

## Distribution of Mercury in Sediments from La Paz Lagoon, Peninsula of Baja California, Mexico

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La Paz lagoon is located in the southeastern portion of the Peninsula of Baja California (Fig. 1). The drainage area of the lagoon has an unique geological setting, a zone of tectonic crustal deformation and is cut by active faults (Angelier et al. 1981, Hausback 1984, Henry 1989). The lagoon is a semi-enclosed shallow marine system, separated from the main part of the La Paz Bay by a sandy barrier named El Mogote. It is connected to the main body of water by means of a tidal channel 300-800 m wide with a maximum depth of 10 m.

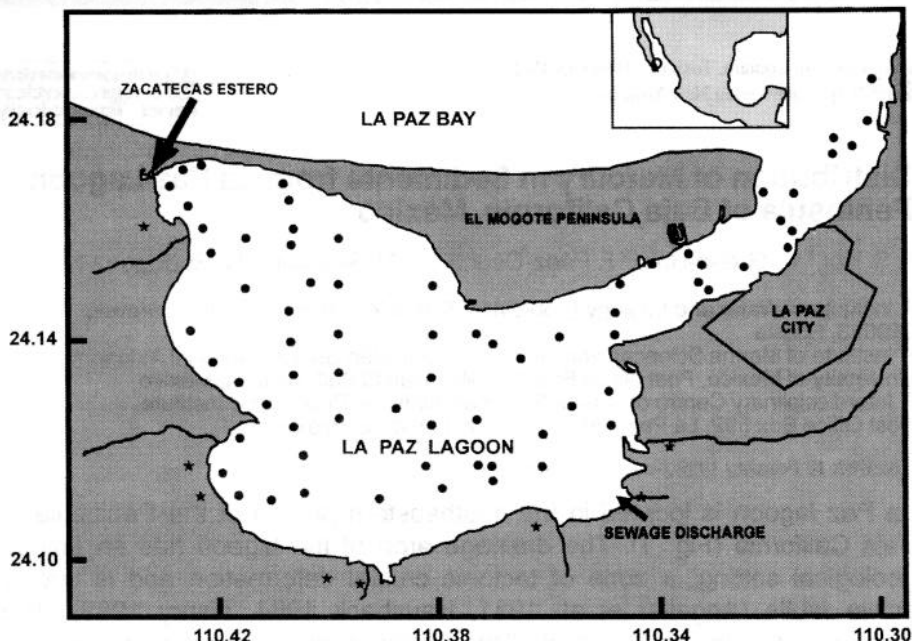
The bottom sediments of the lagoon are predominantly terrigenous, consisting of quartz (on average 54 %), rock fragments (24 %), significant amounts of biogenic carbonates, as well as feldspars, micas, and phosphatic oolites (Godinez-Orta et al. 1997). Terrigenous material enters the lagoon mainly during heavy rains associated with tropical cyclones in July-November. Adjacent to the lagoon (Fig. 1) is the city of La Paz, the capital of the state of Baja California Sur (pop. 160,000), a tourist centre with insignificant industrial development. The wastewater discharge of the city, however, is the only year-long fresh water input to the lagoon.

The present study provides the first measurements of Hg concentrations in the surficial sediments of the lagoon, their spatial distribution, and an evaluation of background levels and possible anthropogenic inputs.

### MATERIALS AND METHODS

A Van Veen grab was used to collect a total of 80 sediment samples from La Paz lagoon (Fig. 1) in October 1996. The subsample for analysis was removed from the uncontaminated interior of the sample using a plastic spoon, transferred to polyethylene bag and stored at -20 °C. Samples from dry streams beds were collected directly by hand from the selected sites (Fig. 1).

The samples were dried at room temperature, then homogenized to a fine



**Figure 1.** Collection sites in La Paz lagoon, Mexico.

powder using an agate mortar and pestle. Particular attention was paid to avoid contamination of samples and working solutions using standard clean-lab procedures. The glassware used was first soaked overnight in a 10%  $\text{HNO}_3$  solution, which also contained  $\text{KMnO}_4$  and  $\text{K}_2\text{S}_2\text{O}_8$ . Then it was heated at 80 °C for 2 hr and immersed in a 2%  $\text{HNO}_3$  solution, containing 0.01% of  $\text{K}_2\text{Cr}_2\text{O}_7$ , where it was stored until used (Kot 1998).

Wet digestion for Hg analysis was done by means of moderate heating of the sample over 15 min with a mixture of oxidizing agents ( $\text{HNO}_3 + \text{H}_2\text{SO}_4 + \text{HClO}_4 + (\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{KMnO}_4$ ) in Kjeldahl flasks. This technique ensures the maximum extraction of Hg from the samples with minimum loss of element (Goryachev and Kot 1997). Hg determinations were achieved using a Yuliya-2/Hitachi flameless atomic absorption spectrophotometer combined with a balanced cold vapour procedure.

