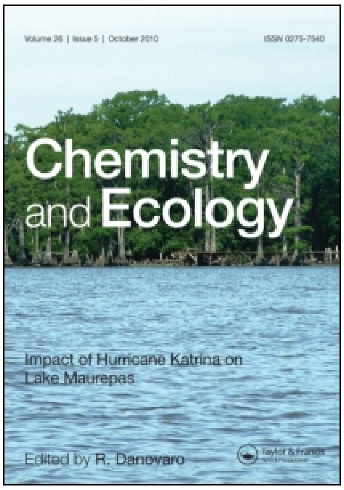

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HEAVY METALS IN MACROALGAE OF HAVANA'S NORTHERN LITTORAL, CUBA

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Copper, iron, lead, manganese, and zinc contents were determined in various phyla of macroalgae typical of the rocky mesolittoral zone of Cuba and widely distributed in the Caribbean Region. The samples were collected in different zones along the shores of Havana City which are more or less influenced by anthropogenic activities. Differences in metal contents were observed due to seasonal variations and differences between sampling sites. Of the analyzed species, only one brown alga, *Padina vickersiae,* is considered as a suitable candidate for the monitoring of metal contamination.

INTRODUCTION

Certain studies (e.g. Amiel and Navrot, 1978, Hershelman *et al.*, 1981; Warren, 1981; Bargagli *et al.*, 1985) have shown that municipal and/or industrial waste waters which are discharged into coastal zones by different routes (shorebased and submarine outfalls or rivers), constitute the main sources of contamination by heavy metals. The environmental effects may vary depending on the characteristics of the discharge zones.

Algae are among the most investigated organisms for detecting metals in the marine environment (Eisler, 1981). Some species of macroalgae have been proposed as bio-indicators in coastal zones (Seeliger and Edwards, 1977; Guimarães *et al.*, 1982; Cullinane *et al.*, 1987). In the present study, the levels of copper, iron, manganese, lead and zinc were determined in six species of macroalgae, typical of the rocky mesolittoral zone of Cuba and widely distributed in the Caribbean area (Taylor, 1960), with the purpose of investigating whether the analyzed species can be used as indicators of this kind of contamination.

The study area was the littoral coastal zone of Havana City. It comprises a location that by direct contact with the open sea, the existence of only small rivers and of waste water via shore-based outfalls of limited discharge capacity (Tritón, Habana del Este and Alamar) could favour the dilution of metals discharged into the sea. Previously, the high level of contamination of Havana Bay and its influence on the western coastal zone has been demonstrated (González *et al.*, 1985), as well as contamination near the main sewage outfall of the city, located at Playa del Chivo.

MATERIALS AND METHODS

Figure 1 shows the sampling sites which include a reference station located at the eastern part of the study area. Table 1 summarizes the species collected during each sampling campaign. The whole plants were collected by hand from the rocky substrate and carried in plastic bags to the laboratory. They were rinsed with twice-distilled water to remove the attached particulate material. The roots were separated and the remaining samples were dried at 105°C, homogenized in an agate mortar, and about 1 g digested in $HNO_3/HCLO_4$ (2 : 1). The residues were dissolved in 1% HNO_3 and analyzed by flame AAS with deuterium background correction. The accuracy was verified using mollusc tissue reference material (MA-M-2/TM) of the International Laboratory of Marine Radioactivity, Monaco; the precision, expressed as the coefficient of variation, was better than 10%. For each metal, the concentrations obtained in the different sampling stations were compared with analysis of variance (ANOVA, $\alpha = 0.05$).

