A PRELIMINARY STUDY OF THE DISTRIBUTION AND MOBILITY OF MERCURY IN WATER AND SEDIMENTS FROM THE SAN JUAN RIVER WATERSHED, NUEVO LEON MEXICO

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ABSTRACT

Monitoring of distribution and fractionation of mercury (Hg) from within the San Juan River Basin that provides water for the Metropolitan Area of Monterrey, Mexico (MAM), was performed. The purpose of this work was to characterize the risk of Hg exposure to human populations that reside in communities nearby the area. Total Hg was quantified from water and surface sediments (0-10 cm) collected from 11 locations during the summer season of 2006. The analysis of Hg was carried out by Cold Vapor Atomic Absorption Spectroscopy (CVAAS). Simultaneously, some relevant physical and chemical parameters were analyzed in water samples and correlated to Hg concentrations to trace the fate of Hg in the watershed. In the river water samples, Hg levels were in the range from 0.17 to 1.14 μg/L. The mean concentration level of Hg in sediment samples was 0.405±0.074 mg/Kg and showed a uniform Hg distribution along the San Juan River Basin, conversely, the fractionation studies showed that chemical speciation plays an important role in stability and low mobility.

Keywords: mercury; fractionation; sediments; waterbodies; San Juan River watershed; Monterrey, Mexico.

INTRODUCTION

According to the United States Environmental Protection Agency (US EPA), mercury (Hg) is a priority contaminant of continuous concern on the global scale [1]. Numerous national and international agencies and organizations have targeted Hg for emission control due to its persistence, bioaccumulation and toxicity in the environment [2]. Although aquatic Hg contamination is a result of atmospheric deposition and terrestrial sources from natural and anthropogenic origin [3], regional emission sources could significantly contribute to Hg loadings through discharges from industrial processes, mining activities, and watershed runoff [4,5]. In the environment, elemental and inorganic Hg is deposited on aquatic sediments where a fraction reacts with sulfate to form mercury sulfide, which is not soluble, and therefore, its bioavailability becomes significantly reduced, whereas a small percentage is converted to methylmercury (MeHg) by bacteria. MeHg is an environmental neurotoxicant which is bioaccumulated and biomagnified in the food web [2]. Therefore, information regarding concentrations and transport of Hg in aquatic ecosystems is needed to predict potential impact on both human and aquatic life.

Worldwide contamination of Hg has been reported in aquatic systems [6-11], including contamination in Mexico [12-14]. However, no data has been published concerning the distribution of Hg contamination in the San Juan River watershed ecosystem. The San Juan River watershed is located in northeastern Mexico and belongs to the Bravo-Conchos River basin. The San Juan River basin has a total surface area of approximately 33 000 Km² comprising the states of Coahuila (40 %), Nuevo Leon (57 %), and Tamaulipas (3 %). The watershed includes a number of smaller tributary basins such as the Cuchillo reservoir in the municipality of China, Nuevo Leon, located at 102 Km eastern Monterrey. The San Juan River supplies the Cuchillo reservoir, which provides water for the Metropolitan Area of Monterrey (MAM) [15-17]. The MAM is the third largest metropolitan area in Mexico and holds a population of approximately four million inhabitants [18]. Although a number of water quality studies have been conducted within the San Juan River watershed, serious problems associated to the persistence of heavy metal pollution have been reported [19,20]. A study conducted in the Santo Catarina River tributary of the San Juan River reported contamination by Fe, Cu, Zn, Cd, and Sr in sediments [17]. Subsequently, Flores-Laureano and Navar [20] assessed the pollution of the San Juan River and its tributary Santo Catarina River during the period 1995-1996. Metals including Al, As, Ba, Cd, Cu, Cr, Fe, Mn, Pb and Fe, exceeded the drinking water quality standards set by the Mexican environmental regulations. Furthermore, this study reported bacteriological and physical parameters that exceeded the drinking water quality standards. Thus, the need for monitoring other relevant priority pollutants such as Hg is mandatory for improving our understanding and assessment of this complex water ecosystem.

The aim of this work was to investigate Hg concentrations in surface water and sediments in the San Juan River watershed and evaluate changes in Hg distribution along different sampling sites followed by an assessment of the degree of environmental impact and human exposure to Hg. In addition, a three-step sequential extraction procedure (SEP) described in the United States Environmental Protection Agency (US EPA) method 3020 [21] was applied to evaluate Hg fractionation and mobility in the sediment samples.

