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

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

Nathália Santos Serrão de Castro¹, Camila Margalho Braga¹, Paulo Arthur de Abreu Trindade², Tommaso Giarrizzo², Marcelo de Oliveira Lima¹

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 sediments are 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), planktovorus (mean 0.566 µg.g⁻¹), omnivorous (mean 0.533 µg.g⁻¹) and detritivorous (mean 0.176 µg/g⁻¹). Forty 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 um 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.

¹Instituto Evandro Chagas, Secretaria de Vigilância em Saúde, Ministério da Saúde - Ananindeua (PA), Brazil.
²Laboratório de Biologia e Manejo dos Recursos Aquáticos, Universidade Federal do Pará (UFPA) - Belém (PA), Brazil.
Study carried out at Instituto Evandro Chagas, Secretaria de Vigilância em Saúde, Ministério da Saúde – Ananindeua (PA), Brazil.
Correspondence: Nathália Santos Serrão de Castro – Instituto Evandro Chagas, Secção de Meio Ambiente – Rodovia BR 316, km 7, s/n – Levilândia – CEP: 67030-000 – Ananindeua (PA), Brazil – Email: n.castro@campus.fct.unl.pt
Financial support: The research reported in this manuscript received funding from the Ministry of Health and from the National Council for Scientific and Technological Development (CNPq), Brazil, which supported the undergraduate scientific fellowship of Camila Margalho.
Conflict of interests: nothing to declare.
INTRODUCTION

Mercury (Hg) is a metal that accumulates along the aquatic food chain, with 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\(^2\).\(^3\).

The Hg is introduced into the environment through different sources, such as atmospheric transport and geochemical pools\(^4\). Its chemical form and physicochemical properties are closed related with its distribution\(^5\). The Hg could be present in the environment as inorganic (\(\text{Hg}^0\), \(\text{Hg}^{1+}\) and \(\text{Hg}^{2+}\)) 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\(^7\). 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\(^8\). 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 (\(\leq 0.50 \mu\text{g} \cdot \text{g}^{-1}\)) preconized by WHO\(^9\)-\(^13\), 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\(^14\)-\(^19\).

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 \(\mu\text{g} \cdot \text{g}^{-1}\) for carnivorous and 0.115 \(\mu\text{g} \cdot \text{g}^{-1}\) 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 (\(n=83/\text{mean} = 7.2 \mu\text{g} \cdot \text{g}^{-1}\) Hg) and from Manoel Urbano (\(n=92/\text{mean} = 14 \mu\text{g} \cdot \text{g}^{-1}\)).

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 \(\text{Ca}^{2+}\) e \(\text{HCO}_3^-\)), 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
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 HNO₃-HClO₄ (1+1), and 5 mL of H₂SO₄. 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 (CV AAS) 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).

### 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 species.

The THg content on muscle ranged from 0.004 to 5.384 µg.g⁻¹. 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).

