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Element concentrations in some species of seaweeds from La Paz Bay and La Paz Lagoon, south-western Baja California, Mexico

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Abstract

La Paz Bay and La Paz Lagoon are water bodies of the Gulf of California that are influenced by waste water discharges from the City of La Paz and from activities of the phosphorite mining company "Rofomex". Because seaweeds concentrate elements from the water and are used as effective indicators of contamination by metals, we investigated their usefulness in this region. Concentrations of certain major elements (Ca, Fe, K and Na) and trace elements (As, Ba, Co, Cr, Cs, Hf, Rb, Sb, Sc, Se, Sr, Ta, Th, U, Zn and Zr) were determined in 12 species of seaweeds from La Paz Bay and La Paz Lagoon using instrumental neutron activation analysis. The contents of trace elements of environmental importance (As, Co, Cr, Fe, Sb, Se and Zn) in all studied samples are within the range of typical levels for a pristine environment not subjected to anthropogenic impact. Somewhat higher concentrations of Cr (81 mg kg^{-1}), Hf (4 mg kg^{-1}), Rb (48 mg kg^{-1}), Sc (6.3 mg kg^{-1}), Ta (0.95 mg kg^{-1}), Th (6.8 mg kg^{-1}), U (33 mg kg^{-1}) and Zn (90 mg kg^{-1}) were found in the green seaweed species *Ulva* (formerly *Enteromorpha) intestinalis*, whereas such elements as As (77 mg kg^{-1}), Sb (1.4 mg kg^{-1}) and Se (1.8 mg kg^{-1}) were mainly concentrated in the species *Sargassum sinicola*, *Codium cuneatum* and *Padina mexicana* respectively. Because of their higher abundance and heterogeneity in elemental composition the seaweeds species *Ulva intestinalis* and *Caulerpa sertularioides* seem to be more suitable for further biomonitoring of heavy metal pollution of the coastal waters in this zone.

Introduction

The development of marine ecosystems is strongly controlled by the biogeochemical cycles of chemical elements, which depend on their interactions with each other and the geological, climatic, physical, chemical and biological processes that occur in the water column and on the interfaces with sediments and the atmosphere (Chester, 2003; De La Lanza & Cáceres, 1994). In coastal marine areas, it is important to understand the biogeochemical cycles of both the major and trace elements because of the possibility of the changes which may occur in them as a result of either natural or man-made alterations to the environment.

Bays, being partly enclosed water bodies, often show strong variations in terms of sediments and chemical composition of the water column. In particular, coastal marine sediments are usually made up of both terrigenous and marine biogenic materials, and their composition can vary depending on hydrodynamic and climatic conditions, the type and strength of material inputs, distance from source and the extent of dilution of natural terrigenous or anthropogenic components, usually enriched in many elements, by silica and carbonates of marine biogenic origin (Chester, 2003).

Some elements are mainly present in the dissolved fraction (ions and molecules) in the sea water, whereas others are incorporated into either colloidal or particulate matter. Particulate and/or dissolved material may interact with each other and alter the biogeochemical fate of the elements in the marine environment. During early diagenesis elements stored in the marine sediments because of the changes in the sediment's pH and redox potential Eh can be released into the interstitial and overlying sea water by dissolution, desorption or autolytic biological processes (Chester, 2003). Any disturbance caused by either physical factors (e.g. currents) or biological factors (e.g. movement of organisms) will stimulate exchanges between the elements in the sediments and those in the seawater.

A variety of organisms, such as seaweeds, can also transfer and accumulate trace elements in the sea (Kennish, 1997). Seaweeds take up metal elements from the aquatic environment, depending on species, exposure time, type of metal and its oxidation state, pH, salinity and presence of organic pollutants (Bernhard & Zattera, 1975; Hassett et al., 1980; Jensen et al., 1976; Myklestad et al., 1978; Phillips, 1977). Contamination of the seaweed surface from simple contact with the elements dissolved in sea water has been observed in both unicellular and pluricellular algae, while metal ions, some of which are essential elements, are also taken up by algae through pores in their cell walls. Consequently, the cell components as well as the composition and structure of the cell walls are important factors in determining the ability of a seaweed species to absorb metals (Kuyucak & Volesky, 1990). For example, in brown seaweeds, the alginates of the cell walls and of the intracellular spaces regulate the exchange of ions, showing an affinity for metals in the following decreasing order: Pb > Cu > Cd > Ba > Sr > Ca > Co > Ni > Zn > Mn > Mg.

Many studies of contaminants and their effects on marine macroalgae have been published since the beginning of the 1960's (see Lobban & Harrison, 1994). Other data have shown that seaweeds can absorb metals such as Pb and Sr (Eide et al., 1980). For example, Ho (1990) found that the seaweed *Ulva lactuca* is an important bioindicator of Cu, Zn and Pb present in sea water. Similar studies were recently done for the coastal zone of Mexico. For example, Robledo & Freile Pelegrín (1997) reported the chemical composition of six species of edible macroalgae from the Yucatan region. Closer to La Paz Bay, Sánchez-Rodríguez et al. (2001) reported the concentrations of elements in various seaweeds from the almost pristine Bay of Loreto, in the central Baja California peninsula.

