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Mercury Concentrations in Muscle and Liver Tissue of Fish from Marshes Along the Magdalena River, Colombia

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Abstract The present research determined the total mercury concentrations in muscle and liver tissue in fish collected from the Magdalena River watershed. A total of 378 muscle samples and 102 liver samples were included in the analysis. The highest mean mercury level in muscle tissue was found in the noncarnivore, *Pimelodus blochii*. However, as a group, carnivores had significantly higher ($p < 0.05$) mercury levels in their muscle tissue than noncarnivores. A significant correlation ($p < 0.05$) was obtained between fish mass and mercury concentrations in muscle or liver in four species. No differences were observed in total mercury concentration based either on species or gender.

Keywords Mercury · Fish · Liver · Trophic level

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Among metals, mercury (Hg) is considered a global pollutant, and fish consumption is a major route by which humans can become exposed (WHO 2000). Hg is released to the atmosphere and aquatic ecosystems by natural process such as volcanism and rock erosion. However, high concentrations of Hg in biota are directly related to anthropogenic activity (Lechler et al. 2000). Human activities such as the chemical industry, gold mining, and the burning of petroleum and coal as fuels are considered as the principal causes of Hg contamination (Limbong et al. 2003). In Latin America, small scale and artisanal gold extraction is possibly the most important source of Hg release to aquatic ecosystems (Veiga 2010).

In anoxic conditions, inorganic mercury is transformed by microorganisms into highly toxic organic forms such as methylmercury (Morel et al. 1998). In fact, more than 70 % of the mercury accumulated in fish muscle tissue is commonly in a methylated form (Redmayne et al. 2000). This form is particularly important because of its propensity to bioaccumulate and biomagnify through the food web, and become a high risk to piscivorous birds, mammals and predacious fish (Scheuhammer et al. 2007). Furthermore, multispecies comparisons featuring individuals of different size and feeding habits provide a better understanding of the Hg biomagnification process within aquatic ecosystems (Dusek et al. 2005). Hg quantification in fish has been mainly based on determinations of the skeletal muscle tissue because it is easy to access and is routinely consumed by humans (Régine et al. 2006). Hg accumulation in fish varies with species and tissue type, and less is known about Hg bioaccumulation in organs like liver, kidney, brain, gills and gonads.

Metal detection in Colombia has been described for fish from the Magdalena River basin, a basin of interest due to the occurrence of gold mining within the watershed

(Mancera and Álvarez 2006). However, little is known about Hg bioaccumulation in fish from other aquatic ecosystems in Colombia, despite a widespread history of small scale and artisanal gold extraction operations in those systems as well (Veiga 2010).

The Magdalena River is considered the principal river of Colombia. Its river basin is located between the central and eastern branches of the Andean mountain range. It receives the San Jorge, Cesar, and Cauca Rivers in the swampy floodplain of the northern lowlands. The basin area covers an area of 273.350 km^2 representing 24 % of the continental country area. Its main stream, the Magdalena River, flows northward about 1,500 km flowing out into the Caribbean Sea. The study area is located in the midlands section of the river, between the municipalities of Puerto Boyacá (130 m above sea level) in the south and San Pablo (75 m above sea level) in the north. Samples were taken from nine marshes within the Magdalena River watershed, spanning from the Antioquia–Santander departments border to the lower reaches of the river as it approaches the Atlantic Ocean (Fig. 1).

There were two primary objectives to the present research: the first was to determine total Hg (THg) concentrations in muscle and liver tissue in different fish species collected from 9 marshes in the Magdalena River watershed. The second was to establish correlations between fish mass, sex and trophic level relative to Hg concentration in muscle and liver.

