ARSENIC CONTENT, GRAIN SIZES AND CHEMICAL CHARACTERISTICS IN SURFACE SEDIMENTS OF THE URÍAS LAGOON, NW MEXICO

Contenido de arsénico, tamaño de grano, y características químicas de sedimentos superficiales en la laguna Urías, noroeste de México

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Key words: coastal lagoons, sediments, trace elements, Gulf of California

ABSTRACT

Aiming to detect possible impacts of human activities on the characteristics of the sediments of the Urías lagoon, which is a lagoonal system surrounded by the urban area of Mazatlán (NW Mexico), we determined the mean percentages of the main particle fractions, pH, CO3²⁻, organic carbon and total arsenic content in the surficial sediments of six different zones of the Urías lagoon. Sand was the dominant size fraction throughout the whole system. The highest organic matter and the lowest pH values were found in adjacent sites to industrial activities, especially to fish processing. Most arsenic concentrations were within the values of the natural local background (12.6-27.3 mg/kg), with the possible exception of sediments close to the industrial area, especially those nearby the fish processing plants, where the mean As (45.2 ± 9.3 mg/kg) exceeded the level which may have adverse effects on marine organisms (41.6 mg/kg). However, it is not excluded that such levels are results rather from the combined effect of the hydrodynamic and sediments dynamic of sediment associated to local enrichments background of the region.

Palabras clave: lagunas costeras, sedimentos, elementos traza, Golfo de California

RESUMEN

La laguna costera Urías se encuentra rodeada por la zona urbana de Mazatlán (noroeste de México). Con la finalidad de detectar posibles impactos de actividades humanas sobre las características de los sedimentos, se determinaron los porcentajes de las fracciones particuladas, pH, CO3²⁻, carbono orgánico y arsénico total en los sedimentos
superficiales en seis zonas de la laguna Urías. En todo el sistema dominó la fracción arenosa. Los mayores valores de carbono orgánico y los menores valores de pH se encontraron en los sitios adyacentes a actividades industriales, en especial aquellos cercanos a las plantas procesadoras de pescado. La mayor parte de los niveles de arsénico se ubican en el intervalo de valores naturales típicos de la región (12.6-27.3 mg/kg), con la posible excepción de los sedimentos de las estaciones cercanas al área industrial, especialmente adyacentes a las plantas procesadoras de pescado, donde la concentración media (45.2 ± 9.3 mg/kg) superó los 41.6 mg/kg, nivel que puede afectar a los organismos marinos. Sin embargo, no se descarta que tales niveles sean resultado del efecto combinado de la hidrodinámica y la dinámica de los sedimentos asociados a los enriquecimientos de arsénico total de la región.

INTRODUCTION

In aquatic ecosystems, pollutants are deposited in sediments, where they are associated frequently to organic or inorganic ligands. However, they may become available to local biota through different mechanisms such as leaching or sediment resuspension, causing ecological damage and possibly becoming a source of concern for human health (Devesa-Rey et al. 2010, Martínez-Santos et al. 2015). Among pollutants, arsenic (As) is a common, widely distributed element present in several mineral forms. Its approximate average concentration on the earth’s crust is 2.0 mg/kg (Wedepohl 1995) due to natural (mostly in hydrothermal active areas) or artificial causes (e.g. mining and smelting activities). Consequently, it may become concentrated to values higher than the limits allowable for drinking waters and for terrestrial/aquatic food for human consumption (Garelick et al. 2009). Additionally, negative effects (i.e., low growth, low development rate) on aquatic organisms and on the structure of benthic communities have been related to As in sediments, even at concentrations of 20 mg/kg (Luo et al. 2010, Marziali et al. 2017).

The Urías lagoon receives effluents from the urban and industrial activities of the city of Mazatlán and its recreational and industrial harbor; and some continental inputs during rainy season. In addition to services to the tourism industry, the main local activities are industrial and artisanal fisheries, food-related industries and one thermoelectric power plant.

There is a considerable literature on the presence and concentrations of heavy metals in the water, sediments and biota of this lagoon, including their probable sources and effects. Most was summarized by Jara-Marini et al. (2011). Some additional information about metal content (Hg, Cd, Pb) in biota may be obtained in Frias-Espericueta et al. (2016), Cardoso-Mohedano et al. (2016) and Gil-Manrique et al. (2017), among others, but there is no information available on distribution and concentrations of As in the sediments of this lagoon.