La Paz Bay and its smaller component, La Paz Lagoon, are particularly interesting for environmental studies because of their proximity to the City of La Paz, the oil reservoirs of Petroleos Mexicanos (PEMEX), the electrical plant owned by the Compañía Federal de Electriciadad, and the activities of the mining company "Roca Fosfórica Mexicana, S.A. de C.V." ("ROFOMEX"), located near the San Juan de la Costa in the western coast of the La Paz Bay. Because of the dry and arid climate of the region, terrigenous material is carried into La Paz Bay and La Paz Lagoon mainly by wind or with episodic discharges of the ephemeral water streams ("arroyos") only after rare but heavy rains. The characteristics of these inputs into the coastal marine environment are largely determined by the different types of rocks (sedimentary rocks, igneous rocks and alluvium, a product of the weathering of the rocks of San Gregorio and San Isidro Formation, and the Comondú geological formation) in the surrounding areas (Figure 1, Hausback, 1984).

The high productivity of coastal waters of La Paz Bay and La Paz Lagoon makes it more interesting to determine the concentrations of elements in the seaweeds, because some of them are edible or could be used as food additives for domesestic animals. It is also necessary to determine which seaweed species are most suitable for future biomonitoring of heavy metal pollution in these areas.

Taking all of this into consideration, as well as the need to increase the use of the region's natural resources in a controlled manner, the present study aimed to determine the concentrations of major and trace elements in some species of seaweeds that occur in La Paz Bay and La Paz Lagoon, and to select species suitable for further biomonitoring of heavy metal pollution of these areas.

Materials and methods

In August 1998, 35 samples of seaweeds were taken from a boat by scuba diving at 19 different locations in La Paz Bay, between Punta Tarabillas and the Espiritu Santo Island (Figure 1, Table 1). The seaweeds were collected by hand directly from the substrate and put into identified plastic bags for later analysis. In the laboratory, they were washed with tap water to get rid of any residues such as sand or shells, and then sorted according to sampling station and species. The seaweeds were identified using taxonomic keys (Abbott & Hollenberg, 1976; Norris, 1975; Silva et al., 1996; Taylor, 1945). They were then left to dry at room temperature, on absorbent paper. Once completely dried, each sample was crushed, sieved and

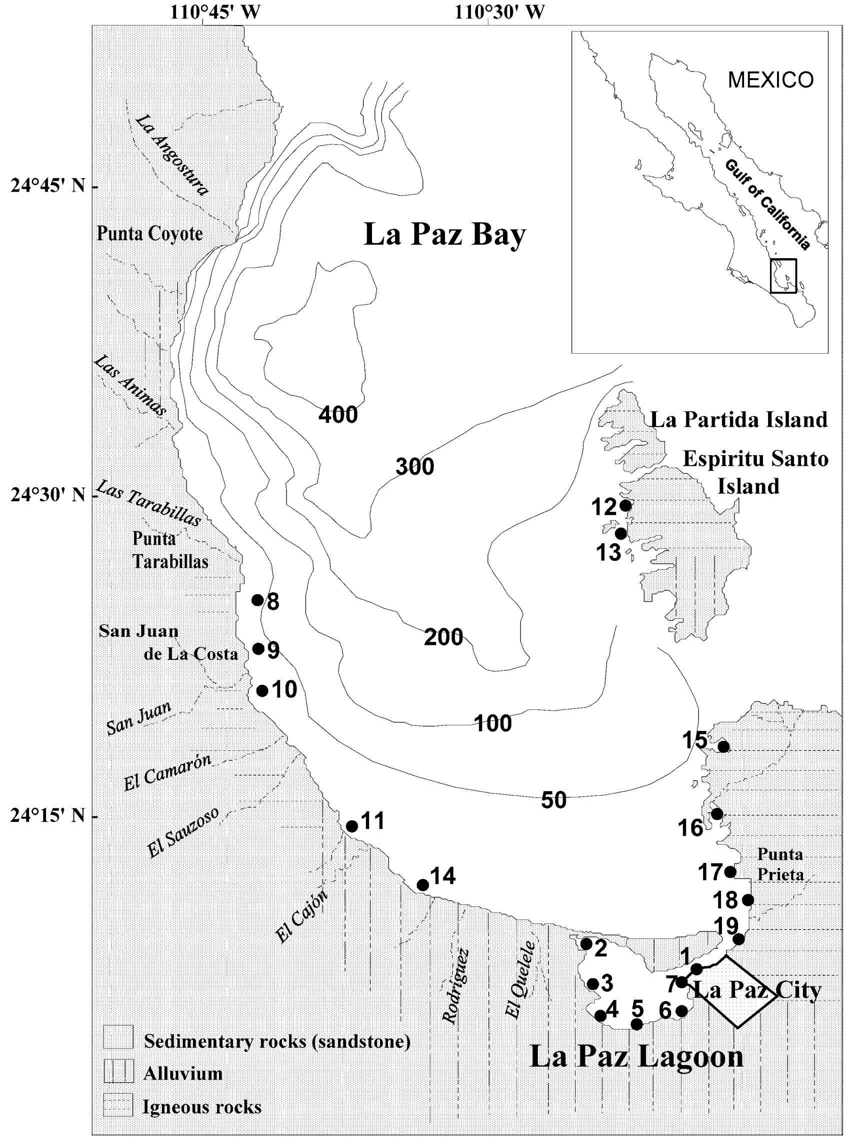

Figure 1. The study area and location of the stations of the seaweed sampling in the La Paz Bay and La Paz Lagoon.

