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Heavy Metals in Clams from Guaymas Bay, Mexico

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The Guaymas Bay, located at the oriental coast in the Gulf of California, México is an important harbor with plenty of urban activity. In the bay, about 1000 of all different types of boats, and 63 effluents from industrial and municipal wastewater, input several types of pollutants in the marine environment (Arreola-Lizarraga et al 2001). Inside the bay, activities of load and unload cause accidental loss of substances and materials (copper, fuel, pesticides, additives) with high contents of heavy metals (Cu, Pb, Ni, Cd, Hg, and Mn) and substances that could modify the chemical presentation of the elements present in the marine environment and in consequence their toxicity (sulfuric acid, phenol, cresol). There are 25 fishery processing industries in the bay which, over many years, discharged wastewater with different levels and types of contaminants that also contribute with the eutrophication of the marine sediment and indeed the bioavailability of the metals. In this environment there are several clam beds that are used as food by the people who live around the bay. Mussels, oysters and several species of clams have been proposed by several studies as quantitative biological indicators of heavy metal pollution in the marine environment (Gutiérrez-Galindo et al., 1999; Shulkin and Kavun 1995). The aim of this study is to evaluate the grade of contamination of heavy metals in the Bay of Guaymas to know if these clams beds are suitable for human consumption.

MATERIALS AND METHODS

Six areas were sampled in the Guaymas Bay. Eighty-four clams were hand collected in a depth between 1 and 5 m with the help of a diver from the Secretaría de Marina. The stations are shown in Figure 1. The species collected were *Chione gnidia* and *Laevicardium elatum*. *C. gnidia* was collected in all the stations while *L. elatum* was only found in one station (station 4'). In station 5 and 5′ the same specie of clams were collected but of a different size. The mean and standard deviation of the biometric and weight measurements of the animals in each station are shown in Table 1. Each clam was weighed and dried in an oven at 70 °C to constant weight for 36 hours and then ground. Individual clams were then digested in acid-washed test tubes with a ratio of 1:5 of concentrated perchloric and nitric acids and slowly boiled to dryness on a hot plate (Van Loon 1985). The cooled, dried sample was redissolved in 1mL of concentrated HCl and 24 mL of

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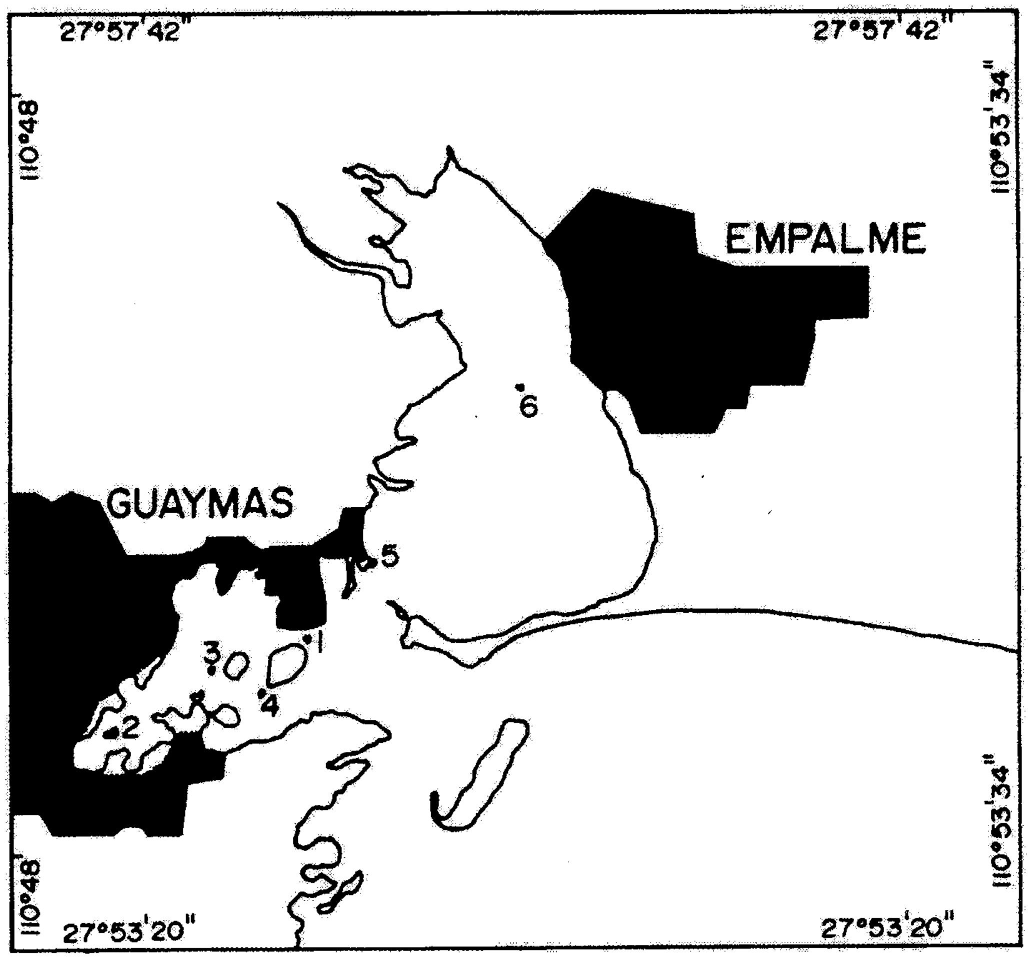

