Trace Metal Distribution Along the Southern Coast of Bahia de La Paz (Gulf of California), México

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The southern tip of The Baja California peninsula is free of sources of industrial pollutants, but studies on plankton and sea-skaters have shown high levels of cadmium, iron, and zinc (Martin and Broenkow 1975; Cheng 1976). Natural processes as atmospheric wash-out or eroded trace-metal-rich land have been suggested to explain such anomalous readings (Cheng 1976).

Much urban activity is found in the south of Bahia de La Paz (Gulf of California), where no information about levels of trace metals in sediments is available. The littoral transport on this bay has built up a sand barrier and formed a coastal lagoon named Ensenada de La Paz. This coastal lagoon has been described as a sediment trap (Lechuga Devéze et al. 1986), and has received much man-made influence, suggesting that this southern portion af Bahia de La Paz could be an effective trace-metal trap also. This work seeks to study the trace metal accumulation in sediments in this area, and contributes to the identification of possible sources of pollution in the Gulf of California.

MATERIAL AND METHODS

Surface sediments (6-m water depth) from Bahia and Ensenada de La Paz, were sampled in 1995. The sampling stations were located according to their proximity to potential pollution sources (Fig. 1). Outside the coastal lagoon is an industrial zone comprising an area of fuel barge offloading and storage, and an area occupied by the diesel-driven power station (sampling stations 1 to 3). The urban activity (La Paz) extends along the inlet of the coastal lagoon (sampling stations 4 to 7). The main urban pollution source until 1992, was the sewage discharges from the city. Since then, these discharges have been decreased (sampling stations 8 and 9). Inside the coastal lagoon (sampling stations 1.0 to 12), there has been a high sediment accumulation.

The samples were obtained with a Van-Been dredge coated with epoxy paint as described by Gutiérrez-Galindo (1994). A subsample was collected from the inside of the sampled sediment using a plastic spoon previously washed with nitric acid. The subsample was tranferred to polypropylene flask and stored at -20°C until analysis using the methods of Word and Mearns (1979).

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Figure 1. Location of the stations in Bahia and Ensenada de La Paz, México

Sediments were size-fractioned through a plastic sieve previously decontaminated with nitric acid. Trace metal content from the $< 65 \mu m$ fraction was obtained in duplicate as per Van Loon (1985). An atomic absorption spectrophotometer (Buck, Sci. 200) equiped with graphite furnace was used.

Copper, iron, manganese, and zinc were quantified using an air-acetylene flame, and lead and cadmium were analyzed by using a graphite furnace. To validate the analytical procedure, samples of marine sediments from the National Research Council of Canada and reference blanks (BCSS-1) were analyzed. All the recoveries of metals studied were over 95%, except iron, which is not contained in the standards used.

Total organic carbon from each sediment sample was calculated using the wet oxidation analysis (Gaudette et al. 1994), using 1N potassium dichromate as oxidant. The results were analyzed statistically using multiple correlation.

RESULTS AND DISCUSSION

Cooper, zinc, manganese, and iron levels are higher in the zones with the higher content of organic matter (Table I,II, Fig.2), particularly in the area where for many years there was the municipal sewage discharge. In this area, the content of organic matter in sediments was 3.5% to 4.2% (Table 1), mainly composed of mud (44% to 70%) and clay (8% to 12%) (Cruz-Orozco et al. 1986). These trace metals levels do not exceed critical limits. According to trace metals in certified sediments (BCSS-1 and MESS-2) from the St. Lawrence Gulf and Beaufort Sea, these values are considered moderate to low. At sampling stations 8 and 9, copper shows high values exceeding 9% and 21% of those standards mentioned, but still remains 10 times lower than standards of contaminated sediments (PACS-1) of Esquilmat Bay (British Columbia). Iron levels do not have a known standard and, compared with those values reported in Osuna-López et al. (1986) and Páez-Osuna and Osuna-López (1987), are considered as natural levels in marine sediments.

