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Heavy Metals in the Oyster *Crassostrea corteziensis* from Urias Lagoon, Mazatlán, Mexico, Associated with Different Anthropogenic Discharges

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According to Cantillo (1998) metals, organochloride compounds and PAH's have been recognized as the most deleterious contaminants to biota in the world marine and estuarine waters, and few studies have documented their concentrations and distribution in tropical and subtropical marine biota. Villanueva and Botello (1998) have reported a metal concentrations increase in the last 25 years in Mexican marine and estuarine environments.

Bivalves are extensively used in monitoring programs in the marine/estuarine environments due their ability to concentrate pollutants (e.g. heavy metals) to several orders of magnitude above ambient levels in sea water (Frías-Espericueta et al. 1999) Páez-Osuna et al. (1995) pointed out that oysters of the genus *Crassostrea* are excellent organisms as biomonitor of marine/estuarine metal pollution in tropical and subtropical coast. Besides, *C. corteziensis* is widely utilized for human consumption and has an important commercial value.

The objective of this study was to determine, during a year, the concentration of seven heavy metals (Cd, Co, Cr, Cu, Ni, Pb and Zn) in the soft tissue of three populations of the mangrove oyster *Crassostrea corteziensis* from a subtropical coastal lagoon which receives shrimp farm, industrial/urban and thermoelectric power plant discharges.

MATERIALS AND METHODS

From May 2003 to March 2004, the mangrove oyster *C. corteziensis* was collected from Estero de Urias lagoon on the Pacific coast of Mexico (Southern Gulf of California) where, in its lower portion, Mazatlan Harbour is located. Three sampling stations were selected according to anthropogenic activities developed in the lagoon: station 1 is influenced directly by the effluents from an aquaculture shrimp farm, station 2 receives effluents from the food industrial zone (i.e., factories of sauce, sausage, fish flour, shrimp packing, and tuna canning) and from fishing boats, while station 3 is influenced by the effluents from a thermoelectric power plant.

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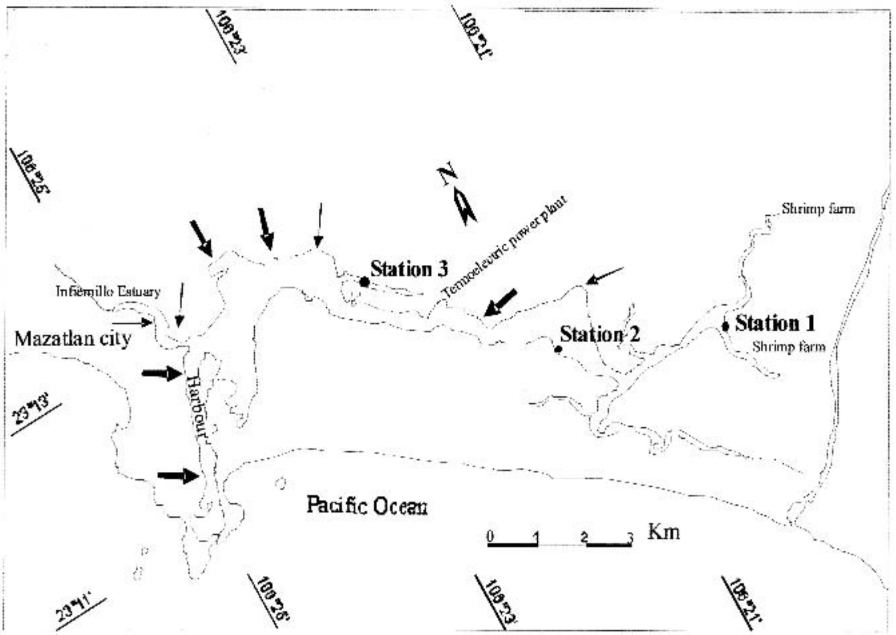

Figure 1. Location of sampling sites. Industrial (➡) and urban (→) discharges.

Samplings were carried out every two months to allow the analysis of organisms in different physiological stages. In each station, 80 oysters with similar size were collected by hand from the mangrove roots (*Rhizophora mangle*) and they were transported to the laboratory.

In the laboratory, prior to analysis, oysters were kept in oceanic seawater for 24 h to defecate the contents in the intestinal tracts. It is important because metal bound to sediments in the intestinal tracts of marine organisms can interfere with the determination of true level of metals incorporated into the bivalves tissues (Lobel et al. 1991). After depuration, oysters were measured and freed of their shells to separate the soft tissue, which was freeze-dried at -45°C and vacuum conditions for 72 h.

Tissues were pulverized and homogenized by grinding in a Teflon mortar. Triplicate sub-samples were digested with a concentrated and quartz-distilled nitric acid and slowly evaporated to dryness (90 °C) and the remainder dissolved in nitric acid 2M. The multiple standard addition method proposed by Miller and Miller (1988) was used. Finally, samples were centrifuged and analyzed by flame atomic absorption spectrophotometry. All material used in heavy metal analysis was completely acid washed (Moody and Lindstrom 1977).