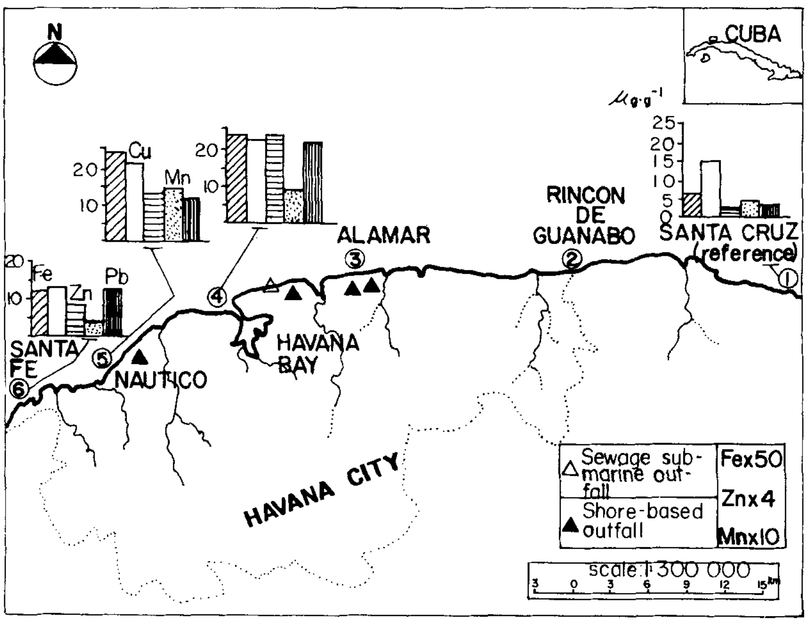

Figure 1 Sampling stations and mean contents ($\mu g.g^{-1}$ dry weight) obtained for *Padina vickersiae*.

RESULTS AND DISCUSSION

The results from the sampling campaigns show that there is no uniformity in the distribution of the studied species. This will limit the comparison of the metal levels found for the different sites for some macroalgae. Table 2a shows the results of the Phaeophyceae studied. In a general sense, *Padina vickersiae* (Figure 1) shows the highest mean metal contents at the bay's mouth and at the Náutico. At the reference site, this species was lowest for iron, zinc and lead and only slightly higher for copper and manganese than samples from Santa Fé. The

Table 1 Macroalgae collected (*) in the studied sites.

	1986																	
	May						*July*						*December*					
Phaeophyceae	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
Turbinaria tricostata	*					*	*					*	*					
Padina vickersiae	*			*	*	*	*			*			*				*	*
Rhodophyceae																		
Laurencia papillosa	*	*					*						*					*
Wurdemannia miniata				*						*						*		
Chlorophyceae																		
Ulva lactuca			*	*	*					*	*					*		
Cladophoropsis membranacea	*	*				*	*	*	*		*	*	*	*	*			*

	1987																	
	February						*April*						*June*					
Phaeophyceae	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
Turbinaria tricostata	*					*	*					*	*					*
Padina vickersiae	*				*		*			*	*	*	*			*	*	
Rhodophyceae																		
Laurencia papillosa	*						*						*					
Wurdemannia miniata				*						*								
Chlorophyceae																		
Ulva lactuca			*	*					*	*	*				*	*	*	
Cladophoropsis membranacea	*	*				*	*	*				*	*	*				*

Sampling sites

1: Santa Cruz (reference site)
2: Rincón de Guanabo
3: Alamar
4: Bay's mouth
5: Náutico
6: Santa Fé

analysis of monthly values for each element shows that the minima were found at the reference station and the maxima at the bay's mouth and at Náutico. Results of ANOVA show significant differences between the reference samples and those from the bay's mouth and Náutico (except for copper) but not between the two latter stations, demonstrating the feasibility of this species to reflect contamination.

For *Turbinaria tricostata,* it was difficult to interpret the results because there were no data from contaminated zones such as the bay's mouth. The mean values and the majority of monthly values for all elements are smaller at the reference site compared with other study sites though only for zinc was this difference statistically significant.

Table 2a Metal contents in Phaeophyceae ($\mu g.g^{-1}$ dry weight); means, SE's and range.

