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Pergamon

*Marine Pollution Bulletin*, Vol. 28, No. 5, pp. 330-333, 1994  
Elsevier Science Ltd  
Printed in Great Britain  
0025-326X/94 \$7.00+0.00

## Spatial and Temporal Variations of Arsenic and Selenium in a Biomonitor (*Modiolus capax*) from the Gulf of California, Mexico

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The Gulf of California occupies an oceanographically unique position among the marginal seas of the Pacific Ocean. Lying between the arid peninsula of Baja California in the west and the almost equally arid states of Sonora and Sinaloa to the east, it constitutes a large evaporation basin, which is open to the Pacific at its southern end (Roden, 1964). It is approximately 1000 km long and 150 km wide on average. In the Mexican states adjacent to the Gulf of California, settlements have developed in valleys and mountainous regions where the main economic activities are agriculture, fishing, tourism, industry and mining. Freshwater input by rivers has only a local impact, mostly during the rainy season. Most river water is used for agricultural and urban purposes and progressively less freshwater is allowed to reach the Gulf of California. Some coastal waters along the peninsula of Baja California may still be considered free of any anthropogenic input of conservative pollutants. The principal sources of contaminants to the coastal waters of the peninsula are municipal discharges in the area of Santa Rosalía, Mulegé and La Paz. The remainder of the west coast of the Gulf of California is affected little by wastewater or industrial discharges.

During May and November 1988 a mussel watch exercise was performed around the coast of the peninsula of Baja California within the Gulf of California. Several studies have confirmed the usefulness of mussels as indicators of trace metal levels in the

coastal marine environment (Goldberg, 1975; Phillips, 1980; Martin, 1985; Farrington *et al.*, 1987). The present study employed the mussel *Modiolus capax* to establish concentrations of arsenic and selenium and to follow their spatial and temporal variations. The species selected for analysis in this study is widespread on the peninsular coast and is also consumed by the local population. In the absence of *Mytilus californianus* or *M. edulis* in the study area, *Modiolus capax* serves as a useful bioindicator for metal contamination. In certain sites studied along the coastal environment of the peninsula, no previous data are available to establish the severity of As and Se contamination.

Samples of *M. capax* were collected from rocky intertidal areas at 14 sites along the peninsula of Baja California, as shown in Fig. 1. The sampling locations were chosen for availability of mussels and their proximity to the human population. Procedures for collection are summarized in Stephenson *et al.* (1979). Samples were placed in metal-free polyethylene bags and stored on dry ice; upon return to the laboratory, they were kept frozen at  $-20^{\circ}\text{C}$  prior to analysis. Samples were prepared for analysis by cleaning shells of epibiota. Forty-five mussels from each sample were split into three groups of 15 mussels each. The gonads were

TABLE I

Variation in size, wet wt and concentration of As and Se in mussels *M. capax* collected from the Gulf of California during 1988. Results are expressed on a dry wt basis ( $\mu\text{g g}^{-1}$ ). Means within the same columns and time periods having the same subscript letter are not significantly different ( $p < 0.05$ , HSD Tukey test).