EXPERIMENTAL

2.1 Study area and sampling

Water and sediment samples were collected in 11 locations from the San Juan River watershed situated in the state of Nuevo Leon in August 2006 (Fig. 1). Shallow water samples were taken nearby the river bank. Surface sediment samples in the depth range 0-10 cm were collected. Six sites were selected along the Santa Catarina River from the eastern suburbs of the city of Monterrey to its junction with the River San Juan; one sample was collected from the La Silla River, at the intersection of this river course and Santa Catarina tributary; three additional sites were located along the San Juan River, between the Boca and the Cuchillo reservoirs; and one sample was collected from the Cuchillo reservoir in the municipality of China, Nuevo Leon, located at 102 Km eastern Monterrey.

Fig. 1. The San Juan watershed and sampling point locations.
Fifty seven percent of the San Juan River watershed has a tropical weather, whereas thirty four percent ranges from semiarid to arid. Monthly rainfall has a bimodal type of distribution, with the first peak occurring in May-June and the second peak, the most important in terms of total depth, occurring during September-October. The annual average rainfall varies from 200 mm to 1500 mm [15]. Metropolitan Area of Monterrey soils are characterized by Feozem, a bimodal type of distribution, with the first peak occurring in May-June and the second peak, the most important in terms of total depth, occurring during

### Table 1. Localization and characteristics of observed water ecosystems.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Site</th>
<th>Latitude (N)</th>
<th>Longitude (W)</th>
<th>Total Hg (µg/L)</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>TDS (mg/L)</th>
<th>Conductivity (μS/cm)</th>
<th>E, (mV)</th>
<th>Salinity (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Santa Catarina River</td>
<td>25° 40' 12&quot;</td>
<td>100° 20' 46&quot;</td>
<td>0.51 ± 0.03</td>
<td>25.0</td>
<td>7.60</td>
<td>358</td>
<td>724</td>
<td>85.1</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>Santa Catarina River</td>
<td>25° 41' 27&quot;</td>
<td>100° 09' 51&quot;</td>
<td>0.85 ± 0.02</td>
<td>31.8</td>
<td>8.35</td>
<td>252</td>
<td>514</td>
<td>94.2</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>Santa Catarina River</td>
<td>25° 40' 18&quot;</td>
<td>100° 7' 46&quot;</td>
<td>1.14 ± 0.01</td>
<td>33.9</td>
<td>8.73</td>
<td>347</td>
<td>709</td>
<td>99.0</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>La Silla River</td>
<td>25° 40' 15&quot;</td>
<td>100° 7' 43&quot;</td>
<td>0.98 ± 0.02</td>
<td>30.6</td>
<td>8.21</td>
<td>354</td>
<td>722</td>
<td>112.8</td>
<td>0.1</td>
</tr>
<tr>
<td>5</td>
<td>Santa Catarina River</td>
<td>25° 40' 16&quot;</td>
<td>100° 7' 43&quot;</td>
<td>0.44 ± 0.04</td>
<td>32.4</td>
<td>8.25</td>
<td>350</td>
<td>714</td>
<td>103.0</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>Santa Catarina River</td>
<td>25° 38' 19&quot;</td>
<td>100° 4' 15&quot;</td>
<td>0.30 ± 0.05</td>
<td>34.4</td>
<td>8.64</td>
<td>339</td>
<td>691</td>
<td>183.4</td>
<td>0.1</td>
</tr>
<tr>
<td>7</td>
<td>San Juan River</td>
<td>25° 35' 50&quot;</td>
<td>99° 59' 58&quot;</td>
<td>0.64 ± 0.02</td>
<td>34.5</td>
<td>8.79</td>
<td>328</td>
<td>669</td>
<td>139.3</td>
<td>0.1</td>
</tr>
<tr>
<td>8</td>
<td>El Cuchillo reservoir</td>
<td>25° 32' 12&quot;</td>
<td>99° 51' 17&quot;</td>
<td>0.94 ± 0.02</td>
<td>31.4</td>
<td>7.61</td>
<td>452</td>
<td>922</td>
<td>111.0</td>
<td>0.2</td>
</tr>
<tr>
<td>9</td>
<td>El Cuchillo reservoir</td>
<td>25° 32' 34&quot;</td>
<td>99° 50' 04&quot;</td>
<td>0.23 ± 0.07</td>
<td>30.1</td>
<td>8.08</td>
<td>352</td>
<td>718</td>
<td>171.7</td>
<td>0.1</td>
</tr>
<tr>
<td>10</td>
<td>El Cuchillo reservoir</td>
<td>25° 31' 40&quot;</td>
<td>99° 37' 19&quot;</td>
<td>0.75 ± 0.02</td>
<td>29.9</td>
<td>9.01</td>
<td>450</td>
<td>917</td>
<td>168.5</td>
<td>0.2</td>
</tr>
<tr>
<td>11</td>
<td>La Silla River</td>
<td>25° 43' 31&quot;</td>
<td>99° 19' 27&quot;</td>
<td>&lt;1 LOD^a</td>
<td>30.7</td>
<td>8.14</td>
<td>302</td>
<td>617</td>
<td>211.9</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Taba 1: <LOD>: below the limit of detection.

