MERCURY IN THE SEDIMENT OF THE UPPER PARNAÍBA RIVER

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ABSTRACT

The contamination of aquatic environments with chemical trace elements can be evaluated by their accumulation in sediments of the water body. Studies on mercury require the use of exclusive extraction techniques that have relatively high costs when compared to the analysis of other trace elements. This study was conducted aiming at determining the mercury concentration in sediments of the Upper Parnaíba River basin, located in a region of agricultural expansion between the states of Piauí and Maranhão. The sediment was collected at 12 sites in the basin. After drying, the quantification of total mercury was performed by the Zeeman atomic absorption spectrometry coupled to a pyrolysis reactor. Mercury concentrations in sediments of the Parnaíba River ranged from 4.2 to 58.5 ng g⁻¹ and presented a low probability of adverse effects on biota. Mercury had no correlation with the variables clay, silt, sand, total organic carbon, iron, and aluminum, demonstrating its possible anthropogenic origin. Although mercury concentrations have a low probability to disturb the balance of the local ecosystem, there is a need for monitoring the region in order to quantify the risks to biota and human health.

INTRODUCTION

The Parnaíba River basin is the second most important in the Northeast of Brazil, located in a region of expansion of the agricultural frontier in the Central-Northeastern direction called Matopiba, which covers the states of Maranhão, Tocantins, Piauí, and Bahia (Freitas & Mendonça, 2016; Santos, 2015, Garcia & Buainain, 2016). However, in spite of providing regional economic development, agricultural activities practiced in an intense and disorderly manner can cause problems of contamination of the soil and water resources by surf

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sediiments in Brazil and in the World, such as Andrade et al. (2017), Bai et al. (2016), Begy et al. (2016), Franz et al. (2013), Franz et al. (2014), Poitrasson et al. (2014), Resongles et al. (2014), Silva et al. (2013), and Voigt et al. (2016). However, due to the need for unique extraction techniques and the cost of analyses, studies involving mercury are in less number (Franklin et al., 2012). In this sense, the studies of Araujo et al. (2015), Cabral et al. (2016), Hu et al. (2015), Remor et al. (2015), Sahoo et al. (2015), and Remor et al. (2018) stand out. Thus, the aim of this study was to determine the total mercury concentrations in sediments of the Upper Parnaíba River basin because it is a new Brazilian agricultural frontier and does not yet have records related to mercury concentration in sediments in rivers of the region.

MATERIAL AND METHODS

Study area

The Parnaíba River basin is located on the border of the states of Piauí, Maranhão, and Ceará, (Figure 1). The Parnaíba River is approximately 1,400 km long. Its main tributaries are the rivers Balsas, Gurguéia, Piauí, Canindé, Poti, and Longá, being considered as the largest river genuinely from northeastern Brazil. It has a drainage area of 331,441.5 km² divided into three large sub-basins, the Low, Medium, and High Parnaíba River, as shown in Figure 1. The Parnaíba River presents a high hydroelectric potential, besides being widely used for urban supply and irrigation.

FIGURE 1. Geographical location of the study area.

The Upper Parnaíba River sub-basin (Figure 1) has a drainage area of 151,630.3 km². Its main tributaries are the rivers Balsas, Uruçuí Preto River, Uruçuí Vermelho, Gurguéia, and Itaueiras. It presents an average annual precipitation of 4,373.6 mm. The Upper Parnaíba River sub-basin is located in the Cerrado macro-region and has a predominantly savanna vegetation. The soils are classified as Oxisols (Latossolo Amarelo, Brazilian Soil Classification System) with a clayey texture, deep profile, good to moderate drainage, and usually considered from acid to very acid (Motta & Gonçalves, 2016). This sub-basin is weakened by activities carried out in the drainage area, such as livestock, mining, generalized deforestation, and inadequate agriculture. In fact, deforested soils become susceptible to erosion, increasing the risk of contamination and decreasing water storage capacity in lakes and reservoirs.