Sites	size (mm)	wet wt (g)	May			
			As		Se	
Punta Estrella	85.1	12.7	10.2	cde	3.57	abc
Puertecitos	81.1	16.0	6.62	e	1.77	e
San Luis Gonzaga	91.8	20.2	12.9	cde	4.02	a
Bahía Angeles G	94.8	15.0	22.7	bc	2.41	cd
Bahía Angeles C	90.1	13.9	13.4	cde	2.59	bcd
Bahía Angeles R	90.6	22.0	53.4	a	2.34	cde
San Rafael	—	—	—	—	—	—
San Fransiquito	94.6	16.7	7.28	de	3.64	ab
Santa Rosalía P	93.9	19.3	13.0	cde	2.03	de
Santa Rosalía M	82.6	11.0	16.6	cd	2.88	abcd
Estero San Lucas	93.9	24.4	6.58	e	1.56	e
Mulegé	87.9	12.4	44.7	ab	4.16	a
Loreto	—	—	—	—	—	—
Bahía La Paz	93.7	17.1	23.0	abc	2.89	abcd
November						
Punta Estrella	90.6	11.0	13.3	ab	3.67	a
Puertecitos	75.3	8.45	17.7	ab	2.54	ab
San Luis Gonzaga	89.8	12.8	9.24	ab	2.60	ab
Bahía Angeles G	84.2	10.9	6.71	b	2.32	ab
Bahía Angeles C	89.5	12.5	14.2	ab	2.34	ab
Bahía Angeles R	93.2	17.8	14.3	ab	2.08	b
San Rafael	75.9	11.9	18.2	ab	2.20	ab
San Fransiquito	—	—	—	—	—	—
Santa Rosalía P	95.4	17.7	12.1	ab	2.26	ab
Santa Rosalía M	98.5	15.4	17.2	ab	2.60	ab
Estero San Lucas	111.3	23.3	10.5	ab	2.15	b
Mulegé	80.6	7.21	24.8	a	2.19	b
Loreto	93.9	12.2	7.07	b	1.93	b
Bahía La Paz	91.6	13.4	18.3	ab	2.71	ab

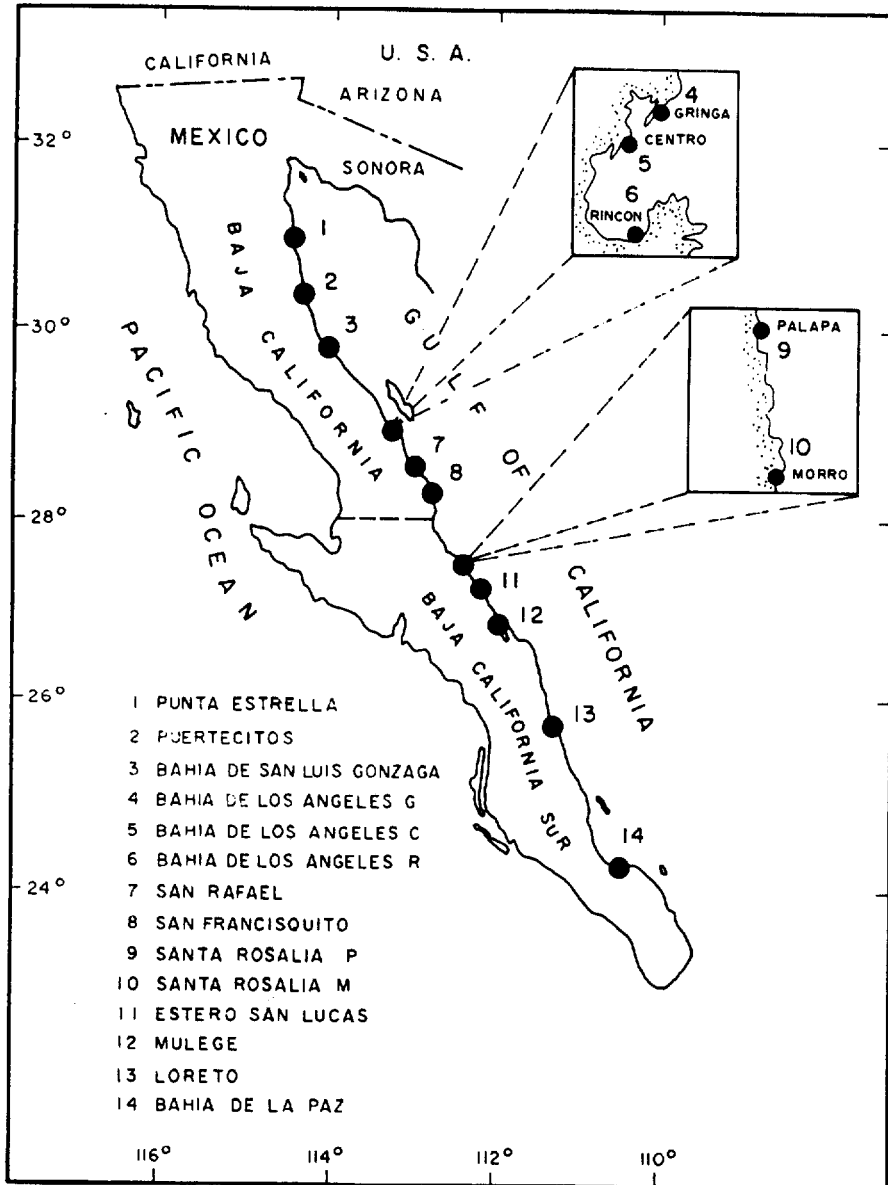


Fig. 1 The study area, showing the sampling sites.