### Table 2. Sequence of extracting agents and operationally defined fractions in the sequential extraction procedure [21,25,26].

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Mercury containing species</th>
<th>Extracting agent</th>
<th>Extraction conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mobile Hg</td>
<td>Alkyl Hg species (MeHgCl, EtHgCl)</td>
<td>4 M HNO3</td>
<td>The sample was extracted with 10 mL of 4 M HNO3 in a microwave oven at 100°C for 10 min. A 3-min ramping time was used to reach the temperature of 100°C. The residue of this step was washed with DDI water</td>
</tr>
<tr>
<td>Semi-mobile Hg</td>
<td>Hg or Hg-M^P</td>
<td>1:2 HNO3 : DDI water</td>
<td>The residue from the previous step was extracted twice with 10 mL of 1:2 HNO3 : DDI water in a water bath heated at 95 ± 2 °C for 20 min. The residue of this step was washed with DDI water</td>
</tr>
<tr>
<td>Non-mobile Hg</td>
<td>HgCl2 (major)</td>
<td>1:6.7 HCl: HNO3 : DDI water</td>
<td>The residue from the previous step was extracted twice with 10 mL of 1:6.7 HCl: HNO3 : DDI water in a water bath heated at 95 ± 2 °C for 20 min.</td>
</tr>
</tbody>
</table>

^aCertain inorganic mercury complexes may be present in both fractions. ^bThis represents a mercury–metal amalgam.
17 (SPSS Inc., Chicago, IL, USA). A two-tailed p < 0.05 was considered statistically significant.

2.2.5 Other physical and chemical parameters
Water quality parameters, including pH, redox potential, temperature, conductivity, dissolved oxygen (DO), total dissolved solids (TDS), and salinity were simultaneously measured in the field. An Orion 290 A pH meter was used for pH and redox potential (Eₐ) measurements; DO was measured using an Orion 835 Dissolved Oxygen meter; and temperature, conductivity and TDS were measured with an Orion 135 probe.

2.2.6 Statistical methods
Pearson’s correlation was used to evaluate the associations between parameters. All statistical analyses were performed with SPSS software version 17 (SPSS Inc., Chicago, IL, USA). A two-tailed p < 0.05 was considered statistically significant.

RESULTS AND DISCUSSION
Eleven representative sampling points of varying degree of pollution of the San Juan River Watershed were selected on the basis of previous reports in this area [19, 20] and unpublished work from our laboratory.