Collection and preparation of samples

Sediment samples were collected using a Petersen sampler at 12 sites (S1, S2, S3, S4, S5, S6, S7, S8, S9, S10, S11, and S12) distributed over a stretch of approximately 90 km on the Parnaíba River (Figure 1). The selection of collection sites aimed at covering urban and agricultural areas and a high degree of preservation area, in addition to the ease of access since the collection process was carried out on a vessel. At each sampling site, five simple samples were collected, constituting a composite sample according to the standards described by ANA (2011). The collection occurred in November 2013, during the dry season. In rivers, the deposition of fine sediments occurs during the period of less precipitation and the washing of this material occurs during the season of more intense rains. In this sense, a single annual collection during the dry season can be satisfactory (ANA, 2011). After collecting, the samples were packed in
polypropylene containers and stored in a refrigerated environment (4 °C). Subsequently, they were dried indoors, avoiding the sunlight, at ambient temperature (20–33 °C).

**Physicochemical analyses**

The particle size analysis was performed with the combination of sedimentation and sieving tests, according to NBR 7181/1984 of ABNT (Brazilian National Standards Organization). The total organic carbon (TOC) was determined by weighing 0.5 g of the sediment sample in a porcelain capsule oxidized at 900 °C by means of a total organic carbon analyzer coupled to a combustion unit for solid samples. A calibration curve obtained with a standard of potassium biphthalate was used for the calculations (Segnini et al., 2008).

Metal quantification was performed in the silt/clay fraction (< 63 μm), as recommended by the World Health Organization (WHO, 1982). For this, the sediment samples were sieved in PVC and nylon sieve with a 63-μm mesh. The extraction of metals aluminum (Al), iron (Fe), and manganese (Mn) was performed by the wet method, following the method 3050B proposed by USEPA (1996). After extraction, the quantification was carried out by means of the flame atomic absorption spectrometry. The accuracy of the data was evaluated using IAEA 356 and IAEA 433 (marine sediment) certified reference materials, with a minimum confidence level of 95%.

Mercury (Hg) quantification was performed by the Zeeman atomic absorption spectrometry coupled to a pyrolysis reactor. The principle of this analysis is based on the thermal destruction of the sample, followed by the measurement of Hg vapor (Castilhos et al., 2006). The accuracy of the data was evaluated using a Mess 3 certified reference material (marine sediment), with a minimum confidence level of 95%.

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**Data analysis**

The data of sediment particle size were analyzed using the Shepard and Pejrup diagrams using the rysgran package (Gilbert et al., 2012) of the statistical software R. The set of physicochemical variables of sediments (sand, silt, clay, TOC, Al, Fe, Mn, and Hg) of the 12 sites was first submitted to the Shapiro-Wilk normality test with a 5% significance. Subsequently, all the variables were auto-scaled following the guidelines described by Moita Neto & Moita (1998). Finally, the auto-scaled dataset was simultaneously summarized in a single principal component analysis (PCA). PCA was performed on the correlation matrix (Pearson) of the variables and the criterion of PC (principal components) retention adopted was the broken-stick, i.e. with eigenvalues higher than that expected at random (Jackson, 1993). In order to interpret the meaning of the retained PCs of the original variables, only the Pearson correlation coefficients higher than 65% were considered.

**RESULTS AND DISCUSSION**

The results of the particle size analysis were used to classify the sediment samples regarding texture and hydrodynamics (Figure 2). The Shepard diagram (Figure 2A) showed that all sampled sites presented a sandy texture, except for S1 and S12, which presented a silty sand texture. The hydrodynamics of all sampled sites is high according to the Pejrup diagram (Figure 2B). The results of texture and hydrodynamics are coherent with each other because in environments with a high hydrodynamic energy, fine particles remain suspended and are transported to lower-energy environments, where they are sedimented (Noronha-D’Mello & Nayak, 2015).