Figure 1. Location of sampling stations in Guaymas Bay.

deionized water in a volumetric flask. The samples were analyzed by atomic absorption (BUCK Scientific, Inc., East Norwalk, Connecticut, Model 200) using an air-acetylene flame. The certified standard reference material DORM-1 (National Research Council of Canada, Ottawa) was used to check the accuracy, and the analytical values were within the range of certified values. All the recoveries of the metals studied were over 95%. All the concentrations of the metals are expressed in $\mu g.g^{-1}$ in dry weight.

The shells of *C. gnidia* do not have an homogeneous growing, therefore with the purpose to make comparisons between specimens of different proportions, an index was developed. We selected four easy measurement features and devised a size index based on summing the length, height and width, divided between the dry weight of the specimen, without shell. This computation was made for each specimen.

The index was used for correlations between the specimens and metal levels. ANOVA analysis was made between size of the clams in the bay and spatial distribution, and a multiple regression between size and the amount of the different heavy metals. All the statistical methods were done using the software STATISTICA, version 5.0.

RESULTS AND DISCUSSION

The relation of the biometric characteristics for *C. gnidia* and *L. elatum*, as well as the concentrations of trace metals for both species are given in Tables 2 and 3.

According to the factor obtained, only the clams from stations 5' and 6 were significantly smaller (F= 57.13, p< 0.000) than the clams collected in the remaining stations. In the calculation of the factor, clams from station 4′ were not included because they are a different specie. The humidity percentage of the clams was 87.5±1.7.

Copper concentrations in the clams were from 4.78 ± 0.97 to 23.04 ± 2.93 μg/g. In station 4, both species had the lowest concentration of copper than all the other stations studied. This station is in the mouth of the bay, an area with a high interchange of water. According to Gutiérrez-Galindo et al. (1999) in mussels (*Modiolus capax*), concentrations lower than 40 μg/g are relatively low. They also found that the accumulation of copper in the organisms is independent of the size, being affected mainly by environmental variations.

The highest significant concentrations of copper were found in front of the city of Guaymas (station 3) and at the dock of CFE-PEMEX (Electricity Federal Commission and Mexican Petroleum) (station 5′) (Figure 1). However, the levels recorded in all the stations are in the range reported previously by several authors as normal for environments with no problems of pollution for this element (Nausen 1983). Páez-Osuna et al (1993) reported concentrations of copper from 8.4μg/g in *Chione californiensis* to 82.9μg/g in *Chione subrugosa*. In terms of human health hazard, humans could tolerate, for prolonged periods, a dietary levels intake of copper as high as 100 mg, although that is 10 to 15 times higher than normal intake (Venugopal and Luckey 1978; Hosch, 1996).

Zinc levels were from 92.4 ± 17.8 to 246 ± 128μg/g (Table 3). No significant differences were found between the different stations or the different sizes of clams in the levels of zinc. Páez-Osuna et al (1991) found concentrations of 118 μg/g in *Chione* sp. collected in the Lavachiste lagoon that is considered suitable for oyster culture. Gutiérrez-Galindo et al. (1999) found no relation between size and zinc levels in mussels. Hosch (1996) found in clams *C. gnidia* collected in the bay of Guaymas, concentrations of zinc from 70.29 ± 6.49 to 180.56 ± 4.25 μg/g and concluded that if someone consumed one dozen clams with an average of 96 μg/g, there would be no risk to human health.