3.1 Water quality
Sampling locations with coordinates and environmental conditions during sampling with total Hg concentration found in filtered river samples are shown in Table 1. Water samples from San Juan River watershed recorded temperature ranging 24.0-34.5°C, salinity from 0.079±0.028 mg/Kg of total Hg in sediments samples. In contrast, the available fraction of Hg, including methylmercury (MeHg), thus making the mobile fraction represented 20±8% of total Hg. The mobile fraction contains most of the total Hg represented nearly 9% of the total Hg (0.038 mg/Kg), whereas the mobile fraction represented 71±10% of total Hg in sediments. The non-mobile fraction is related to sediment quality criteria for Hg have been set in some countries [33, 35], it is necessary to evaluate the reactivity, solubility and potential bioavailability of Hg in sediments [36] (Table 2). The levels of Hg extracted from sediment samples can be seen in Fig. 2. The distribution of Hg in the fractions was similar across the sampling site locations. Results showed that Hg was mainly distributed in the non-mobile Hg fraction (0.29 ± 0.07 mg/Kg), which accounted for 71±10% of total Hg in sediments. The non-mobile fraction is related to elemental and strongly bound Hg compounds. The semi-mobile fraction of Hg represented nearly 9% of the total Hg (0.038 mg/Kg), whereas the mobile fraction represented 20±8% of total Hg. The mobile fraction contains most of the available fraction of Hg, including methylmercury (MeHg), thus making it the most toxic fraction. Total Hg content in this fraction corresponded to 0.079±0.028 mg/Kg of total Hg in sediments samples.

Fig. 2. Sequential chemical fractionation of Hg in sediment samples from San Juan River watershed.
Table 3. Mercury content in the sediment samples from San River watershed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Site</th>
<th>Mercury content (mg/kg dry weight)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Santa Catarina River</td>
<td>0.297 ± 0.008</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.533 ± 0.004</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.410 ± 0.006</td>
</tr>
<tr>
<td>4</td>
<td>La Silla River</td>
<td>0.459 ± 0.005</td>
</tr>
<tr>
<td>5</td>
<td>Santa Catarina River</td>
<td>0.313 ± 0.007</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>0.470 ± 0.005</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>0.495 ± 0.010</td>
</tr>
<tr>
<td>8</td>
<td>San Juan River</td>
<td>0.450 ± 0.011</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>0.317 ± 0.016</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>0.408 ± 0.012</td>
</tr>
<tr>
<td>11</td>
<td>El Cuchillo reservoir</td>
<td>0.300 ± 0.017</td>
</tr>
</tbody>
</table>

*The values are means ± 95% confidence level (n=3).

3.3 Association between Hg and environmental parameters in the San Juan River watershed.

In this study, associations between Hg concentrations and several environmental factors were estimated using the Pearson’s correlation coefficient (r). Correlation tests having P-values < 0.05 indicated strong association between tested variables. The statistical analysis revealed a highly significant positive correlation (r=0.01) between total Hg in sediments and the non-mobile Hg fraction (r=0.862).

There was a strong positive correlation (r=0.05) between total Hg levels in water samples and the semi-mobile Hg fraction in sediments (r=0.650). Pearson correlation analysis indicated that total Hg concentrations in water samples were negatively correlated with the redox potential measured in the samples (r=-0.660, p<0.05). However, Pearson’s correlation analysis indicated that Hg levels in water samples were not associated with pH (r=0.195, p>0.05).

The concentration of total Hg and MeHg in aquatic environment can be influenced by several physical and chemical parameters including temperature, pH, salinity, organic carbon, redox potential, bacterial activity, inorganic and organic complexing agents and organic matter content [37,38]. Alkaline pH values and total Hg average concentrations below the US EPA ambient surface water quality criteria [30] were observed within the San Juan River Watershed. The weak correlation between Hg content and some physicochemical variables could indicate the influence of the local anthropogenic activities [39].

CONCLUSIONS

The San Juan River watershed was characterized by relatively low levels of Hg. The slightly higher Hg concentrations found at some monitoring points could be related to diffuse sources of Hg, such as anthropogenic and industrial activities. Concentrations of Hg in water samples varied from 0.17 to 1.14 μg/L and were below the maximum concentration for Hg established by the Mexican environmental regulations. Additionally some of the physicochemical parameters such as pH, TDS and temperature exceeded the drinking water safety levels. On the other hand, Hg concentrations in surface sediments were very similar among all the sampling sites and ranged from 0.289 to 0.501 mg/Kg. A significant amount of Hg in sediments was found to be associated with the non-mobile fraction that corresponds to a number of very stable chemical species with low mobility.

The study was conducted to help assess the need for a more comprehensive survey of Hg distribution in this ecosystem, which may eventually have an impact on the health of the nearly four-million inhabitant metropolitan area of Monterrey, known to harbor the largest metallurgical urban zone in northern Mexico.

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