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Heavy metals in the rock oyster *Crassostrea iridescens* (Filibranchia: Ostreidae) from Mazatlan, Sinaloa, Mexico

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Abstract: Two populations of *Crassostrea iridescens* were sampled off Mazatlan and in a zone free of anthropogenic activity. The bivalves were collected from February 1992 to February 1993. Concentrations of Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn were determined by flame atomic absorption spectrophotometry. Annual mean values in the sampling zone off Mazatlan were higher in Co, Cu, Fe, Mn, Ni and Zn than in the sampling zone free of anthropogenic activity; however, differences were not statistically significant at 95% confidence level. Urban discharges in the coastal zone in front of Mazatlan city, have little or no heavy metal concentrations dissolved or particulated.

Key words: *Crassostrea iridescens*, heavy metals, urban discharges, oyster.

In the Pacific region of Mexico, the rock oyster *Crassostrea iridescens* (Hanley 1954), is present along the coast, and it is associated with subtidal rocky substrates (Páez-Osuna *et al.* 1995). The species is geographically distributed from La Paz, Gulf of California, to northern Peru (Keen 1971). Recently, its reproductive cycle was described by Frías-Espericueta *et al.* (1997): there is a resting phase from November through January; a maturation phase from April to May; and a spawning phase from July to October.

Bivalves are extensively used in monitoring programs in the marine environment due to their ability to concentrate pollutants to several orders of magnitude above ambient levels in sea water (Al-Madfa *et al.* 1998). According to Phillips and Rainbow (1993) an ideal biomonitor should fulfill several requisites: should be sessile or sedentary in order to be representative of the study area; should be abundant in study areas, easy to identify and sample at all times of year, and should have sufficient tissue for analysis of the contaminant of interest; should be hardy, tolerating wide ranges of contaminant concentration, thereby permitting the design of transplant experiments and laboratory studies of contaminant kinetics; and should be strong accumulators of the relevant trace metal. These characteristics, its wide distribution and commercially valuable seafood species, makes *C. iridescens* a very suitable species as an indicator of pollution (biomonitor) for heavy metals.

Regarding heavy metals, various processes influenced by anthropogenic activities may contribute to increase concentrations in natural waters (Singh and Steinnes 1994): (1) run-off from agricultural and urban areas, (2) discharges from mining, factories and municipal sewer systems, (3) leaching from dumps and former industrial sites, (4) atmospheric deposition.

The purpose of this study was to evaluate the concentration of eight heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn) in two different sites in Mazatlan, Sinaloa, Mex. One site with little influence and another without urban discharge influence.

MATERIALS AND METHODS

Individuals of *C. iridescens* were collected (9-10 samplings) from two sites along the coast of Mazatlan, Sinaloa, Mexico from February 1992 through February 1993. One station was located in front of Mazatlan, which receives little urban wastewater (23° 15' 41.5"N and 106° 15' W). The second station was located north of the city between 23° 28' and 23° 29' N and 106° 36' and 106° 37' W, an area characterized by the absence of significant anthropogenic activity. Oysters were sampled by scuba diving, collecting organisms of similar size to minimize the effect of body weight (Anonymous 1980; Marina and Enzo 1983). In the laboratory, after taking biometric measurements, the soft tissue of each composite sample of 15-20 organisms was dried at 70 °C. All glassware and plastic devices used in the manipulation of the samples were completely acid-washed (Moody and Lindstrom 1977). Pulverization and homogenization were achieved by grinding the tissue samples in a teflon mortar. Samples and blanks for analysis were prepared by digesting aliquots of dry material with concentrate quartz-distilled nitric acid using the standard addition method and the metal concentrations were determined by flame atomic absorption spectrophotometry (Páez-Osuna *et al.* 1993a, 1995). The heavy metal concentration confidence intervals were calculated using the method proposed by Miller and Miller (1987). The performance of the method was evaluated by analyzing a reference material mussel homogenate MA-M-2/MT (Anonymous 1985). The concentrations found for Cd, Co, Cr, Cu, Ni and Zn were in the acceptable range reported, only Fe and Mn were underestimated (Páez-Osuna *et al.* 1995) (Table 1).

TABLE 1

Heavy metals concentrations (μg/g, dry weight) in the reference material MA-M-2/TM; mean ± standard deviation (n=6).