stored for further chemical analysis. Element contents in sub-samples of seaweeds were determined at the V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences, using instrumental neutron activation analysis (INAA). A 100 mg fraction of each sample was taken, then folded in aluminium paper and irradiated jointly with standard reference materials SRM 1646a "Estuarine sediment", IAEA-356 "Polluted marine sediment" and SD-N-1/2 "Contaminated marine sediment" (IAEA) by thermal neutrons (2.8×10^{13} n $s^{-1}cm^{-2}$). The induced radioactivity of each sample was measured using a semi-conductor gamma ray spectrometer, supplied with a high resolution Ge(Li) detector coupled with a 4096 channel "Nokia" analyzer. Gamma ray spectrometric standard reference sources were used to calibrate the instrument (^{152}Eu) (Sánchez-Rodríguez et al., 2001; Shumilin et al., 2000). In this manner, the content of the following elements in the seaweed dry tissues was determined: As, Ba, Br, Ca, Co, Cr, Cs, Fe, Hf, K, Na, Rb, Sb, Sc, Se, Sr, Ta, Th, U, Zn, and Zr.

Table 1. The study area, location of the stations and species of seaweeds collected in the La Paz Bay and La Paz Lagoon in August 1998.

	Coordinate of station		
Station	Latitude, °N	Longitude, °W	Specie
1	24°08′04″	110°21′00″	*Enteromorpha intestinalis* (Linnaeus) Link; *Caulerpa sertularioides* (S.G. Gmelin) Howe
2	24°10′18″	110°25′81″	*Enteromorpha intestinalis* (Linnaeus) Link; *Caulerpa sertularioides* (S.G. Gmelin) Howe
3	24°08′25″	110°25′36″	*Enteromorpha intestinalis* (Linnaeus) Link; *Caulerpa sertularioides* (S.G. Gmelin) Howe
4	24°06′76″	110°25′08″	*Caulerpa sertularioides* (S.G. Gmelin) Howe
5	24°06′67″	110°23′16″	*Caulerpa sertularioides* (S.G. Gmelin) Howe; *Halimeda discoidea* Decaisne *Spyridia filamentosa* (Wulfen) Harvey
6	24°07′05″	110°21′34″	*Enteromorpha intestinalis* (Linnaeus) Link
7	24°08′49″	110°21′28″	*Enteromorpha intestinalis* (Linnaeus) Link; *Dictyota divaricata* Lamouroux; *Padina mexicana* Dawson1944
8	24°25′08″	110°40′00″	*Enteromorpha intestinalis* (Linnaeus) Link; *Dictyota divaricata* Lamouroux; *Sargassum sinicola* Setchel & Gardner *Amphiroa beauvoisii* Lamourox
9	24°23′64″	110°40′00″	*Enteromorpha intestinalis* (Linnaeus) Link; *Codium cuneatum* Setchell & Gardner; *Sargassum sinicola* Setchel & Gardner
10	24°21′69″	110°40′84″	*Gelidiopsis tenuis* Setchell & Gardner
11	24°15′52″	110°36′76″	*Dictyota divaricata* Lamouroux; *Padina mexicana* Dawson; *Sargassum sinicola* Setchel & Gardner
12	24°30′10″	110°23′08″	*Gelidiopsis tenuis* Setchell & Gardner
13	24°29′23″	110°23′46″	*Gelidiopsis tenuis* Setchell & Gardner
14	24°12′06″	110°33′28″	*Codium cuneatum* Setchell & Gardner; *Gelidiopsis tenuis* Setchell & Gardner
15	24°19′11″	110°19′27″	*Caulerpa sertularioides* (S.G. Gmelin) Howe; *Spyridia filamentosa* (Wulfen) Harvey
16	24°16′23″	110°19′78″	*Caulerpa sertularioides* (S.G. Gmelin) Howe
17	24°13′27″	110°18′73″	*Spyridia filamentosa* (Wulfen) Harvey; *Digenia simplex* (Wulfen) C. Agardh
18	24°12′16″	110°18′04″	*Galaxaura oblongata* (Ellis & Solander) Lamouroux; *Amphiroa beauvoisii* Lamourox
19	24°10′47″	110°18′45″	*Caulerpa sertularioides* (S.G. Gmelin) Howe; *Halimeda discoidea* Decaisne; *Padina mexicana* Dawson

Results

Seaweed species

The location of sampling stations where seaweeds were collected is shown in Table 1. Twelve species were found, belonging to all three divisions (Chlorophyta, Phaeophyta and Rhodophyta). The greatest variety of species was found at Stations 8 and 11, while Stations 3, 6, 13 and 16 were poorest in species abundance, with only one species present. The green macroalgae *Enteromorpha intestinalis* and *Caulerpa sertularioides* were the most widespread during the observation period, being found in 7 stations.

