

## Heavy Metals in Surface Sediments from Huizache-Caimanero Lagoon, Northwest Coast of Mexico

M. G. Frías-Espéricueta, J. I. Osuna-López, P. J. López-Saenz, G. López-López, G. Izaguirre-Fierro

Faculty of Marine Sciences, Autonomous University of Sinaloa, Post Office Box 610, Mazatlán 82000, Sinaloa, Mexico

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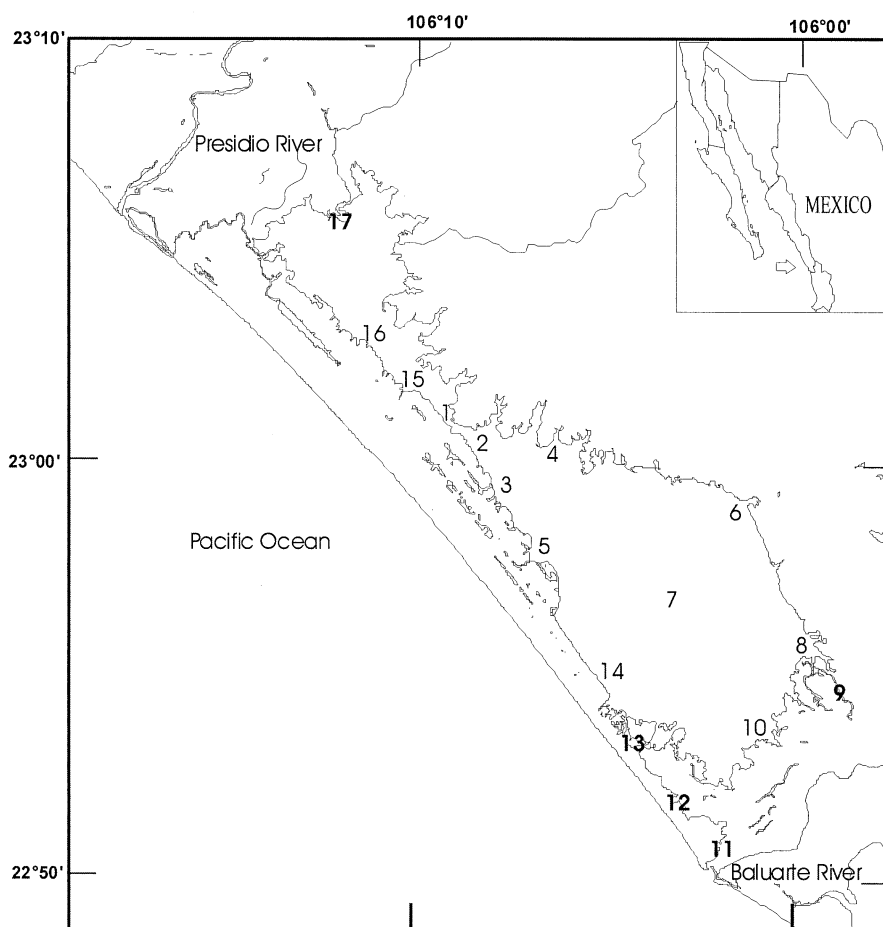
Elevated concentrations of heavy metals in coastal regions result from the natural and anthropogenic processes. In Mexico, in spite of environmental policy efforts to reduce environmental risk to safeguard the natural environment and to protect human health, studies carried out for more than 25 years have demonstrated high concentrations of some heavy metals in lagunar and estuarine ecosystems (Villanueva and Botello 1998).

Identifying distribution and accumulation patterns of anthropogenic chemicals present in the marine/coastal environment, is an important step in determining the extent to which these compounds are potentially available for uptake by aquatic organisms (Chase et al. 2001).

Huizache-Caimanero is a subtropical lagoon which has a surface of 175 km<sup>2</sup> and is located in the subtropical Pacific coast (SE Gulf of California) (Fig. 1). This lagoon is connected with two rivers: 1) Presidio River (at North) which directly receives rural and agricultural discharges; and 2) Baluarte River (at South) which receives agricultural, urban and aquaculture discharges. The purpose of this study was to assess the concentration of seven heavy metals (Cd, Co, Cu, Fe, Ni, Pb and Zn) and organic matter in surface sediments of the Huizache-Caimanero lagoon. This is of ecological concern, because this lagoon is a nursery and feeding area for many commercially important crustacean (shrimps and crabs) and fish species; which supports 21 fishermen associations.

### MATERIALS AND METHODS

17 surface sediment samples were obtained from the Huizache-Caimanero lagoon (Fig. 1). Upper 5 cm layer of sediment were carefully taken to avoid disturbing and placed in plastic bags. Munsiri et al. (1995) pointed out that the upper 5 cm layer is more biologically and chemically active than deeper layers, and exchanges of substances between soil and water occur in this layer. Sediment samples were transported in coolers (4 °C) to the laboratory. All material used in sampling and heavy metal treatment were acid washed (Moody and Lindstrom 1977).