dissected and discarded to minimize variation in body weight due to the reproductive cycle (Ouellette, 1981). In each case, a 5 g sample of homogenized mussel tissue was treated with 5 ml of 40% (w/v)  $Mg(NO_3)_2 \cdot 6H_2O$  and dried at 80°C overnight. The dry residues were ashed at 500°C for 5 h. The ash was diluted with 25 ml of 4 M HCl. Procedural blank digests were also prepared. The analysis of As and Se was carried out with a Thermo Jarrel Ash, Smith Hieltje 12 Atomic Absorption Spectrophotometer fitted with an AVA 440 hydride generation system. The accuracy of the method used was tested using Standard Reference Materials from the National Bureau of Standards (SRM 1572 citrus leaves for As, and SRM 1577a bovine liver for Se). Replicate analysis showed agreement of 100% and 85% with certified values, respectively. Mean values for elements were analysed statistically by means of ANOVA and Tukey HSD 'post hoc' tests. Variances were checked for homogeneity by means of the Box's small sample F approximation (Wilkinson, 1990). A simple linear correlation analysis between wet wt, size and concentration of As and Se was also performed.

Mean concentrations of As and Se and the results from the 'post hoc' analysis for samples of *M. capax* taken during May and November 1988 are presented in Table 1. The geographical variation of these element levels and their temporal variability are shown in Fig. 2.

In May, the maximum value for As ( $53.4 \mu g g^{-1}$  dry wt), was found in mussels from the area of Bahía de los Angeles R (site 6), and the minimum value ( $6.58 \mu g g^{-1}$  dry wt) in samples from Estero San Lucas (site 11). The second highest As value ( $44.7 \mu g g^{-1}$  dry wt) was found in mussels from Mulegé (site 12). High levels of As in mussels therefore occurred in the central-northern region and the south of the peninsula (Fig. 2). The maximum Se value for May ( $4.16 \mu g g^{-1}$  dry wt) was found in samples from Mulegé (site 12) and the minimum value ( $1.56 \mu g g^{-1}$  dry wt) in mussels from Estero San Lucas (site 11). In general, Se presented less regional variability than that found for As. The ratios for maximum and minimum concentrations were 8.1 and 2.7 for As and Se, respectively (Table 1).

In November, the concentrations of As found in mussels were generally slightly lower and less variable