For this reason, we compared the total As concentrations of six different areas of the Urías lagoon and determined their relationships to the physical and chemical characteristics of their surface sediments, aiming to determine the association between sediment characteristics and the presence and concentration of As.

MATERIALS AND METHODS

The Urías Lagoon is classified as a coastal lagoon with an internal barrier (Lankford 1977) and a longitude of 17 km (surface area: 18 km²), located in the southern part of the state of Sinaloa (southeastern Gulf of California, Mexico). Its depth ranges from 1 to 3 m, with the exception of the navigation channel, where it reaches 12 m. Its hydrodynamics is tidally governed, with a 1 m tidal average (Montaño-Ley et al. 2008).

As the lagoon does not continuously receive freshwater it presents a high salinity gradient in the upper lagoon, causing anti-estuarine circulation, and it has a salinity range of 25.8 to 38.4 g/L (Cardoso-Mohedano et al. 2016). Other potential sources of contaminants in surrounding areas are the municipal slaughterhouse, shrimp farms and the open-air municipal solid waste dump (Ochoa-Izaguirre and Soto-Jiménez 2013).

Surface sediments were collected at six sampling sites chosen for their location close to the discharge of effluents from some human activities, such as shrimp farms (SF), a thermoelectric power plant (PP), fishmeal plants (FP), an industrial park (IP), a commercial harbor (HA), and a recreational fishing fleet area (RF) (Fig. 1). The urban area of Mazatlán city extends between stations RF and IP.
At each site, samples were obtained with a Van Veen grab at nine equidistant points (10 m) forming a square grid of 20 × 20 m and covering an area of 400 m² (nine sediment samples/sampling site) (Fig. 2). Sediments in contact with the grab were discarded; samples were obtained from the underlying 3 cm, placed in individual, acid-cleaned plastic bags and transported to the laboratory.

One set of nine samples in each one of six selected sites was obtained in the rainy season and sampling was repeated in the dry season (N = 54 samples for dry season and 54 samples for rainy season).

In the laboratory, samples were divided in two equal parts: one was used for determination of particle sizes following Folk (1974). The second was dried in an oven at 60 °C, pulverized in an agatha mortar and three subsamples were taken for analysis using standard methods: pH according to APHA (2012) and carbonates and organic carbon (OC) as in Loring and Rantala (1992). For total arsenic, samples were digested according to Araújo et al. (2009) and the supernatant was analyzed with an atomic absorption spectrophotometer (AAnalyst 800, Perkin-Elmer).

For quality assurance/quality control (QA/QC), all materials used for As analysis were acid-washed using HNO₃ and HCl (2M). The accuracy was determined with a marine sediment reference material PACS-2 (National Research Council of Canada), obtaining a mean recovery value of 98.0 ± 16.2 %. The coefficient of variation for As standards was 4.2 %.

Values were not normal or homoscedastic (Kolmogorov-Smirnov and Bartlett’s tests). For comparison we used the nine data for each sampling site (six sampling sites) (54 data for rainy season and 54 data for dry season: a total of 108 samples) which were compared using Kruskall-Wallis tests.
separating different means with Dunn’s tests. Pearson correlations were calculated to identify relationships between variables. All tests were performed with $\alpha = 0.05$ (Zar 1999).

RESULTS

For particle size (Table I), sand was the dominant fraction in all stations (except in the IP station during the rainy season). During the rainy season, values decreased progressively from the innermost station SF (84.8 ± 7.9 %) to the central part of the basin (station IP, 37.9 ± 21.5 %), which was significantly lower ($p < 0.05$) than all sampling stations. The significantly highest value (76.8 %) was at the station closest to the lagoon mouth (RF). During dry season, no significant difference ($p > 0.05$) was observed between most of the sampling stations.

Conversely, the silt fraction had values increasing from inner to central areas during rainy season, decreasing to outer areas (RF station). However, during the dry season only FP and RF stations were significantly lower ($p < 0.05$) than those of the inner areas. Finally, clay had the highest percentages at stations IP and HA during rainy and dry season, respectively; and the lowest percentages were found in the inner stations, and at the one closest to the mouth of the lagoonal system (Table I).

