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Original Article

Mercury in fish and sediment of Purus River, Acre State, Amazon

Mercúrio em peixe e em sedimento do Rio Purus, Estado do Acre, Amazônia

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Abstract

Core subject: To quantify the Hg content of sediment and fish collected along the Purus River (Acre State, Amazon) in order to identify if those samples could be a potential route of Hg exposure to the population of Manoel Urbano (a riverside community). **Methods:** The total mercury (THg) was quantified using the Cold Vapor Atomic Absorption technique. **Results:** We collected 06 samples of sediment and 264 samples of fish. The Hg in sediments ranged between 0.038 and 0.065 μg.g^{-1}. The results indicate that sediment is in agreement with "uncontaminated" Amazonian rivers. The carnivorous species presented the highest level of Hg on muscle (mean 0.927 μg/g^{-1}), followed by piscivorous (mean 0.873 μg.g^{-1}), planktophagus (mean 0.566 μg.g^{-1}), omnivorous (mean 0.533 μg.g^{-1}) and detritivorous (mean 0.176 μg/g^{-1}). Fourty four percent (44%) of the total species collected presented mean levels of THg on muscle, a percentage greater than the threshold recommended by WHO. **Conclusion:** Some species may be a route for Hg exposure. The sediment is within the normality. The authors suggest that other factors, such as culture and society, should be considered for future researches in order to promote the population healths.

Keywords: mercury; fish; sediment; Purus; Amazon.

Resumo

Tema central: Quantificar o teor de mercúrio (Hg) em sedimentos e em peixes coletados ao longo do rio Purus, no Estado do Acre, Região Amazônica, a fim de identificar se essas amostras conferem uma via potencial de exposição do Hg para a população de Manoel Urbano (uma comunidade ribeirinha). **Métodos:** O mercúrio total (HgT) foi quantificado utilizando a técnica de absorção atômica por vapor frio. **Resultados:** Seis amostras de sedimentos e 264 amostras de peixes foram coletadas. O Hg em sedimentos de fundo variou entre 0,038 e 0,065 μg.g^{-1} (média de 0,050 μg.g^{-1}). Os resultados indicam que os sedimentos estão de acordo com rios amazônicos "não contaminados". As espécies carnívoras apresentaram o mais alto nível de Hg no músculo (média de 0,927 μg/g^{-1}), seguido por piscívoros (média de 0,873 μg/g^{-1}), planctófagos (média de 0,566 μg/g^{-1}), onívoros (média de 0,533 μg/g^{-1}) e detritívoros (média de 0,176 μg/g^{-1}). Além disso, 44% do total de espécies coletadas apresentaram níveis médios de HgT no músculo superior ao limite recomendado pela Organização Mundial da Saúde (OMS). **Conclusão**: Algumas espécies podem ser uma via para a exposição ao Hg. O sedimento encontra-se dentro na normalidade. Os autores consideram que outros fatores, como a cultura e a sociedade, devem ser considerados para pesquisas futuras a fim de promover a saúde dessa população.

Palavras-chave: mercúrio; peixe; sedimento; Purus; Amazônia.

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INTRODUCTION

Mercury (Hg) is a metal that accumulates along the aquatic food chain, whith carnivorous fish presenting the higher concentrations, and undergoes biomagnification in almost all food chains, which ultimately results in a very high environmental exposure to consumers[1,2].

The Hg is introduced into the environment thru different sources, such as atmospheric transport and geochemical pools[3]. Its chemical form and physicochemical properties are closed related with its distribution[4,5]. The Hg could be present in the environment as inorganic (Hg^0, Hg^{1+} and Hg^{2+}) and organic forms. The organometallic compounds result from the action of microorganisms that transform the inorganic form into organic forms[6].