Materials and Methods

Between October and November 2008, three sampling campaigns were completed at 9 marshes from midland Magdalena River (Fig. 1). In a downstream progression, the names of the marshes were: 1 (Palagua), 2 (Samaria), 3 (Rio Viejo), 4 (Barbacoas), 5 (Chucurí), 6 (El Opón), 7 (Juan Esteban), 8 (Bija), 9 (Tabacurú). Fish were captured using gill nets with different mesh size to obtain a wide range of fish lengths. Once captured, each individual was measured for length, weighed and sexed. Taxonomic keys were used (Maldonado et al. 2009) to verify species identification. A total of 378 individuals (176 carnivores and 202 noncarnivores) belonging to 24 species were collected. Muscle tissue from all 378 fish was analyzed for THg. Six fish species comprised more than 70 % of the total collection. These were: *Caquetaia kraussii*, *Curimata mivartii*, *Cyphocharax magdalenae, Leporinus muyscorum*, *Prochilodus magdalenae,* and *Triportheus magdalenae*. Liver tissue was collected from a subset (102) of the fish from within these six species.

Samples of muscle and liver were excised, approximately 0.6 g each, and stored frozen until laboratory analysis. Samples were digested with sulfuric acid (H_2SO_4), nitric acid (HNO_3) and potassium permanganate ($KMnO_4$; EPA 1998). THg content was determined by flameless atomic absorption spectrometry, using a Buck Scientific 410 Cold vapor Mercury Analyzer (Buck Scientific, Inc, Norwalk CT). Hg concentrations are expressed as µg/g wet weight. Quality assurance was determined using sample duplicates, calibration standards, blank samples and certified material (DORM-3 fish protein from the National Research Council of Canada). The DORM-3 certified value for THg was 0.382 ± 0.060 µg/g. Our analyses yielded 0.360 ± 0.014 µg/g ($n = 5$). Recoveries were reported at 94 % for THg for the DORM-3 reference material. Variation coefficients for duplicate samples were estimated to be less than 5 %. The detection limit for THg in fish muscle tissue was 0.01 µg/g.

Prior to any statistical comparisons, the distribution of the muscle and liver total Hg concentrations were tested for normality (Shapiro–Wilk's test). The data were not normally

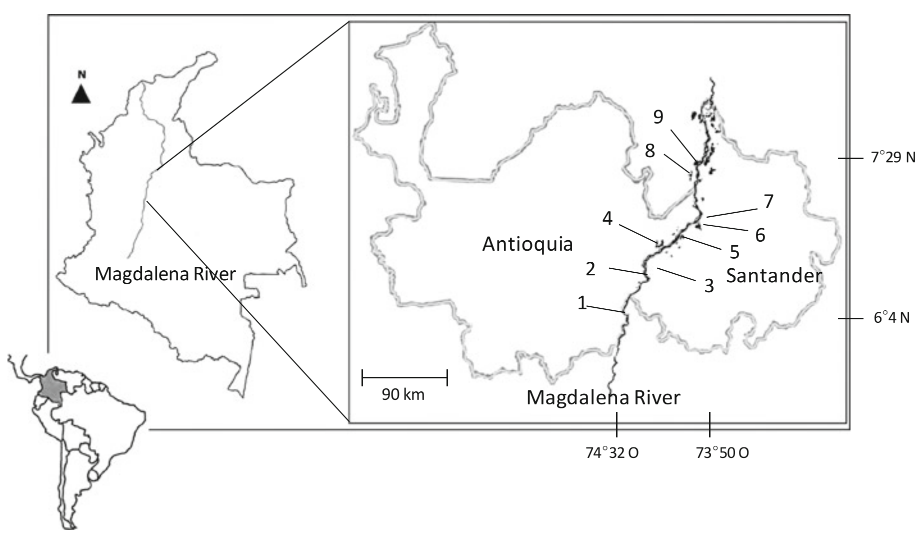

Fig. 1 Study area and marsh locations in midlands of the Magdalena River. The *numbers* on the map in the *right panel* correspond to marsh locations within the watershed. From south to north the marsh names are: *1* Palagua, *2* Samaria, *3* Rio Viejo, *4* Barbacoas, *5* Chucurí, *6* El Opón, *7* Juan Esteban, *8* Bija, *9* Tabacurú

distributed in any of the comparisons ($p < 0.05$ in all cases). Non-parametric statistics were used on the results throughout. The Mann–Whitney test was used for paired comparisons. The Kruskal–Wallis test was used for multiple comparisons. Non-parametric post hoc (multiple rank comparison) test was used to determine which mean ranks differed significantly from one another. Spearman's rank correlation coefficients were generated to assess whether parameters were correlated with each other. In all cases, statistical significance was inferred if $p < 0.05$.