Major elements (Ca, Fe, K and Na)

The concentrations of the major elements in the samples vary depending on algal species and sampling location (Table 2, Figures 1–3). Ca was present at high levels in *Halimeda discoidea* (30.2%) collected at the Station 5 in the southern part of the bay in the La Paz Lagoon area. Two species were found to have a high concentration of Fe: *Padina mexicana*, in samples taken at the south-eastern end of the bay at the Station 11 located in front of the El Cajón Arroyo (1.6%), and *Enteromorpha intestinalis*, in samples taken from a Station 8 located south of San Juan de La Costa (1.4%). The highest accumulation of K was found in samples of *Enteromorpha intestinalis* which were collected in

Table 2. Concentrations of the elements in the samples of macroalgae collected in the La Paz Bay and the Lagoon of La Paz.

		Content of elements (mg kg^{-1})																			
Specie	Station	Na (%)	K (%)	Ca (%)	Fe (%)	Rb	Cs	Th	Sr	Ba	Sc	U	Zr	Hf	Ta	Cr	Co	Zn	As	Sb	Se	Br
E. intestinalis	1	0.8	0.1	5.5	1.2	33	3.3	2.2	650	245	4.8	7.5	50	1.2	0.2	15	3.5	50	16	0.5	0.7	4.3
	2	0.7	–	5.0	0.7	18	2.2	1.3	670	150	2.7	1.6	50	0.6	0.1	10	2.9	40	9	0.6	0.4	10.6
	3	0.3	–	2.5	0.9	15	2.3	1.3	395	23	3.7	5.0	50	1.5	0.1	13	4.7	70	3	1.0	1.1	2.7
	6	0.5	–	2.8	1.2	18	2.8	1.3	185	165	3.6	6.2	48	1.2	–	11	4.2	90	3	0.4	0.6	1.7
	7	0.3	–	2.7	0.8	15	2.5	2.2	210	87	3.8	1.0	–	0.8	0.3	11	4.2	50	6	0.4	0.5	1.3
	8	1.0	3.1	8.5	1.4	22	2.4	3.2	645	390	5.1	0.9	230	4.0	0.3	57	3.9	50	13	0.2	0.5	3.1
	9	1.9	–	12.2	1.3	49	3.5	6.9	700	425	6.3	33.3	85	2.7	0.9	81	3.4	50	8	0.3	1.4	2.0
C. cuneatum	9	3.1	0.8	2.2	0.4	6	0.7	0.7	200	140	1.4	0.9	35	0.7	–	15	2.3	30	31	1.4	0.7	5.5
	14	15.2	0.9	4.0	0.1	–	0.1	0.1	630	43	0.2	12.6	4	0.1	–	2	0.4	10	48	0.3	0.4	6.7
C. sertularioides	1	0.4	0.1	2.3	0.4	3	1.1	1.0	215	90	2.0	3.1	60	1.2	0.2	24	1.7	30	21	0.4	1.2	1.2
	2	0.4	0.1	3.0	0.2	2	0.7	0.4	255	50	0.9	6.6	45	0.2	0.2	5	1.1	20	13	0.7	0.7	1.9
	3	0.3	0.1	1.0	0.3	9	1.4	0.8	145	–	1.5	2.8	–	0.4	0.1	4	2.4	40	13	0.4	0.7	1.1
	4	0.3	–	1.0	0.3	4	1.4	0.8	140	55	1.4	3.0	–	0.4	0.1	5	2.1	30	6	0.2	0.5	1.3
