Mercury in Amazonian fish from Madeira River basin, Rondônia State, Brazil

P. A. S. Gali[1], D. M. Bonotto[1], E. G. da Silveira[2] & W. R. Bastos[2]
[1]*Departamento de Petrologia e Metalogenia,*
Instituto de Geociências e Ciências Exatas-UNESP, Rio Claro, Brazil
[2]*Departamento de Geografia,*
Fundação Universidade Federal de Rondônia-UNIR, Porto Velho, Brazil

Abstract

This investigation was carried out at the Madeira River basin, located in the state of Rondônia, Brazilian Amazon. Fish from Madeira, Jaciparaná, and Jamari rivers between 7 and 11° parallels south and between 62 and 65° meridians west in Rondônia state, Brazil, were sampled and chemically analyzed for mercury in order to evaluate if the inputs of this metal into the food-chain is occurring in levels reaching values above those recommended by the World Health Organization. This is because such an element is very dangerous when ingested by humans and its presence was extensively identified some years ago in the area, since it was utilized as an amalgam in processes for recovering alluvial gold.
Keywords: mercury, fish, statistical distribution, Madeira River basin, health hazard.

1 Introduction

In aquatic systems, heavy metals (including mercury) and other elements are mainly transported in the solid phase, either sorbed onto particle surfaces and coatings, or incorporated into mineral grains. Thus, 90-99 percent of the total metal load in rivers is transported in the particulate phase, depending on the geochemical behavior of the metal and the nature of the physical and chemical environment [1]. Upon discharge to river waters, metal speciation or complexation, and other physical-chemical parameters such as pH, redox conditions, and nature of the solid-metal species interaction, determine the partitioning of the metal between solid and liquid phases, controlling its

dispersion throughout the aquatic environment, where adsorption on fine particles has been recognized as a key process in its transport [2-4].

The sources of trace metals in aquatic systems determine their distribution ratio between the aqueous and solid phases, when the metal contents of river solids depend significantly on allochthonous influences. Mining activities involve the extraction, processing, and disposal of large quantities of rock, being responsible, very often, by the release of metals that are introduced either directly or indirectly to rivers and streams [5]. The major problem affecting mercury during mining activities is related to the fact that it is widely utilized as an amalgam in processing alluvial gold ores, mainly in rainforest areas [6, 7].

The gold exploitation in several areas of the Brazilian Amazon has caused environmental problems due to the presence of mercury in the biosphere, whether in liquid, ionic or vapour form. Special attention has been given to mercury inputs at the Madeira River in the Amazon area by numerous investigators [6, 8-13] since is one of the largest tributary of Amazon River and the gold mining was officially allowed and practiced since the Andean headwaters, causing the release of metallic mercury to the atmosphere and waterways [14].

The gold mining activities on the Madeira River extended from the Bolivian headwaters, on the Beni River, down to the city of Porto Velho, capital of Rondônia State, and, despite to be practically absent in the present days, mercury has been evaluated in the aquatic system by local authorities and environmentalists due to the possibility of occurring contamination in people [15]. Contamination of the aquatic food-chain of the Madeira River tributaries has been demonstrated [20], being reported that 86% of the piscivorous fish collected in the Beni River exhibited high mercury concentrations, i.e. values exceeding by almost four times the WHO safety limit [16].

This investigation focused the mercury presence in fish of the Madeira River basin, Brazilian Amazon, following the previous interest in the area due to possible intoxication on animal and human population due to the ingestion of this metal in food.

2   Material and methods

The Madeira River is one of the largest tributaries of the Amazon River, extending from Bolívia and crossing the city of Porto Velho, capital of Rondônia State in Brazil, which is the most populated site (population approximately 300,000, according to the 1999 census) along it. The Aw-tropical rainy climate (Köppen classification) characterizes Rondônia State, i.e. the relative air humidity ranges from 74.2 up to 90.8% and air temperature from 20.7 up to 32.2°C [17]. The wet season (average rainfall = 250 mm/month) occurs between October and April, whereas the dry season (average rainfall = 20 mm/month) between May and September [17]. Such rain regime influences directly the water level height of the Madeira River (Fig. 1).

