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Cd, Cu, Pb, and Zn in Lagoonal Sediments from Mazatlán Harbor (SE Gulf of California): Bioavailability and Geochemical Fractioning

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Mazatlán harbor is located in the subtropical Pacific coast (SE Gulf of California), and it is situated in the lower and intermediate part of the coastal lagoon system known as "Estero de Urías". The lagoon has an area of *ca.* 16 Km^2 with an orientation axes semi-parallel to the coast. The climate of the region is tropical subhumid with a monthly average temperature ranging from 19.7°C in February to 28.0°C in August. Annual average precipitation is about 800 mm, occurring mainly during the rainy season (García, 1973). The lagoon system receives freshwater inputs from land runoff and untreated or partially treated industrial, shipping and domestic effluents from local point sources. These materials include particulate metals, which partially settle to the bottom in calm hydrodynamic conditions while the rest are transported downstream to the coastal adjacent waters. Metals from natural and anthropogenic sources can generate anomalous concentrations in the sediments mainly those from less energetic semienclosed areas as mangrove swamps. Several studies (e.g. Harbison, 1986; Tam and Yao, 1998) have shown that mangrove sediments have a high capacity to retain heavy metals from tidal water and stormwater runoff, and therefore often act as sinks for heavy metals.

The purpose of this study was to assess the sediment metal quality in the lagoon system and to know the potential risk of Cd, Cu, Pb and Zn on the biological communities that are associated to lagoon environments including mangrove forests. For a better estimation of anthropogenic input, an enrichment factor was calculated for each metal considering the earth's crust concentrations (Sinex and Wright, 1988; Grant and Middleton, 1990). In addition, the relative metal bioavailability was evaluated by sequential extraction (Tessier *et al.*, 1979); this technique allows a better estimation of the contaminant potential of these metals bounded to sediments.

MATERIALS AND METHODS

Eigtheen surface sediment samples were collected with a 0.3 m^2 Van Veen grab at five selected sites from the Lagoon system on November 1994 (Fig. 1). Representative sites of the lagoon system were selected considering the type of human activities, bathymetry and morphology. Site A is located in a small and shallow water body (6x10^5 m^3) connected with the main lagoon via a narrow channel, and characterized by the presence of mangroves (*Rhizophora mangle*) in the inner portion. This site receives inputs from land runoff during the rainy season (July-October) and untreated domestic effluents from 30% of Mazatlán population (4x10^3 m^3/day). Sites B and C are located in the main industrialized area of the port and are

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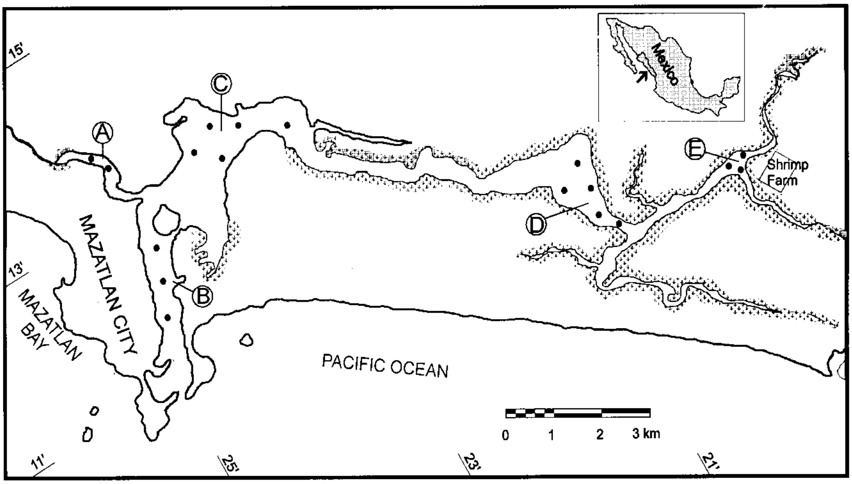

Fig. 1. Location of sampling sites in Mazatlán harbor (SE Gulf of California).

subject to regular effluents discharges from the harbor facilities, sandblasting of boats, food processing industry of fish and shrimp and a power plant cooling system. Sites D and E receive freshwater inputs from land runoff by a group of tidal channels bordered by mangroves (*R. mangle, Laguncularia racemosa and Avicennia germinans*). Additionally, site E receives effluents from semi-intensive shrimp farm (220 ha) while site D only acts as a filter system for freshwater runoff without any direct anthropogenic discharges. It is obvious that heavy metals and other contaminants could to be transported from the other sites to site D.

