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Methylmercury Concentrations in Six Fish Species from Two Colombian Rivers

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Abstract The objective of this study was to determine whether fish collected from the La Miel or Nechí Rivers (Colombia) differed in muscle methyl mercury (meHg) concentration. Two fish from six different species were collected from markets adjacent to each river. Overall, fish collected from the market adjacent to the Nechí River contained higher levels of meHg. This result however is being driven by very high meHg concentrations in four individual fish, three of which are Pimelodid, long-whiskered catfish. These catfish may represent ideal sentinel organism for the detection of meHg contamination in Colombian rivers.

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Mercury (Hg) enters the environment through natural and anthropogenic pathways leading to concerns regarding its occurrence and fate within the aquatic environment (Clarkson and Magos 2006). This heavy metal is of global concern due to its distribution, persistence, bioaccumulation, and toxicity in the environment, especially in organic forms such as methyl mercury (meHg; Hylander and Goodsite 2006). Hg and meHg have been detected in water, sediment, and fish throughout Latin America (Durrieu et al. 2005).

Mercury pollution in Latin America is a growing problem due to the recent and rapid expansion of artisanal gold mining (Veiga et al. 2006). Colombia ranks second in gold production in South America and gold mining is the major source of Hg pollution within Colombia (Malm 1998). Artisanal gold mining involving Hg amalgamation in the extraction process commonly occurs in Colombia on a large scale basis, mostly south of Bolivar and northeast of Antioquia (Olivero et al. 2002). During the gold mining process Hg is vaporized entering the air, where it is transported to the aquatic environment (Veiga et al. 2006). Hg together with sediments from the mining area are transported to the northern countryside of Colombia where they have been detected in these aquatic ecosystems (Marrugo et al. 2008).

Mercury has been shown to accumulate in aquatic systems, but especially in fish, through transformation to methyl mercury (Clarkson and Magos 2006). More than 70% of Hg accumulated in fish muscle tissue is commonly in its methylated form (Raymond and Rossmann 2009). In studies examining Hg in fish collected from Latin America, piscivorous predators demonstrate greater Hg concentration in muscle tissue compared to non-carnivorous species, displaying biomagnifications (Alonso et al. 2000; Marrugo et al. 2008; Olivero-Verbel et al. 2004). Bioaccumulation of Hg in fish is an important concern in human health exposure through fish consumption as it could lead to adverse health effects, especially in populations consuming high levels of Hg contaminated fish (Clarkson et al. 2003). Although, some information about mercury concentrations in fish from gold mining areas and industrial impacts does exist, knowledge about these problems in Colombia continues to be incipient.

This project had two different objectives. The first was to determine whether the fish collected from two different river systems in Colombia had different tissue concentrations of meHg in their muscle tissue. Muscle tissue was the focus of this research, as all of the fish sampled were taken from markets, and as such were destined to be food. The second objective was to determine whether trophic level of the fish collected was related to the body burden of Hg. Given the propensity for meHg to biomagnify across trophic levels, it was our a priori hypothesis that predatory fish would have higher concentrations of meHg in their fish tissues than fish feeding at lower trophic levels.

Materials and Methods

Fish were collected from February 23rd to 26th, 2011 from two Colombian Rivers. The La Miel River has had historically low levels of low impact gold mining, whereas the Nechí river, has a large degree of artisanal and professional gold extraction activity. In both watersheds, fresh fish were purchased directly from subsistence fishermen, one in the municipality of El Bagre located beside the Nechí River Northern of Antioquia department and other in a small fisherman settlement located beside the La Miel River, 60 km from the municipality of Norcasia in Caldas department. Therefore, the exact location of collection of the individuals within the watersheds is uncertain.

Two individuals from 6 different species (*Sorubim cuspicaudus, Pseudoplatystoma magdaleniatum, Triportheus magdalenae, Pimelodus* spp., *Prochilodus magdalenae, Leporinus muyscorum*) were collected from each river. The species *L. muyscorum*, *Pimelodus* spp., *P. magdalenae* and *T. magdalenae* are all benthic omnivores, while fish *S. cuspicaudus* and *P. magdaleniatum* are piscivorous predators. The length and body mass of the fish collected are given in Table 1. The fish tended to be larger when taken from the Rio Nechí than they were in La Miel, however the small sample sizes for each species precluded statistical analysis of the individuals.

Immediately after purchase, fish were measured for length and weighed for mass. Clean muscle tissue (approximately 3 g) sample were taken from each individual immediately behind and below the dorsal fin; sections of muscle were cut out on site. Samples were macerated and homogenized independently and then stored in polypropylene tubes and held on ice until being returned to the laboratory at the University of Antioquia, Medellin, Colombia.