Results and Discussion

The number of fish sampled, as well as mean values for their mass, length and THg concentrations in white muscle and liver are given in Tables 1 and 2.

The number of fish captured at each marsh varied from a high of 70 individuals in Barbacoas to only 7 in Samaria. The species captured at each site was also quite variable. We selected six marshes and the most representative species (*P. Magdalenae*, n = 69) to make marsh to marsh comparisons. Results from a nonparametric analysis of variance (Kruskall–Wallis test) indicated significant ($p < 0.05$) differences in THg concentrations in the muscle tissue of this species across the six marshes (Fig. 2). Post hoc pairwise comparisons indicated that tissue from the fish collected in the Palagua marsh contained the highest mean THg concentration value compared with Barbacoas, J. Esteban, Rio Viejo and Tabacurú.

Fourteen species that included more than seven individuals were selected to run the Kruskal–Wallis test for THg in muscle and hepatic tissue among species. A total of 378 muscle samples and 102 liver samples were included in the analysis. There were no significant differences among the 14 species with respect to muscle or hepatic THg concentration (data not shown, $p > 0.05$ in both cases).

Both white muscle and liver tissue were analyzed for THg in 6 species (*P. magdalenae, C. mivartii, C. kraussii,*

Table 1 Mean values (±SD) for fish mass, length and total mercury (THg) levels in muscle tissue for fish species captured in nine marshes from the Magdalena River, Colombia

Species	n	Trophic level	Fish mass (g)		Standard length (cm)		Muscle THg (μg/g)	
			Mean	SD	Mean	SD	Mean	SD
P. magdalenae	69	Noncarnivore	286	99	24.1	2.8	0.097	0.215
C. mivartii	54	Noncarnivore	200	75	22.6	2.8	0.057	0.066
C. kraussii	46	Carnivore	165	108	16.7	3.6	0.157	0.121
C. magdalenae	41	Noncarnivore	56	21	12.9	1.9	0.058	0.069
T. magdalenae	37	Noncarnivore	104	45	19.1	2.5	0.216	0.185
L. muyscorum	25	Noncarnivore	241	88	25.2	2.7	0.125	0.086
Ctenolucius hujeta	11	Carnivore	81	107	18.0	3.8	0.350	0.798
P. blochii	10	Noncarnivore	34	31	13.0	2.9	0.371	0.399
Centrochir crocodili	9	Noncarnivore	59	13	14.8	1.8	0.087	0.058
Cynopotamus magdalenae	9	Noncarnivore	150	101	21.8	3.9	0.243	0.133
Trachelyopterus insignis	9	Carnivore	97	46	16.2	2.8	0.160	0.065
Ageneiosus pardalis	7	Carnivore	318	171	29.6	5.7	0.118	0.034
Hemiancistrus cf wilsoni	7	Noncarnivore	180	131	27.4	7.6	0.049	0.030
Sorubim cuspicaudus	7	Carnivore	705	332	44.6	8.9	0.358	0.221
Hypostomus hondae	6	Noncarnivore	274	152	25.6	4.9	0.050	0.039
Dasyloricaria filamentosa	5	Noncarnivore	38	5	19.6	1.3	0.055	0.015
Eigenmannia humboldtii	5	Carnivore	104	16	41.5	2.6	0.172	0.105
Aequidens pulcher	4	Carnivore	38	47	10.4	7.4	0.410	0.213
Hoplias malabaricus	4	Carnivore	371	114	27.6	3.2	0.111	0.030
Sternopygus macrurus	4	Carnivore	428	190	64.9	12.5	0.138	0.053
Plagioscion surinamensis	3	Carnivore	279	90	26.6	2.7	0.123	0.048
Gilbertolus alatus	2	Noncarnivore	24	3	11.4	0.1	0.253	0.062
Hoplosternum magdalenae	2	Noncarnivore	97	87	15.4	8.3	0.043	0.015
Pseudoplatystoma magdaleniatum	2	Carnivore	2,162	1,433	56.5	12.1	0.170	0.056
Total	378							