This study provided Hg distribution data for 419 samples of fish from Madeira, Jaciparaná, and Jamari rivers in the Madeira River basin between 7 and

11° parallels south and between 62 and 65° meridians west in Rondônia state, Brazil (Fig. 2). The samples were obtained between April 1994 and January 1998 in the central market located at the city of Porto Velho, as well collected directly from the rivers after using roads and small boats, because the selected area is not suitable for navigation. The specimens were identified according to their popular name during the fieldwork. Afterwards, they were stored in polyethylene bags that were kept in iceboxes and transported up to the laboratory.
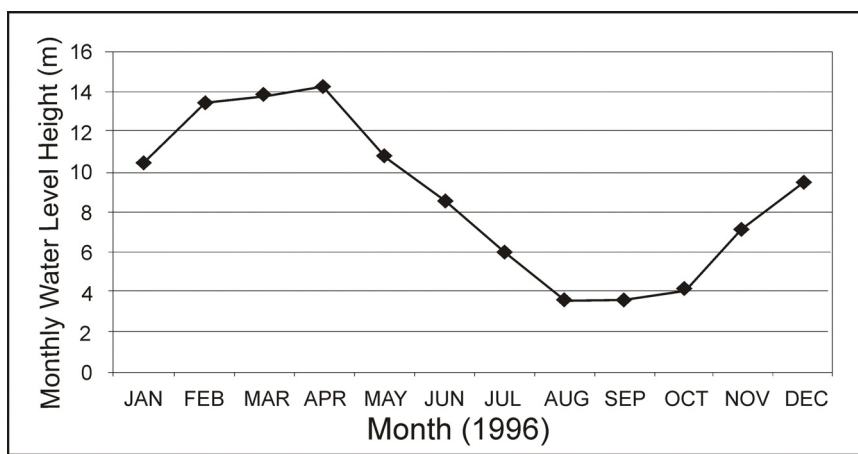

Figure 1:   The average monthly water level height of the Madeira River during 1996 [17].

The weight and length of the specimens were recorded at the laboratory according to standard procedures [18]. It was also indicated if their skin contains scales or not, as well their possible scientific name based on criteria applied to Amazonian fish [18]. Then, a fillet was cut from the back of the specimen and maintained under freeze (-5 °C) up to the time of analysis.

Digestion and extraction procedures were used for Hg analysis in the samples. About 0.5 g of each sample was weighed in Teflon beakers/tubes, 1 mL of 30% H_2O_2 was added plus 2 mL of a 1:1 H_2SO_4-HNO_3 mixture and 5 mL of 5% $KMnO_4$. This material was inserted in a 630 W microwave oven and maintained there (temperature~55°C) during about 35 minutes. Alternatively, digestion was also performed in an opened system. Afterwards, the solution was brought to room temperature (~25°C) and the excess $KMnO_4$ was neutralized with some drops of 12% hydroxylamine hydrochlorate. The volume was raised up to 10 mL with ultra pure water prepared on a Milli Q system that uses ion exchange resin and Millipore 0.22 µm filter.

The analyses of total Hg concentrations were done using atomic absorption spectrophotometers with cold vapor generation. The equipment utilized is a Perkin Elmer model FIMS-400 atomic absorption spectrophotometer, containing a cylindrical cell with quartz window, an Hg lamp (253.7 nm), a specific detector