The Amazonian population diet varies according to the season and presents diversity in the consumption of regional fruits[7,8]. Although, this scenario have been changing slowly due to the recent advances in the Brazilian social programs (direct cash transfer programs) which increased the financial support capacity of some populations, diversifying the diet of these individuals and becoming less dependent of the hydrological cycles [9]. In spite of this newly social context, fish continues to be the major source of protein intake for most of the Amazonian population, especially children. Some of the fish species that are commercially available contains Hg levels that extrapolate the safe limit (≤0.50 $\mu g.g^{-1}$) preconized by WHO[10-15], leading to the development of environmental biomonitoring programs in order to measure the concentration of this metal into different fish species and assess the risk of exposure for this population[16–19].

In Amazon, Hg can be released in the aquatic ecosystems by anthropogenic (mainly via gold mining activity) and natural process (such as soils lixiviation)[20,21]. In this context, the mercury levels of Amazonian population, even the ones located at non-canonical exposed area, usually extrapolate the maximum safe limit allowed by WHO[22-25].

Brabo et al.[26] conducted a study to quantify Hg in various abiotic and biotic matrices from Acre State and Purus Rivers (both located at the west end of Western Amazonia), including fish samples from Rio Branco (the capital of Acre State), Sena Madureira, Brasiléia and Assis Brazil cities (small riverine villages located at Acre State). The results revealed that water, bottom sediments and suspended solids were in accordance with a non-impacted area and also that Hg lithogenic input is more significant than the external contribution. Regarding the aquatic biota, 1186 commercially samples of fish were captured. Among them, 613 were classified as carnivorous and 513 as non-carnivorous. The Hg content followed the standard profile of bioaccumulation where the concentration was 1.287 µg.g for carnivorous and 0.115 µg.g for non-carnivorous species.

The ratio between fish ingestion and Hg exposure in the population of Acre State is encompassed by some factors, considering the consumer economical status, and, of utmost importance, a great proportion of the population (independent of its social context) shows high levels of Hg on hair[27]. In this context, Martins[28] identified key aspects of feeding habits of non-urban population of Acre that contributed significantly to identify possible and alternatives causes of Hg exposure, such as the cultivation of beans on the small ravines (or beaches) created during the dry season. As a result, sediment and cultivars presented low levels of Hg, but some populations presented high levels of Hg on hair: individuals from Sena Madureira (n=83/ mean =7.2 µg.g Hg) and from Manoel Urbano (n=92/ mean =14 µg.g).

The present study aims to assess if the fish species from the Purus River confer a risk of exposure to Hg for a riparian population living at Manoel Urbano (Acre State). Furthermore, the analysis of the river bottom sediment was performed in order to identify any recent anthropogenic input of Hg.

METHODOLOGY

Area of study

The Purus River Basin has a transfrontier position, being located at Amazonas (73%) and Acre State (21%), as well as Peru (5.5%) and Bolivia (0.5%)[29]. The Purus River (the main tributary of the Basin) presents native forest, low anthropogenic impact and wetlands along the oxbow parts[29]. This river has an extension of 3700 Km, emerges in the Contamana Mountain (Peru) and recedes into Solimões River[30,31]. The waters of the Purus River are classified as white, presenting a bicarbonate profile (rich in Ca^{2+} e HCO^{3-}), weakly acid to neutral pH (from 6.5 to 7) and high dissolved materials and salts that are carried from Andes[32].

Manoel Urbano is located at the central part of the State of Acre along the Purus River. In 2010, the city had a population of 7,981 habitants and a demographic density of 0.75 hab/Km^2 [33].

Sample collection

The present study collected 264 samples of 18 fish species and 06 samples of sediment along 06 points (with a distance of 5 km between each sample point) of the Purus River, in the period November 2013 (Figure 1).