The levels of iron were from 85.6 ± 28.2 to 397 ± 154 μg/g (Table 3). All the levels are in the range reported previously by other authors. Páez-Osuna et al (1993) reported mean values of 352 and 319 μg/g in *C. californiensis* collected in

Table 1. Biometric measurements, dry weight, and size index of the clams collected in the Guaymas Bay.

Station	Length (cm)	Tall (cm)	Wide (cm)	Dry weight (g)	Size Index*
1 (n = 7)	8.94 ± 0.52	8.10 ± 0.59	5.70 ± 0.35	3.85 ± 0.83	6.08 ± 1.00^{a}
2 (n =12)	8.64 ± 0.80	7.71 ± 0.63	5.24 ± 0.62	4.63 ± 1.21	4.94 ± 1.22^{a}
3 (n = 8)	7.72 ± 0.61	6.60 ± 0.49	4.67 ± 0.31	2.93 ± 1.11	7.13 ± 1.99^{a}
4 (n = 2)	8.15 ± 0.21	7.60 ± 0.28	5.20 ± 0.42	4.89 ± 1.43	4.44 ± 1.11^{a}
4'(n =11)	9.66 ± 0.39	10.28 ± 0.52	7.59 ± 0.44	12.37 ± 1.72	
5 (n =10)	8.09 ± 0.55	7.21 ± 0.71	4.89 ± 0.57	3.63 ± 0.99	5.84 ± 1.25^{a}
5'(n =13)	5.77 ± 0.29	5.05 ± 0.25	3.65 ± 0.30	0.69 ± 0.15	21.73±4.55^{b}
6 (n =21)	4.13 ± 0.53	3.67 ± 0.55	2.35 ± 0.35	0.39 ± 0.15	28.96±7.83^{c}

*Means in a row followed by different letters indicate that they were significantly ($p<0.05$) different.

Table 2. Mean and standard deviation of Cd, Pb, Mn, Ni, Cu, Fe y Zn levels in clams from the Guaymas Bay, Sonora.

Station	Cu	Zn	Fe	Mn
1	15.26 ± 3.40^{a}	128 ± 23.02^{a}	101 ± 37.29^{a}	5.39 ± 1.25^{a}
2	17.30 ± 3.76^{a}	246 ± 128.0^{b}	85.6 ± 28.23^{a}	8.78 ± 2.63^{a}
3	23.04 ± 2.93^{b}	144 ± 61.49^{a}	91.8 ± 16.33^{a}	6.20 ± 1.27^{a}
4	8.86 ± 1.83^{c}	105 ± 13.12^{a}	160 ± 3.69^{a}	1.59 ± 0.02^{a}
4'	4.78 ± 0.97^{c}	111 ± 17.00^{a}	270 ± 76.03^{b}	5.06 ± 1.46^{a}
5	16.33 ± 2.42^{a}	112 ± 19.72^{a}	110 ± 18.17^{a}	7.71 ± 7.74^{a}
5'	20.93 ± 5.43^{b}	92.4 ± 17.79^{a}	280 ± 88.34^{b}	26.9 ± 26.20^{b}
6	14.80 ± 4.44^{a}	148 ± 29.91^{a}	397 ± 154.5^{c}	20.0 ± 10.3^{b}

Station	Pb	Cd	Ni
1	1.13 ± 0.44^{ab}	0.78 ± 0.31^{ab}	4.68 ± 1.16^{a}
2	1.24 ± 0.48^{ab}	0.21 ± 0.26^{b}	5.17 ± 1.25^{a}
3	0.51 ± 0.30^{b}	0.31 ± 0.34^{b}	4.51 ± 1.95^{a}
4	2.68 ± 0.24^{a}	1.67 ± 0.20^{a}	5.41 ± 0.70^{a}
4'	1.73 ± 0.71^{ab}	0.75 ± 0.69^{ab}	7.44 ± 1.21^{a}
5	1.88 ± 0.90^{ab}	1.28 ± 0.56^{ab}	6.02 ± 1.23^{a}
5'	2.41 ± 0.84^{a}	1.01 ± 0.67^{ab}	5.91 ± 2.06^{a}
6	4.03 ± 2.04^{c}	1.08 ± 0.94^{ab}	23.65 ± 8.63^{b}

Means in a row followed by different letters indicate that they were significantly ($p<0.05$) different.

sites with typical marine conditions. They also reported means of 518 and 1061µg/g of iron in clams *C. subrugosa* collected in an environment with moderate contamination from industrial and agricultural effluents. The content of iron in the clams (Table 2) was affected more by the size and the specie than for the site in which they were collected ($r = -0.81$, $p < 0.001$). According to Nir et al (1990) the uptake of iron in oysters decreases with age.