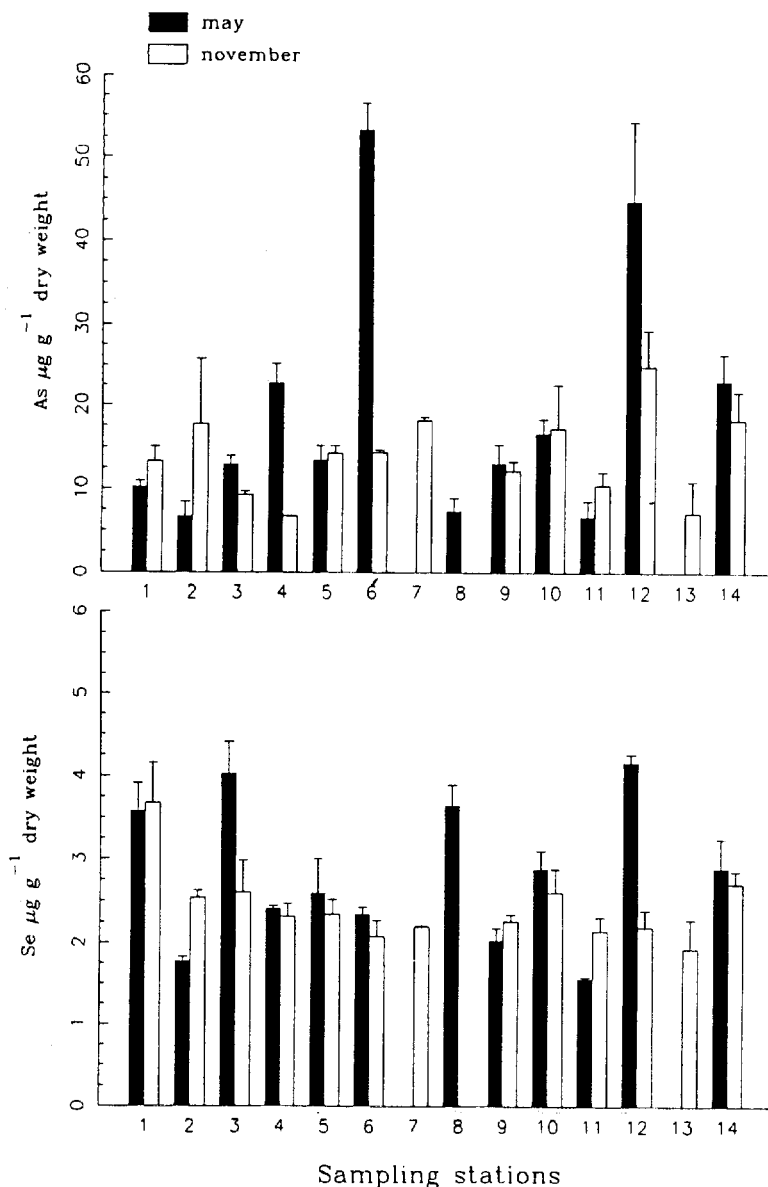


Fig. 2 Geographical variations of As and Se concentrations in *M. capax* (means  $\pm$  standard errors,  $\mu\text{g g}^{-1}$  dry wt) from the Gulf of California during 1988.

than those of May. The maximum value of As in *M. capax* ( $24.8 \mu\text{g g}^{-1}$  dry wt) was detected in Mulegé (site 12) and the minimum value ( $6.71 \mu\text{g g}^{-1}$  dry wt) in Bahía de los Angeles G (site 4). The maximum value of Se ( $3.67 \mu\text{g g}^{-1}$  dry wt) was found in mussels from Punta Estrella (site 1) and the minimum value ( $1.93 \mu\text{g g}^{-1}$  dry wt) in samples from Loreto (site 13). The maximum/minimum ratios calculated for the November samples were 3.7 and 1.9 for As and Se, respectively (Table 1). In November, Se concentrations in mussels showed less variation between sites, by comparison to data for May. Selenium concentrations appeared to vary little throughout the Gulf of California (Fig. 2).

The correlation analysis between animal weight or size and the concentrations of As and Se in *M. capax* showed that the biological characteristics had no significant effect ( $p < 0.05$ ) on the variability of these elements.

The sites studied along the Gulf of California represent a variety of hydrographic conditions. The annual water temperature range is large, and increases from

about  $9^{\circ}\text{C}$  near the mouth of the Gulf to  $22^{\circ}\text{C}$  near the Colorado River estuary at the head of the Gulf. Surface salinities in the northern two-thirds of the Gulf range between  $35\text{‰}$  and  $35.8\text{‰}$  (Roden, 1964). Variations in salinity and temperature in the Gulf of California may contribute to spatial and temporal variations of As and Se in mussels. With respect to temperature effects, both As and Se exhibit enhanced accumulation in mussels at higher temperatures. The accumulation of As also increases in mussels at lower salinities (Fowler & Benayoun, 1976; Ünlü & Fowler, 1979). Spatial and temporal variations of As and Se in the region may also be affected by their bioavailability and by the reproductive state of the mussels. Coimbra *et al.* (1991) reported effects of the reproductive cycle on metal accumulation in mussels.