The concentrations of the major elements, Al and Mn were determined using atomic absorption spectrophotometry, while neutron activation analysis was used for Fe. Details of the methodology applied are presented in Rodríguez-Figueroa et al. (1998). Organic carbon and carbonates were determined by standard method of wet oxidation (Rauret et al. 1987, UNEP 1995). Statistical analyses were conducted using GraphPad Prism 2.01 and Systat for Windows 5.0.

## RESULTS AND DISCUSSION

The analytical results for the Hg and major component of the lagoon

sediments and the dry stream soils from La Paz lagoon are summarized in Table 1. The spatial distribution of Hg (Fig. 2) in the lagoon sediments is strongly patterned. The area can be divided into three distinct zones. The first zone, characterized by concentrations of Hg  $<0.015 \mu\text{g/g}$  includes the northern part from the end of the channel to Estero Zacatecas. The sediments of this zone are coarse-grained (mainly sands) (Cruz-Orozco et al 1989) with low organic carbon content ( $<0.7 \%$ ). The second zone includes near-shore areas in the western and southern part of the lagoon where the concentrations vary from 0.015 to  $0.035 \mu\text{g/g}$ . These sediments are fine-grained sands with a relatively high content of organic carbon (0.8-1.8 %). The third zone corresponds to areas with concentration of Hg higher than  $0.035 \mu\text{g/g}$ , with a maximum value of  $0.050 \mu\text{g/g}$ . These high concentrations occur in the muddy sediments of the 10 m deep depression in the NW portion of the lagoon and in front of Chametla, a village on the southern shore, and near the discharge site of waste water-treatment facility for La Paz.

The mean Hg content of the dry stream sediments was  $0.02 \mu\text{g/g}$ . The highest levels were found near the waste water discharge site and near Chametla village. Soils from other areas had contents less than  $0.01 \mu\text{g/g}$ .

Table 2 shows a significant ( $p<0.001$ ) positive correlation between Hg concentrations and Fe content ( $r=0.50$ ) as well as organic carbon ( $r=0.48$ ) and a negative association ( $p<0.05$ ) of Hg with carbonates ( $r=-0.30$ ) in the lagoon sediments. In case of the adjacent dry streams, however, no significant correlations were detected. Fe presents usually in sediments as oxyhydroxide compounds and agglomerates of this element with organic matter, therefore the correlation of Hg is probably related with these oxyhydroxides, fully or partially associated with organic compounds. The negative correlation with carbonates may be explained by the presence of newly formed marine biogenic carbonates or ancient carbonates of sedimentary rocks with inclusions of pelitic material brought from the drainage basin of the Comondú geological subprovince (Hausback 1984).

To confirm the geochemical associations of the analyzed components, all of the data were also subjected to principal component analysis (Davis 1973). The results, Table 3, show the the highest eigenvalues for two principal factors, accounting for 62.13 % of the accumulated variance; factor 1 indicates strong positive loadings of Hg, together with Fe and organic carbon, in agreement with the results obtained in the linear analysis. Factor 2 is less clear, but indicates negative loading for carbonates, Mn and Al with low loading for Hg.

The concentrations of Hg found in the La Paz area are lower than typical background values for uncontaminated marine deposits (e.g. Tyrrhenian

**Table 1.** Mean ( $\pm$ SD) concentration of Hg ( $\mu\text{g/g}$ ), Mn ( $\mu\text{g/g}$ ) and major components (%) in the stream and lagoon sediments of the La Paz lagoon. The number of determinations (n) and the 95% confidence interval are enclosed within parentheses (- unavailable)