Metal	Reported concentrations	Class of results	Concentration found
Cd	1.16-1.54	A	1.27 ± 0.08
Co	0.75-1.07	B	1.01 ± 0.10
Cr	0.95-1.62	B	1.28 ± 0.13
Cu	7.53-8.44	A	6.74 ± 2.24
Fe	229.2-268.2	B	171.3 ± 29.1
Mn	60.7-75.3	B	53.9 ± 4.9
Ni	0.89-2.04	C	2.07 ± 0.19
Zn	152.8-166.7	B	192.2 ± 24.4

Certified with satisfactory (A) or acceptable (B) degree of confidence; values not certified (C) (Anonymous 1985).

RESULTS

Table 2 and 3 list heavy metal concentrations in the soft tissue of *C. iridescens* in both stations.

There were no significant correlations between metal concentration and body length (T-students, $p > 0.05$). Boyden (1974) suggested that for some metals the concentrations in small organisms may be greater than those in large organisms. With regard to the correlation coefficient between metal concentrations, only Cu-Zn revealed a significant coupling with $r = 0.95$ ($p=0.005$) and $r = 0.88$ ($p=0.05$) for stations 1 and 2, respectively (Fig. 1).

TABLE 2

Heavy metals concentrations (µg/g, dry weight) in soft tissue of Crassostrea iridescens collected in station 1.

Date	Length (cm)	Cd	Co	Cr	Cu	Fe	Mn	Ni	Zn
February 1992	9.63	2.5±0.2	5.3±0.5	1.7±0.2	39±13	111±19	15.9±1.4	3.7±0.3	670±85
March 1992	10.76	2.4±0.2	4.4±0.5	1.9±0.2	35.8±11.1	171±29	14.2±1.4	4.4±0.4	668±86
April 1992	7.88	2.6±0.2	5.3±0.6	2.1±0.2	53±16.7	110±22	13.0±1.2	9.8±1	730±96
May 1992	9.02	2.2±0.2	5.3±0.6	1.7±0.2	38.8±12.7	130±23	14.2±1.5	3.1±0.3	639±85
July 1992	9.04	2.8±0.2	4.5±0.5	1.8±0.2	51.1±16.8	143±28	20.3±2.1	3.7±0.4	707±98
September 1992	8.53	2.9±0.2	5.3±0.6	2±0.2	102±32.6	271±50	17.3±1.6	4±0.5	788±110
November 1992	8.85	2.8±0.2	5.1±0.6	2.9±0.3	107±34.7	194±39	16.8±1.7	4.2±0.5	795±115
December 1992	9.83	3.3±0.3	6.5±0.7	2.3±0.4	110±35.8	170±33	16.8±1.7	5.9±0.8	822±116
January 1993	9.21	2.6±0.3	5.4±0.6	1.8±0.3	118±39.1	164±33	11.5±1.2	4.1±0.5	798±117
February 1993	8.59	3.1±0.3	5.4±0.6	1.6±0.3	52.9±17.3	186±39	14.2±1.5	3.7±0.5	670±100

The intervals of concentrations for Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn were: 2.2-3.3, 4.4-6.5, 1.6-2.9, 35.8-118, 110-271, 11.5-20.3, 3.1-9.8 and 639-822 µg/g (dry weight), respectively, for station 1; while for station 2: 1.9-3.9, 4.5-5.4, 1.7-2.8, 32.3-112, 15-377, 11-19.2, 2.8-8.2 and 604-843 µg/g (dry weight), respectively.

In station 1 the highest concentration of Cd, Co, Cr, Cu and Zn was determined in autumn-winter months; while the Ni, Fe and Mn its highest value occurred in the Spring-Summer months (Table 2). Regarding station 2 the highest concentration of Cd, Co, Cu, Fe and Zn was found in autumn-winter; and Cr, Mn and Ni in spring-summer months (Table 3). There were no significant differences between the highest values of spring-summer and autumn-winter. Only Ni, in both stations, differed (means comparison test, $p > 0.05$, see Miller and Miller 1987).

Mean values of Co, Cu, Fe, Mn, Ni and Zn were higher in station 1 than in station 2, only Cd and Cr mean values were higher in station 2. However, no significant difference was observed (means comparison test, $p > 0.05$).

In both stations the decreasing order of metals values was the same.

Zn>Fe>Cu>Mn>Co>Ni>Cd>Cr

DISCUSSION

Around the world, the coastal zones are subject to the direct release of urban and industrial discharges, such inputs are known to contain heavy metals, which may increase trace

TABLE 3

Heavy metals concentrations (µg/g, dry weight) in soft tissue of Crassostrea iridescens collected in station 2.