**Figure 1.** Location of sampling sites into Huizache-Caimanero lagoon.

Samples were oven-dried at 70°C and finely ground for analysis. Organic matter content was analyzed by the chromic acid oxidation method (Loring and Rantala 1992). For Cd, Co, Cu, Fe, Ni, Pb and Zn metal concentrations, triplicate sub-samples were digested with a concentrated nitric/hydrochloric acid mixture (3:1, v/v) (Breder, 1982; De Gregori *et al.*, 1996) and slowly evaporated to dryness (90 °C) and the remainder dissolved in nitric acid (2M). After that, samples were centrifuged and analyzed by flame atomic absorption spectrophotometry. Reference material sediment homogenate BCSS-1 (UNEP 1995) was used to establish accuracy and precision of the method, and values were satisfactory except for Cr and Mn (37 and 44% of recovery, respectively) and these metals were not included. Differences in average concentrations among stations were assessed by an one-way analysis of variance, and correlations with the T-students test (Zar 1984).

## RESULTS AND DISCUSSION

Values of organic matter and heavy metal are shown in table 1. It is important to comment that no mangle forest is present in this lagoon. Organic matter content into the lagoon ranged from 0.34 to 2.66 %. The highest values were observed at the mouths of rivers (stations 11, 13 and 17) and fishing zone (stations 14 and 16), because shrimp fishing is carried out with a plastic cast net (Known as “atarraya”), where fishermen put commercial shrimp food in the sediments to attract shrimps (this practice is calling “purineo”), which enrichment the sediment by organic carbon. This is of ecological concern, because an accumulation of organic matter favors oxygen depletion in the surface layer of soil and develops toxic microbial metabolic in the water ( $H_2S$ ,  $NO_2^-$  and  $FeS_2$ ) (Boyd, 1995), affecting distribution of species.

**Table 1.** Organic matter content (%) and heavy metal concentrations ( $\mu g/g$ , dry weight, Fe in percent) in surface sediments from Huizache-Caimanero lagoon.

Station	OM	Cd	Co	Cu	Fe	Ni	Pb	Zn
1	0.59	0.58	8.2	24.1	2.3	8.4	36.6	91.4
2	1.72	0.79	4.2	7.2	0.6	5.4	21.7	35.6
3	2.39	0.38	8.56	17.6	1.9	6.7	36.1	68.6
4	1.61	0.44	4.77	10.9	0.9	4.5	25.8	45.2
5	1.95	0.55	9.6	18.7	2.1	8.9	41.7	78.6
6	1.21	0.10	7.8	15.6	1.8	7.6	30.5	64.6
7	1.69	0.79	9.2	21.6	2.2	8.8	50.8	103.7
8	0.41	0.29	8.1	16.5	1.8	6.9	42.8	87.9
9	0.34	0.26	5.7	7.4	1.9	3.3	29.5	67.2
10	1.51	0.87	5.8	8.8	1.2	3.3	32.3	59.6
11	2.38	0.29	6.1	6.6	2	4.9	49.7	82.2
12	1.16	0.65	4.7	6.4	1	2.5	28.8	52.8
13	2.66	0.92	5.9	12.3	1.5	4.2	49.9	75.6
14	2.43	0.63	7.9	14.2	2	6.8	38.7	74.9
15	1.11	0.17	9.9	23.1	1.3	9.9	68.9	93.7
16	2.62	0.79	7.8	11.8	1.3	5.2	25.9	41.2
17	2.33	0.59	8.6	22.8	1.7	6.1	51.5	108.3

Interval concentrations of metals were 0.10-0.92, 4.2-9.9, 6.4-24.1, 6000-23000, 2.5-9.9, 21.7-68.9 and 35.6-108.3  $\mu g/g$  for Cd, Co, Cu, Fe, Ni, Pb and Zn, respectively (Table 1).

Cd was found in lowest concentration followed, in ascending order by Ni, Co, Cu, Pb, Zn, and Fe, reflecting the abundance of these elements in sediments of Huizache-Caimanero lagoon. All Cd values were lower than 1  $\mu g/g$ , a value reported by Buchman (1989) as maximum soil concentration.

With regard to Cu and Zn, the permissible limits are 25 and 100  $\mu g/g$  (Buchman 1989), respectively. In our study, only stations 1, 7 and 17 for Cu; and station 7

and 17 for Zn; showed close values to these limits. Station 17 is located next to a zone which receives agricultural effluents (Presidio river) derived mainly from the vegetables fields which are characterized by the use of large quantities of metallic fungicides with high content of Cu (cupravit) and Zn (zineb).