	5	0.4	–	2.5	0.6	4	1.4	0.9	360	66	2.6	5.4	–	0.5	–	8	3.5	50	5	0.1	0.2	2.8
	15	0.9	–	3.7	0.3	1	0.3	0.4	420	40	1.0	4.0	34	0.2	–	4	1.2	20	16	0.5	0.8	2.4
	16	3.5	–	6.8	0.4	11	0.6	0.9	910	65	1.5	10.3	38	0.6	0.1	5	1.3	40	11	0.6	0.4	5.7
	19	0.8	–	5.7	0.4	12	1.2	0.8	1160	82	1.5	0.3	76	0.3	–	6	1.4	50	20	1.0	1.0	1.3
H. discoidea	5	1.0	0.3	30.2	0.6	2	1.3	0.9	7245	105	2.5	4.3	10	1.0	–	14	3.0	40	18	0.5	1.2	6.3
	19	2.1	–	26.2	0.2	2	1.2	0.6	6485	95	0.9	1.8	38	0.2	–	5	1.4	20	9	0.7	0.4	7.2
D. divaricata	8	0.7	–	5.1	0.6	15	0.9	2.2	1230	280	2.3	6.0	80	1.1	0.1	23	2.0	40	33	0.2	0.4	2.4
	11	0.7	0.4	6.0	0.8	20	0.8	2.2	1175	330	4.2	6.5	90	1.4	0.5	19	3.2	30	28	0.4	1.4	1.6
P. mexicana	11	1.0	–	14.7	1.6	25	1.6	4.1	3275	515	5.9	4.8	69	3.2	0.5	49	5.5	50	20	0.1	1.8	1.7
	18	0.1	0.1	22.4	1.0	13	2.1	1.7	4755	240	3.8	4.3	43	0.9	–	14	3.5	40	17	0.7	0.7	1.4
	19	1.0	0.2	20.4	0.6	16	2.0	1.2	4345	220	2.4	2.1	29	0.5	–	9	2.0	40	18	0.4	0.3	1.4
S. sinicola	8	0.7	0.4	3.3	0.1	8	0.7	0.2	1735	73	0.5	7.2	15	0.8	–	4	1.4	30	77	0.2	1.6	4.9
	9	0.6	–	4.1	0.2	8	0.4	0.5	1775	74	0.6	1.4	45	0.2	–	8	1.2	30	55	–	1.2	7.1
	11	0.5	–	5.0	0.1	10	0.3	0.3	2355	130	0.5	1.5	20	0.1	–	5	1.1	20	45	0.5	0.3	6.6
G. oblongata	17	0.7	0.7	21.8	0.3	8	0.8	0.5	5750	81	0.9	10.20	28	0.2	–	5	2.1	40	15	0.2	1.0	9.4
A. beauvoisii	8	0.4	–	26.5	0.1	6	0.5	0.3	6620	72	0.3	0.2	10	0.1	–	3	0.2	10	8	0.5	0.2	1.6
G. tenuis	10	0.6	–	2.9	0.1	6	0.4	4	335	120	0.3	4.3	–	0.3	–	4	1.4	20	3	0.3	0.9	5.5
	12	2.4	0.4	3.4	0.2	4	0.5	0.6	380	10	0.8	4.5	39	0.2	0.3	8	1.9	30	13	0.5	0.7	9.5
	13	2.3	0.3	3.5	0.2	4	0.4	0.4	320	25	0.7	4.2	30	0.1	–	3	1.8	20	12	0.7	0.9	10.2
	14	2.3	0.2	5.2	0.1	1	0.3	0.3	715	130	0.2	5.8	32	0.1	–	2	0.7	30	14	1.0	1.6	12.4
S. filamentosa	5	0.5	–	2.4	1.2	17	4.0	1.8	225	80	5.1	6.3	65	1.1	–	12	7.2	60	6	0.2	1.2	3.7
	16	0.6	–	7.7	0.5	3	1.2	0.8	990	63	1.9	2.5	45	0.5	0.1	7	1.6	20	3	0.3	0.5	4.2
	17	0.7	–	8.1	0.6	11	1.7	1.5	1100	205	2.2	3.3	22	1.5	0.2	10	2.3	80	3	0.4	0.7	6.2
D. simplex	17	1.2	1.4	9.2	0.1	33	2.7	1.7	1150	110	2.8	11.5	10	1.1	0.3	14	4.0	90	28	0.5	0.5	7.1