Table 2 Mean values (±SD) for fish mass, length and total mercury (THg) levels in muscle and liver tissue for a subset of 102 fish of 6 species captured in nine marshes from the Magdalena River, Colombia

Species	Trophic level	Fish mass (g)		Standard length (cm)		Muscle THg (µg/g)		Liver THg (µg/g)		n
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	
P. magdalenae	Noncarnivore	286	99	24.1	2.8	0.097	0.215	0.102	0.090	32
C. mivartii	Noncarnivore	200	75	22.6	2.8	0.057	0.066	0.061	0.118	21
C. kraussii	Carnivore	165	108	16.7	3.6	0.157	0.121	0.177	0.458	17
T. magdalenae	Noncarnivore	104	45	19.1	2.5	0.216	0.185	0.095	0.150	15
C. magdalenae	Noncarnivore	56	21	12.9	1.9	0.058	0.069	0.167	0.085	11
L. muyscorum	Noncarnivore	241	88	25.2	2.7	0.125	0.086	0.086	0.049	6
Total										102

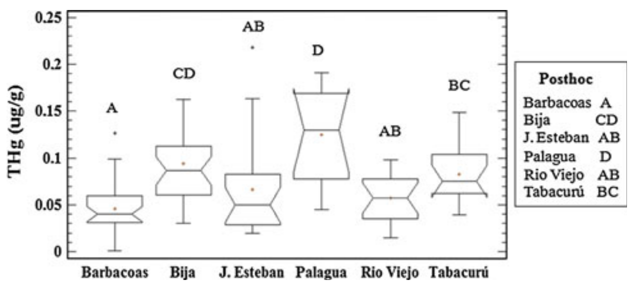

Fig. 2 Comparison of mercury in muscle tissue for *Prochilodus magdalenae* in six marshes from the Magdalena River, Colombia. For each site, the mean, median, upper quartile, lower quartile, maximum, minimum and outlier are presented. *Letters* that are not shared among the marsh groups indicate significant differences between marshes. Post hoc pairwise comparisons placed the fish into four groups (*A–D*)

Table 3 Relationship between fish weight and Hg concentration in liver and muscle tissue of three fish species from the Magdalena River

Species	*p* value	r-Spearman's	Tissue
C. kraussii	0.000	0.563	Muscle
C. magdalenae	0.001	0.355	Muscle
Sorubim cuspicaudus	0.027	0.611	Muscle
C. kraussii	0.003	0.738	Liver

T. magdalenae, Cyphocharax magdalenae and *L. muyscorum*). There was not a significant difference between THg levels in the two tissues in four of the species. However, THg levels in muscle tissue were significantly higher in *P. magdalenae* and *Cyphocharax magdalenae.*

Correlations were determined between fish mass and THg concentration in muscle or liver tissue in fourteen and six species, respectively. Significant correlations were obtained only in *C. kraussii, Cyphocharax magdalenae* and *S. cuspicaudus* in white muscle tissue and *C. kraussii* in liver tissue (Table 3). These findings are consistent with the results of Dorea et al. (2006), where significant correlations between muscle THg concentration and body mass were found in only three (*Cychla* spp., *Myleus torquatus, Hydrolycus scomberoides*) of the 12 fish species that they analyzed.

