

## **Anomalous Levels of Heavy Metals in Sediments from Guaymas Bay, Mexico**

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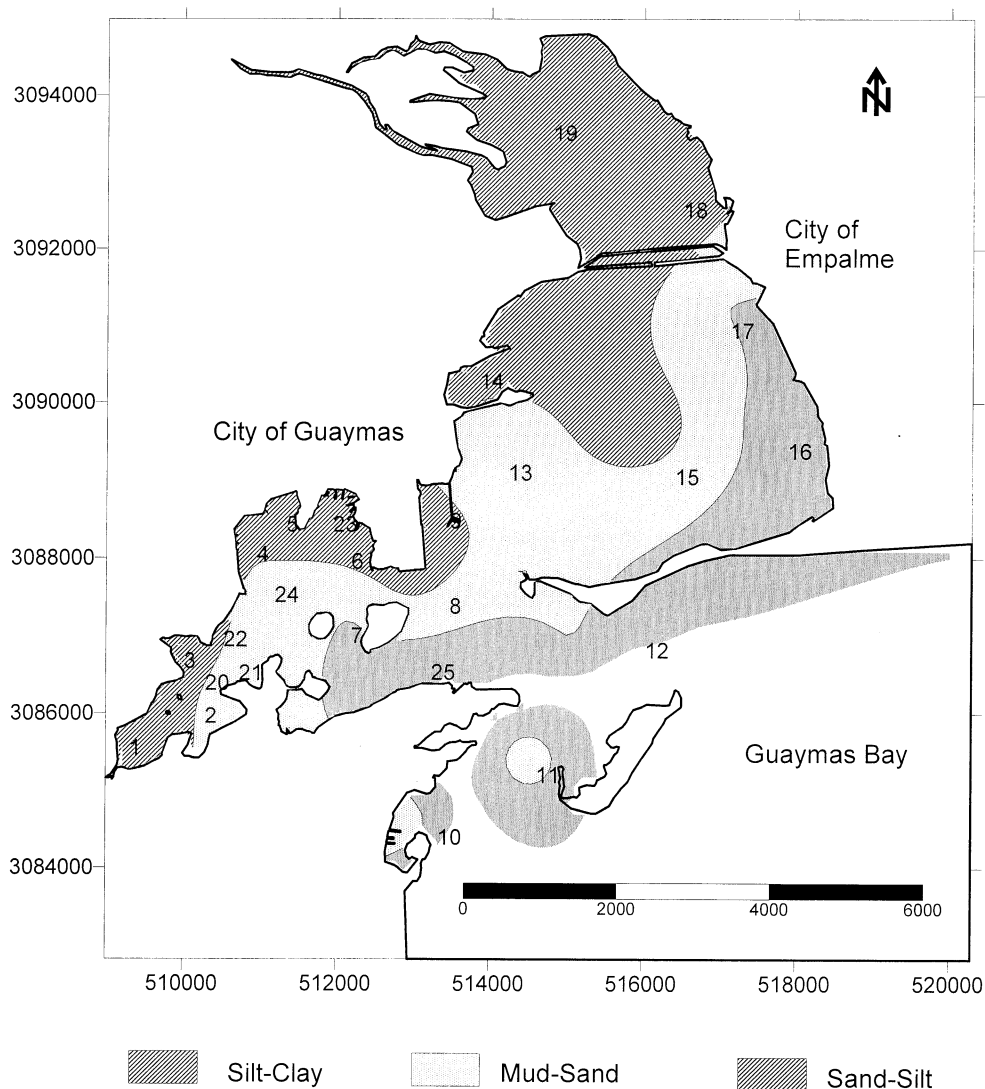
Guaymas Bay (27°55'N, 110°52'W) is located in the state of Sonora on the eastern shores of the Gulf of California, México. The harbor contains many urban activities. There are about 1000 types of boats and 63 effluents from industrial and municipal wastewater supplying pollutants into the marine environment (Arreola-Lizarraga et al. 2001). Dock activities that cause accidental contamination of the bay include copper, fuel, pesticides, and industrial additives. There are 25 fish processing plants along the bay, which over many years, discharged wastewater with contaminants that contribute to eutrophication of the marine sediment and bioavailability of metals (Méndez et al. 2002). This study evaluated the degree of contamination by heavy metals in marine sediments in Guaymas Bay using a geo-accumulation index.