Fish were collected using cast nets and gillnets with different mesh sizes (35, 50 and 70 mm between opposite knots). Then, the specimens were identified using taxonomic guides[34-36]. Some additional information as total weight (g), total length (cm), trophic level using the Fishbase database[37], and stomach content were collected. The muscle and liver samples were placed in plastic bags, identified, frozen and transported in coolers to the

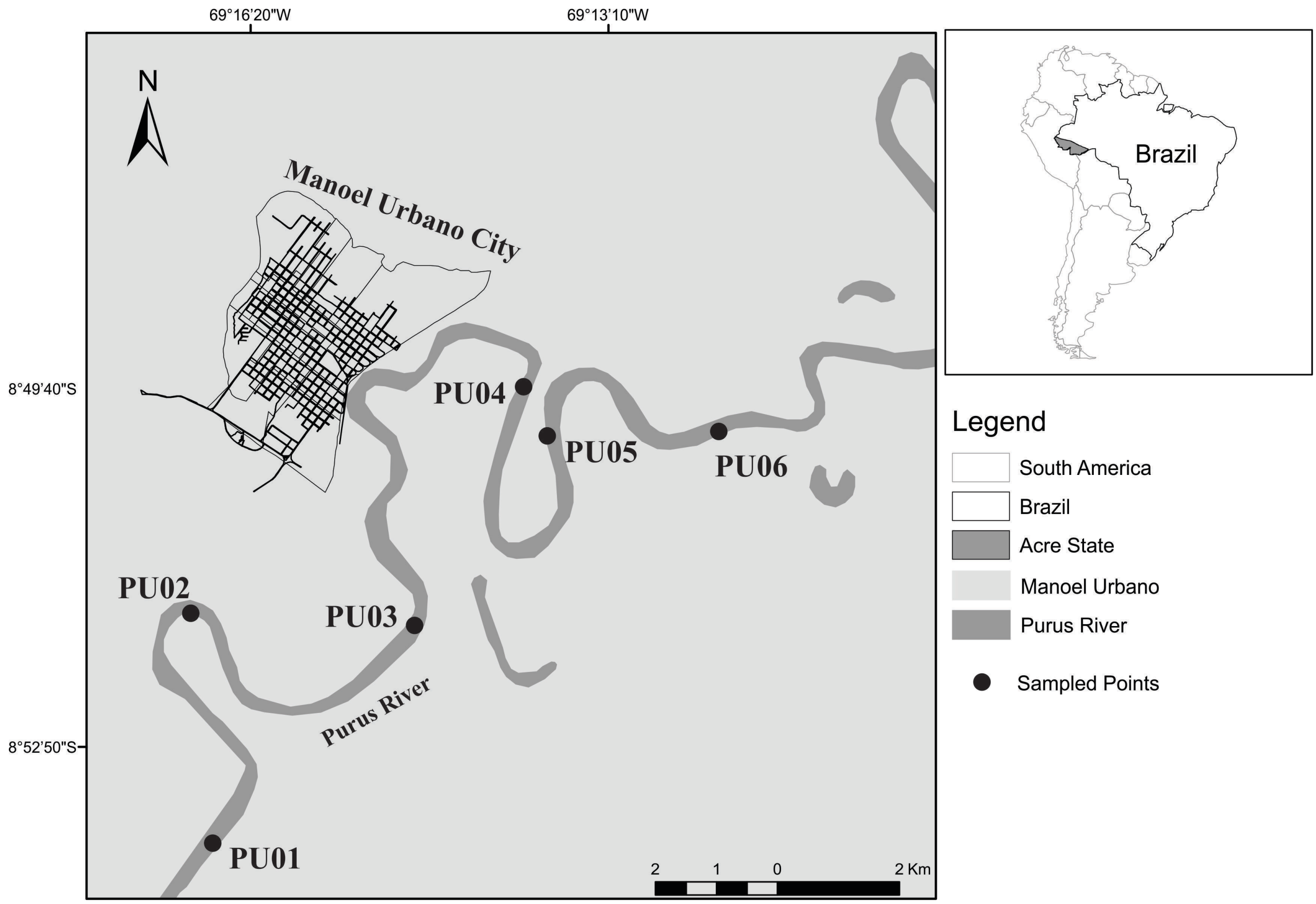

Figure 1. Map showing the geographic location of Manoel Urbano and the sampling points along the Purus River

laboratory. The samples were stored in glass vials, homogenized and stored at –20 °C until the laboratory analysis.