Species/Site	*Fe*	*Cu*	*Zn*	*Mn*	*Pb*
P. vickersiae					
Santa Cruz (1)	326.2 ± 150.3	15.5 ± 7.0	10.0 ± 4.6	46.9 ± 17.5	4.4 ± 3.7
	(80.0 – 507.4)	(2.3 – 21.6)	(2.8 – 14.9)	(27.9 – 68.7)	(2.1 – 11.9)
Bay's mouth (4)	1156.3 ± 408.4	22.3 ± 3.5	92.0 ± 42.1	85.9 ± 48.4	21.5 ± 17.8
	(686.2 – 1411.9)	(18.3 – 24.3)	(44.0 – 109.2)	(32.2 – 126.3)	(8.9 – 41.8)
Náutico (5)	1159.3 ± 438.0	21.4 ± 7.1	52.2 ± 11.3	143.5 ± 33.6	12.3 ± 5.2
	(598.2 – 1819.4)	(13.1 – 31.2)	(41.0 – 64.1)	(96.5 – 184.6)	(8.4 – 21.3)
Santa Fé (6)	582.4 ± 555.3	12.3 ± 1.0	30.9 ± 27.8	38.4 ± 13.3	12.0 ± 7.8
	(249.3 – 1122.4)	(3.2 – 23.0)	(9.2 – 62.2)	(27.8 – 53.3)	(5.9 – 20.8)
T. tricostata					
Santa Cruz (1)	18.9 ± 10.9	5.6 ± 3.1	8.4 ± 1.5	2.4 ± 1.5	<1.5
	(3.9 – 34.5)	(1.3 – 10.5)	(5.4 – 9.3)	(0.94 – 4.7)	
Santa Fé (6)	26.0 ± 21.3	5.0 ± 3.0	11.7 ± 2.2	2.8 ± 1.6	<1.5
	(1.2 – 56.7)	(<1.3 – 7.7)	(9.3 – 13.4)	(1.2 – 5.2)	

Table 2b Metal contents in Rhodophyceae ($\mu g.g^{-1}$ dry weight)

Species/Site	*Fe*	*Cu*	*Zn*	*Mn*	*Pb*
L. papillosa					
Santa Cruz (1)	107.2 ± 78.4	8.1 ± 6.8	14.1 ± 6.9	10.5 ± 3.7	4.8 ± 3.3
	(50.4 – 206.2)	(<1.3 – 18.6)	(6.0 – 22.5)	(6.8 – 14.9)	(1.5 – 9.8)
Rincón de Guanabo (2)	215.3	10.5	29.0	25.5	<1.5
Santa Fé (6)	408.6	28.1	55.4	46.2	8.0
W. miniata					
Bay's smouth (4)	1124.4 ± 96.1	16.3 ± 5.3	56.9 ± 0.69	20.4 ± 8.6	7.6 ± 0.89
	(1040.2 – 1261.3)	(9.1 – 20.4)	(56.3 – 57.8)	(15.4 – 30.3)	(6.5 – 8.6)

Table 2c Metal contents in Chlorophyceae ($\mu g.g.^{-1}$ dry weight)

