4
	Isla del Amor, *A.* c.f. *citrinellus* normal morphs	0.029 ± 0.017 μg/g	7
	P. Momotombo, *A.* c.f. *citrinellus*	0.17 ± 0.24 μg/g	10
	P. Momotombo, *A.* c.f. *citrinellus* gold morphs	0.257 ± 0.307 μg/g	7
	P. Momotombo, *A.* c.f. *citrinellus* normal morphs	0.164 ± 0.307 μg/g	2
	M. Chiltepe, *A. labiatus*	0.047 μg/g	1
	P. Momotombo, tilapia	0.18 ± 0.17 μg/g	11
	P. Momotombo, *P. managuensis*	0.355 μg/g	1
Water	Lakewide average, epilimnion	2.7 ± 0.1 ng/L	5
Fishes	Site #2, *A.* c.f. *citrinellus* (all taxa)	0.090 ± 0.121 μg/g	14
	Site #2, *A. zaliosus*	0.065 ± 0.008 μg/g	6
	Site #2, *A.* "short"	0.054 ± 0.021 μg/g	5
	Site #2, *A.* "chancho"	0.199 ± 0.267 μg/g	3
	Site #2, *P. managuensis*	0.120 ± 0.073 μg/g	7

Surface water total mercury concentrations in Lake Apoyo exceeded those of lakes in Western Maryland, which receive atmospheric mercury deposition from coal-fired energy plants and coal-mine runoff, and were lower than in sites contaminated by gold mining in the Rio Negro in Brazil (Fig. 3; Castro et al., 2002; Barbosa et al., 2003). The uniformity of our results in the five locations along the circumference of the lake suggests that the surface waters are well mixed. There are no known industrial emissions upwind of the lake. The relatively high mercury concentrations are likely due to volcanic thermal vents inside the lake.

The total mercury concentrations in the epilimnion of Lake Managua were much higher and more variable than in Lake Apoyo. Not all the mercury found in Lake Managua can be explained by emissions from the chlorine/alkali factory. Total mercury in water and fishes in Puerto Momotombo suggested a separate, localized site of mercury in this region of the lake. We observed a bimodal distribution of mercury concentrations in both *A.* c.f. *citrinellus* and tilapias from Puerto Momotombo (Fig. 2a), as well as variance in the total mercury concentrations in water from two points in the area (Table 3a). Two potential sources of mercury on the north side of Lake Managua are runoff from a volcanic geothermal energy plant and contamination from gold mining using amalgamation techniques. A geothermal energy plant dumps untreated water from the geothermal deposits onto the ground on the lakeside slope of the Momotombo Volcano, which then runs freely into the lake. The mineral contents of these waters are not known, although it is known that natural sources of mercury in the environment include volcanoes, which emit 29 tons per year to the atmosphere in Central and South America alone (Nriagu and Becker, 2003), and faults, which can be detected by mercury emissions (Crenshaw et al., 1982).

Also, just to the east of the Momotombo Volcano lies the Sinecapa River watershed in which lies the La India gold mine complex, heavily exploited during the colonial period

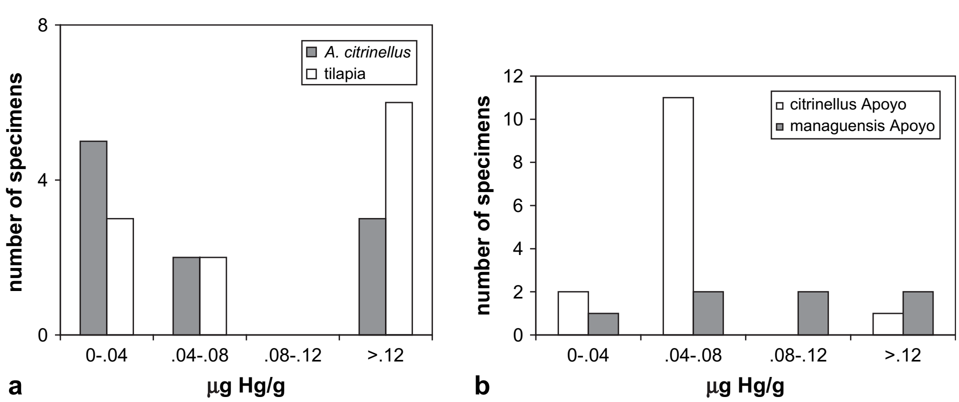

Fig. 2. (a) Frequency distribution of total mercury concentrations in fishes, Puerto Momtomobo, Lake Managua. (b) Frequency distribution of total mercury concentrations in fishes, Lake Apoyo.

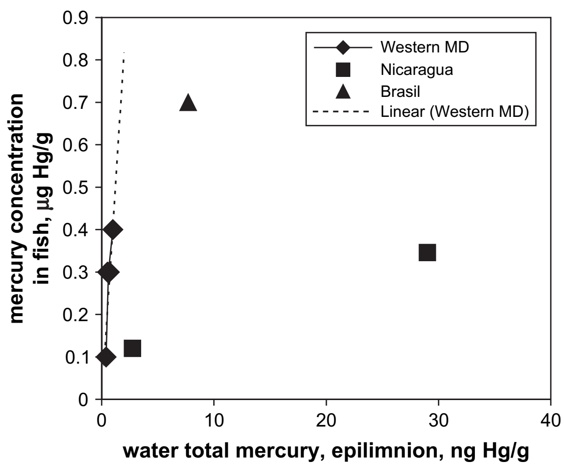

Fig. 3. Comparison of total mercury levels in water and in top predator fishes, Western Maryland (Castro et al., 2002), Brazil (Barbosa et al., 2003) and Nicaragua (this study).