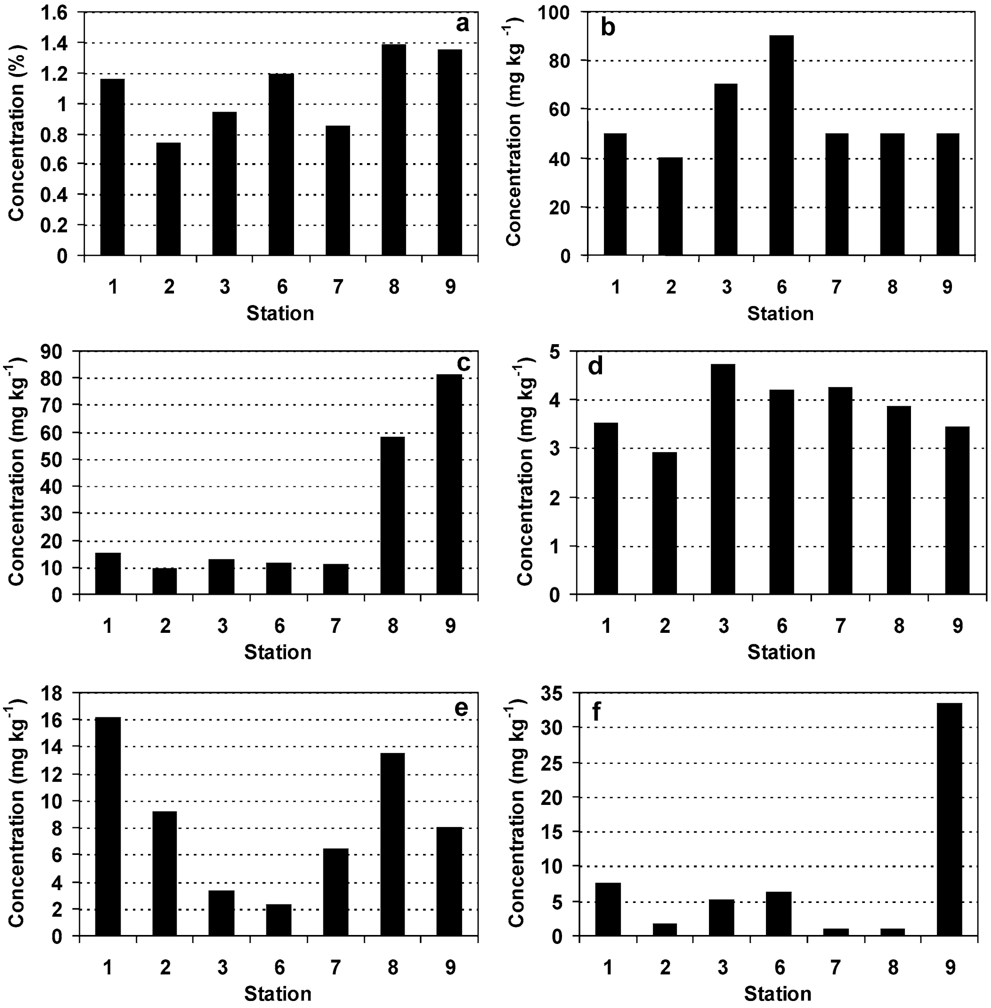

Figure 2. The spatial distribution of the concentration of selected elements in the samples of the seaweed *Enteromorpha intestinalis* from the La Paz Bay and La Paz Lagoon: (a) iron; (b) zinc; (c) chromium; (d) cobalt; (e) arsenic and (f) uranium.

La Paz Bay at Station 8. The highest concentration of Na (15.2%) was detected in *Codium cuneatum* which was collected at Station 14 in the southern part of the La Paz Bay (Figure 1, Table 2).

Trace elements (As, Ba, Rb, Co, Cr, Cs, Hf, Sc, Ta, Sb, Se, Sr, Th, U, Zn and Zr)

*S*trontium had the same tendency to accumulate as Ca, displaying the highest concentration (7245 mg kg^{-1}) in *Halimeda discoidea* from Station 5 (Table 2). In general, the highest concentrations of most of the trace elements (Cr, Hf, Rb, Sc, Se, Ta, Th, U and Zr) were detected in *Enteromorpha intestinalis* collected at Stations 8 and 9 near San Juan de la Costa on the western side of La Paz Bay. The species *Enteromorpha intestinalis* from Station 9, in La Paz Bay in front of the mining area of San Juan de la Costa, displays the highest concentrations of uranium (33 mg kg^{-1}) and of chromium (80 mg kg^{-1}) (Table 2, Figure 2). Nevertheless, higher concentrations of Co were found in *Spyridia filamentosa* (7.2 mg kg^{-1}) and *Enteromorpha intestinalis* (4.7 mg kg^{-1}) from Stations 3 and 6 respectively, located in the semi-closed La Paz Lagoon (Table 2, Figure 2) and in *Padina mexicana* (5.5 mg kg^{-1}) from Station 11.

Maximum values of 90 mg kg^{-1} of Zn were found in *Enteromorpha intestinalis* and *Digenia simplex*, in areas near the City of La Paz, to the south (Station 6) and south-east (Station 17) of La Paz Bay (Table 2).

Arsenic revealed a different pattern, showing the highest levels in *Sargassum sinicola* collected at Stations 8 (77 mg kg^{-1}) and 9 (55 mg kg^{-1}) in La Paz Bay, in the areas of Punta Tarabillas and San Juan de la Costa respectively. Concentrations of antimony, another environmentally important element, were highest in *Codium cuneatum*, reaching 1.4 mg kg^{-1} in samples from the western side of La Paz Bay (Station 9).

As can be seen from Tables 1–2 and Figures 2–3, the seaweeds *Enteromorpha intestinalis* and *Caulerpa sertularioides* were the most frequent and widespread in the study area, and showed a good range in the contents of accumulated heavy metals.

Discussion

This study shows that concentrations of elements in the seaweeds collected in La Paz Bay and La Paz Lagoon vary depending on species and sampling location, probably because many variables affect the accumulation of elements in algae including the abundance of these elements in the surrounding water (Barnett and Ashcroft, 1985; Sánchez-Rodríguez et al., 2001). Strong correlations have been demonstrated between the levels of dissolved Cu, Pb, Ni and Cr in the water and in algae (Haritonidis & Malea, 1995; Jordanova et al., 1999; Seeliger & Edwards, 1977). Biological,