The sediments were collected using Van Veen Grab sampler. Then, the samples were identified, stored in plastic bags, dried at room temperature, fractionated until reach a granulometry of 270 mesh and stored at room temperature until the laboratory analysis.

Analysis of total mercury

The samples were analyzed according to Akagi et al.[38]. Approximately, 0.5 g of homogenized muscle, 0.3 g of homogenized liver and 0.2 g of sediment were weighted and transferred to 50 mL Pirex® volumetric flasks, added 1 mL of deionized water, 2 mL of HNO_3-$HClO_4$ (1+1), and 5 mL of H_2SO_4. Samples were then heated on a hot plate to 200-230 °C for 30 minutes. After cooling, the mixture were completed to 50 mL with deionized water, then THg was analyzed by Cold Vapor Atomic Absorption Spectrometry (CVAAS) with the Mercury Analyser, model HG-201, produced by SANSIO. All analyses were performed in duplicate and were accompanied by quality control from certified reference material (DOLT-4 and DORM-3).

Descriptive statistics and correlation calculations were evaluated (significance level of 95% or p<0.05) using the software MINITAB 17 (Minitab Inc.).

RESULTS

Levels of mercury in fish

A total of 264 individuals belonging to 3 orders, 11 families and 18 species were collected. Table 1 shows the number of collected species, the popular and scientific names, trophic levels, feeding habit and mean HgT content on muscle and liver of each specie

The THg content on muscle ranged from 0.004 to 5.384 $\mu g.g^{-1}$. The carnivorous species presented the highest level of Hg on muscle (mean 0.927 $\mu g.g^{-1}$), followed by piscivorous (mean 0.873 $\mu g.g^{-1}$), planktophagus (mean 0.566 $\mu g.g^{-1}$), omnivorous (mean 0.533 $\mu g.g^{-1}$) and detritivorous (mean 0.176 $\mu g.g^{-1}$).

The species *Calophysus macropterus, Hydrolycus scomberoides, Rhaphiodon vulpinus, Cetopsis coecutiens, Sorubim lima, Pinirampus pirinampu, Plagioscion squamosissimus and Hypophthalmus edentatus* presented mean levels of THg on muscle greater than the threshold recommended limit for human consumption of

Table 1. The popular and scientific names of the collected species, the feeding habit, the number of samples and the mean HgT (μg.g⁻¹) are shown