The results given in Table 1 are similar to those found along the California coast of the USA. Hayes & Phillips (1986) reported concentrations of As in resident and transplanted mussels (*Mytilus californianus*) of  $6\text{--}29 \mu\text{g g}^{-1}$  dry wt at collection sites in

California. Johns *et al.* (1988) reported Se levels of 3–5 µg g<sup>-1</sup> dry wt in benthic bivalves (*Corbicula* sp. and *Macoma balthica*) from San Francisco Bay. It appears likely that the lower values reported here for As and Se in *Modiolus capax* represent baseline levels of these elements in relatively pristine locations.

We appreciate the financial support of Consejo Nacional de Ciencia y Tecnología (CONACyT) México (agreement PCCNCNA-050364) and Secretaría de Educación Pública (agreement 880532).

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*Marine Pollution Bulletin*, Vol. 28, No. 5, pp. 333–335, 1994  
 Elsevier Science Ltd  
 Printed in Great Britain  
 0025-326X/94 \$7.00+0.00

## Heavy Metal Concentrations in Selected Organisms from İzmir Bay, Turkey

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Heavy metal contamination of the environment has been recognized as a serious pollution problem. In particular, mercury has received much attention due to the well known toxic effects of this metal (Förstner & Witmann, 1982). It is of importance to establish baseline levels of trace elements in the environment.

The effect of some heavy metals on algal growth and their biochemical and physiological properties, as well as their accumulation in algal species, has been studied by a number of authors. Phillips (1977) has advised on the use of macroalgae as indicator organisms for monitoring metal levels in marine environments.

The Bay of İzmir is one of the largest bays on the Aegean coast of Turkey, extending about 24 km in an east–west direction, with an average width of about 5 km. İzmir city and harbour, and several industries are located on the inner coastline of the Bay. Untreated or partially treated industrial and domestic wastewaters are discharged directly or carried by streams into the Bay. Rapid increases in wastewater volumes have triggered extensive pollution of the Bay, starting in the

early 1960s. As a result, the inner bay in particular is heavily polluted.

As part of a programme carried out to estimate the degree of heavy metal pollution, samples of macroalgae and other organisms were collected for the inner part of İzmir Bay (Fig. 1). The concentrations of heavy metals in organisms of the Bay have been previously investigated by Tuncer (1988) and IMST (1988). The present study reports the distribution of Hg, Cd, Pb, Cr, Cu and Zn in species of marine macroalgae and other organisms collected from İzmir Bay.

Samples were collected by trawling in the intertidal zone, as applicable. Algae were kept in plastic bags at

TABLE 1  
 Trace metal concentrations (µg g<sup>-1</sup> wet wt) in seaweeds of İzmir Bay.

Species	n	Hg	Cd	Pb	Cu	Zn
<i>Ulva</i> sp.	9	Min: 0.020	nd	0.63	1.18	4.77
		Mean: 0.038	0.13	3.31	1.82	8.02
		Max: 0.084	0.56	9.34	2.11	13.38
<i>Codium</i> sp.	11	Min: 0.027	nd	0.72	0.51	2.73
		Mean: 0.036	0.14	3.13	0.92	4.89
		Max: 0.053	0.47	6.72	1.74	8.60
<i>Gracilaria</i> sp.	4	Min: 0.025	0.14	2.00	1.07	5.85
		Mean: 0.071	0.38	3.78	1.95	7.50
		Max: 0.099	0.66	6.08	2.55	10.04
<i>Bangia</i> sp.	2	Min: 0.031	0.10	4.08	2.50	15.69
		Mean: 0.045	0.12	4.49	2.55	15.69
		Max: 0.059	0.14	4.90	2.59	15.69
<i>Codium bursa</i>	3	Min: 0.025	0.12	0.94	0.52	1.54
		Mean: 0.031	0.18	1.64	0.63	1.98
		Max: 0.042	0.26	2.27	0.89	2.77
<i>Phyllophora nervosa</i>	1	0.064	0.32	4.04	1.32	6.10
<i>Dazia</i> sp.	1	0.046	0.46	3.84	0.73	3.55

n: Number of samples. Min: Minimum. Max: Maximum.