An aliquot of 0.7 g in duplicate from each individual was used for total mercury analysis. Prior to total mercury measurement, samples were digested with sulfuric acid (H_2SO_4), nitric acid (HNO_3) and potassium permanganate

Table 1 Body mass, fish length and muscle meHg concentrations for the 24 fish collected from markets adjacent to the Nechí and La Miel Rivers

	Nechí River			La Miel River		
	Mass (g)	Length (cm)	meHg (ng/g)	Mass (g)	Length (cm)	meHg (ng/g)
Pseudoplatystoma magdaleniatum	18,123	106	***433***	924	44	56
	990	48	134	932	45	56
Leporinus muyscorum	340	24	130	278	25	65
	391	29	***593***	162	21	64
Sorubim cuspicaudus	648	46	***465***	998	48	91
	703	48	***934***	1,021	50	92
Prochilodus magdalenae	578	30	114	240	24	8
	616	31	127	198	23	65
Pimelodus spp.	163	26	80	46	16	25
	197	27	111	83	18	78
Triportheus magdalenae	91	19	62	45	9	27
	100	20	40	28	8	85

Methyl mercury concentrations that exceed 400 ng/g are presented in bold and italics

($KMNO_4$; EPA 1998). Total Hg (THg) content was determined by the manual cold vapour technique (US EPA 1998) using a (give the make and model of the machine) flameless atomic absorption spectrometer. Method accuracy was verified by using appropriate sample duplicates, calibration standards, blank samples and certified material DORM-3 Fish protein from National Research Council of Canada. DORM-3 concentration material was 0.330 ± 0.012 µg/g (Certified value 0.382 ± 0.060 µg/g, n = 3).

An additional aliquot (2 g) of the fish tissue collected in Colombia was shipped on blue gel ice to the Aquatic Toxicology Laboratory at the University of Nebraska at Omaha, and then fish tissue samples weighing between 0.5 and 0.7 g were placed into 1.5 mL conical microcentrifuge tubes. Samples were packaged and forwarded, on dry ice to a commercial laboratory (Quicksilver Scientific, Lafayette, CO), for methylmercury and mercury (II) analysis, according to previously published methods (Shade 2008). Method accuracy was verified by using appropriate sample duplicates, calibration standards, blank samples and certified reference materials TORT-2 (lobster hepatopancreas) and DOLT-4 (dogfish liver). Recoveries were reported at 101% for meHg and 105% for HgT for the TORT reference material, and as 93% for meHg and 105% for HgT for the DOLT reference material.

Results and Discussion

Total Hg, methyl Hg and Hg II were measured by different methods in two different laboratories. When all of the fish samples (n = 24) were analyzed together, there were strong intercorrelations among the three measured traits (Table 1), suggesting a high degree of repeatability among the different metrics and between the two laboratories.

The portion of meHg from THg in the analyzed sample was in average 56% for both sample location. This corroborates the significant proportion of meHg found in fish from Hg polluted aquatic ecosystem. For this reason, even though meHg average values does not exceed the World Health Organization limit for fish consumption (500 ng/g), there is still a risk for frequent fish consumers and local fish protein diet dependent. In contrast, Marrugo et al. (2008) in the Mojana region – Colombia, found that in different fish species mercury was present almost completely as the methylated form, with percentages between 80.5% and 98.1%. The last demonstrates that in other freshwater aquatic ecosystem, mercury is being methylated in lest proportion compared with what was found in the Mojana region in the San Jorge River, Colombia.

Overall, fish from the Nechí River contained approximately five times (268 vs. 56 ng/g) the meHg concentration that fish did when collected from the La Miel River. These

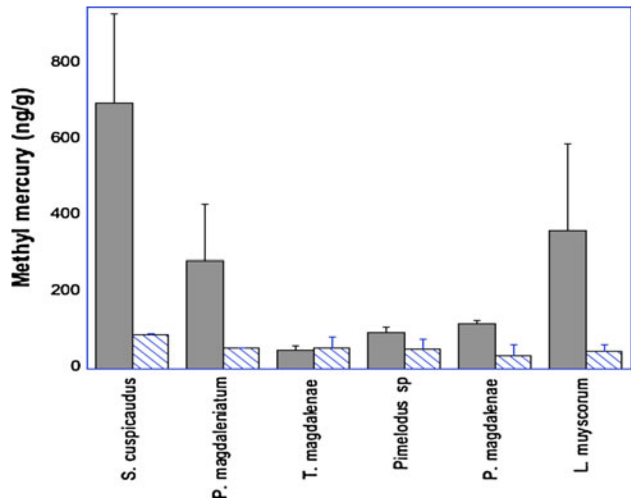

Fig. 1 The concentration of methylmercury from each of six species taken from the Nechí River (*solid bars*) and La Miel River (*striped bars*). Results from a two-way ANOVA indicated a significant difference between the fish from the two river systems, but no significant differences among fish species

