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Macroalgae as Biomonitors of Heavy Metal Availability in Coastal Lagoons from the Subtropical Pacific of Mexico

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Despite the fact that a relatively rich algal flora exists along the broad range of coastal environments in Mexico (Abbott and Hollenberg, 1976; Serviere-Zaragoza et al., 1993) their viability as biomonitors of trace metals has not been studied. Macroalgae have been known to concentrate heavy metals to levels several times those found in the surrounding waters. This is due to their accumulation of metals by active and passive processes responding essentially to metals present in solution (Bryan, 1969; Seeliger and Edwards, 1977; Leal et al., 1997).

Spatial or temporal trends in contamination provided by data on metal levels in macroalgae may not correspond to those found in other biomonitor species such as mollusks and barnacles. Consequently a biomonitoring program of metal contamination is more complete when barnacles and bivalve results are considered together with macroalgae data. A project was initiated to establish levels of trace metals, pesticides and petroleum hydrocarbons in a range of marine organisms from the subtropical Pacific coast of Mexico. Attention was given to bivalves, barnacles and macroalgae, which are known to be among the most effective and widely used biomonitors of pollution (Rainbow and Phillips, 1993). In a previous work (Páez-Osuna et al., 1999) regional variations of heavy metal concentrations in tissues of barnacles from the subtropical Pacific coast of Mexico were determined and reported. This work reports on concentrations only of trace metals in the macroalgae and is the first study of its kind to be conducted in the area.

MATERIALS AND METHODS

The study area includes twelve locations (Table 1). With the exception of Puerto Vallarta and Monteón Beach the rest are classified (Lankford, 1977) as coastal lagoons. These ecosystems constitute important fishery areas and play key roles as nursery grounds for commercially relevant species of shrimp and fish. In Table 1 is shown a summary of the main activities developed in each location and the associated drainage basin.

About 0.5-1.0 kg of fresh algae were handpicked from the intertidal regions of the twelve different locations along the Pacific subtropical coast of Mexico (Table 1) in April 1996. Samples were stored in polyethylene bags and kept at 4°C during transport. In the laboratory, any epiphytes, sediments and adhering animals were removed with seawater for each collection site. The samples were then dried for 7

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days at 60°C and ground to a powder using a teflon mortar. Blanks and aliquots (051.0 g) of the homogenized tissues were digested with concentrated quartz-distilled nitric acid. The digests were slowly evaporated to dryness and the residues were dissolved in 1 M nitric acid and analyzed by flame atomic absorption spectrophotometry. Concentrations of each metal were determined quantitatively by the multiple standard addition method. The samples were spiked with roughly 0, 1, 2 and 4 times the expected amount of metal in each aliquot of sample (Páez-Osuna et al. 1993). All glassware and plastic devices were thoroughly acid-washed (Moody and Lindstrom, 1977). All metal concentrations were expressed as µg g^{-1} dry weight. Spinach IAEA-331 supplied by the International Atomic Energy Agency's Analytical Quality Control Services was analysed by the same technique. The results and the NIST certified values (Zeisler et al., 1995) for this material are presented in Table 2. Ni appeared to be overestimated with this method, and therefore results for this element are only briefly discussed. Differences in average concentrations of each metal between the three main genera studied were assessed by one-way analysis of variance and the Tukey's multiple comparison test using the GraphPad Prism 2.0 for Windows 97 (GraphPad Software Inc., San Diego CA). Data sets were analyzed for normality using the Kolmogorov-Smimov test and proved to follow a Gaussian distribution.

RESULTS AND DISCUSSION

The results of the analysis of the seven metals studied in the nine species of macroalgae from all sites are summarized in Table 3. Certain species were absent in some sites and more than one species were present in other. Fe, Mn and Zn were the most abundant elements in the 16 populations of macroalgae examined, followed by Cu, Ni, Co, Cr and Cd. Enteromoroha clathrata (Roth) Grev. and Ulva lactuca Linnaeus from Yavaros lagoon were rather exceptional as they consistently had higher levels of Mn than Fe. The levels of most of the metals studied vary widely depending on site and species.

E. clathrata collected from Guaymas Harbor and Yavaros lagoon, Enteromorpha intestinalis (L.) Link from Mazatlán Harbor, U. lactuca from Manzanillo Harbour, and Spyndia filamentosa (Wulf) Harv. from Altata-Ensenada del Pabellón lagoon were the macroalgae that accumulated high levels of Fe. Conversely, Enteromorpha linza (L.) J. Ag. from Altata-Ensenada del Pabellón lagoon and C. amplivesiculatum from Lobos lagoon contained relatively low levels of Fe. The higher concentrations of Mn were found in E. clathrata and U. lactuca collected in Yavaros lagoon. Intermediate levels of Mn were in evidence in S. filamentosa from Altata lagoon and Gracilaria subsecundata S. and G. from Ceuta lagoon. The rest of the macroalgae populations exhibited values between 10-115 µg g^{-1}.

