MERCURY IN THE SEDIMENT OF PELOTAS RIVER BASIN, BRAZIL

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ABSTRACT
Many studies have determined the concentration of trace elements in river sediments in Brazil. Notwithstanding, mercury assessments are scarce, especially because of exclusive extraction techniques and expensive analysis techniques. Still, this element is known for its toxicity, persistence, and bioaccumulation, making its presence in the environment an important factor for biota and human health. For this reason, the objective of this study was to determine the mercury concentration in the sediment of the Pelotas River basin, located on the border of the states of Santa Catarina and Rio Grande do Sul. The sediment was collected at eight locations of the Pelotas basin and, after drying, the mercury was quantified by atomic absorption spectrometry based on the Zeeman-background correction, coupled to a pyrolysis reactor. The mercury concentrations in the sediments of the Pelotas River varied from 40.5 ng g⁻¹ to 62.0 ng g⁻¹ and presented a positive correlation with the fraction of silt and clay. The concentrations of mercury found in sediments of the Pelotas River basin have a low probability of negatively affecting the biota. Nonetheless, given the persistence and bioaccumulation potential of this element, the aforementioned region needs further studies to quantify the risks it may cause on the local biota and human health.

INTRODUCTION
During the last few years, research in the field of sedimentology has been focused on sediment production, quantification, and transportation (Sousa et al., 2012; Vanzela et al., 2014; Cerquetani & Martins Filho, 2006). Additionally, studies have concentrated on the impacts of contaminated sediments on the environment, especially because sediment is considered the main fixator and carrier element in aquatic environments (Pejman et al., 2015; Cembranel et al., 2017a). Among the main contaminants, mercury (Hg) has received special attention because of its high toxicity, environmental persistence, and bioaccumulation potential, which negatively affects humans and environments worldwide (Kim et al., 2016).

Countless human activities contribute to increase Hg concentrations in the environment, including coal-based thermoelectric plants, incineration of organic products, gold mining, industrial manufacturing processes of organochlorine products, caustic soda, batteries, thermometers, fluorescent light bulbs, and their disposal, along with the production of drugs and fungicides (Kim et al., 2016). As an illustration, when Hg based pesticides are applied to crops, these areas are considered major sources of Hg to watercourses and groundwater.

In aquatic environments, microorganisms can transform Hg into methylmercury (CH₃Hg), considered even more toxic than the original element. Consequently, this substance accumulates in the tissue of aquatic animals in higher quantities than those found in the environment. The toxic effect of Hg on humans and other living organisms depend on factors such as chemical form, environmental concentration, exposure routes, and vulnerability of the exposed organisms (Kim et al., 2016). In humans, elevated concentrations of Hg can cause neurological, nephrological, immunologic, cardiac, and reproductive disturbances, along with genetic problems and reduction of cognitive functions (Oliveira et al., 2013; Gibb & O’Leary, 2014).

Several studies have already determined the concentrations of trace elements in river sediments in Brazil, notably Melo et al. (2012), Santos et al. (2013), Botero et al. (2014), and Voigt et al. (2016). Nevertheless,
studies involving Hg are scarce, especially because of the complex technical requirements of exclusive extraction and the high costs of analyses (Franklin et al., 2012). Some of the noteworthy studies are: Siqueira & Aprile (2012); Hortellani et al., (2013); Almeida et al., (2014); Araujo et al. (2015); Remor et al. (2015); Rocha et al., (2015); and Sahoo et al. (2015).

The Pelotas River basin is a very fragile area, known for its high hydroelectric and industrial potential and intense agricultural activities. Looking to improve the quality of this environment and to prevent its exposure to highly dangerous chemical agents, environmental diagnoses are performed in order to propose management measures and to remediate areas already contaminated or with high contamination risks. Overall, this study aimed to determine the concentrations of Hg in the sediment of the Pelotas River basin.