In both seasons, organic matter and arsenic showed the same trend, increasing from the mouth of the lagoon (RF) to the FP station, and decreasing progressively towards the inner stations. The sediments with the highest OC contents were at the SF and FP stations during both seasons, while the lowest were those from RF, close to the lagoon entrance (Table I).

Carbonates had no discernible trend in either season, reaching the highest values in front of the PP station both in the rainy and dry seasons (9.2 ± 1.4 and 15.1 ± 0.8 %, respectively), which were significantly ($p < 0.05$) higher than the other stations (Table I). Carbonates were fairly homogeneous, ranging between approximately 6.1 and 8.6 % throughout the whole basin, with the exception of the PP station, as commented above (Table I).

A significant ($p < 0.05$) acid pH value was registered in the FP station (6.3 ± 1.1) during the rainy season. The highest values were those of the PP station and of the outermost stations (RF and HA) in both seasons (Table I).

The total arsenic intervals for rainy and dry seasons were 13.0–41.6 and 16.6–48.8 mg/kg, respectively. The highest As contents were those of the stations located adjacent to fishmeal plants and

| TABLE I. MEAN SIZE FRACTIONS, CO$_2^-$, AND OC, pH, AND TOTAL ARSENIC OF SURFACE SEDIMENTS OF SIX STATIONS OF THE URÍAS LAGOON, ADJACENT TO SHRIMP FARMS (SF), POWER PLANT (PP), FISHMEAL PLANT (FP), INDUSTRIAL PARK (IP), COMMERCIAL HARBOR (HA), AND RECREATIONAL FISHING FLEET AREA (RF). N = 54 FOR EACH SEASON (DRY AND RAINY) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Site            | Sand* (%        | Silt* (%)       | Clay* (%)       | CO$_2^-$ (%)    | OC* (%)         | pH*             | As* (mg/kg)     |
| SF              | 84.8 ± 7.9a     | 9.6 ± 8.9b      | 3.8 ± 5.4b      | 7.1 ± 0.1b      | 6.1 ± 1.2ab     | 7.0 ± 0.2b      | 13.0 ± 2.8d     |
| PP              | 65.3 ± 14.2a    | 18.5 ± 14.1b    | 4.2 ± 5.4b      | 9.2 ± 1.4a      | 4.6 ± 2.4c      | 8.1 ± 0.2a      | 20.7 ± 1.9c     |
| IP              | 66.4 ± 25.3a    | 25.8 ± 21.2ab   | 7.8 ± 5.1b      | 6.1 ± 0.3b      | 7.5 ± 1.2a      | 6.3 ± 1.1c      | 41.6 ± 8.9a     |
| HA              | 37.9 ± 21.5b    | 42.6 ± 16.6a    | 19.5 ± 8.5a     | 6.8 ± 0.2b      | 5.4 ± 0.4bc     | 7.3 ± 0.1b      | 35.0 ± 4.4ab    |
| IP              | 64.9 ± 7.8a     | 21.3 ± 3.0ab    | 13.7 ± 6.9ab    | 6.4 ± 0.1b      | 2.4 ± 0.9d      | 7.7 ± 0.2ab     | 26.7 ± 9.2bc    |
| HA              | 78.2 ± 10.3a    | 13.5 ± 12.4b    | 5.8 ± 5.5b      | 6.2 ± 0.1b      | 1.4 ± 0.7d      | 7.9 ± 0.2a      | 20.6 ± 2.9cd    |

*Non parametric tests; different letters indicate significant differences between values in the same column/by season (one-way ANOVA test, $\alpha = 0.05$)
industrial activities (FP and IP stations), although both were not significantly different from the mean value of the HA station. The lowest values were those of stations SF and PP in both seasons (Table I).

Sand was inversely related to silt and clay; however, the correlation was positive between these materials. Regarding chemical characteristics, \( \text{CO}_3^{2-} \) was related directly to pH and inversely to OC. Arsenic was significantly (\( p < 0.05 \)) correlated with OC and clay, and inversely with pH (Table II).