The levels of Co and Cr in the macroalgae were often <7 µg g^{-1}. E. linza and U. lactuca from Altata-Ensenada del Pabellón lagoon and Manzanillo Harbour, respectively, accumulated Co to a greater extent than the other macroalgae (Table 3). with the exception of E. intestìnalis from Mazatlán Harbour, the other algae normally contained between 10 and 90 µg g^{-1} of Zn. Similarly, with the exception of clathrata from Guaymas Harbour, the rest of algae had between 1.9 and 20 µg g^{-1} Cu. The levels of Ni in most of the algae were <10 µg g^{-1}. Only the algae collected from Ohuira, Altata-Ensenada del Pabellón and Ceuta lagoons, and Mazatlán and

Table 1. A summary of the characteristics of selected locations and sites sampled in the subtropical Pacific coast of Mexico

Location	Species	Substratum/description of site and surroundings
Guaymas Harbor 27° 55.5'N; 10° 52.7' W	E. clathrata	Rocks/Fisheries, shipyards, urban sewage
Lobos Lagoon 27° 23.1'N; 110° 33.0' W	C. amplivesiculatum	Sediments/Fisheries, intensive agriculture
Yavaros Lagoon 26° 41.3'N; 109° 32.4' W	E. clathrata U. Lactuca	Wood pier pilings/Fish-meal factories, agriculture
Agiabampo Lagoon 26° 21.8'N; 109° 10.0' W	E. linza	Sediments/Fisheries, rural communities
Ohuira Lagoon 25° 39.4'N; 108° 56.7' W	E. clathrata	Sediments/Fisheries, intensive agriculture
Navachiste Lagoon 25° 33.5'N; 108° 52.5' W	C. amplivesiculatum	Sediments/Fisheries, shrimp farming, agriculture
Altata Lagoon 24° 29.4'N; 107° 42.6' W	E. linza S. filamentosa	Wood pier pilings/Fisheries, shrimp farming, intensive agriculture, urban sewage
Ceuta Lagoon 24° 2.8'N; 107° 7.0' W	G. subsecundata	Mangrove roots/Fisheries, shrimp farming, rural communities
Mazatlàn Harbor 23° 12.6'N; 106° 23.3' W	E. intestinalis U. Lactuca	Mudflats/Fish and shrimp factories, shipyards shrimp farming, urban sewage
Monteòn Beach 20° 59.0'N; 105° 19.8' W	P. durvillaei	Sand beach/rural communities
Puerto Vallarta Harbor 20° 37.6'N; 105° 14.2' W	E. flexuosa C. Isabelae	Jetty rock/Urban sewage, port operations
Manzanillo Harbor 19° 04.5'N; 104° 17.9' W	U. lactuca	Mangrove roots/Urban sewage, shipyards, port operations

Table 2. Concentration (µg/g dry weight) of elements in IAEA-331 Spinach. Mean concentration ± standard deviation (n=6).

Element	NIST certified concentrations	Concentration found (n=6)
Cd	2.89±0.07	2.84±0.04
Co	0.39±0.05	0.65±0.15
Cr	1.92±0.04	1.22±0.12
Cu	12.2±0.6	11.2±0.9
Fe	293±6	266±25
Mn	75.9±1.9	79.0±6.3
Ni	2.14±0.10	5.10±0.35
Zn	82±3	74±6

Manzanillo Harbors showed a greater concentration than the rest of the algae. Relatively low levels of 2.2 µg g^{-1} or less of Cd were found in most of the algae.

Table 3. Trace metal concentrations in macroalgae from the subtropical pacific coast of Mexico (µ/g dry weight).