MATERIAL AND METHODS

Study area

The Pelotas River basin is located on the border of the Brazilian states of Santa Catarina and Rio Grande do Sul (Figure 1). The Pelotas River is the main affluent of the Uruguay River, composing one of the largest basins of Southern Brazil. It possesses a 13,227 km² drainage area, 62% in the state of Santa Catarina, and 38% in the state of Rio Grande do Sul. The climate of the region is considered temperate, with average yearly rainfall of 1623 mm, distributed throughout the year, but having higher concentrations from May to September.
The soil was classified using the Spatial Analysis Tools from the ArcGIS 10 software. Images were used from the Digital Elevation Models, belonging to the TOPODATA project of the Brazilian National Institute for Spatial Research (INEP). The use of soil used in areas of influence was classified by using images from an orbital sensor taken on January 30, 2014, by the Landsat 8 satellite. The classification was done in a supervised manner, using the Maximum Likelihood algorithm from the SCP (Semi-Automatic Classification Plugin) plugin of the open source QGIS software, version 2.14.5. Figure 1 illustrates the soil use classes, wherein pastures occupy 52.79% of the total area of influence, followed by vegetation (45.16%), agriculture (0.92%), and urban area (0.46%). Furthermore, the basin houses industrial activities such as timber, pulp & paper, construction, and agriculture. The hydroelectric potential becomes apparent due to the extremely wavy relief and the presence of the Machadinho and Barra Grande hydroelectric power plants (HPP), as well as the possibility of installing the Pai Querê and three other HPPs, which are under licensing process now.

Sample collection and preparation

Sediment samples were collected from eight sites within the Pelotas River basin, using a Petersen sampler. Six locations in the Pelotas River (PEL 00, PEL 01, PEL 02, PEL 03, PEL 04, PEL 05) and two in its tributaries (TRI 01 – Contas River and TRI 02 –São Sebastião do Arvoredo Stream) (Figure 1). Five samples were collected from each location, constituting a composite sample by the norms of ANA (National Water Agency). Sampling was carried out in February 2014, a period with the lowest annual rainfall average. This is important because the fine river sediments are deposited during the dry season, and are washed away during the rainy season. Thus, only one yearly sampling during the dry season is sufficient for analysis (ANA, 2011). After collecting the samples, they were transported in a refrigerated vehicle (4 ºC) and later dried out in an enclosed area, away from the sun and at room temperature.

Physicochemical analyses

Particle size analyses were conducted with a combination of sedimentation and sieving procedures, according to the NBR 7181/1984 standard of the Brazilian Association of Technical Norms (ABNT). The total organic carbon (TOC) was determined by the modified Walkley-Black method (Coser et al., 2012). The chemical elements were only quantified in the silt + clay fraction (<63 μm), as recommended by the World Health Organization (WHO, 1982). In order to do so, after drying, the sediment samples were sieved through a PVC and nylon sieve with a 63 μm mesh net.

The elements aluminum (Al), iron (Fe), and manganese (Mn) were extracted on a wet basis, using the 3050B method of USEPA (UNITED STATES ENVIRONMENTAL PROTECTION AGENCY). This extraction method was developed to quantify the fractions of metals that could become environmentally available.

After extraction, these elements were quantified by flame atomic absorption spectrometry (FAAS). Data accuracy was evaluated by the analytical methods for IAEA 356 and IAEA 433 certifications as reference materials (marine sediment), which were in line with the results at the 95% confidence level.

Total mercury (Hg) was quantified by atomic absorption spectrometry based on Zeeman-background correction, with a pyrolysis reactor. First, the solid sample (sediment) is thermally disrupted, and then the Hg vapor is measured (Castilhos et al., 2006; Fiori et al., 2013). The accuracy of these data was evaluated by comparing it to Mess-3 sample (marine sediment), i.e. certified reference material, checking the consistency of at least 95%.

Data analysis

Sediment particle-size analyses were interpreted through the ternary diagrams of Shepard (1954) and Pejrup (1988) to determine texture and hydrodynamics, respectively. These interpretations were performed in the R environment using the RYSGRAN package (Gilbert et al., 2012).

The set of sediment physicochemical variables was summarized in a Principal Component Analysis (PCA) by the PCORD 5.0 software. This assessment reduces the set of original variables into a set of Principal Components (PC), looking to maintain the maximum variability of the original set. PCA was performed on the Pearson correlation matrix of variables, adopting the broken-stick retention criterion, i.e. with eigenvalues higher than those randomly expected (Jackson, 1993). To interpret the meaning of retained PCs of original variables, only Pearson correlation coefficients higher than 70% were considered (Jolliffe, 1986).