Pb varied from 21.7 to 68.9  $\mu\text{g/g}$ , all stations showed a value higher than 10  $\mu\text{g/g}$ , which is the permissible limit reported. A possible source of this metal is the atmospheric transport from vehicle emission from cities and several roads surrounding the study area. Since sediments act as integrators and amplifiers of metal concentrations (Che and Cheung 1998), discharges from various years may cause the elevated levels observed in the sediments of the present study.

According to Vazquez et al. (1994) Fe is known to adsorb strongly on sediment particles and the major metal-binding in the surface layers of sediments are iron oxyhydroxides ( $\text{FeOOH}$ ) (Chapman et al. 1998). Station 1 showed the highest value with 23,000  $\mu\text{g/g}$ , which is located very close to human populations.

Merian (1991) pointed out that the average reported concentration for Ni in non-contaminated soils is in the 7-50  $\mu\text{g/g}$ . In the present study highest value of 9.9  $\mu\text{g/g}$  was detected in station 15.

Regarding station 7, which is located at center of the lagoon (Fig. 1) showed the highest concentrations of Cu, Zn and Pb. It would therefore seem possible that anthropogenically Cu, Zn and Pb are being transported to this area and allowed to settle to the lagoon bed in this region of probably weak currents. Besides, another important reason for these metal levels in Huizache Caimanero lagoon could be the enclosed nature of the system together with irregular access to tidal flushing; which allows metal accumulation. Evidently, more oceanographic information is required for a better explanation.

In table 2, only correlation between OM and cadmium was observed, in spite of organic matter is recognized as a preferential site for metal because its ability of complexation and adsorption, which leads to a strong correlation between it and metals (Green-Ruiz and Páez-Osuna 2003). Regarding metals, the good correlation in some metals (i.e. Zn and Cu), indicates a common enrichment for these metals due to similar physical/chemical properties of the elements involved (Carbonell et al. 1998) and/or both metals are associated with the same mineral facies (Rosales-Hoz and Carranza-Edwards 1998); however, due to sample size, some correlation coefficients could be significant by the high number of degrees of freedom (Boyd 1995).

Table 3 presents a comparison of metal levels in the Huizache-Caimanero lagoon with other zones of Mexico and the world. Cd, Cu, Ni, Pb and Zn values found in the present study are lower than those determined in the Thames estuary (UK), Deep Bay (Hong Kong) and Ho Chi Ming (Vietnam). However, Huizache-

**Table 2.** Correlation coefficients between organic carbon content and heavy metals concentrations ( $P \leq 0.05$ ;  $*P \leq 0.001$ ).

	OM	Cd	Co	Cu	Fe	Ni	Pb	Zn
OM	1.00	0.448	--	--	--	--	--	--
Cd		1.00	--	--	--	--	--	--
Co			1.00	0.869*	0.648	0.857*	0.617	0.698*
Cu				1.00	0.524	0.849*	0.587	0.745*
Fe					1.00	0.503	--	0.7053*
Ni						1.00	0.534	0.577
Pb							1.00	0.826*
Zn								1.00

-- not significant

Caimanero lagoon showed higher values than others lagoons from Mexico (San Andres lagoon), while Sonoran coast (NW of Mexico) and Urias lagoon showed an interval concentration of each metal higher than Huizache-Caimanero lagoon.

**Table 3.** Comparative heavy metal concentrations ( $\mu\text{g/g}$ , dry weight) in surface sediments.

Site	Cd	Cu	Ni	Pb	Zn	Reference
Thames estuary, UK	1.3	61	34	179	219	Attrill and Thomas (1995)
Deep Bay, Hong Kong				127.8	284.9	Che and Cheung (1998)
Ho Chi Ming, Vietnam		71.1		70.9	321.2	Phuong et al. (1998)
San Andres lagoon, Mexico	1.11	4.85	5.96	11.8	10.1	Vazquez et al. (1994)
Infiernillo estuary, Mexico	0.9	42.7	21.7	5.1	66.8	Osuna-López et al. (1997)
Coatzacoalcos river, Mexico	2.27	25	28.5	32.1	80	Rosales-Hoz and Carranza-Edwards (1998)
Sonoran coast, Mexico	0.5-2.51				6.5-390	García-Rico et al. (2003)
Altata-Ensenada del Pabellon lagoon Mexico		5.6-64	14.7-31	46-294	19-176	Green-Ruiz and Páez-Osuna (2003)
Urias lagoon, Mexico	0.8-1.4	24-90		37-128	84-359	Soto-Jimenez and Páez-Osuna (2001)
Huizache-Caimanero lagoon, Mexico	0.1-0.9	6.4-24	2.5-9.9	21.7-69	35-108	This study

In conclusion, Huizache-Caimanero lagoon shows a moderate environmental problem due Pb values determined. In this context, more studies about Pb

bioavailability and sources are required, because these concentrations may affect fisheries in terms of environmental/biological conservation.

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