differences are consistent with the contention higher levels of gold extraction activity in the Nechí River lead to higher levels of meHg in the local fish tissue. This result, however, may be misleading in that there are only pronounced differences in tissue meHg in three of the six fish species collected (*S. cuspicaudus, P. magdaleniatum, and L. muyscorum),* whereas the other three species did not appreciably differ between watersheds (Fig. 1). A two-way ANOVA was run to evaluate the influence that fish species and river system had on tissue methylmercury concentration. Results of the two-way ANOVA indicated significant effects due to river system (F test = 12.12, $p > 0.005$) but not due to fish species (F = 2.97, $p = 0.57$), but not due to the fish-species/river system interaction term (F = 2.32, $p = 0.107$, Fig. 1). When the methylmercury concentrations from the fish from the two river systems were analyzed separately, neither of the one way ANOVAs indicated significant differences among the six fish species within either river system ($0.05 > p$ in both cases).

When taken together, the fish collected differed dramatically in body size (Table 2). Furthermore, when the fish from the two river systems are compared, the fish taken from the Nechí River tended to be larger. Body mass was not correlated with muscle meHg concentration for the fish collected from either the Nechí River (n = 12, $r^2 = 0.04$, $p > 0.05$) or La Miel Rivers (n = 12, $r^2 = 0.20$, $p > 0.05$) or for both watersheds taken together (n = 24, $r^2 = 0.002$, $p > 0.05$). One fish (*P. magdaleniatum*, body mass 18,123 g) collected from the Nechí River was much larger than all of the others, and this individual may have biased the relationship the mass/meHg relationship for all of the

Table 2 Correlation (r) matrix table among meHg, HgII and total mercury in fish from La Miel and Niche Rivers, Colombia, South America

	meHg	Hg II	HgT
meHg		0.9173	0.8958
Hg II			0.9397
HgT			

The corresponding linear regression to these correlations was statistically significant at the $p < 0.01$ level in all cases

other individuals. However, when that individual was removed from analysis, there was still no statistical correlation between body mass and the muscle meHg concentrations in the Nechí River fish ($n = 11$, $r^2 = 0.16$, $p < 0.05$) or when all of the fish from both rivers were considered together ($n = 23$, $r^2 = 0.06$, $p < 0.05$).

Muscle tissue from only four individual fish contained meHg levels that exceeded 400 ng/g (Table 1). All four of these fish were collected from the Nechí River and three of the four individuals (two *S. cuspicaudus* and a *P. magdaleniatum* were Pimelodid, long-whiskered catfish. The fourth fish was a *L. muyscorum*. This omnivorous Characid grazes on invertebrates, plant material and detritus. As such, it was somewhat surprising that the Characid contained such high levels of meHg. Of the three, *P. magdaleniatum* is considered to be the most valuable to the local, artisanal fishery. It migrates throughout the watershed and is a pisciverous predator (Ríos et al. 2008). The piscivorous feeding habits of *P. magdaleniatum* specifically, and the Pimelodid catfish in general may make them particularly susceptible to meHg bioconcentration. As such, these catfish may represent ideal sentinel organisms to be used as indicators of Hg contamination in Colombian rivers.

It is interesting to note that there was pronounced variation in the meHg concentration between the two *P. magdaleniatum* and *L. muyscorum* collected from the Nechi River (Table 1). Clearly, trophic status was not the sole driving force responsible for muscle meHg concentration. These individuals were sampled at the local market therefore it is possible that they came from very different geographical areas within the river. Furthermore, both *P. magdaleniatum* and *L. muyscorum* are migratory (Ríos et al. 2008) which further complicates their Hg exposure history and may help to explain how two individuals sampled from the same market can vary so much in meHg muscle concentration.

The World Health Organization (2000) has set guidelines for human consumption of meHg in fish tissue at 500 ng/g, and fortunately only two of the 24 fish collected in this study exceeded that criteria. However, it is disconcerting that fish, particularly the Pimelodid catfish, can differ widely in muscle concentrations of meHg when purchased from the same local marketplace. Results from this study do not suggest that meHg contamination of fish flesh is widespread across watersheds and species in the gold mining regions of Colombia. It does suggest, however that in gold mining regions, individual, highly contaminated fish are reaching the marketplace. The health consequences of periodic consumption of these contaminated fish remains to be elucidated.

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