Date	Length (cm)	Cd	Co	Cr	Cu	Fe	Mn	Ni	Zn
February 1992	8.62	3.5±.02	5.3±0.5	1.8±0.3	32.3±10.2	86±17	11.0±1.2	3.8±0.4	606±90
March 1992	7.92	3.4±0.2	5.3±0.6	2.2±0.2	41.4±13	15±20	11.3±1.1	2.9±0.3	741±94
April 1992	9.45	2.6±0.2	4.5±0.5	2.8±0.3	34.8±11.5	118±24	11.1±1	2.8±0.4	604±84
May 1992	9.85	1.9±0.1	5±0.5	1.8±0.3	39.4±13.1	108±18	19.2±2	3.38±0.4	608±78
September 1992	8.57	3.1±0.2	5.1±0.6	2.7±0.3	77.1±24.7	205±42	12.1±1.2	8.2±0.8	722±97
November 1992	8.72	2.9±0.3	4.6±0.5	2.1±0.4	69.2±23	197±35	14.0±1.4	3.5±0.5	722±108
December 1992	9.85	3.1±0.2	5.4±0.6	2.1±0.3	80.3±26.7	229±45	16.3±1.7	4.8±0.6	755±104
January 1993	8.98	3.9±0.4	4.9±0.5	2.1±0.4	112±35.3	141±24	11.3±1.2	4.4±0.5	843±108
February 1993	8.65	3.7±0.4	5.2±0.5	1.7±0.3	49.7±16.3	377±75	17.0±1.8	3.6±0.4	641±94

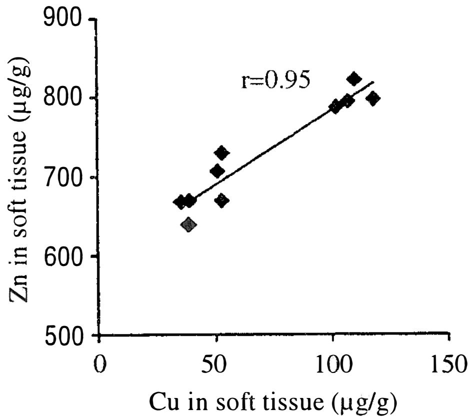
metal concentrations in the coastal zone, some of which are toxic and can endanger human health (Al-Madfa *et al.* 1998). In the present study, station 1, which receives little urban discharges, apparently showed the highest annual mean values of the majority of metals.

Concerning correlations between heavy metal concentrations in the soft tissue of *C. iridescens*, only Cu-Zn in both stations were significant. These correlations may be attributable to the fact that *C. iridescens* metabolically requires Cu and Zn in the same proportion during its life cycle, and similar physical/chemical properties of the metals involved in the metabolic processes (Szefer *et al.* 1994). Paéz-Osuna and Marmolejo-Rivas (1990a) found the same correlations in *Crassostrea corteziensis* from the Port of Mazatlán, Sinaloa, Mexico.

Trace metal seasonal variations have been reported for several species of molluscs (Bryan 1973). The causes of seasonal fluctuations have been associated with the food supply, changes in the run-off of particulate metal to the sea, due to high precipitation (Fowler and Oregioni 1976), variations related to the reproductive cycle (Latouche and Mix 1981; Paéz-Osuna and Marmolejo-Rivas 1990 b).

In stations 1 and 2, the peak of Mn was determined in July and May, respectively. According to Frías-Espericueta *et al.* (1997) in these months *C. iridescens* was in the maturation phase and close to spawning. Marina and Enzo (1983) found in *Donax trunculus* that Mn plays an important role in those phases prior to spawning, possibly as an enzymatic catalyst (Galtsoff 1964). Watling and Watling (1976) found in C*horomytilus meridionalis* that the trace metal distribution changes as a function of growth and maturation.

In the present work, essential metals were accumulated in amounts higher than non-essential metals. This order suggests that *C. iridescens* accumulates heavy metals according to the biological effect of metals and/or the concentration in the surrounding seawater. Páez-Osuna and Marmolejo-Rivas (1990a) found that, when the levels of trace metals in the oyster *Crassostrea corteziensis* were correlated with those in the particulate fraction of the month immediately preceding, a significant relationship was obtained for several metals. This is the result of specific mechanisms as uptake, transport, storage and excretion of metals (Simkiss and Mason 1983, Phillips and Rainbow 1989).