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

<table>
<thead>
<tr>
<th>Specie</th>
<th>Popular name</th>
<th>Trophic level</th>
<th>Feeding habit</th>
<th>Mean HgT, muscle / ± SD</th>
<th>Range Muscle</th>
<th>Mean HgT, liver / ± SD</th>
<th>Range liver</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolycus scomberoides</td>
<td>Payara</td>
<td>4.5</td>
<td>Piscivorous</td>
<td>1.386 ± 1.089</td>
<td>0.055-2.432</td>
<td>1.044 ± 1.184</td>
<td>0.116-2.781</td>
<td>4</td>
</tr>
<tr>
<td>Raphidiodon vulpinus</td>
<td>Biara</td>
<td>4.5</td>
<td>Carnivorous</td>
<td>1.109 ± 0.626</td>
<td>0.136-2.359</td>
<td>1.755 ± 1.405</td>
<td>0.124-4.562</td>
<td>15</td>
</tr>
<tr>
<td>Cetopsis coecutiens</td>
<td>Candirú-Açu</td>
<td>3.9</td>
<td>Carnivorous</td>
<td>0.900 ± 0.741</td>
<td>0.224-1.853</td>
<td>5.770 ± 4.225</td>
<td>1.323-9.991</td>
<td>4</td>
</tr>
<tr>
<td>Sorubin lima</td>
<td>Duckbill catfish</td>
<td>4.1</td>
<td>Carnivorous</td>
<td>0.772 ± 0.490</td>
<td>0.076-1.287</td>
<td>1.447 ± 1.632</td>
<td>0.163-3.933</td>
<td>5</td>
</tr>
<tr>
<td>Pinirampons pirinampu</td>
<td>Flatwiskered catfish</td>
<td>4.5</td>
<td>Piscivorous</td>
<td>0.617 ± 0.279</td>
<td>0.316-0.868</td>
<td>2.546 ± 2.418</td>
<td>0.195-5.025</td>
<td>3</td>
</tr>
<tr>
<td>Plagioscion squamosissimus</td>
<td>South American silver croaker</td>
<td>4.4</td>
<td>Piscivorous</td>
<td>0.617 ± 0.279</td>
<td>0.316-0.868</td>
<td>2.546 ± 2.418</td>
<td>0.195-5.025</td>
<td>3</td>
</tr>
<tr>
<td>Hypophthalmus edentatus</td>
<td>Highwaterman catfish</td>
<td>2.9</td>
<td>Planktrophagous</td>
<td>0.566 ± 0.136</td>
<td>0.358-0.827</td>
<td>1.725 ± 1.087</td>
<td>0.592-3.560</td>
<td>10</td>
</tr>
<tr>
<td>Anodus elongates</td>
<td>Charuto</td>
<td>3.4</td>
<td>Omnivorous</td>
<td>0.453 ± 0.118</td>
<td>0.169-0.711</td>
<td>0.404 ± 0.215</td>
<td>0.048-0.966</td>
<td>44</td>
</tr>
<tr>
<td>Roeboideos affinis</td>
<td>Cacunda</td>
<td>3.7</td>
<td>Omnivorous</td>
<td>0.273 ± 0.085</td>
<td>0.120-0.349</td>
<td>0.278 ± 0.174</td>
<td>0.098-0.588</td>
<td>6</td>
</tr>
<tr>
<td>Carinata inornata</td>
<td>Branquinha</td>
<td>2.0</td>
<td>Detritivorous</td>
<td>0.239 ± 0.146</td>
<td>0.124-0.440</td>
<td>0.157 ± 0.069</td>
<td>0.086-0.245</td>
<td>4</td>
</tr>
<tr>
<td>Triportheus angulata</td>
<td>Sardinha Papuda</td>
<td>2.7</td>
<td>Omnivorous</td>
<td>0.224 ± 0.097</td>
<td>0.032-0.487</td>
<td>0.140 ± 0.078</td>
<td>0.015-0.347</td>
<td>122</td>
</tr>
<tr>
<td>Psectrogaster amazonica</td>
<td>Branquinha Cascuda</td>
<td>2.0</td>
<td>Detritivorous</td>
<td>0.196 ± 0.071</td>
<td>0.126-0.267</td>
<td>0.121 ± 0.056</td>
<td>0.068-0.180</td>
<td>3</td>
</tr>
<tr>
<td>Pimelodus blochii</td>
<td>Bloch’s catfish</td>
<td>3.1</td>
<td>Omnivorous</td>
<td>0.172 ± 0.052</td>
<td>0.081-0.220</td>
<td>0.727 ± 0.621</td>
<td>0.144-1.945</td>
<td>7</td>
</tr>
<tr>
<td>Potamorhina altamonzica</td>
<td>Mocinha</td>
<td>2.0</td>
<td>Detritivorous</td>
<td>0.141 ± 0.070</td>
<td>0.005-0.280</td>
<td>0.157 ± 0.093</td>
<td>0.035-0.331</td>
<td>14</td>
</tr>
<tr>
<td>Prochilodus nigricans</td>
<td>Black prochilodus</td>
<td>2.4</td>
<td>Detritivorous</td>
<td>0.128 ± 0.057</td>
<td>0.050-0.196</td>
<td>0.232 ± 0.095</td>
<td>0.111-0.345</td>
<td>6</td>
</tr>
<tr>
<td>Schizodon fasciatus</td>
<td>Aracu-Pintado</td>
<td>2.5</td>
<td>Omnivorous</td>
<td>0.068 ± 0.027</td>
<td>0.020-0.097</td>
<td>0.021 ± 0.010</td>
<td>0.010-0.035</td>
<td>6</td>
</tr>
<tr>
<td>Mylosoma duriventre</td>
<td>Silver Dollar fish</td>
<td>2.8</td>
<td>Omnivorous</td>
<td>0.065 ± 0.036</td>
<td>0.004-0.094</td>
<td>0.169 ± 0.230</td>
<td>0.020-0.577</td>
<td>5</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>264</td>
</tr>
</tbody>
</table>

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.\(^{48}\) who reported a mean Hg content of 0.054 µg.g\(^{-1}\) for the bottom sediment of Iaco 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)

<table>
<thead>
<tr>
<th>Collection point</th>
<th>N</th>
<th>HgT</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>1</td>
<td>0.056</td>
</tr>
<tr>
<td>02</td>
<td>1</td>
<td>0.038</td>
</tr>
<tr>
<td>03</td>
<td>1</td>
<td>0.039</td>
</tr>
<tr>
<td>04</td>
<td>1</td>
<td>0.042</td>
</tr>
<tr>
<td>05</td>
<td>1</td>
<td>0.065</td>
</tr>
<tr>
<td>06</td>
<td>1</td>
<td>0062</td>
</tr>
<tr>
<td>Mean</td>
<td>-</td>
<td>0.050</td>
</tr>
<tr>
<td>Total</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

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 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 represent 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. 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 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.

REFERENCES


Accepted on: Aug. 29, 2016