![FIGURE 2. Textural composition and hydrodynamic conditions of the bottom sediment in the Parnaíba River. A: Shepard diagram; B: Pejrup diagram.](image)

PCA is shown in Figure 3. Two PCs were considered apt to be evaluated according to the broken-stick criterion, totaling 87.24% of explanation of the data set variability (Figure 3). PC1 is composed of the variables silt, clay, TOC, Al, and Fe in the positive quadrant and sand in the negative quadrant. PC1 separated the sampled sites into three groups: the first group was composed of S1 and S12 and presented the highest values of silt, clay, TOC, Al, and Fe; the second group was composed of S3, S5, S6, S7, S8, and S10 and presented the highest values of sand; and the third group was composed of S2, S4, S9, and S11 and presented intermediate values for the variables that compose PC1 (Figure 3). PC2 was composed of the variable Hg in the negative quadrant and Mn in the positive quadrant. PC2 separated the sampled sites into three groups: the first group was composed of S1 and S2 and presented the highest values of Hg; the second group was composed of S10 and S12 and presented the lowest values; and the third group was composed of S3, S4, S5, S6, S7, S8, S9, and S11 and presented intermediate concentrations of Hg (Figure 3).
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According to the PCA (Figure 3), Hg presented a negative correlation with Mn and is not correlated with the natural variables clay, silt, sand, TOC, Al, and Fe. When the concentration of a metal in the sediment is positively correlated with the variables clay, silt, TOC, Al, and Fe indicates that the concentration is of geogenic origin (Davuthuouglu et al., 2010; Remor et al., 2018). In this fraction, the elements are bound to silicates (Favas et al., 2015) or complexed with organic matter (Strom et al., 2011) and hence unavailable for biota. Elements of anthropogenic origin are found predominantly in the most unstable sediment fractions, which are vulnerable to small changes in environmental conditions (Bartoli et al., 2012). Thus, it is possible that Hg concentrations in some collection sites are derived from anthropic activities, especially at S1, S2, and S3 (Figure 4), located near the more urbanized area of the Upper Parnaíba River basin. Other studies have reported an increase of Hg concentration in sediments due to urbanization (Andrade et al., 2017; Cabral et al., 2016; Cavoura et al., 2017; Hu et al., 2015). Therefore, anthropic activities have been increasing Hg concentration in sediments of sites near the urban areas due to the inadequate disposal of residues containing this element, such as batteries, fluorescent lamps, thermometers, electronic components, among others (Micaroni et al., 2000).

FIGURE 3. Principal component analysis of physicochemical variables of the sediment of the Parnaíba River.

FIGURE 4. Mercury concentration in the bottom sediment of the Parnaíba River.
The sites S4, S5, S6, S7, S8, S9, S10, S11, and S12, which are more distant from the urban area, presented lower concentrations of Hg in the sediment (Figure 4). In the influence area of these sites, the most relevant anthropic activities are the agriculture and livestock. Therefore, these activities are not contributing to increasing Hg in sediments of the Parnaíba River.

The total concentrations of Hg found in sediments of the Upper Parnaíba River ranged from 4.2 to 58.5 ng g⁻¹ (Figure 4; Table 1). These concentrations do not present risks to biota when taking into account the limits proposed by CONAMA Resolution No. 454/2012 for sediments, in which Hg values below 170 ng g⁻¹ present a low probability of adverse effects on biota and Hg concentrations above 486 ng g⁻¹ would cause effects on organisms exposed to Hg. However, Castro et al. (2016) found low concentrations of Hg in sediments but detected higher concentrations in the muscles of carnivorous fish.

TABLE 1. Total mercury concentration (ng g⁻¹) in sediments of fluvial environments in Brazil.