Specie	Popular name	Trophic level	Feeding habit	Mean HgT, muscle / ± SD	Range Muscle	Mean HgT, liver / ± SD	Range liver	N
Calophysus macropterus (Lichtenstein, 1819)	Zamurito	3.2	Omnivorous	2.482 ± 1.942	1.284-5.384	4.572 ± 4.831	1.236-11.700	3
Hydrolycus scomberoides (Cuvier, 1819)	Payara	4.5	Piscivorous	1.386 ± 1.089	0.055-2.432	1.044 ± 1.184	0.116-2.781	4
Rhaphiodon vulpinus (Spix & Agassiz, 1829)	Biara	4.5	Carnivorous	1.109 ± 0.626	0.136-2.359	1.755 ± 1.405	0.124-4.562	15
Cetopsis coecutiens (Lichtenstein, 1819)	Candirú-Açú	3.9	Carnivorous	0.900 ± 0.741	0.224-1.853	5.770 ± 4.225	1.323-9.991	4
Sorubim lima (Bloch & Schneider, 1801)	Duckbill catfish	4.1	Carnivorous	0.772 ± 0.490	0.076-1.287	1.447 ± 1.632	0.163-3.933	5
Pinirampus pirinampu (Spix, 1829)	Flatwhiskered catfish	4.5	Piscivorous	0.617 ± 0.279	0.316-0.868	2.546 ± 2.418	0.195-5.025	3
Plagioscion squamosissimus (Heckel, 1840)	South American silver croaker	4.4	Piscivorous	0.617 ± 0.279	0.316-0.868	2.546 ± 2.418	0.195-5.025	3
Hypophthalmus edentates (Spix & Agassiz, 1829)	Highwaterman catfish	2.9	Planktophagous	0.566 ± 0.136	0.358-0.827	1.725 ± 1.087	0.592-3.560	10
Anodus elongates (Agassiz, 1829)	Charuto	3.4	Omnivorous	0.453 ± 0.118	0.169-0.711	0.404 ± 0.215	0.048-0.966	44
Roeboides affinis (Günther, 1868)	Cacunda	3.7	Omnivorous	0.273 ± 0.085	0.120-0.349	0.278 ± 0.174	0.098-0.588	6
Curimata inornata (Vari, 1989)	Branquinha	2.0	Detritivorous	0.239 ± 0.146	0.124-0.440	0.157 ± 0.069	0.086-0.245	4
Triportheus angulatus (Spix & Agassiz, 1829)	Sardinha Papuda	2.7	Omnivorous	0.224 ± 0.097	0.032-0.487	0.140 ± 0.078	0.015-0.347	122
Psectrogaster amazonica (Eigenmann & Eigenmann, 1889)	Branquinha Cascuda	2.0	Detritivorous	0.196 ± 0.071	0.126-0.267	0.121 ± 0.056	0.068-0.180	3
Pimelodus blochii (Valenciennes, 1840)	Bloch's catfish	3.1	Omnivorous	0.172 ± 0.052	0.081-0.220	0.727 ± 0.621	0.144-1.945	7
Potamorhina altamozonica (Cope, 1878)	Mocinha	2.0	Detritivorous	0.141 ± 0.070	0.005-0.280	0.157 ± 0.093	0.035-0.331	14
Prochilodus nigricans (Spix & Agassiz, 1829)	Black prochilodus	2.4	Detritivorous	0.128 ± 0.057	0.050-0.196	0.232 ± 0.095	0.111-0.345	6
Schizodon fasciatus (Spix & Agassiz, 1829)	Aracu-Pintado	2.5	Omnivorous	0.068 ± 0.027	0.020-0.097	0.021 ± 0.010	0.010- 0.035	6
Mylossoma duriventre (Cuvier, 1818)	Silver Dollar fish	2.8	Omnivorous	0.065 ± 0.036	0.004-0.094	0.169 ± 0.230	0.020-0.577	5
Total								**264**

fish established by WHO (0.5 μg.g⁻¹). Those species represents 44% of the total species collected.

The Hg content on liver ranged from 0.010 to 11.700 μg.g⁻¹. The highest Hg content on liver was observed in carnivorous (mean 2.991 μg.g⁻¹), followed by piscivorous (mean 2.045 μg.g⁻¹), planktophagos (mean 1.725 μg.g⁻¹), omnivorous (mean 0.902 μg.g⁻¹) and detritivorous (mean 0.167 μg.g⁻¹). The species that presented more accumulation of THg into liver were *C. coecutiens* (mean 5.770 μg.g⁻¹), *C. macropterus (*4.572 μg.g⁻¹), *P. pirinampu* and *P. squamosissimus* (mean 2.546 μg.g⁻¹, both). The Pearson analysis revealed a moderate corratio between muscle and liver (0.577).

Our data indicate a good corratio between the trophic level with the THg into muscles (r=0.644; p=0.001), as well as a good corratio between THg into muscles with length (r=0.505; p=0.001) and with weight (r=0.408; p=0.001). The data is in agreement with other studies that evaluated the same parameters[13,39].

Analysis of HG into sediment

The analytical results of Hg in bottom sediments (n=6) ranged between 0.038 and 0.065 μg.g⁻¹ and mean values observed was 0.050 μg.g⁻¹ (Table 2).