Lead shows a relation with organic matter (Table 2). There is a stronger association with the area used for yachts and vessel anchorage (Fig. 2). The probable source could be some fuel spills from boat transit and there could have some effect from their antifouling bottom paint. Despite this influence, the critical levels are not exceeded.

There is a clear association of trace metal distribution with human activities. The high Mn and Fe, and sediments rich in organic matter correlations (Table 2) could be a response to low values of dissolved oxygen. The magnitude of desorption processes in sediments can be reduced when the sediments become hypoxic or anoxic. Then the Fe and Mn precipitate as oxides and are trapped in the sediments (Louma 1992).

Cadmium shows an unique distribution not related to organic matter content in sediments (Table 1 and 2). It is concentrated in sediments outside the coastal lagoon

Stations	Sand	Mud	Clay	Organic matter	
1	100			0.44	
2	100			0.50	
3	100			0.75	
4	100			1.13	
5	94.86	5.56		1.52	
6	93.81	6.19		0.57	
7	90.59	5.51	3.49	0.49	
8	48.41	43.67	7.92	3.47	
9	17.85	70.58	11.57	4.22	
10	93.50	6.50		0.51	
11	98.41	1.58		0.71	
12	98.69	1.30		0.56	

Table 1. Percentage of sand, mud, and clay at stations of Bahia and Ensenada de La Paz (Cruz-Orozco et al. 1989), and organic matter content (this work).

(Fig. 2) with values exceeding critical levels. There are some differences of sediment composition inside the coastal lagoon and the bay.

Whereas the coastal lagoon is composed of aluvial sediments, the sediment source of the bay is from sedimentary and volcanic rocks from the Monterrey formation. This structure has a mineral composition rich in phosphates with a purity greater than 28% (INEGI 1984), leading to industrial exploitation for fertilizers. This mining activity is done north of the bay, and cadmium is a common impurity of such an activity (Mann and Ritchie 1995).

High cadmium levels in this study may have their origin in the wind erosion of the Monterrey formation and mining activities. The cadmium-rich particles are transported southward by coastal currents and deposited in areas close to the great sand barrier named "El Mogote". Cheng (1976) found high levels of cadmium in *Hallobates* sp (sea-skaters) collected at Bahia Falsa, 10 km away at sampling station 1. Martin and Broenkow (1975) reported high concentrations of cadmium in plankton collected in the southern Gulf of California. According to these authors, the accumulation of cadmium in the trophic chain can be probably explained by the atmospheric route or by marine current transport. Páez-Osuna et al. (1986) working at Bahia de Mazatlán (continental side of the Gulf of California) did not show such anomalous levels of cadmium in sediments, but the same authors have found high cadmium levels in *Pennaeus californiensis* from the Pacific coast of Baja California



Figure 2. Metal levels at twelve stations from Bahia and Ensenada de La Paz, México.

	Cu	Zn	Mn	РЬ	Cd	Fe	О.М.
Cu P=	1.00						
Zn P=	0.79 (0.002)	1.00					
Mn P=	0.87 (0.000)	0.88 (0.000)	1.00				
Pb P=	0.52 (0.081)	0.41 (0.188)	0.24 (0.446)	1.00			
Cd P=	-0.25 (0.44)	-0.20 (0.541)	-0.49 (0.108)	0.18 (0.564)	1.00		
Fe P=	0.70 (0.012)	0.59 (0.043)	0.85 (0.000)	-0.06 (0.855)	-0.63 (0.027)	1.00	
M.O. <i>P</i> =	0.92 (0.000)	0.74 (0.006)	0.84 (0.001)	0.55 (0.061)	-0.21 (0.512)	0.60 (0.039)	1.00

Table 2.- Multiple correlations between trace metals and organic matter (O.M.) i sediment.

peninsula (Páez-Osuna and Mayen 1995).

Those findings and our conclusion indicate that main cadmium anomalies are around the southern tip of Baja California peninsula, and probably have their origin in the mineral composition of rocks and its transport by strong erosion activity.

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