**DISCUSSION**

The higher percentages of clay of the central part of the Urías lagoon coincide with the higher As sediment content. This agrees with the inverse relationship between grain sediment and As content, even with other metals (Li et al. 2016, Tansel and Rafuudin 2016, Zhao et al. 2016). This distribution coincides also with the tidal hydrodynamic model developed by Montañó-Ley et al. (2008) for the Urías lagoon, according to which the highest accumulation of metals would occur in the central lagoon. Besides, the freshwater input from Jabalines creek to Urías lagoon could contribute to explain this distribution.

The low OC content determined in the PP station is due to high \( \text{CO}_3^2^- \) content in sediments (Table I), while the high OC content of stations SF and FP (6.1 ± 1.2 and 7.5 ± 1.2 %, respectively) seem due to contributions to the Urías lagoon sediments from urban and industrial wastewaters and shrimp farms (Páez-Osuna 2001).

Most of the remaining values were close to those determined by Osuna-López et al. (1986), Soto-Jiménez and Páez-Osuna (2001) and Jara-Marini et al. (2008) in some of the central and inner stations of the Urías lagoon. However, lower contents of OC were reported by Frias-Espericueta et al. (2004) in the surface sediments of the Huizache-Caimanero (HC) coastal lagoon (southern Sinaloa state). This could be due to the poorer mangrove development and sparser population densities in areas surrounding the HC lagoon.

The mean OC interval of the present study (1.4-7.5%) is lower than the mean OC content in sediments of anthropogenic-polluted lagoons (3.0-12.0 %; Magni et al. 2008), but within the interval of several coastal lagoons around the world (1.7-45.9 %), where some coastal lagoons receive high industrial and urban discharges (Raygoza-Viera et al. 2014).

The pH values found at stations SF and FP (7.0 ± 0.3 and 6.8 ± 0.9, respectively) coincide with the results of Agraz-Hernández (1999), who related the low pH values determined in mangrove areas or close to shrimp farms of Urías lagoon to the presence of decomposing organic matter. These stations had significantly lower pH values than the PP station, probably because of the buffering effect of the high number of bivalve shells found in the sediment of the latter, which explain also the significantly higher mean \( \text{CO}_3^{2-} \) content of PP sediments in comparison to other stations.

The significant (\( p < 0.05 \)) negative correlation between pH and As observed in the present study, is in accordance with several studies, and is the result of the release of As ions from the weak-bounded fractions of the sediments under acidic conditions (Rivera-Hernández and Green-Ruiz 2016).

The enrichment of As in sediments with high load of organic matter (positive correlation between As, OC and clays), as specifically observed in the FP station (fishmeal plant) of the present study, comes from the high capacity of OC (especially humic and fulvic acids) to trap this and other elements (Wang and Mulligan 2006, Ruiz-Fernández et al. 2009, Bejarano-Ramírez et al. 2017), which is due to their negative charged surfaces which adsorb trace elements behaving as cations (Tukura et al. 2007).

**TABLE II. CORRELATION COEFFICIENTS BETWEEN SEDIMENT CHARACTERISTICS**

<table>
<thead>
<tr>
<th></th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
<th>( \text{CO}_3^{2-} )</th>
<th>OC</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silt</td>
<td>-0.919**</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td>-0.585**</td>
<td>0.427**</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{CO}_3^{2-} )</td>
<td>-0.179</td>
<td>0.167</td>
<td>0.025</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OC</td>
<td>-0.139</td>
<td>0.133</td>
<td>0.067</td>
<td>-0.121</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>0.067</td>
<td>-0.145</td>
<td>-0.053</td>
<td>0.326*</td>
<td>-0.674**</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>-0.188</td>
<td>0.166</td>
<td>0.304*</td>
<td>-0.052</td>
<td>0.239*</td>
<td>-0.247*</td>
</tr>
</tbody>
</table>

*\( p < 0.05 \), **\( p < 0.01 \), OC: organic carbon
However, there is no correlation between OC and clay, as expected according to the literature (Rivera-Hernández and Green-Ruiz 2016); this can be due to the fact that industrial sources of OC do not necessarily follow the same pattern than the sources of clay, as well as their distribution.

During the rainy season, the continental runoff may cause an increase in the trace elements concentration of coastal lagoons sediment (Tukura et al. 2007, Rodríguez-Iruretagoiena et al. 2016). Variations in the content of sediment metal are generally associated with changes in organic carbon (Magni et al. 2008).