RESULTS AND DISCUSSION

Particle size analysis was used to classify the sediment samples by texture and hydrodynamics (Figure 2). The Shepard Diagram (Figure 2A), on the other hand, displays the texture variability among locations. The PEL 02 site showed a silty clay texture, while PEL 01 and PEL 04 had sandy silty clay textures and PEL 00 a silty clayey sand texture. Both TRI 01 and PEL 03 sites had a clayey sandy textures while TRI 02 revealed a sandy clayey silt texture and PEL 05 a silty sand texture.

The hydrodynamics in PEL 00, PEL 03, PEL 05, and TRI 02 was high according to the Pejrup diagram (Figure 2B). On the other hand, PEL 01, PEL 02, PEL 04, and TRI 01 presented moderate hydrodynamics. The sites with elevated hydrodynamics had higher proportions of sand, from about 52% to 72%. In high hydrodynamic-energy environments, fine particles remain suspended and then transported to environments with lower energy levels, where they are sedimented (Noronha-D'mello & Nayak, 2015).
Figure 3 exhibits the PCA for the set of physicochemical variables of sediments. According to the broken-stick criterion, two PCs were considered for the analysis; they comprised 69.22% of the total variability. In the positive quadrant, the PC 1 is composed of the variables sand, Al, and gravel; yet, in the negative one, it is composed of the variables clay, silt, and Hg (Figure 3). The PC 2 in the negative quadrant is composed of the variables Mn and Fe. Conversely, TOC was taken as uninterpretable by the broken-stick criterion, thus presenting lower variability among the locations than the random variability (Jackson, 1993). Therefore, no significant statistical difference among the sampled locations was registered. The PC 1 separated the sites into three groups: the first, formed by PEL 03 and PEL 05, which had the highest results for sand, Al, and gravel; the second, by PEL 02, TRI 02, and PEL 01, where the highest levels of clay, silt, and Hg were found; and the third, by PEL 00, TRI 01, and PEL 04, with intermediate values for the variables included in PC 1 (Figure 3). PC 02 separated PEL 02 from the rest of sites since it had the highest levels of Mn and Fe, and the lowest concentrations of the variables forming PC 02 (Figure 3).
The positive correlation between the finer portion of sediments (silt and clay) and Hg contents (Figure 3) is due to the larger surface area of fine particles, increasing their adsorption capacity (Oliveira et al., 2011; Cembranel et al., 2017b). Thus, clay is considered an important factor for Hg adsorption in soils and sediments (Araújo et al., 2015). The PCA shows the lack of correlation between Hg and the contents of TOC, Al, Fe, and Mn. In this experiment, only the fractions of elements environmentally available were quantified, confirming the association between most of the Hg found and the fine portion of sediments (silt and clay). This result points out the complexing minerals as absorbent agents for Hg, albeit they are commonly unavailable for reactions with the aquatic environment, i.e. there is a low probability of it being incorporated by the aquatic biota (Araújo et al., 2015).

By observing the PCA results, it seems that the largest fraction of Hg found in sediments is in its least reactive form (adsorbed to complexing minerals), which is hardly available to the ecosystem. Elements of anthropogenic origins are predominantly found in sediment parts that are more unstable, which are vulnerable to small environmental changes (Bartoli et al., 2012). Hence, we believe the largest fraction of Hg in sediments from the Pelotas River is most likely of geogenic origin. However, thorough studies in this region are still necessary to confirm these results.

Figure 4 shows the Hg concentrations in the sediment of the Pelotas River. The locations presenting higher concentrations (PEL 01, PEL 02, PEL 04, and TRI 02) were the same that had higher quantities of fine sediments (silt and clay) and moderate hydrodynamics (Figure 2). This supports the results obtained in the PCA (Figure 3), which showed a correlation of Hg concentrations with silt and clay fractions.