The results are higher when the data are compared with the results obtained by Brabo et al.[26] who found an mean value of 0.023 μg.g⁻¹ for the Purus River (closer to Sena Madureira city) and 0.026 μg.g⁻¹ for the bottom sediment of the Iaco River (one of the main tributary of the Purus River) while the results are similar with the ones observed by Mascarenhas et al.[40] who reported a mean Hg content of 0.054 μg.g⁻¹ for the bottom sediment of Acre River. The values found in this study are below the background set for "uncontaminated" Amazonian rivers <0.200 μg.g⁻¹.

Table 2. Levels of HgT in bottom sediment (μg.g^{-1})

Collection point	N	HgT
01	1	0.056
02	1	0.038
03	1	0.039
04	1	0.042
05	1	0.065
06	1	0062
Mean	-	0.050
Total	**6**	

DISCUSSION

There is no direct evidence of gold mining activity in the Acre State. Although, its geographical location may be a determinant factor for the comprehension of Hg flow in this ecosystem, given that Peru, Bolivia and Amazonia have been historically affected by gold extraction. In spite of this scenario, most of the studies identified that the abiotic samples in this region were within the normality and were in agreement with a non impacted area[26-28], and our data are in agreement with this idea.

It is premature to evaluate if *C. macropterus, H. scomberoides, R. vulpinus, C. coecutiens, S. lima, P. pirinampu, P. squamosissimus and H. edentatus* represents any real risk to human health. Although, according to our observations, all of them are commercialized and consumed by the population of Manoel Urbano (except for *C. coecutiens*).

There are few studies regarding the economic fishing potential of the Purus River. de Almeida et al.[41] characterized the fishing activity in Manoel Urbano and other small villages, unraveling the fishing sector into Manoel Urbano, revealing peculiarities about the fishing activity, such as: the preponderance of lake fishing, the use of motorized canoes rather than boats, gillnetting is the main methods used for fish capture, the absence of a central market for fish commercialization (improving the ratio between fishermen and consumers) and the decreasing of fishing activity during the dry season. This work provided a list of some species that are commercialized in the region, but used the popular their names, thus decreasing our capacity to successfully compare our results. Although, Filhote/Piraíba covers 29% of the tons landed in the main ports of the region; Branquinha (a detritivorous fish also reported in our work) cover 11%.

Most of the species cited in this work migrate (such as *C. macropterus, H. scomberoides, R. vulpinious, S. Lima, P. pirinampu, P. amazonica, P. nigricans, S. fasciatus and M. duriventre*), and some of them (*H. scomberoides, P. Pirinampu* and *P. nigricans*) had being identified into different rivers in Amazonia, such as Solimões and Madeira-Tapajós interfluves[42,43]. *C. macropterus* and *P. pirinampu* had been identified also in Colombia and Venezuela where it has commercial potential[44,45]. Other studies also identified the specie *R. vulpinus* as potential to accumulate Hg into muscle[16,46]. Special emphasis should be attributed to *P. squamosissimus* and *H. edentatus* which are significant for the economy of the fisheries activity in Amazon and presented higher values of Hg into muscle[47].

The socio-economical behavior of the population of Acre (reported by Santos et al.[27] and Martins[28]) put in evidence that the Hg flow dynamic goes beyond the geopolitical barriers, and may be dependent of anthropologic features, such as cattle activities and ancient diet heritage that corroborate with the idea that those populations have alternative origins of protein intake (rather than fish). Thus, the relationship between food, culture and society should be considered in future studies in order to understand the high values of Hg observed on hair of this population.

CONCLUSION

Considering that species with higher Hg content on muscle were the ones that presented higher trophic position, the ingestion of some fish species may be a route of exposure for the population of Manoel Urbano.

Purus is an international river and merit special attention given that the route of Hg exposure may be associated with gold mining activities in other countries, such as Peru.

The population of Manoel Urbano is composed by a miscellaneous of factors, where the triad food, culture and society should be addressed for future studies in order to better design the route of Hg exposure and, consequently, promote health in this population.

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