### **MATERIALS AND METHODS**

Sediment samples at 25 stations were obtained with a Van Veen grab (Figure 1), using a GPS Magellan 315 for locating stations, which were chosen for their proximity to potential pollution sources. The samples taken were stored in polyethylene bottles previously decontaminated with nitric acid and kept frozen until chemical analysis. Grain size distribution was evaluated using calibrated sieves (Folk 1974).

For heavy metal analysis, the sample fraction smaller than 65µm was used. Total digestion was carried out in Teflon beakers using nitric and hydrofluoric acids (proportion 3:1) (Van Loon 1985). An atomic spectrophotometer (BUCK Scientific #200A) using flame air/acetylene was used to determine the amount of copper, zinc, nickel, cadmium, manganese and lead present. Metal recovery was between 95 and 102%. Validation of the analytical procedure was determined with samples of marine sediments from the National Research Council of Canada and reference (BCSS-1, MESS-2, and PACS-1), which are from the Gulf of St. Lawrence, Beaufort Sea, and Esquimalt Bay, B.C., respectively.

These standards were also used to evaluate the level of contamination of the sediment samples. BCSS-1 and MESS-2 are sediments with low and moderate pollution, while PACS-1, is considered as polluted area. A second approach for



**Figure 1.** Location of sampling stations in Guaymas Bay, Sonora, México and texture of sediments (UTM grid coordinates used).

evaluating the level of heavy metal contamination is the geo-accumulation index (Müller 1979), which is:

$$I_{geo} = \log ([M]_i / (1.5([M]_r))$$

where,  $[M]_i$  and  $[M]_r$  are concentrations of heavy metals in the area studied and the mean of the element in the terrestrial matrix.

## RESULTS AND DISCUSSION

Levels of copper, manganese, zinc, lead, nickel, and cadmium are shown in Table 1.

The highest concentrations of copper were 295, 339, and 275  $\mu\text{g/g}$  at stations 6, 8, and 9, respectively (Figure 1). Station 8, is in front of the main dock in which several types of materials as copper, grain, and various chemical compounds are unloaded. The BCSS-1 and MESS-2 standards have copper concentrations between 18.5 and 39.3  $\mu\text{g/g}$ , lower than the concentrations in Guaymas Bay. The PACS-1 standard has  $452 \pm 16$   $\mu\text{g/g}$  copper, higher than any sample in this study.

According to the index of geo-accumulation ( $I_{\text{geo}}$ ; Müller 1979), only the area surrounding station 8 ( $I_{\text{geo}} = 2.03$ ) would be classified as moderately to highly polluted with copper. Stations 4, 5, 6, 9, 21, and 25, with  $I_{\text{geo}}$  between 1.08 and 1.83, have moderate pollution with copper.

Copper is associated with fine sediment particles and organic matter (Green-Ruiz 2000). High levels of copper are associated with dumping of municipal wastewater, hydrocarbons, and boat repairs (Leoni and Sartori 1996; Shriadah 1998; Gibbs and Guerra 1997). The highest copper concentrations were found in silt and clay sediments.

The highest concentrations of zinc were recorded at stations 5, 10, and 24 (Figure 1), with 476, 359 and 366  $\mu\text{g/g}$ , respectively. Remaining stations show zinc concentrations close at those reported for MESS-2 and BCSS-1 ( $172 \pm 16$  and  $119 \pm 12$   $\mu\text{g/g}$ ). The concentrations reported for PACS-1 is  $824 \pm 22$   $\mu\text{g/g}$ , almost double the highest concentrations obtained in this study. Stations 5 and 24 are near dumping sites of municipal wastewater and station 10 is an important area of industrial activities (Green 2000; Ruelas-Inzunza 1998).

Only station 5 ( $I_{\text{geo}} = 2.18$ ) is classified as an area with moderate to strong zinc pollution, and stations 4, 6, 10, and 24 are classified as moderately polluted with zinc ( $I_{\text{geo}}$  of 1.05 to 1.80). No relationship was found between particle size and concentration of zinc.

The highest concentration of manganese was recorded at station 9 (247  $\mu\text{g/g}$ ). All other stations recorded manganese typical of sediments with low to moderate levels of pollution, according the MESS-2 and BCSS-1 standard, (365 and 229  $\mu\text{g/g}$  zinc, respectively). None station is considered by  $I_{\text{geo}}$  as being contaminated with manganese.