The accuracy and precision of the method used was established by means of a reference material mussel homogenate MA-M-2/TM (IAEA 1985), and values were satisfactory except for Fe and Mn (63.8 and 71.6% of recovery, respectively), and these metals were not included in the study. Differences in average concentrations among stations were assessed by an one-way analysis of variance ($p<0.05$) (Miller and Miller 1988).

RESULTS AND DISCUSSION

Table 1 shows heavy metals concentrations found in the present study. No similar seasonal fluctuations were observed between metals, indicating that metal levels in the soft tissue of *C. corteziensis* is in function of anthropogenic sources. In each sampling and each station, no values of Cr were obtained because concentrations in the soft tissue of *C. corteziensis* were very close to or below the detection limit (0.65 μg/g).

Table 1. Heavy metal concentrations (μg/g, d.w.) in the soft tissue of *C. corteziensis* from Estero de Urias lagoon.

Sampling	Station	Cd	Co	Cu	Ni	Pb	Zn
May	1	1.1±0.03	1.3±0.03	76.2±5	1.4±0.07	6.4±0.2	1337±20
	2	1.2±0.03	1.4±0.02	88.2±6	1.6±0.10	8.9±0.3	1667±25
	3	1.2±0.02	1.6±0.03	110±7.4	1.3±0.06	8±0.3	2281±34
July	1	5.6±0.10	1.8±0.04	48±3.2	1.4±0.07	12.5±0.5	1692±25
	2	6±0.15	1.7±0.03	54±3.6	1.7±0.08	15.8±0.4	1270±19
	3	4.7±0.12	1.4±0.03	90±6	0.7±0.03	15±0.5	1962±29
September	1	1.5±0.04	1.9±0.04	40.7±2	1.8±0.10	6.4±0.2	1751±26
	2	3.7±0.11	1.8±0.04	84.7±5	2.5±0.13	19.4±0.5	2229±33
	3	1.5±0.04	1.9±0.04	107±7	1.7±0.08	8.4±0.3	2296±34
November	1	2±0.05	1.9±0.03	33.8±2	1.8±0.10	10.4±0.4	1146±17
	2	3±0.09	2.1±0.04	79.8±5	2.7±0.14	12.5±0.4	2352±35
	3	1.2±0.03	2±0.02	83±5.5	1.9±0.10	8.6±0.3	2354±35
January	1	3.9±0.10	1.8±0.02	54.8±4	2.6±0.10	18±0.6	1879±28
	2	4.2±0.12	1.8±0.04	79.5±5	2.9±0.14	18.9±0.6	1780±26
	3	2.8±0.07	1.9±0.03	101±7	2.1±0.10	16.5±0.5	2297±34
March	1	1.3±0.03	2±0.04	51.9±3	1.7±0.08	7.5±0.3	1323±20
	2	1.4±0.04	2.1±0.03	85±5.6	2.7±0.13	7.9±0.3	1770±26
	3	1.2±0.03	1.9±0.03	109±7.3	1.7±0.08	7.1±0.3	2531±37

Regarding Cd and Pb, interval of concentrations were 1.1-6 and 6.4-19.4 μg/g, respectively, and station 2 showed the highest values in each sampling. According to Landis and Yu (1999), waterborne Cd is probably the largest problem because it is common in the aquatic environment, and an important source is the deposition of municipal sewage sludge, and Estero de Urias lagoon, directly receives this kind of source from Mazatlan city. Regarding Pb, the source of this metal could be governed by input from point sources, which could be the canned industries (Tuna and sardine) (Albert and Badillo 1991), although more studies must be carried out to elucidate Pb source.

Páez-Osuna and Marmolejo-Rivas (1990) who carried out a study, during a twelve-month period, in the same lagoon with the same oyster, found a Cd and Pb intervals of 0.8-1.8 and 1.5-15 μg/g, which are lower than those reported in the present study, indicating a probably increase of Cd and Pb in the lagoon. It could be by the enclose nature of the system together with irregular access to tidal flushing; which allows metal accumulation.

Muñoz-Barbosa et al. (2000), who carried out a metal monitoring study on the Northwest coast of Baja California, Mexico; found a higher interval for Cd (1-11 μg/g) but a lower interval for Pb (<L.D.-0.6 μg/g); these authors used the mussel *Mytilus californianus* as a biomonitor. Besides, Cd values of the present study are lower than those reported by Paéz-Osuna et al. (1991) and Páez-Osuna et al. (1993), who reported an annual Cd average of 10.3 and an interval of 2-15 μg/g, from Navachiste and Altata-Ensenada del Pabellón lagoons (Both in Sinaloa state, Mexico), respectively; both coastal lagoons are associated with agricultural drainage basins.

Zn was an order of magnitude higher than copper, because Zn is less toxic than Cu to oysters and they can uptake more without adverse effects. Intervals of 33.8-110 and 1146-2531 μg/g, were observed for Cu and Zn, respectively. In each sampling, thermoelectric power plant (Station 3) showed the highest Cu and Zn levels. Apparently, this power plant is contributing to increases Cu and Zn levels in the ecosystem. Michel and Zegel (1998) pointed out that corrosion of the water pipelines could be the Zn source. However, more studies are required to determine if the thermoelectric power plant is a point source of Cu and Zn wastes to the Estero de Urias lagoon.