Location	Species	Cu	Ni	Co	Cd	Fe	Zn	Mn	Cr
Guaymas	E. clathrata	22.6	9.8	5.3	1.4	1862	85.2	27	4.9
Lobos	C. amplivesiculatum	4.3	4.7	4.3	1.9	259	10.5	34	2.8
Yavaros	E. clathrata	18.0	7.4	4.9	0.7	1909	58.7	4204	5.8
	U. lactuca	15.0	3.8	4.9	0.9	458	20.6	2515	6.3
Agiabampo	E. linza	4.7	3.7	3.7	1.4	594	13.5	25	2.1
Ohuira	E. clathrata	6.1	27.4	3.8	1.6	673	13.1	131	1.7
Navachiste	C. amplivesiculatum	3.0	8.8	2.3	2.2	454	22.8	37	2.1
Altata	E. linza	8.1	10.2	10.4	1.4	274	23.2	70	2.9
	S. filamentosa	7.4	13.3	6.8	3.7	1318	29.2	288	7.0
Ceuta	G. subsecundata	4.5	26.3	4.6	1.6	607	20.0	163	2.3
Mazatlàn	E. intestinalis	8.9	11.7	1.1	0.3	4030	99.8	114	3.8
	U. lactuca	6.8	29.1	0.5	0.2	670	8.8	58	3.2
Monteòn	P. durvillaei	1.9	3.5	4.0	5.6	487	36.7	22	1.2
Puerto	E. flexuosa	6.3	4.9	4.6	1.0	443	25.6	11	2.0
Vallarta	C. isabelae	6.3	5.3	1.8	1.7	895	87.7	36	1.8
Manzanillo r	U. lactuca	8.1	32.9	11.7	1.3	2532	29.9	65	4.4

However, the two algae S. filamentosa from Altata and Padina durvillaei Bory from Monteón Beach had high Cd values.

Higher seawater metal availabities in solution have presumably led to a greater accumulation of these metals in the algae. The main source of these metals in the harbor waters is related to the discharge of domestic and industrial effluents (Osuna-López et al. 1989). Considering the limited number of sites where U. lactuca was collected (Manzanillo, Mazatlán and Yavaros), the results reveal for Manzanillo Harbour a degree of contamination for Ni, Fe and Zn.

The relatively elevated levels of some metals as Mn, Cu and Fe, in the macroalgae from Yavaros and Altata-Ensenada del Pabellón lagoons are possibly related with agricultural effluents which contain residues of fertilizers and pesticides, including metallic fungicides (e.g. Manzate (Mn), Maneb (Mn), Cupravit (Cu)). These are applied in significant amounts in the intensively farmed catchment areas that border such coastal lagoons (Páez-Osuna et al. 1993).

The multiple comparison of mean metal concentrations in the three main algae groups present (i.e. Enteromorpha at seven sites (n=7), Codium at three sites (n=3), and U. lactuca also in three sites (n=3)) revealed significant ($P<0.05$) differences only in the case of Cd, where Codium showed a higher Cd concentration than the others genera. In Yavaros lagoon and Mazatlán Harbor were collected in the sites 3 and 9 simultaneously U. lactuca and Enteromorpha and it was observed that in both sites the filamentous algae showed a higher ability to concentrate Cu, Co, Fe, Zn and Mn than the foliaceous macroalgae.

Maximum levels of Mn in Enteromorpha species found here were high compared with those reported in Hong Kong waters (Ho, 1987b), the Kuwait coast (Buo-Olayan) and Subrahmanyam, 1996) or the northern Adriatic (Munda and Hudnik, 1991), but similar to the levels from the Goa coast of India (Agadi et al., 1978). The maximum concentrations of Mn, particularly in the macroalgae of Yavaros lagoon, were more elevated than the levels reported for most Phaeophyceae (Fuge and James, 1973; Zingle et al., 1976; Burdon-James et al., 1982).

Similarly, maximum values of Fe in Enteromorpha species in this work were high compared to the data from Kuwait and the Goa coast, but low in comparison to data for E. flaxuosa from contaminated Hong Kong waters (Ho, 1987). The rest of the metals studied here were at lower or comparable levels than those reported for this genus (Agadi et al., 1978; Munda and Hudnik, 1991; Buo-Olayan and Subrahmanyam, 1996).

In this study, with the exception of Mn levels in U. lactuca that were more elevated than those reported from the coasts of Kuwait (Buo-Olayan and Subrahmanyam, 1996), Cuba (Ramirez et al., 1990) and Goa (Agadi et al., 1978), the rest of the metal concentrations were low or similar to those in the literature. In the case of Codium amplivesiculatum and Codium isabelae from three sites of the Pacific sub-tropical coast of Mexico, the levels of Cd found were high in relation to Codium vermilara and Codium effusum from northern Adriatic (Munda and Hudnik, 1991); Cu, Zn and Mn resulted comparable among the four species.

The lowest concentration of Cu, Ni, and Cr were observed in P. durvllaei from El Monteón Beach, an uncontaminated rural site. In contrast, the level found of 5.6 µg g^{-1} of Cd indicates that this species is a good accumulator of this metal and the site has a high bioavailability of Cd, which is probably related to the natural enrichment of Cd in the Pacific waters associated with upwelling (Segovia-Zavala et al., 1998).