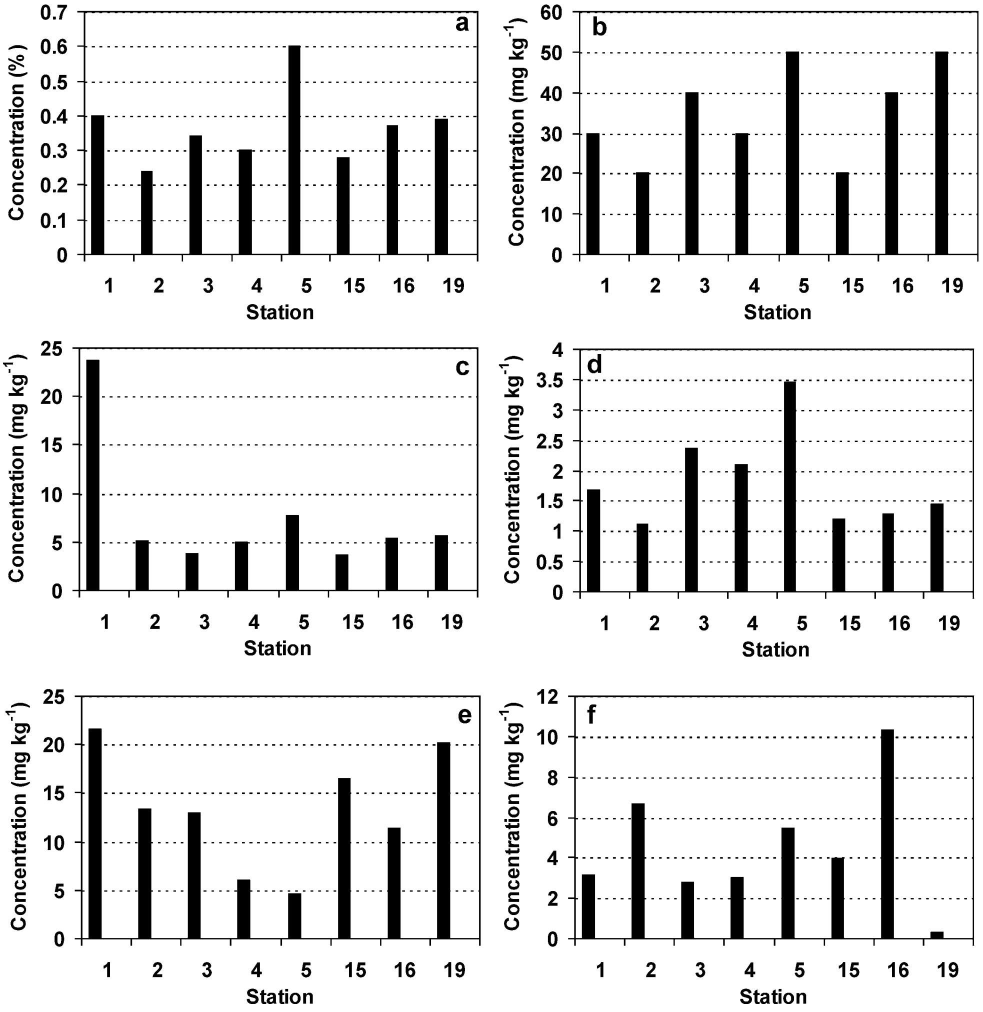

Figure 3. The spatial distribution of the concentration of selected elements in the samples of the seaweed *Caulerpa sertularioides* from the La Paz Bay and La Paz Lagoon: (a) iron; (b) zinc; (c) chromium; (d) cobalt; (e) arsenic and (f) uranium.

physical and chemical conditions affect both the distribution and the role of the elements, compounds and residues in a system (Hassett et al., 1980). Furthermore, seaweeds have a high potential capacity for storing trace metals, depending on the species of alga and the metal (Phillips, 1977; Myklestad et al., 1978). Previous studies (Khristoforova et al., 1983; Ostapczuk et al., 1997; Sánchez-Rodríguez et al., 2001; Sueur et al., 1982) have shown that members of the Phaeophyta have the highest capacity for storing metals. In this study, however, algae belonging to the Chlorophyceae (e.g. *Enteromorpha intestinalis*) from the area near San Juan de la Costa generally accumulated most elements (Cr, Hf, Rb, Sc, Se, Ta, Th, U and Zr). This distinctive feature of this area is probably a result of the weathering of the natural rocks of the drainage basins (mainly sedimentary and volcanic rocks), as well as due to the influence of nearby phosphorite mining operations on the seawater and the marine sediment composition. It was clear that near the mouths of the Las Tarabillas Arroyo and Arroyo San Juan, at Station 9, in front of San Juan de La Costa, concentrations of 33 mg kg^{-1} of U and 80 mg kg^{-1} of Cr in *E. intestinalis* are higher than those found in the same specie from other stations (Table 2, Figure 2). These concentrations are also higher than those found by Sánchez-Rodríguez et al., (2001) for macroalgae in Loreto Bay, where maximum values of $\sim$4 mg kg^{-1} for uranium and of 36 mg kg^{-1} for chromium were found in *Sargassum sinicola*.