<table>
<thead>
<tr>
<th>Site</th>
<th>State</th>
<th>Minimum</th>
<th>Mean</th>
<th>Maximum</th>
<th>Impact</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parnaíba River</td>
<td>PI/MA</td>
<td>4.2</td>
<td>13.4</td>
<td>58.5</td>
<td>M; A; U</td>
<td>This study</td>
</tr>
<tr>
<td>Lake Violão</td>
<td>PA</td>
<td>130.0</td>
<td>240.0</td>
<td>590.0</td>
<td>NR</td>
<td>Sahoo et al., 2015</td>
</tr>
<tr>
<td>Paraíba do Sul River</td>
<td>RJ/MG</td>
<td>22.2</td>
<td>56.1</td>
<td>158.3</td>
<td>M; OF</td>
<td>Araujo et al., 2015</td>
</tr>
<tr>
<td>Ivinhema River</td>
<td>MS</td>
<td>25.0</td>
<td>78.0</td>
<td>125.0</td>
<td>M; A</td>
<td>Remor et al., 2015</td>
</tr>
<tr>
<td>Purus River</td>
<td>AC</td>
<td>38.0</td>
<td>50.0</td>
<td>65.0</td>
<td>NR</td>
<td>Castro et al., 2016</td>
</tr>
<tr>
<td>Grama River</td>
<td>MG</td>
<td>45.0</td>
<td>56.3</td>
<td>76.0</td>
<td>M</td>
<td>Mendes et al., 2016</td>
</tr>
<tr>
<td>Rio River</td>
<td>MG</td>
<td>7.0</td>
<td>94.5</td>
<td>268.0</td>
<td>M</td>
<td>Mendes et al., 2016</td>
</tr>
<tr>
<td>Pardo River</td>
<td>SP</td>
<td>10.0</td>
<td>20.0</td>
<td>90.0</td>
<td>M; U</td>
<td>Machado et al., 2016</td>
</tr>
<tr>
<td>Pelotas River</td>
<td>SC/RS</td>
<td>40.5</td>
<td>48.7</td>
<td>62.0</td>
<td>NR</td>
<td>Remor et al., 2018</td>
</tr>
</tbody>
</table>

Impact: anthropic activities developed in the drainage basins correlated with the increase in Hg concentrations in sediments of the respective rivers cited by the authors, where: M – mining, OF – organomercurial fungicides, A – agriculture/livestock, U – urbanization, and NR – not reported.

Regardless of the Hg concentrations in sediments of the Upper Parnaíba River be lower than those found in other studies shown in Table 1, monitoring the sediment is essential in the region since the local population develops activities and uses this natural resource for activities of production, consumption, and recreation. In addition, the bioaccumulation characteristics, degree of toxicity, and biomagnification of Hg have the need to be monitored in the environment and at all trophic levels.

CONCLUSIONS

The concentrations of Hg found in sediments of the Upper Parnaíba River indicated a low probability of adverse effects on biota. However, Hg concentration at sites near the urban area is higher than in other sampled sites. In this sense, it is necessary to monitor a possible increase in the Hg concentration in the sediment caused by urbanization and verify whether the current levels can cause damage to biota and human health due to its high toxicity, persistence, and bioaccumulation in the environment.

The study of Ferreira et al. (2017) in the Upper Paraguay River plateau demonstrates the bioaccumulation potential of Hg. These researchers found Hg concentrations in the sediment of 100 ng g⁻¹, while in the muscle of carnivorous fish of the region, it exceeded 600 ng g⁻¹, evidencing their persistence and bioaccumulation. In addition, the highest concentration found in the basin (S1) is approximately 14 times higher when compared to the lowest concentration (S5) (Figure 4). In this context, detailed studies are essential in the region aiming at proving the bioaccumulative capacity and degree of Hg toxicity in order to quantify the risks to aquatic biota and human health (Remor et al., 2018).

The results found in our study were compared with other studies carried out in Brazilian fluvial environments, as shown in Table 1. In this sense, the values of the total Hg concentration found were, on average, lower when compared to those observed in other regions.

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