In the laboratory physical and chemical properties of sediment samples were determined by standard methods, including organic carbon (Loring and Rantala, 1992), carbonates (Rauret *et al.* 1987) and particle size (Folk, 1974). For bulk metal analysis, aliquots of sediments were digested with aqua regia inverted in a Teflon decomposition manifold system (Breder, 1982). The selective leaching technique proposed by Tessier *et al.* (1979) was used to extract the metals into five fractions operationally defined (Table 1). Metal concentrations of Cd, Cu, Pb and Zn in the bulk and geochemical fraction extracts were determined by flame atomic absorption spectrophotometry with a Shimadzu AA-630-12. The concentration of 'total' metals obtained in bulk extracts and the sum of the metals obtained in the sequential extraction fractions varied less than 10%. Accuracy for the bulk metal analysis was checked by determination of the metals in an intercalibration sample IAEA sediment standard material SD-N-1/2 (IAEA, 1985). Differences in average concentrations were evaluated by a one-way analysis of variance and a Tukey's multiple comparison test (Zar, 1984) using the GraphPad Prism (version 2.0) software. The enrichment factors, EFs, for each element were calculated from the formulae (Sinex and Wright, 1988, Grant and Middleton, 1990): $EF=(M/Al)_{sample}/(M/Al)_{crust.}$. The earth's crust values are from Martin and Maybeck (1979) and represent the average composition of the surficial rocks exposed to weathering.

RESULTS AND DISCUSSION

Table 2 shows the physical and chemical characteristics and the average bulk metal

Table 1. Selective extraction scheme (modified from Tessier *et al.*, 1979).

Fraction	Reagent	Extractant Volume (ml)	Experimental conditions
F1	1M $MgCl_2$ (pH 7)	15	Shaking time 1h at room temperature
F2	1M NaOAC (pH 5) adjusted with HOAc	20	Shaking time 5-6h at room temperature
F3	0.04M NH_2 OH-HCl 25% (v/v) HOAc, (pH2)	35	Intermitent shaking each 30 -45 min for 6 h at 96 ± 3°C
F4	0.02M HNO_3 + 10 ml 30% H_2O_2 pH 2 adjusted with HNO_3	16	Occasional agitation for 2 h at 85 ±2°C
	30% H_2O_2 pH 2 adjusted with HNO_3	6	Occasional agitation for 3 h at 85 ± 2°C
	3.2M NH_4OAc in 20% (v/v) HNO_3	10	Shaking time 30 min
F5	HNO_3-HCl 1:3 v/v (regia inverted solution)	15	Overnight at 130°C
Total	HNO_3-HCl 1:3 v/v (regia inverted solution)	15	Overnight at 130°C

Table 2. Physical and chemical characteristics of sediments.

Site	n	%$CaCO_3$	% C_{org}[a]	Mz[b]	Cd	Cu[c]	Pb[d]	Zn[c]
A	2	4.7 ±0.5	8.1 ±3.2	8.2 ±1.8	1.1 ±0.4	68.1 ±7.6	55.0 ±15.1	206 ±21.3
B	3	5.0 ±3.8	3.1 ±1.5	3.9 ±2.1	0.8 ±0.4	40.7 ±11.9	128 ±42.0	151 ±39.9
C	5	5.0 ±3.6	4.3 ±1.3	5.0 ±1.6	1.4 ±0.6	90.6 ±23.3	67.0 ±15.4	359 ±76.5
D	5	4.6 ±2.5	3.6 ±1.0	8.5 ±2.0	0.9 ±0.3	24.1 ±11.6	37.4 ±10.8	84.3 ±38.7a
E	3	3.8 ±1.2	4.3 ±1.6	8.5 ±1.7	1.0 ±0.2	35.7 ±11.7	58.6 ±15.2	133 ±41.3