The highest concentration of nickel (58.5  $\mu\text{g/g}$ ) was recorded at station 14 near the dock serving CFE and PEMEX (Electricity Federal Commission and Mexican Petroleum). Remaining stations recorded similar or lower concentrations of nickel than the MESS-2, BCSS-1, and PACS-1 standards ( $49.3 \pm 1.8$ ,  $55.3 \pm 3.6$ , and  $44.1 \pm 2.0$   $\mu\text{g/g}$ , respectively). With the low concentrations in PACS-1, it was now

**Table 1.** Concentrations of copper, manganese, zinc, lead, nickel, and cadmium ( $\mu\text{g/g}$  dry weight) in sediments from Guaymas Bay, Sonora.

Station	Cu	Mn	Zn	Pb	Ni	Cd
1	18.9	81.2	54.7	25.7	4.9	0.4
2	129	120	192	49.9	11	0.3
3	69.8	92.8	126	48.2	7.0	1.8
4	175	120	219	14.5	14.9	1.8
5	235	130	477	81.0	28.5	4.8
6	295	146	229	46.3	26.9	4.9
7	77.6	115	109	36.6	15.4	0.60
8	339	177	135	36.3	26.5	1.8
9	275	247	111	30.8	28.4	0.70
10	90.8	151	360	56.5	32.3	5.1
11	45.9	144	35.5	23.7	17.0	2.5
12	4.7	45.7	19.7	6.4	10.2	1.6
13	107	179	87	26.6	31.0	3.9
14	78.0	135	72.7	26.3	58.5	2.9
15	41.8	192	59.9	20.3	28.1	2.5
16	5.1	12.2	3.4	11.4	11.3	1.2
17	32.9	203	40.2	25.1	26.7	2.8
18	25.7	156	32.9	27.2	24.6	2.3
19	25.9	138	37.8	20.3	23.2	2.2
20	93.6	134	202	47.4	16.3	0.88
21	219.6	95.8	206	70.0	18.1	0.87
22	124	114	195	59.8	17.8	ND
23	76.7	183	100	29.9	14.9	0.92
24	138	177	367	49.9	25.4	4.1
25	183	104	199	50.2	17.6	1.18

ND= Not Detected

used for comparison with our results. No station was considered as contaminated with nickel using the  $I_{\text{geo}}$ .

The highest concentration of lead ( $81 \mu\text{g/g}$ ) was recorded at station 5, close to the dumping out of municipal wastewater. This value is higher than the highest concentration reported by Hosch (1996), which was  $69.19 \mu\text{g/g}$ . The PACS-1 standard ( $404 \pm 20 \mu\text{g/g}$ ) was almost five times higher than the highest concentration in Guaymas Bay. The remaining stations are in agreement with levels reported by Hosch (1996), but are higher than the concentrations of lead reported in the MESS-2 and BCSS1 standards ( $21.9 \pm 1.2$  and  $22.7 \pm 3.4 \mu\text{g/g}$ , respectively).

The three stations with the highest concentrations of zinc are the same ones with the highest concentrations of lead. A significant correlation ( $r = 0.81$ ;  $P < 0.001$ ) was found between these elements.

According to the  $I_{geo}$ , station 5 is moderately to strongly contaminated by lead ( $I_{geo}=2.10$ ). Stations 2, 3, 6, 10, 20, 21, 22, 24, and 25 are moderately polluted by lead ( $I_{geo}$  = ranging from 1.33 to 1.90).

The highest concentration of cadmium ( $5.1 \mu\text{g/g}$ ) was recorded at station 10, near the canning factories. This concentration is higher than the PACS-1 standard ( $2.38 \pm 0.20 \mu\text{g/g}$ ). Stations 5, 6, 13, 14, and 24 also have higher concentrations than PACS-1. The values reported by MESS-2 and BCSS-1 ( $0.24 \pm 0.01$  and  $0.25 \pm 0.04 \mu\text{g/g}$ , respectively) are 10 times lower than the highest level of cadmium measured in this study. Hosch (1996) did not analyze sediments near the canning factories and reported a site near the main dock having  $2.36 \mu\text{g/g}$ . This area (station 6) is the second most polluted station, after station 5. Both stations have the twice of the levels reported by Hosch (1996) (Table 1). Most of the high concentrations of cadmium were found in areas with the fine particle size.