for absorption on the Hg wavelength, a system of flow injection analysis, and a cold vapor generator system. The parameters of calibration utilized in this equipment consisted on an Ar flow of 50 mL.min^{-1}, a 3% HCl flow of 9-11 mL.min^{-1}, and a 0.2-0.5% NaBH$_4$+NaOH flow of 5-7 mL.min^{-1}. The concentrations of the analytical solutions for obtaining the calibration curve of the equipment varied between 2 and 40 μg.L^{-1}, and were prepared from a 2 μg.mL^{-1} stock solution preserved with 5% HNO$_3$ + 0.01% K$_2$Cr$_2$O$_7$. Each aliquot representing the sample (0.5 g) was divided in three sub-aliquots. All analytical determinations were made in triplicate for each sub-aliquot, yielding, therefore, nine measurements for each sample. The final result for each sample (Table 1) corresponded to the mean value of the nine readings.
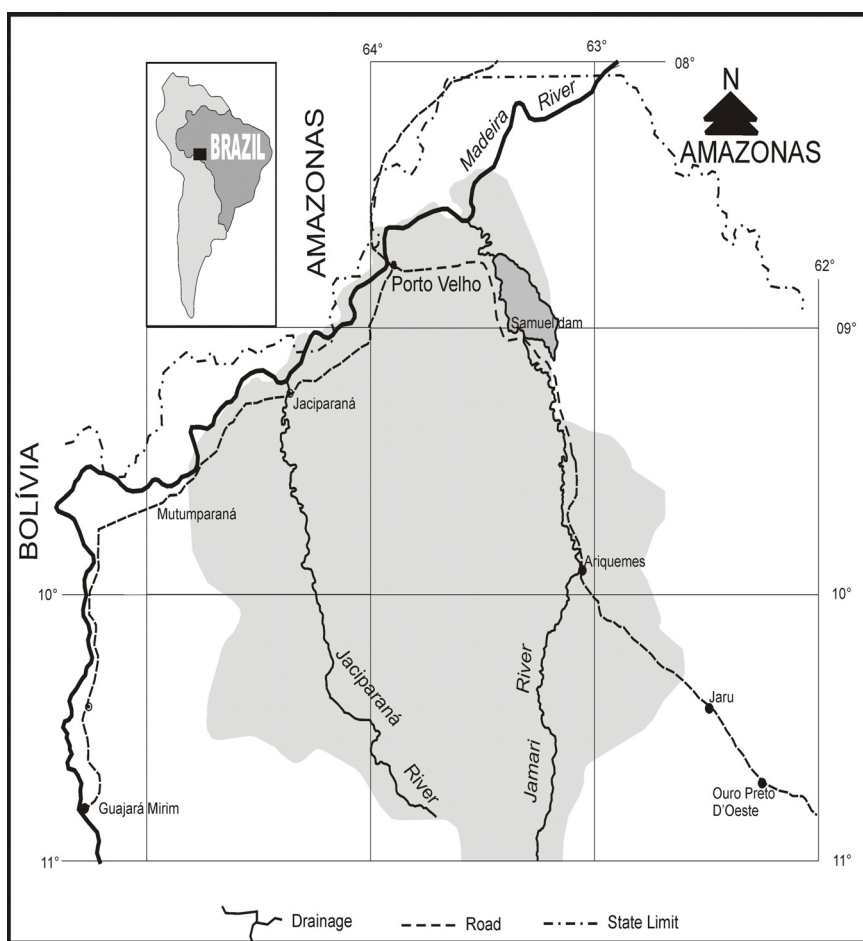

Figure 2: Location of the area for sampling fish in Rondônia State, Brazil.

Table 1: Average Hg content in fish from the Madeira River basin, Brazil.

Popular name	Scientific name	N*	Hg (ppm)
Acará	*Geophagus* sp.	10	0.09
Acari Bodó	*Lipsarcus pardalis*	1	0.04
Apapá	*Pellona* sp.	1	0.81
Aruanã	*Osteoglossum bicirrhossum*	2	0.68
Bacu	*Pterodoras granulosus*	1	0.01
Bico de Pato	*Hemisorubim platyrhynchos*	3	0.53
Bicudo	*Boulengerella ocellata*	4	0.90
Branquinha	*Potamorhina latior*	16	0.09
Cará	*Cichlasoma spectabile*	3	0.29
Caratinga	Not identified	1	0.04
Cascudinho	*Pareiorhapis duseni*	7	0.04
Cascudo	*Plecostomus* sp.	3	0.04
Croatá	*Platynematichthys notatus*	2	1.86
Curimatã	*Prochilodus* sp.	38	0.12
Curimba	Not identified	1	0.08
Dourado	*Brachyplathystoma flavicans*	4	0.43
Filhote	*Brachyplathystoma filamentosum*	7	0.96
Jacundá	*Crenicichla reticulata*	5	0.37
Jaraqui	*Semaprochilodus taeniurus*	7	0.18
Jatuarana	*Hemiodus notatus*	9	0.10
Jaú	*Paulicea leutkeni*	2	0.52
Lírio Braço de Moça	*Platystomatichthys sturio*	4	0.46
Mandi	*Pimelodus* sp.	6	0.34
Mandubé	*Ageneiosus brevifilis*	3	0.95
Mapará	*Hypophtalmus edentatus*	18	0.56
Matrinchã	*Brycon* sp.	1	0.05
Pacu	*Mylossoma* sp.	21	0.07
Peixe Cachorro	*Hydrolycus scomberoides*	9	0.97
Pescada	*Plagioscion squamosissimus*	14	0.33
Piau	*Laemiyta* sp.	4	0.07
Piau Apará	Not identified	3	0.21
Piau Aracu	*Laemolyta* sp.	6	0.16
Piau Botafogo	*Shizodon vittatum*	3	0.04
Piau Cabeça Gorda	*Leporinus friderici*	5	0.20
Piau Cabeça de Meia	*Schizodon fasciatum*	14	0.14
Pintado	*Pseudoplatystoma* sp.	22	0.92
Piramutaba	*Brachyplathystoma vaillanti*	1	0.09
Piranha	*Serrasalmus* sp.	46	0.80
Pirapitinga	*Colossoma bidens*	3	0.08
Pirarucu	*Arapaima gigas*	4	0.26
Sardinha	*Triportheus elongatus*	11	0.26
Surubim	*Pseudoplatystoma fasciatus*	1	0.38
Tambaqui	*Colossoma macropomum*	8	0.15
Traíra	*Hoplias malabaricus*	34	0.46
Tucunaré	*Cichla ocellaris*	49	0.36
Tucunaré açu	*Cichla* sp.	2	0.30