![Graph](image_url)

**FIGURE 4.** Mercury concentrations in the bottom sediments of the Pelotas River.

The Hg concentrations in the bottom sediments of the Pelotas River varied from 40.5 ng g\(^{-1}\) to 62.0 ng g\(^{-1}\) (Figure 4; Table 1). Our findings were compared to those of other studies in Brazilian river environments, as shown Table 1. In general, the highest levels of Hg found in this research were lower than those reported by other authors. Furthermore, according to the CONAMA resolution nº 454/2012 (Brazilian National Environmental Committee), Hg concentrations lower than 170 ng g\(^{-1}\) (level 1) have smaller probabilities of adversely affecting the biota, and only those above 486 ng g\(^{-1}\) (level 2) could. Therefore, the concentrations found in the Pelotas River show a low probability of risk to the biota. Nevertheless, Castro et al., (2016) demonstrated the bioaccumulation potential of Hg when studying the Purus River. These researchers found Hg concentrations between 38 and 65 ng g\(^{-1}\) in the sediment of the Purus River, while in carnivorous fish muscle, it reached up to 5384 ng g\(^{-1}\), with an average of 927 ng g\(^{-1}\). This outcome demonstrates the high toxicity, persistence, and bioaccumulation potential of this element. In this context, it is important to emphasize the need for further studies to quantify the risks to aquatic biota and human health in the Pelotas River basin.
TABLE 1. Mercury concentration in sediments of river environments in Brazil.

<table>
<thead>
<tr>
<th>Location</th>
<th>Coordinates</th>
<th>Hg (ng g⁻¹)</th>
<th>Impact</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Latitude Longitude</td>
<td>Min Aver Max</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pelotas River *</td>
<td>29°29'36&quot;S 50°07'38&quot;W</td>
<td>40.5 48.7 62.0</td>
<td>This study</td>
<td></td>
</tr>
<tr>
<td>Teles Pires River</td>
<td>09°25'19&quot;S 56°32'20&quot;W</td>
<td>90.0 148.0 250.0</td>
<td>M; A</td>
<td>Wasserman et al., 2007</td>
</tr>
<tr>
<td>Paranaíta River</td>
<td>09°28'09&quot;S 56°41'45&quot;W</td>
<td>50.0 83.6 140.0</td>
<td>M; A</td>
<td>Wasserman et al., 2007</td>
</tr>
<tr>
<td>Botafogo River</td>
<td>07°42'51&quot;S 34°52'53&quot;W</td>
<td>1.0 138.7 250.0</td>
<td>I</td>
<td>Lima et al., 2009</td>
</tr>
<tr>
<td>Paraíba do Sul River</td>
<td>21°40'00&quot;S 41°10'00&quot;W</td>
<td>22.2 56.1 158.3</td>
<td>M; FO</td>
<td>Araujo et al., 2015</td>
</tr>
<tr>
<td>Ivinhema River</td>
<td>22°49'31&quot;S 53°33'12&quot;W</td>
<td>25.0 78.0 125.0</td>
<td>M; A</td>
<td>Remor et al., 2015</td>
</tr>
<tr>
<td>Paraná River</td>
<td>22°43'31&quot;S 53°18'15&quot;W</td>
<td>36.0 55.0 67.0</td>
<td>NR</td>
<td>Remor et al., 2015</td>
</tr>
<tr>
<td>Violão Lake</td>
<td>06°24'00&quot;S 50°21'10&quot;W</td>
<td>130.0 240.0 590.0</td>
<td>NR</td>
<td>Sahoo et al., 2015</td>
</tr>
<tr>
<td>Purus River</td>
<td>08°52'50&quot;S 69°13'10&quot;W</td>
<td>38.0 50.0 65.0</td>
<td>NR</td>
<td>Castro et al., 2016</td>
</tr>
</tbody>
</table>

*This study: Impact: human activities conducted in the drainage basins correlated to the increase of Hg concentration in the sediments of their respective rivers, as cited by the authors. M: gold mining; GO: organomercurial fungicides; A: Agriculture; I: Industrial production of chloride and soda; NR: non-reported group.

CONCLUSIONS

This study found no correlation between human activities and mercury concentrations in the sediment of the Pelotas River basin and its tributaries. The mercury concentrations found in the sediment have little chance of causing adverse effects on local biota. Yet, the high toxicity, persistence, and bioaccumulation potential of mercury emphasizes the need for further investigations in this region with the purpose of quantifying risks it may cause to aquatic biota and human health.

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