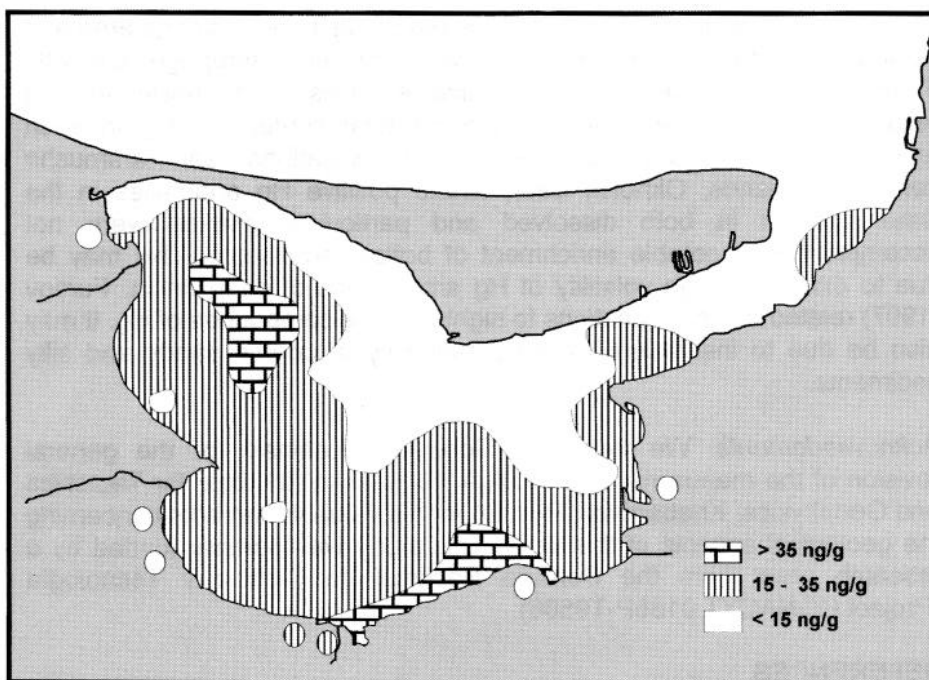
	Lagoon sediments	Stream sediment
Hg	0.020 $\pm$ 0.011 (0.018-0.023, n=72)	0.016 $\pm$ 0.009 (0.009-0.024, n=8)
Fe	1.50 $\pm$ 0.73 (1.3-1.7, n=72)	2.00 $\pm$ 1.10 (1.1-2.9, n=8)
Mn	180 $\pm$ 97 (150-200, n=68)	300 $\pm$ 150 (170-430, n=8)
Al	7.7 $\pm$ 2.3 (7.1-8.2, n=68)	-
C-org	1.10 $\pm$ 0.85 (0.84-1.30, n=65)	1.10 $\pm$ 0.45 (0.73-1.60, n=7)
CaCO <sub>3</sub>	22. $\pm$ 21 (17. -28. n=63)	

**Table 2.** Correlation matrix for Hg and major components in the stream and lagoon sediments of La Paz lagoon

	Hg	CaCo3	C-org	Fe	Mn	Al
Lagoon sediments						
Hg	1.00	-0.30 <sup>a</sup>	0.48 <sup>b</sup>	0.50 <sup>b</sup>		
C-org			1.00	0.70 <sup>b</sup>		
Mn					1.00	0.40 <sup>b</sup>
Stream sediments						
Fe				1.00	0.89 <sup>a</sup>	

Only are presented those correlation coefficients significant at  $p < 0.05^a$  and  $p < 0.001^b$ .

Sea, 1.62  $\mu\text{g/g}$ , Bargagli et al. 1988; Shirami Sea, 0.06-0.55  $\mu\text{g/g}$ , Takeuchi 1972; Okhotsk Sea, 0.39 $\pm$ 0.17  $\mu\text{g/g}$ ). They are also lower than average abundance of this element in sedimentary rocks (Shales, 0.4  $\mu\text{g/g}$ , Turekian and Wedepohl 1961) and soil data (0.03-0.8  $\mu\text{g/g}$ , Bowen 1966; 0.01-0.5  $\mu\text{g/g}$ , Fergusson 1990).



**Figure 2.** Distribution of Hg in the sediments from La Paz lagoon, Mexico.

**Table 3.** Results of the analysis of principal components for major components and Hg content in sediments of the lagoon La Paz.

Variable	Factor 1	Factor 2
Hg	0.78	0.17
Carbonates	-0.14	-0.47
C-org	0.84	-0.19
Fe	0.87	-0.08
Mn	-0.29	-0.77
Al	0.24	-0.77

Eigenvalues			
Factor	Eigenvalue	% var.	% cum. var.
1	2.25	37.42	37.42
2	1.48	24.71	62.13

This points to low natural background levels of Hg in the drainage area and in the waters of the La Paz lagoon as well as limited anthropogenic inputs. From this, we conclude that the active tectonics in the basin and Hg “expiration” are not always reflected on total content of Hg in such environments. This is in agreement with investigations near Paramushir vent (Kuril islands, Okhotsk Sea), where positive Hg anomalies in the water column in both dissolved and particulate phases were not accompanied by notable enrichment of bottom sediments. This may be due to extremely high volatility of Hg emanations of deep origin. Fursov (1997) related these emanations to highly volatile compounds of Hg. It may also be due to insufficient trapping capability of coarse sandy and silty sediments.

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