* N = number of samples.

3   Hg content in selected fish

The average values of the Hg content in the analyzed fish are greatly variable, ranging from 0.01 to 1.86 ppm (Table 1). The species sampled are widely spread over the area, being commonly consumed by the population. However, considering the number of specimens sampled per specie, the economic importance and the use in alimentation, four types were selected for initial evaluation of the data obtained. They are: *Prochilodus* sp., *Serrasalmus* sp., *Hoplias malabaricus*, and *Cichla ocellaris*. A summary of the parameters obtained for these fish is shown in Table 2.

The WHO safety limit [16] for ingestion of mercury in fish is 0.5 ppm and considering the range of values reported in Table 2, only the specimens of *Prochilodus* sp. do not reach the maximum allowable limit in any analyzed sample. These fish ingest organic matter and microorganisms associated to mudstone at the bottom of lakes and margins of rivers, realizing long migration for reproduction. *Serrasalmus* sp., *Hoplias malabaricus*, and *Cichla ocellaris* are classified as carnivorous fish, and among them the average Hg content is higher in *Serrasalmus* sp. (0.8 ppm) that exceeds the WHO safety limit of 0.5 ppm.

However, such contamination level is lower than that found in other piscivorous fish in the Amazon area, since values exceeding by almost four times the WHO safety limit have been reported [8]. The same relationship between the Hg content and the alimentation pattern of the specie had been identified in previous studies developed in Brazil, with the higher Hg contents occurring in individuals of higher trophic levels [10-13].

Table 2:   Weight, length, and Hg content in fish from the Madeira River basin, Rondônia State Brazil.

	Serrasalmus sp.	*Prochilodus* sp.	*Hoplias malabaricus*	*Cichla ocellaris*
Number of samples	46	38	34	49
Weight (g)				
Minimum value	500	200	250	100
Maximum value	2100	2000	1200	2000
Average value	884	556	533	560
Length (cm)				
Minimum value	14	22	20.5	21
Maximum value	36.5	42.5	46	44
Average value	27	28	31	29
Hg (ppm)				
Minimum value	0.1908	0.0029	0.1018	0.0627
Maximum value	2.1681	0.3380	1.1876	0.8432
Average value	0.8051	0.1203	0.4628	0.3551

4 Statistical analysis of the data

The Hg content data obtained for *Prochilodus* sp., *Serrasalmus* sp., *Hoplias malabaricus*, and *Cichla ocellaris* were submitted to statistical analysis, as reported in Table 3. All data adjust to a normal distribution (Fig. 3), inclusive those obtained for *Cichla ocellaris* that indicate a bi-modal normal distribution.

Table 3: Statistical distribution of the mercury content in fish from the Madeira River basin, Rondônia State, Brazil.