but closed today. There is, nonetheless, considerable panning for gold in the watershed by artisan gold miners using mercury amalgamation techniques. Mercury losses during panning are compounded by its evaporation over an open flame to recover gold, resulting in atmospheric deposition of volatile mercury into the watershed. Mercury contamination of watersheds has occurred as a result of uncontrolled amalgamation techniques in gold mining in China (Dai et al., 2003) and in Indonesia (Ayhuan et al., 2003). Additional testing is required to determine if the volcanic source or use of mercury in the gold mining in the Sinecapa are contributors to the mercury load in this part of Lake Managua.

Industrial chlorine production utilizing mercury electrodes has been the cause of significant mercury contamination in several locations. Releases from a chlorine/alkali production facility have contaminated the Ulhas Estuary system on the Arabian Sea, resulting in high concentrations of dissolved (40–610 ng Hg/l) and particulate (1.13–6.43 µg Hg/g) mercury concentrations (Ram et al., 2003). A prior study showed similar mercury concentrations in sediments near the chlorine factory in Lake Managua (overall surface average 0.62 ± 0.46 µg Hg/g, $n = 17$; in front of chlorine/alkali factory, 20 cm below substrate surface 4.4–9.2 µg Hg/g, $n = 4$; Lacayo et al., 1991).

The bimodal distribution of mercury concentrations in *A.* c.f. *citrinellus* and tilapias in Puerto Momotombo could also be due to trophic differences among the individuals of both taxa. The relatively low trophic position of tilapias suggests low levels of mercury accumulation. Nonetheless, 27% of the tilapias sampled in Puerto Momotombo had relatively high mercury levels (>0.3 µg Hg/g), a similar proportion to that of *A.* c.f. *citrinellus* from the same site, which presumably occupies a higher trophic position. Furthermore, neither taxon exhibited statistically significant body weight–mercury concentration relationships. Tilapias are known to undergo trophic shift from particulates and small fishes as juveniles, to plankton and detritius as adults (De Moor et al., 1986), which may significantly influence mercury accumulation. Furthermore, it is thought that multiple species of both tilapias (McKaye et al., 1995) and *A.* c.f. *citrinellus* (McKaye et al., 2002) are found in the lake, which may be distinguished by important differences in trophic position, leading to variance in mercury accumulation (Barbosa et al., 2003; Ikingura and Akagi, 2003). Whereas the mercury levels in *A.* c.f. *citrinellus* in our study correspond well to a previous study (Lacayo et al., 1991), we measured much higher concentrations in tilapia than the lakewide and local averages of another previous study (lakewide average 0.026 µg Hg/g, $n = 29$; Puerto Momotombo 0.012 ± 0.007 µg Hg/g, $n = 4$; Gutiérrez, 2001). Bimodal mercury concentration distributions were found, however, in both taxa in one of the sites (Puerto Momotombo). This pattern could be produced by multiple species with unique trophic levels in each taxon, which is likely to occur in other portions of the lake. We consider trophic variation in the taxa to be an unlikely cause of the bimodal mercury distributions, as this pattern would likely be repeated in some other part of the lake. It could also be produced by a local mercury release such as volcanic mercury emissions, especially from the perforations in the surface water for geothermal energy extraction, or from gold extraction activities in a nearby river.

Total mercury concentrations in water alone do not determine the uptake rate of mercury in fishes. The bioavailability of mercury sources in an aquatic ecosystem may be even more important than the total mercury concentrations to the uptake rate in fishes and other fauna. Bioavailability is influenced by a variety of factors such as biological oxygen demand, pH, alkalinity, and other ions (Lange et al., 1993; Driscoll et al., 1995) and may influence concentrations of mercury in fish (Gorski et al., 2003). Now that accurate direct measurements of mercury and methylmercury in water are available, more sophisticated models for mercury uptake can be developed. We recommend methylmercury measurements in the epilimnion in these lakes.

We compared mercury concentrations in top predators of lakes in Western Maryland (Largemouth bass, *Micropterus salmoides*) with those of the two Nicaraguan lakes studied (*P. managuensis*), relative to the total mercury concentrations in the epilimnion of each lake (Fig. 3). Fish muscle total mercury concentrations in Nicaraguan lakes were far lower than predicted from the uptake ratios determined from the Maryland lakes. Mercury uptake in the Nicaraguan lakes is far below the levels in three lakes in Western Maryland (Castro et al., 2002), and below the level found in the Rio Negro in Brazil (Barbosa et al., 2003), according to a linear model of mercury uptake in top predator fish relative to total mercury concentration in the epilimnion. The reasons for the lower uptake ratios in Nicaraguan lakes are not clear, but could be important in predicting and even controlling mercury uptake in lakes where pollution may have occurred or intervention options are considered.

Although we found fishes with mercury concentrations meriting health concerns for consumers, we expected to find much higher mercury concentrations in these fish based on the very high mercury concentrations in the water column. We need to understand better the relationship between mercury in the water column and fish in tropical lakes. Further research is needed to determine the chemical and physical status of mercury in these lakes, and detailed taxonomic and trophic status of the fishes analyzed. Further study of the mercury movements from the chlorine/alkali factory can aid in development of improved remediation techniques at mercury spill sites.

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