Considering the results obtained in this work, it is possible to conclude that macroalgae were efficient biomonitors reflecting suspected or known localized increases in metal abundance. However, more experimental and field studies are obviously needed with macroalgae if they are to be used as biomonitors. The main disadvantage to using macroalgae as biomonitors in the subtropical pacific coast of Mexico is related with the uncertainty of the uptake metal patterns among the different species present.

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REFERENCES

Abbott IA, Hollenberg GJ (1976) Marine algae of California, Stanford University Press, Stanford

Agadi VV, Bhosle MB, Untawale AG (1978) Metal concentrations in some seaweeds of Goa (India). Bot Mar 21:247-250

Bryan GW (1969) The absorption of zinc and other metals by the brown seaweed Laminaria digitata. J Mar Biol Ass United Kingdom 49: 225-243
Buo-olayan AH, Subrahmanyam MNV (1996) Heavy metals in marine algae of the Kuwait coast. Bull Environ Contam Toxicol 57: 816-823
Burdon-Jones C, Denton GRW, Jones GB, Mcphie KA (1982) Regional and seasonal variations of trace metals in tropical Phaeophyceae from north Queensland. Mar Environ Res 7: 13-30
Fuge R, James KH (1973) Trace metal concentrations in brown seaweeds, Cardigan Bay, Wales. Mar Chem 1: 281-293
Ho YB (1987) Metals in 19 intertidal macroalgae in Hong Kong waters. Mar Pollut Bull 18: 564-566
Lankford RA (1977) Coastal lagoons of Mexico. Their origin and classification In: Wiley M (Ed) Estuarine Processes, Academic Press, New York, p 1983
Leal MCF, Vasconcelos MT, Sousa-Pinto, I, Cabral JPS (1997) Biomonitoring with benthic macroalgae and direct assay of heavy metals in seawater of the Oporto coast (North West Portugal). Mar Pollut Bull 34: 1006-1015
Moody JR, Lindstrom PM (1977) Selection and cleaning of plastic containers for storage of trace element samples. Anal Chem 49: 2264- 2267
Munda IM, Hudnik V (1991) Trace metal content in some seaweeds from the northern Adriatic. Bot Mar 34: 241-249
Osuna-López JI, Páez-Osuna F, Marmolejo-Rivas C, Ortega-Romero P (1989) Metales pesados disueltos y particulados en el Puerto de Mazatlán. An Inst Cienc Mar Limnol UNAMexico 16: 307-320
Páez-Osuna F, Osuna-López JI, Izaguirre-Fierro n G, Zazueta-Padilla, HM (1993) Heavy metals in clams from a subtropical coastal lagoon associated with an agricultural drainage basin. Bull Environ Contam Toxicol 50: 915-921
Páez-Osuna F, Bójorquez-Leyva H, Ruelas-lnzunza J (1999) Regional variations of heavy metal concentrations in tissues of barnacles from the subtropical Pacific coast of Mexico. Environ lnternat 25: 647-654
Rainbow PS, Phillips DJH (1993) Cosmopolitan biomonitors of trace metals. Mar Pollut Bull 26: 593-601
Ramírez M, Gonzalez H, Ablanedo N, Torres I (1990) Heavy metals in macroalgae of Havana's northern littoral, Cuba. Chem Ecol 4: 49-55
Seeliger U, Edwards P (1977) Correlation coefficients and concentration factors of copper and lead in sewater and benthic algae. Mar Pollut Bull 8: 16-19
Segovia-Zavala JA, Delgadillo-Hinojosa F, Alvarez-Borrego S (1998) Cadmium in the coastal upwelling area adjacent to California-Mexico border. Estuar Coast Shelf Sci 46: 475-481
Serviere-Zaragoza E, Gonzalez-Gonzalez J, Rodríguez-Vargas D (1993) Ficoflora de la region de Bahia de Banderas, Jalisco-Nayarit. In: Salazar- Vallejo S, Gonzalez NE (Eds) Biodiversidad Marina y Costera de Mexico, CONABIO, CICRO, Chetumal, Mexico, p 420
Zeisler R, Becker DA, Gills TE (1995) Certifying the chemical composition of a biological material-a case study. Fres J Anal Chem 352: 111-115
Zingde MD, Singral SYS, Moraes, CF, Reddy CVG (1976) Arsenic, copper, zinc and manganese in the marine flora and fauna of coastal and estuarine waters around Goa. Indian J Mar Sci 5: 212-217