Trophic level was simplified to a comparison between carnivorous and noncarnivorous species. Fish species trophic levels were obtained from Maldonado et al. (2009). Trophic level was a strong determinant of THg accumulation among the fish species. The difference in THg concentration based on feeding level was more noticeable for muscle than hepatic tissue (Fig. 3). This is consistent with the concept of biomagnification, as reported by others

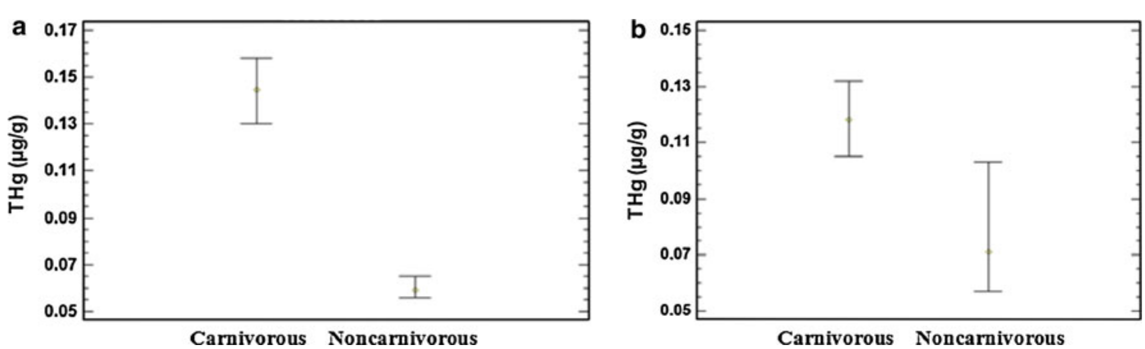

Fig. 3 Comparison between mercury concentration in muscle and hepatic tissue and trophic level in fish species captured in the Magdalena River. The carnivorous species had significantly higher ($p < 0.05$) concentrations of THg in white muscle than did the noncarnivorous species. **a** Muscle tissue, **b** hepatic tissue

(Dorea et al. 2006). The carnivorous species had significantly higher ($p < 0.05$) concentrations of white muscle THg than did the noncarnivorous species (Fig. 3). Comparisons between the THg in white muscle from male and female fish were determined for 14 different species. In none of the 14 comparisons were significant differences found in THg due to sex ($p > 0.05$ for all comparisons). It has been implied that female fish bioaccumulate less Hg than males, due to the shedding of fat-laden eggs (Madenjian et al. 2011). Curiously, in this study, significant differences were not found in any of the 14 comparisons.

There is only one other study (Olivero et al. 1998) that quantified Hg concentrations in fish from the lower Magdalena River. In that study, the ranges for Hg in muscle tissue were 0.022–0.516 µg/g for *C. kraussii.* 0.118–0.233 µg/g for *S. cuspicaudus* and 0.023–0.198 µg/g for *P. magdalenae*. For the last two species, the values found during the present study were consistently higher than those documented by Olivero and co-workers.

Frequent fish consumption of carnivorous species from midland Magdalena River represents a higher risk to human health compared with the noncarnivorous species. However, some of the noncarnivorous species also had very high Hg content. Overall, more than 95 % of the sampled fish individuals indicated THg concentrations below the World Health Organization limit of 0.5 µg/g for Hg in fish for human consumption (WHO 2000). Nevertheless, prolonged low-level exposure to the various forms of Hg may be affecting individuals in populations of frequent fish consumers (Holmes et al. 2009). Therefore, a greater risk may exist for frequent consumers of fish particularly those species such as *P. magdalenae, C. kraussii, L. muyscorum* and *S. Cuspicaudus.*

This study provides information on mercury distribution in fish organs in relation to their trophic level with clear differences observed between carnivorous and noncarnivorous species. A long-term monitoring program should be established in the contaminated areas for the purpose of providing an early fish consumption warning to the public for those species where such a warning is warranted.

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