Means differ significantly (P<0.05) among sites:[a]B, C, D and E< A; [b]B and C< A, D and E; [c]B, D and E< A and C; [d]A, D and E< B and C.

concentrations in the surface sediment samples from the sites investigated. Fine sediments covered most of the sites with considerable levels of organic carbon and characteristics of reducing environment (black color and H_2S odor). The organic carbon in sediments clearly reflected the anthropogenic activities described for each site: high concentration originated mainly by domestic effluents (8.1±2.2% for site A), food industry (4.3±1.8 % for site C) and shrimp pond discharges (4.3±1.3% for site E). In site D, where no any direct anthropogenic discharges are received, the organic carbon was 3.6±1.0%. Sites A, D and E with mangrove sediments had significantly (p<0.05) high concentrations of fine material (grain size parameter Mz≥8.2) retained by the prevalent hydrodynamic (relative calm) and the presence of the mangrove roots.

Values obtained for Cd ranged from 0.8 to 1.4 mg/kg, Cu 24.1 to 90.6 mg/kg, Pb 37.4 to 128 mg/kg, and Zn 84.3 to 359 mg/kg. Site C which is currently subject to regular discharges of effluents from the fish and shrimp processing industry, canning and fish flour production, and the power cooling plant, showed the highest levels of Cd, Cu and Zn. Site B had the highest level of Pb, this site receives inputs from the sports fleet (yachts), fishery boats, passenger liners and ferry-boats and from various companies dedicated to supply fuel for ships. For most of the metals, sediments from site D showed significantly lower levels than the rest of the sites; although not considered as strictly clean, this place could be considered as an area with background levels on a regional basis. The results of EF calculated for individual metals in each site are shown in Fig. 2. Cd and Pb concentrations showed values from 4.2 to 6.6 and from 2.1 to 8.7 times the background crust level, suggesting a moderate enrichment for all sites. Cu and Zn levels were from slightly to moderately enriched (EF 1.2 to 3.1) in sites A, B and C, while in sites D and E they show a depletion relative to the baseline value (EF<1). Sediments from sites A, B and C are characterized by receiving anthropogenic influence and appear as "hot spots", with a significantly elevated EF for all metals studied, particularly Cd and Pb.

In order to examine the potential impact of metals on the biota, a sequential extraction procedure was applied to sediments from the five selected sites. Cd was mainly associated (60-100%) to the exchangeable fraction in the sediments from all sites (Fig. 2). These results are similar to other woks carried out previously in aquatic