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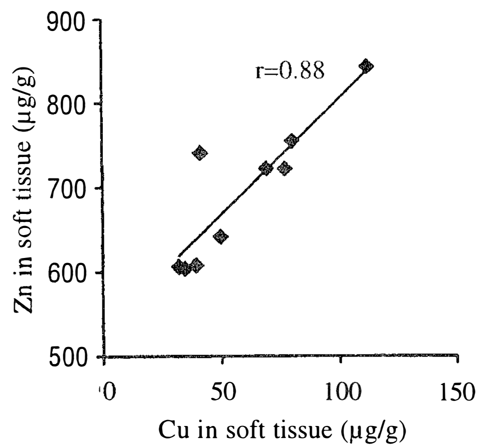

Fig. 1. Relatinoship between Zn and Cu (µg/g, dry weight) in the soft tissue of the oyster *Crassostrea tridescens* along study period. A: station 1; B: station 2.

Zn showed the highest concentrations. Generally, oysters have been considered as strong accumulators of zinc, and these organisms accumulate high concentrations of zinc in detoxified granules (George *et al.* 1978). With regard to Cu, Eisler (1981) observed that some species could exhibit high Cu concentrations due to the proximity to anthropogenic source or to biotic/abiotic factors capable of modifying Cu uptake and retention. Rainbow (1988), and Depledge and Rainbow (1990), found that heavy metals are taken up and accumulated by marine invertebrates to tissue and body concentrations usually much higher on a wet weight basis than concentrations in the surrounding seawater. Metal accumulation strategies fall along a gradient from the strong accumulation of all metal taken up, to the regulation of the body metal concentration to an approximately constant level; by balancing metal excretion/uptake (Rainbow 1993). Zn, Fe, Cu, and Mn are biologically essential and play an important role as cofactor in enzymatic processes (Singh and Steinnes 1994).

Comparing metal concentrations in oysters from this study with other bivalves collected in other zones of the world (Table 4), our values are lower than those reported by Goldberg *et al.* (1978) for a polluted zone (except for Ni), besides metal concentrations of this study are slightly higher than those of Langebann lagoon (South Africa), an area relatively unpolluted with respect to trace metals, and according to Watling and Watling (1976), these values represent near-background levels and that metal uptake is "normal". However, and according to Rainbow (1993), defining a background concentration for a metal is too difficult, given the role of biological variables.

A general conclusion is that urban discharges in the coastal zone in front of Mazatlan city, have little or no heavy metal concentrations dissolved or particulated. This work requires future investigations to analyze urban discharges. However, the analysis of total coliform feces (Ortiz-Arellano, in prep.) revealed higher values in station 1 than station 2.

TABLE 4

Average heavy metals concentrations in bivalves from different areas. Concentrations are expressed in μg/g, dry weight.

Species	Area	Cd	Cr	Cu	Fe	Mn	Ni	Zn	Ref.
Pinctada radiata	Arabian Gulf	0.49		2.79			7.08		a
Tellina sp	NW Coast Mexico	6.0	2.7	119	1338	27	3.8	806	b
Saccostrea iridescens	Mazatlan, Mexico	3.6		20	93	9.4	1.7	402	c
Crassostrea gigas	Langebaan Lagoon (South Africa)	9		33		12	1	424	d
Crassostrea virginica	Gulf Coast (USA)	5.1		134	258	13.5	2.6	1741	e
Crassostrea iridescens	Mazatlan, [1] Mexico	2.7	2	70.8	164.9	15.4	4.7	728	f
Crassostrea iridescens	Mazatlan, [2] Mexico	3.1	2.1	59.6	164	13.7	4.2	694	g

(a) Al-Madfa *et al.* (1998), (b) Páez-Osuna *et al.* (1993b), (c) Páez-Osuna and Marmolejo-Rivas (1990b), (d) Watling and Watling (1976), (e) Goldberg *et al.* (1978), (f) and (g) this study.
[1] Station 1, [2] Station 2.

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RESUMEN

Dos poblaciones de *Crassostrea iridescens* fueron muestreadas en la zona costera de la ciudad de Mazatlan y en una zona libre de actividad antropogénica. Los bivalvos fueron colectados de febrero de 1992 a febrero de 1993. Concentraciones de Cd, Co, Cr, Cu, Fe, Mn, Ni y Zn fueron determinados por espectrofotometría de absorción atómica. Los valores medios anuales en la estación de

muestreo de la ciudad de Mazatlán fueron mayores en Co, Cu, Fe, Mn, Ni y Zn que los determinados en la zona libre de actividad antropogénica; sin embargo, las diferencias no fueron significativas al nivel de confianza del 95%. Una conclusión es que las descargas urbanas en la zona costera en frente de Mazatlán no tiene, o tiene, bajas concentraciones de metales pesados disueltos o particulados.

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