In the present study, the sediments of stations SF, PP, FP and IP had significant (p < 0.05) higher OC during the rainy season, but a higher As content in those stations was not observed in the Urías lagoon sediments during the rainy season. This indicates that the As content in sediments is not necessarily related to the alternation of dry and rainy seasons, which was also shown in the case of Cd and Pb by Jara-Marini et al. (2008) in the same lagoon, which had an interval of 3.2-3.3 and 47.9-56.5 mg/kg in dry season, and 3.1-3.3 and 50.7-58.9 mg/kg in rainy season, respectively.

The concentrations of As in the Urías lagoon sediments lie within the ranges determined in most lagoons and coastal areas in different regions worldwide (Table III). Although the environmental concentrations of As may depend on the presence and distance of natural sources, they are more frequently related to human activities prevailing in the area under study.

Some activities are commercial harbor discharges, wastes from the fertilizer industry or effluents from agricultural fields (Mirlean et al. 2003, Shumilin et al. 2005, Jara-Marini and García-Rico 2006). Other sources detected were urban wastewater and solid waste dumps (Bloundi et al. 2009), as well as preservatives used by the local wood industry together with urban waste dumps (Pradit et al. 2010). Most total arsenic concentrations determined in the Urías lagoon are higher than the value reported by Wedepohl (1995) as mean continental crust (2.0 mg/kg), which is in accordance with Luo et al. (2010), who pointed out that As and other metals can occur naturally in higher concentrations in different zones of the world.

In this context, As content in the Urías lagoon lied within the local background range proposed by SGM (1997): from 12.6 to 27.3 mg/kg in the nearest 10 km, although in areas farther afield they increase to 46.0-69.1 mg/kg. This indicates a possible natural origin of most As inputs and a generally low degree of human impact, which results rather from the combined effect of the hydrodynamic and sediment dynamics.

Values higher than the local background were determined at the IP and FP stations, although only FP exceeded the probable effect level (PEL) of As in the marine environment (41.6 mg/kg; Long et al. 1995). However, all the samples exceeded the ERL (8.2 mg/kg) proposed by Long et al. (1995), which could cause some physiological alterations in the benthic fauna of the Urías lagoon. Considering the generally high As content of seafood and fish (Manía et al. 2015), this could also indicate that the fish and seafood processing plants operating near to the FP

| TABLE III. TOTAL ARSENIC CONCENTRATIONS IN SURFACE SEDIMENTS IN COASTAL LAGOONS |
|-----------------------------------------------|------------------|
| International | Range (mg/kg) |
| Patos lagoon, Brazil | 11.9-46.4 (Mirlean et al. 2003) |
| Nador lagoon, Morocco | 4.0-76.0 (Bloundi et al. 2009) |
| Coastal areas of China | 5.6-13.0 (Luo et al. 2010) |
| Gorgan Bay, Caspian Sea | 3.3-14.3 (Bagheri et al. 2015) |
| Songkhla lagoon, Thailand | 0.8-70.7 (Pradit et al. 2010) |
| Mexico | |
| Urías lagoon, Mazatlán, Sinaloa | 13.0-48.3 (this work) |
| La Paz lagoon, Baja California Sur | 0.8-44.0 (Shumilin et al. 2001) |
| Magdalena-Almejas lagoon, Baja California Sur | 1.0-34.0 (Shumilin et al. 2005) |
| Coastal zone of Sonora | 0.05-13.5 (Jara-Marini and García-Rico 2006) |
| La Paz lagoon, Baja California Sur | 0.9-20.1 (Pérez-Tribouillier et al. 2015) |
Sand was the main size fraction of the Urías lagoon sediments, although clay increases significantly in inner stations, especially in those adjacent to industrial activities. The highest content of OC and the lowest pH values were detected in the station close to the fish processing plant (FP) that operates in the area. All the contents of As in this study exceeded the ERL (8.2 mg/kg), and the sites near the fish processing plants exceed the levels with adverse effects on marine organisms (41.6 mg/kg). This station had also the highest arsenic concentration, which coincides with the significant positive correlation between As and OC, explained by the complexation of As with humic and fulvic acids ligands. However, pH values varied relatively little, and the significant negative correlation between pH and As indicates that As$^{5+}$ is preferably adsorbed by sediments.

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