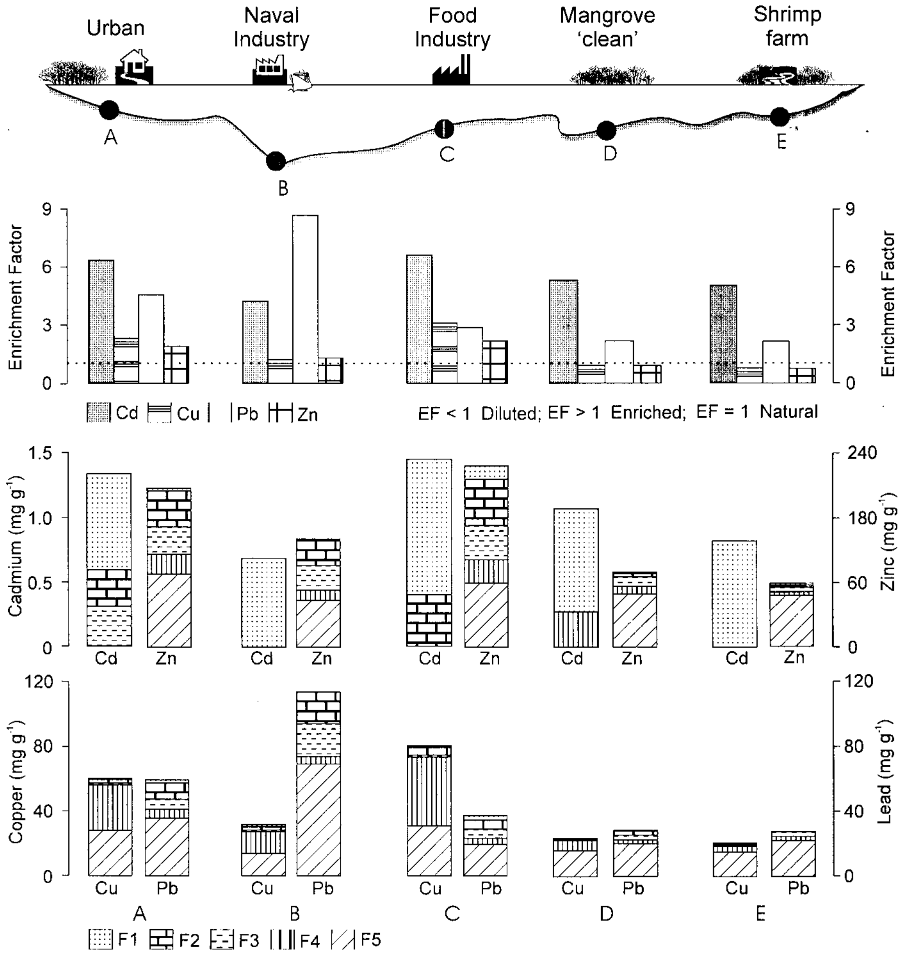

Fig. 2. Enrichment factors of Cd, Cu, Pb and Zn and their distribution in different geochemical fractions for all sampling sites in Mazatlán Harbor.

sediments (e.g. López-Sanchez *et al.* 1996; Ramos *et al.* 1999). However, exchangeable Cd is common in oxidized sediments (Kersten and Förstner, 1987) and its presence in fine sediments could indicate an oxidation of these sediments during sampling and extraction (Rule and Alden, 1992). In this study, no special attempts were made to purge the atmosphere above the collected sediments dominated by fine material partially anaerobic. Cu was bounded mostly in the residual or lithogenic (F5) fraction in mangrove sediments (>80%) and the rest was associated to F4 (15-18%). Cu associated to F4 was probably bounded to organic compounds as humic complexes (i.e. Cu-humate) rich in mangrove sediments, which reduce the total levels due to a migration from sediment phase to water (Salomons and Förstner, 1984) explaining the EF<1 in sites D and E. In sediments affected by anthropogenic activities (sites B and C), Cu was mainly associated to the organic fraction (40-60%) and second category F5 residual contained about 30-40% of the total.

Pb distribution in the different geochemical fractions was similar to that of poor or enriched mangrove sediments. The residual fraction contributed with a high percentage (70-90%) of Pb total and the rest was distributed in F2 and F4 confirming the natural source of this metal in the sites D and E. Significant amounts of Pb were extracted in F2 (12-20%), F3 (12-15%) and in a lesser extent in F4 (<10%) in sites where the bulk concentration was elevated. This suggests that anthropogenic Pb discharged in sites A and B, is immobilized in sediments by fixing reactions involving carbonates, oxide minerals and organic matter. Finally, a high portion of Zn (70-80%) was found in the residual fraction (F5) in sediments from sites D and E, with little contribution of F3 (5%) and F4 (5%). However, mangrove sediments from site A that are influenced by domestic effluents showed a significant percentage (about 40%) associated with non-lithogenic fractions (F2, F3 and F4). At sites B and C, the inert fraction (F5) that corresponds to detrital or lattice-bound Zn contained only 30% of total Zn, while the carbonated, oxide and organic matter fractions contributed with 30%, 25% and 10-15%, respectively.