Hg content range (ppm)	Average Hg content (ppm)	Frequency	Frequency percentage	Cumulative percentage
Serrasalmus sp. (N = 46)				
0.1908 - 0.2861	0.2400	4	8.7	8.7
0.2861 - 0.4289	0.3600	3	6.5	15.2
0.4289 - 0.6430	0.5400	12	26.1	41.3
0.6430 - 0.9641	0.8000	15	32.6	73.9
0.9641 - 1.4456	1.2000	8	17.4	91.3
1.4456 - 2.1675	1.8100	3	6.5	97.8
2.1675 - 3.2499	2.7100	1	2.2	100.0
Prochilodus sp. (N = 38)				
0.0018 - 0.0040	0.0029	1	2.6	2.6
0.0040 - 0.0088	0.0064	0	0	2.6
0.0088 - 0.0194	0.0141	0	0	2.6
0.0194 - 0.0429	0.0312	1	2.6	5.2
0.0429 - 0.0948	0.0689	8	21	26.2
0.0948 - 0.2095	0.1523	26	68.5	94.7
0.2095 - 0.4630	0.3366	2	5.3	100
Hoplias malabaricus (N = 34)				
0.1000 - 0.1506	0.1253	2	5.9	5.9
0.1506 - 0.2268	0.1887	2	5.9	11.8
0.2268 - 0.3416	0.2842	11	32.3	44.1
0.3416 - 0.5144	0.4280	9	26.5	70.6
0.5144 - 0.7747	0.6445	4	11.8	82.4
0.7747 - 1.1667	0.9707	5	14.7	97.1
1.1667 - 1.7570	1.4618	1	2.9	100
Cichla ocellaris (N = 49)				
0.0500 - 0.0771	0.0636	1	2	2
0.0771 - 0.1189	0.0980	1	2	4
0.1189 - 0.1833	0.1511	9	18.5	22.5
0.1833 - 0.2827	0.2331	14	28.6	51.1
0.2827 - 0.4359	0.3594	6	12.2	63.3
0.4359 - 0.6722	0.5542	15	30.6	93.9
0.6722 - 1,0366	0.8547	3	6.1	100

Statistical tests of correlation were performed between weight and length and between the Hg content and weight for the data obtained for *Prochilodus* sp., *Serrasalmus* sp., *Hoplias malabaricus*, and *Cichla ocellaris*. Fig. 4 plots all

relationships found among these parameters, where it is possible to see that the weight of the specimens is directly related to their length, as expected. The Hg content raises in accordance with the weight of the carnivorous fish *Serrasalmus* sp., *Hoplias malabaricus*, and *Cichla ocellaris* (Fig. 4), evidencing the cumulative effect of mercury in tissues, i.e. the increase in weight is normally related to the age of the specimen, that causes a longer assimilation of Hg present in food, not in the metallic form, but bio-available in the ionized (organic) form. Beyond the Hg content values in the non-piscivorous fish *Prochilodus* sp. not exceed the WHO safety limit of 0.5 ppm, the Hg content and weight in these fish are not related (Fig. 4), reinforcing the importance of the alimentation habit on the Hg bioaccumulation.
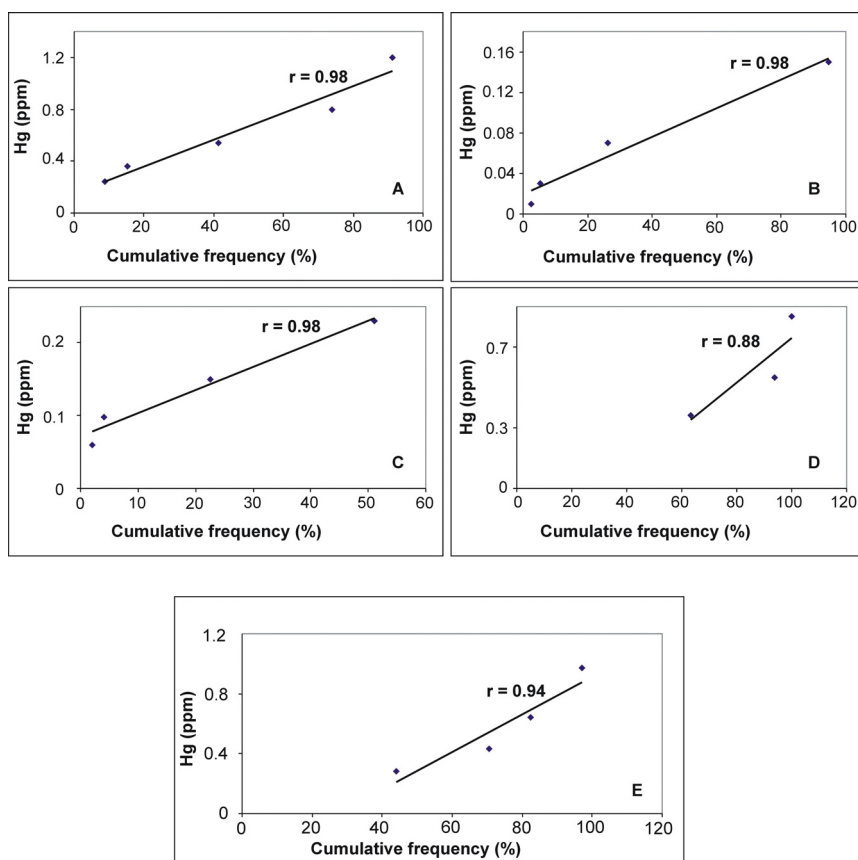