A possible explanation for this selective accumulation of metals may be that fact that the initial process of rapid absorption of elements by the seaweeds could be a result of electrostatic attraction of metal ions, since this mechanism does not directly depend on factors which influence the metabolism of algae (a temperature, a light, pH, the availability of nitrogen or the age of organisms), but is related to the abundance of elements in the surrounding water. This could then be followed by the active uptake of metal ions which are transported across the cellular membrane and introduced into the cytoplasm (Crist et al., 1988, 1990; Levine, 1984). To verify this, additional studies need to be carried out, with systematic observations of macroalgae and corresponding concentrations of elements in the water, taking into account the possible supply of metals into the marine environment from natural sources (Hausback, 1984; Rodríguez Castañeda, 2002).

The highest amounts of both Ca and Sr were found in the green alga *Halimeda discoidea* collected in the southern part of the bay, near La Paz Lagoon, and in La Paz Bay, south of Punta Prieta. Macroalgae incorporate Sr through a process involving the exchange of intracellular polysaccharides, whereas Ca ions are used to maintain membranes and the cell wall (Lobban & Harrison, 1994). In fact it has been observed that during ionic exchanges, polysaccharides in brown seaweeds have an affinity for divalent cations such as Ca^{2+} (Karez & Pereira, 1995). This would explain the high concentrations of calcium found in samples of *Padina mexicana* collected in Stations 18 and 19, in the area of Punta Prieta. Both species, *Halimeda*, and to a much lesser extent *Padina*, accumulate calcium carbonate (Lobban & Harrison, 1994).

Selenium, on the other hand, reached its highest concentration (1.8 mg kg^{-1}) in *Padina mexicana* collected at Station 11, in front of the El Cajón Arroyo mouth, which receives terrigenous sediments from a drainage basin of volcanic rocks (Figure 1, Table 2). Since Se is an enzymatic cofactor, it is likely that its accumulation in this seaweed is regulated by metabolic processes (Lobban & Harrison, 1994).

As for Zn, an element that is frequently used to monitor strongly polluted areas, maximum values of 90 mg kg^{-1} were found in *Enteromorpha intestinalis* and *Digenia simplex* collected in the areas close to the City of La Paz, in the southern (Station 6) and southeastern (Station 18) parts of the bay. However, these levels were lower than levels in seaweeds in areas of high human impact (1000 to 2000 mg kg^{-1}). It has been suggested that Zn is taken up both by absorption and by active transport, since it is an important nutrient in algal metabolism (Lobban & Harrison, 1994).

This information is not only useful in determining the pollution status of the La Paz Bay. It is known that seaweeds help reduce the levels of metals in the environment, and removal rates depend on the concentrations of dissolved metals and water pH value (Bernhard & Zattera, 1975; Jensen et al., 1976).

Arsenic showed a preference for the seaweed *Sargassum sinicola* which was collected in Stations 8 and 9, located near Punta Tarabillas and San Juan de la Costa respectively. This feature of As can be attributed to its affinity with this species of seaweed as well as to the spatial distribution of As in the surface sediments, which in these areas showed concentrations of 10 to 20 mg kg^{-1}, apparently because of the weathering products of phosphatic rocks (Rodríguez Castañeda, 2002).

The highest concentrations of the antimony, another important environmental indicator, were found in *Codium cuneatum*, with maxima in samples from the western side of La Paz Bay (Station 9): this can be related to the fact that sediments supplied to this area are influenced by the weathering products of igneous rocks from the surrounding region.

On the basis of our results we conclude that La Paz Bay has not suffered seriously from human impacts, but that the geological characteristics of this region encourage a natural increase in certain elements in the sediments, which is then reflected in the macroalgae. Several macroalgae have been described as excellent bio-indicators because the levels of metals in their tissues are proportional to the concentrations of metals in the surrounding waters (Bryan & Hummerstone, 1973; Försberg et al., 1988; Föster, 1976; Fuge & James, 1973). Results obtained so far from seaweeds collected in the coastal waters of La Paz Bay show that there is localized variation in each of the different areas of the bay, and that the accumulation of some elements is probably determined by their relative concentration in the surrounding water, by a species' particular metabolic processes, and by local environmental conditions.

Conclusions

We found that seaweeds belonging to the Chlorophyceae accumulated the highest contents of the elements studied, with *Enteromorpha intestinalis* as an example for Ba, Cr, Cs, Hf, Rb, Sc, Ta, Th U, and Zr. The variations in the concentrations of these elements in the algae can be related to the influence of local factors such as naturally occuring higher contents of some elements in the water and sediments of certain parts of the bay, or the localized and limited effect of mining operations in the area near San Juan de la Costa.

Of the major and trace elements found in the sediments and seaweeds of the La Paz Bay, the contents of As, Cr, Sb, Se and Zn, usually associated with an intense human activity, did not suggest the existence of such impact on the environment, but did reflect the geological composition of the rocks of the region and the particular characteristics of this water body. Because of their abundance and good range of elemental content the seaweeds *Enteromorpha intestinalis* and *Caulerpa sertularioides* appear most suitable for further biomonitoring of the heavy metal pollution of the coastal waters in this zone.

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