Bioavailability is a function of particular geochemical fractions where metals are associated and may be influenced by physiological factors of organisms such as age, sexual condition, and diet (Tessier and Campbell, 1987; Phillips and Rainbow, 1993). Theoretically fractions F1, F2 and F4 are recognized as the major reservoirs for biologically available metals under favorable conditions and the amount of associated metal constitute a greater danger than the total amount (Kersten and Förstner, 1991). In shallow lagoonal and mangrove sediments with low redox potential, as Estero de Urías, the metal associated to F4 is not directly bioavailable because the sulfide fraction is included. However, metals in the sulfide fraction are converted to more soluble and available forms upon aeration and partial oxidation of the sediments (Kersten and Förstner, 1987), which could occur under natural conditions such as storms and very low tides.

Table 3 shows the amount of potentially bioavailable Cd, Cu, Pb and Zn in selected sites from Mazatlán harbor. The bulk of Cd found was bioavailable in sediments from most of the studied sites. Mangrove sediments in site D (presumably clean) and E (with shrimp pond effluents) showed <25% of the Cu, Pb and Zn total. Site A showed about 30% of bioavailable Cu, Pb and Zn (21.1, 17.5 and 72.2 $\mu g\ g^{-1}$, respectively). About 60% of Cu, 40% of Pb and 30% of the total of Zn total in sediments from sites B and C were potentially available to organisms. Results for the same metals in the soft tissue of barnacles collected in sites B, C and D in the 1995-1996 period in Mazatlán

Table 3. BSAF values in barnacles* from selected sites respect to average metal bioavailable fraction (C_{BF}) in sediments. Levels in µg g^{-1}.

Metal		Site B	Site C	Site D
Cadmium	C_{BF}	0.7±0.4	1.4±0.6	1.1±0.3
	$C_{barnacle}$	4.1±3.9	4.4±3.6	1.8±0.3^{a}
	BSAF	6	3	2
Copper	C_{BF}	16.7±6.9	48.1±15.3	7.5±3.2^{a}
	$C_{barnacle}$	148±220	124±89	26.1±3.6^{a}
	BSAF	9	3	3
Lead	C_{BF}	24.1±11.3	12.2±1.2	5.1±0.9^{a}
	$C_{barnacle}$	14.8±23.5	12.4±5.2	15.5±3.0
	BSAF	1.1	1.0	3
Zinc	C_{BF}	45.1±15.2	102.5±23.5	15.4±8.5^{a}
	$C_{barnacle}$	5589±3440	30030±46040	1676±225^{a}
	BSAF	124	293	109

* Data from Ruelas-Inzunza and Páez-Osuna (1998). Means differ significantly ($P<0.05$) among sites: ^{a}D< B and C;

harbor (Ruelas-Inzunza and Páez-Osuna, 1998) could be discussed in this context (Table 3). For instance Cd concentrations registered in barnacles from sites B (4.1±3.9 µg/g) and C (4.4±3.6 µg/g) were two times more elevated than those from site D (1.8±0.3 µg/g). Similarly, Cu from barnacles collected in sites B and C was 6-8 times higher than those from site D. Zn from sites B and C was 3-6 times higher than that from site D. In the case of Pb, the highest level was detected in barnacles from site B; the value was from two to three times more concentrated than in sites C and site D. These results reveal a similar tendency to results obtained with sediments in either bulk levels and bioavailable fractions.

A bioconcentration factor (BSAF), defined as the ratio of the metal concentration in barnacles used as biomonitors ($C_{barnacle}$) to the bioavailable metal in the sediments (C_{BF}), was calculated in anthropogenically affected sites (B and C) and compared with a reference site (D) (Table 3). Results indicated that BSAF values for Cd and Cu were similar in sites C and D and significantly higher in site B, while site C had the highest values for Zn ($p>0.05$). The bioconcentration of metals in function to the biologically available amount was in the following order: Zn>>Cu>Cd>Pb. This reflects a high storing of Zn in the soft tissue of barnacles in comparison with sediments and much lesser extent of Cu and Cd. However, BSAF values from Pb of 1 to 3 revealed that the capacity of barnacles for bioaccumulation of this metal is more limited in relation to the bioavailable levels in sediments.

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