Other anthropogenic sources of Cu in the Estero de Urias lagoon include leaching from antifouling paints (Mazatlan Harbour) and discharges of wastewater in contact with metal surfaces, such as tanks and pipelines (Michel and Zegel 1998). However, copper can also originate from natural sources. Regarding Zn, this metal has many industrial uses, although it is ubiquitous in the environment.

Páez-Osuna and Marmolejo–Rivas (1990) determined a Cu interval of 25-83 μg/g in the soft tissue of *C. corteziensis*, but the Zn interval was lower (710-1600 μg/g) than those reported in the present study. Apparently, there is an increase of Zn in the Estero de Urias lagoon. In spite of this Zn levels, NOAA (1989) reports a range of 3000-5000 μg/g of Zn for contaminated sites. In this context, Estero de Urias lagoon could be considered as a moderate Zn contaminated lagoon.

Studies carried out in other coastal lagoons from NW of Mexico, Navachiste (Páez-Osuna et al. 1991) and Altata-Ensenada del Pabellón (Páez-Osuna et al. 1993) reported higher values of 67 and 147 μg/g of Cu and lower data of 509 and 727 μg/g of Zn, respectively. Muñoz-Barbosa et al. (2000) found a lower interval of 4-9.1 μg/g in the soft tissues of *Mytilus californianus* from the NW coast of Baja California than those found in the present study.

Ni, as Cd and Pb, showed the highest values in station 2, with an interval of 0.7-2.9 µg/g; while Co no showed any tendency along study period. Páez-Osuna and Marmolejo-Rivas (1990) found a higher Ni interval (2.2-6 µg/g) those reported in the present study; and Páez-Osuna et al. (1991) and Páez-Osuna et al. (1993) found similar values in *C. corteziensis* from Navachiste and Altata-Ensenada del Pabellón lagoons, respectively.

The statistical analysis reveals that Cd values found in station 2 were statistically different ($p<0.05$) than those found in the others stations; with exception of station 3 in sampling I (May). Regarding Pb, comparison among station 2 and 3 were not different in sampling II (July), and among station 1 and 2, no difference was observed in sampling V (January) and VI (March). Only Zn values found in stations 2 and 3 were not different in sampling IV (November). Finally, Cu values determined in station 3, were not different with station 2 only in the sampling IV (November), and comparison between station 3 and 1 was always different.

Table 2. Comparative heavy metal concentrations (µg/g, d.w.) in soft tissues of bivalves from other areas of the world.

Site	Species	Cd	Cu	Pb	Zn	Reference
Acajutla, El Salvador	*Ostrea iridescens*	<1.15	622	<LD	2040	Michel and Zengel (1998)
Mauritanian coast	*Crassostrea gigas*	10	68		300	Roméo et al. (2000)
Bilbao estuary, Spain	*Scrobicularia plana*	60	103.6	140.3	2751	Ruiz and Sain-Salinas (2000)
Sepetiba Bay, Brazil	*Crassostrea rhizophorae*	29.8			80724	Rebelo et al. (2003)
Urias lagoon, Mexico	*Crassostrea corteziensis*	2.63	76.48	11.57	1884	This study

In spite of an apparent increase of Cd and Pb concentrations in the Estero de Urias lagoon, the mean value found in the present study is lower than those determined in *C. gigas*, *S. plana* and *C. rhizophorae* from Mauritanian coast, Bilbao estuary (Spain), and Sepetiba Bay (Brazil), respectively (Table 2). Regarding Cu and Zn, only data determined in *S. plana* from Mauritanian coast is lower than those reported in Table 2.

Besides, the mean Cd, Cu, Ni and Zn values reported in the present study are lower than the World Mussel Watch 85th percentile value of 221, 680, 4.7, 4500 µg/g, respectively; only Pb (11.57 µg/g) was higher than the 85th percentile value of 8.6 µg/g (Cantillo 1998).

Table 3 compares the metal concentration found in the present study to the levels of concern; it can see that the greatest concern would be from Pb exposure. People would have to consume 26.6 g (wet wt.) of soft tissue of the mangrove oyster

Crassostrea corteziensis from Estero de Urias lagoon, Mazatlán Sinaloa, Mexico, to reach the daily limit for Pb.

Table 3. Oral intake per person (in grams, wet weight) of soft tissue of oysters *C. corteziensis* for reach levels of concern proposed by USFDA (1993) and WHO (1998).

Metal	*C. corteziensis* from Estero de Urias	Levels of concern µg/person/day
Cd	85.9	55
Cu	161	3000
Ni	2608	1200
Pb	26.6	75

The observed increase in metal concentrations suggests that Estero de Urias lagoon has anthropogenic trace metal inputs, probably from Industrial/Urban discharges and Harbour activities (Cd, Pb and Ni) and from Thermoelectric power plant (Cu and Zn). Values found in the station close to the shrimp farm were lower than the other stations. Cd and Pb levels found in the present study are of ecological concern, because metal levels in organisms depend mainly on their environmental levels and could affect fisheries (bivalve, fish, shrimp) in terms of environmental/biological conservation.

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