Stations 5, 6, and 10, with an  $I_{geo} = 4, 4.04$ , and  $4.09$ , respectively, are very strongly polluted by cadmium. Stations 11, 13, 14, 15, and 17, with  $I_{geo}$  = ranging from  $3.04$  to  $3.76$ , are strongly to very strongly polluted by cadmium. Stations 3, 4, 8, 12, 16, 18, and 19, with  $I_{geo}$  ranging from  $2.37$  to  $2.96$ , moderately to strongly polluted, and stations 9, 20, 23, and 25 with  $I_{geo}$  ranging from  $1.15$  to  $1.97$  are moderately polluted by cadmium. Further studies are required to evaluate the origin of this element. Several studies have reported elevated levels of cadmium in sediments (Méndez et al. 1998), mussels (Méndez et al. 2002) plankton (Martín and Broenkow 1975), and insects (Cheng et al. 1976) collected along the Baja California Peninsula.

According to the Geo-accumulation Index, the level of pollution with copper, zinc, and lead in some areas of Guaymas Bay are from moderate to high, while the level of cadmium in the bay is very high.

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## REFERENCES

- Arreola-Lizárraga JA, Padilla-Arredondo G, Burrolla-Sánchez MS, Urias-Laborín D, Dorado-Villanueva F, Hernández-Ibarra A, López-Tapia MR, Méndez-Rodríguez LC, y Acosta B (2001) Diagnóstico de la contaminación marina de la Bahía de Guaymas, Sonora y proximidades. VIII Congreso de la asociación de investigadores del Mar de Cortés A.C. y al II Simposium Internacional sobre el mar de Cortés. Mayo 29 - Junio 1 del 2001. Ensenada, B.C. México.
- Cheng L, Alexander GV, Franco PJ (1976) Cadmium and other metals in sea-skaters. *Water Air Soil Pollut* 6:33-38

- Folk R.L (1974) Petrology of sedimentary rocks, Hemphill, Austin, Texas.
- Gibbs RJ, Guerra C (1997) Metals of the bottom muds in Belice City harbor, Belice. *Environ Pollut* 98:135-138
- Green-Ruiz-Ruiz CR (2000) Geoquímica de metales pesados y mineralogía de la fracción arcillosa de los sedimentos de cuatro puertos del Golfo de California. Doctoral Thesis, UNAM. Mazatlán, Sinaloa. 329 p.
- Hosch G (1996) Prospective mapping of total cadmium, copper, zinc and lead contamination in water, sediment and clams (*Chione gnodia*) of Guaymas Bay, Sonora, México. Masters Thesis. University of Hull, England
- Leoni L, Sartori F (1996) Heavy metals and arsenic in sediments from the continental shelf of the northern Tyrrhenia/Eastern Ligurian seas. *Mar Environ Research* 41(1):73-98
- Martin JH, Broenkow WW (1975) Cadmium in plankton: Elevated concentrations off Baja California. *Science* 190:884-885
- Méndez L, Acosta B, Alvarez-Castañeda ST, Lechuga-Devéze CH (1998) Trace metal distribution along the southern coast of Bahía de La Paz (Gulf of California), México. *Bull Environ Contam Toxicol* 61:616-620.
- Méndez L, Salas-Flores, LM, Arreola-Lizarraga A, Alvarez-Castañeda ST, Acosta B (2002) Heavy Metals in Clams from Guaymas Bay, México. *Bull Environ Contam Toxicol* 68:217-223
- Müller G (1979) Schwermetalle in den sedimenten des Rheins-Veränderungen seit 1971. *Umschau* 79:778-783.
- Ruelas-Inzunza J (1998) Balanos (*Balanus eburneus*, *Fistobalanus dentivarians* y *Megabalanus coccopoma*) como bioindicadores de la contaminación por metales en las aguas del puerto de Mazatlán, Sinaloa. Tesis de Maestría en Ciencias del Mar. Universidad Nacional Autónoma de México. 121 pp.
- Shriadah MA (1998) Metals pollution in marine sediments of the United Arab Emirates creeks along the Arabian Gulf shoreline. *Bull Environ Contam Toxicol* 60:417-424.
- Van Loon J (1985) Selected methods of trace metal analysis: biological and environmental samples. John Wiley & Sons, New York