Figure 3: The average Hg content in a) *Serrasalmus* sp., b) *Prochilodus* sp., c) *Cichla ocellaris* (N=25), d) *Cichla ocellaris* (N=24), and e) *Hoplias malabaricus* plotted on a probability graph.
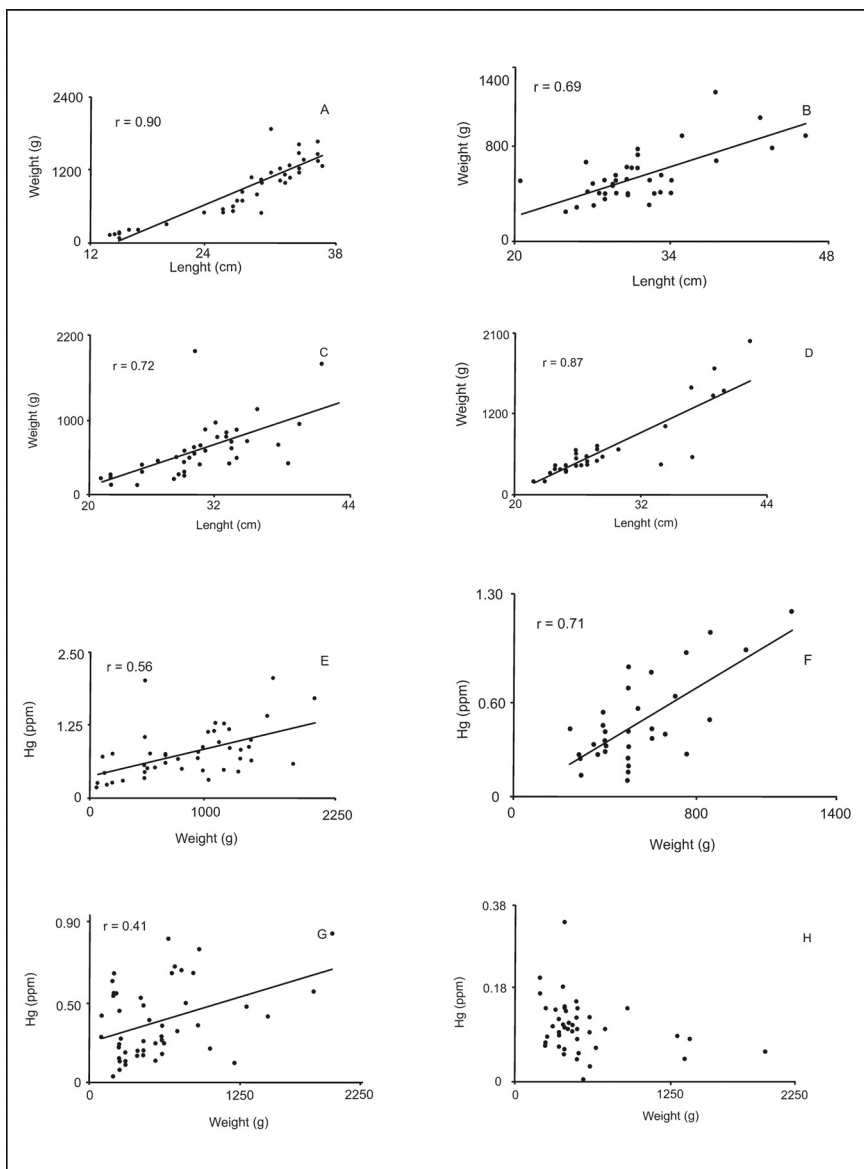
Figure 4:   The relationship between weight and length in a) *Serrasalmus* sp.,
b) *Hoplias malabaricus*, c) *Cichla ocellaris*, d) *Prochilodus* sp.,
and the relationship between the Hg content and weight in
e) *Serrasalmus* sp., f) *Hoplias malabaricus*, g) *Cichla ocellaris*, and
h) *Prochilodus* sp.

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