The levels of manganese were from 1.59 ± 0.02 to 26.9 ± 26.20µg/g. The highest concentrations of manganese were recorded in station 5' (Table 3). The concentration of manganese was negatively correlated with size ($r = -0.57$, $p< 0.001$). This is in agreement with several studies made using oysters and bivalves (Lytle and Lytle 1990; Gutiérrez-Galindo et al. 1999; Páez-Osuna et al. 1991, 1995) although most of these studies also mentioned that the sampling site has a strong influence due to the sediment composition and perturbations by anthropogenic activities and upwelled waters (Gutiérrez-Galindo et al 1999; Lytle and Lytle 1990) This element is not found in the list for FAO (Nausen 1983).

The highest value of manganese recorded for Páez-Osuna et al (1991) in the Navachiste lagoon, México was 23.2 µg/g, in *Chione* sp. In other species of mussels, concentrations of manganese from 3.5µg/g in *Mytilus edulis* to 31µg/g in *Mytella strigata* have been reported (Páez-Osuna et al 1988). According to these studies these values are from areas with no environmental problems. Considering that this lagoon is suitable for the culture of these organisms, the values obtained in the present study could be considered normal.

The levels of lead recorded were from 0.51 ± 0.29 to 4.03 ± 2.04 µg/g. The highest levels were from station 6. The highest mean with error standard of cadmium concentration recorded by Hosch (1996) was 1.04 ± 0.10 µg/g. According to FAO (Nausen 1983) the highest limit of lead considered safe for the ingestion of mollusks is 10 µg/g, which was not found in any organism. The size of clams was negatively correlated with the concentration of lead ($r = -0.72$, $p< 0.001$). This is in agreement with Pip (1995) who explained that younger animals may accumulate metal in higher concentrations than older organisms, although Bourgoin (1990) noted that a correlation between age and size may not necessarily exist in bivalves.

The levels of cadmium in clams were from 0.21 ± 0.26 to 1.28 ± 0.559 µg/g. The highest levels of cadmium were found in stations 4 and 5. Previously Hosch (1996) reported a mean with an error standard of 1.50 ± 0.075 µg/g. The levels of cadmium in stations 2 and 3 were significantly lower than the levels found in the clams from station 4 but not in 4', although *C. gnidia* and *L. elatum* did not have significant differences between them in their levels of cadmium. No correlations were found between the size of the organisms and their cadmium concentration. This is in agreement to Giusti et al (1999) who found no trends between body size and cadmium in soft tissue of *Mytulis edulis*. According to FAO (Nausen 1983) the limit of cadmium in bivalves for human ingestion is 2 µg/g. Several clams were over this value in stations 4, 5, 5' and 6. We are in agreement with Hosch (1996) who reported that high levels of cadmium reflected a serious problem of pollution in the bay that could affect the marine environment and humans.

The levels of nickel found in the clams were from 4.68 ± 1.16 to 23.65 ± 8.63μg/g. The lowest value recorded was 1.83μg/g while the highest was 46.56 μg/g. In station 6, the highest values of nickel were recorded. Although these clams together with those collected in station 5' show the smallest size, statistically their contents of nickel were different. (Table 2). Although a negative relation between the size and nickel content in soft tissue of the clams was found ($r = -0.75$, $p < 0.001$), it is possible that the high levels of nickel found in the smaller clams are more associate with the transport of this element from the area in which there are activities of load and unload of petrochemical substances to this site. Giusti et al (1999) also found levels as high as 42.9μg/g of nickel in small mussels collected in a site close to petrochemical plants. Station 6 has a mean that is almost three times higher than that obtained in other stations and 3 times higher than the highest value reported by Páez-Osuna et al (1988) which is 8.1 μg/g. This could indicate a pollution problem of this metal in this area of the bay. Also, high concentrations of nickel could be from the discharges at the fiscal dock and the dock of PEMEX and the thermoelectric power station, together with some spills from shrimp boats. According to FDA (1993), 1200 μg/Ni/day is the maximum tolerable daily intake although individuals sensitive to nickel should not consume more than 50μg/Ni/day. Therefore, the intake of shellfish depends greatly on the tolerance of the people to the elements in the food.

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