Species/Site	*Fe*	*Cu*	*Zn*	*Mn*	*Pb*
C. membranacea					
Santa Cruz (1)	407.2 ± 322.0	14.7 ± 14.9	28.1 ± 22.8	28.2 ± 32.4	3.5 ± 1.6
	(130.1 – 922.2)	(3.4 – 40.8)	(4.0 – 62.4)	(7.5 – 93.4)	(<3.0 – 6.7)
Rincón de Guanabo (2)	1558.2 ± 1365.1	20.4 ± 9.3	49.0 ± 23.5	30.8 ± 22.8	9.9 ± 5.6
	(236.1 – 3950.2)	(11.3 – 29.6)	(31.8 – 92.1)	(14.1 – 73.9)	(<3.0 – 19.8)
Alamar (3)	470.1 ± 292.2	19.3 ± 18.8	27.3 ± 3.4	11.9 ± 3.9	<3.0
	(263.1 – 676.4)	(6.1 – 32.6)	(24.9 – 29.7)	(9.2 – 14.7)	
Náutico (5)	735.0	5.6	15.4	45.9	18.7
Santa Fé (6)	234.2 ± 220.0	16.7 ± 10.9	40.7 ± 28.1	12.5 ± 10.1	7.6 ± 5.7
	(50.5 – 597.2)	(6.3 – 29.3)	(7.3 – 74.1)	(1.8 – 31.0)	(<3.0 – 15.9)
U. lactuca					
Alamar (3)	129.0 ± 72.8	6.2 ± 3.3	15.9 ± 2.8	6.7 ± 2.6	2.7 ± 1.0
	(29.6 – 195.2)	(4.4 – 11.2)	(14.1 – 20.0)	(4.6 – 9.6)	(1.6 – 3.7)
Bay's mouth (4)	176.0 ± 47.7	11.1 ± 6.1	19.9 ± 2.4	9.0 ± 2.8	3.5 ± 2.3
	(119.1 – 260.1)	(5.2 – 13.7)	(16.8 – 22.1)	(5.9 – 13.2)	(2.0 – 8.2)
Náutico (5)	125.2 ± 70.3	8.4 ± 2.7	10.2 ± 7.4	8.2 ± 3.7	2.6 ± 0.61
	(58.1 – 221.3)	(5.4 – 11.6)	(3.9 – 20.8)	(3.0 – 11.5)	2.0 ± 3.3

Comparing the level of the metal contents in these brown algae, the extreme values coincide. Iron predominated at all sites in agreement with other reports for algae and macrophytes (Eisler, 1981). The lowest values were found for lead which is often considered to be among those elements which apparently have no biological function (Viarengo, 1985). In *Turbinaria tricostata,* zinc took the second place in content. Usually, in *Padina vickersiae,* manganese was found at higher concentration. However, at the bay's mouth, the zinc content was nearly ten times higher than at the reference site and therefore displaced manganese from the second place. Also the sediments of this sampling area were found enriched in this element (González *et al.*, 1988). This could support our hypothesis that the high zinc content reflects the capacity of this species to concentrate zinc, considered as a fundamental attribute for any organism used in chemical monitoring (Widdows, 1985). In the same way, the presence of this species at the reference station as well as at the bay's mouth, reflects its resistance to high concentration of contaminants, a further condition necessary for a biological indicator (Kristoforova and Maslova, 1983). Differences in the contents of metals in *Turbinaria tricostata* were less evident than in *Padina vickersiae. Turbinaria tricostata,* by its low frequency of occurrence in contaminated zones, and low bioconcentration factors for metals, was not very well suited for such studies.

The occurrence of Rhodophyceae (Table 2b) is also restricted. *Wurdemannia miniata* was found only at the bay's mouth and showed relatively low variability in its metal content over many months. On the other hand, *Laurenica papillosa* showed a remarkable variability even in the reference zone, where the average values were lower than those at Santa Fé and Rincón de Guanabo. Both red algae, in the order of metal contents, show the same pattern: $Fe > Zn \geq Mn > Cu > Pb$. This elemental pattern seemed not to be influenced by the degree of heavy metal contamination (González *et al.*, 1988).

Chlorophyceae (Table 2c): *Ulva lactuca* was found at the central stations of the study area. This species has been reported as characteristic of zones with a high content of organic matter (Valle *et al.*, 1985). At the bay's mouth the mean metal contents were all higher than at other sampling sites. However, this finding was again only statistically significant for zinc. Because of the convincing results we obtained with *Padina vickersiae,* we omitted *Ulva lactuca* as a possible means of chemical monitoring although this species has been recommended as a potential indicator of contamination by heavy metals in inshore areas (Boyden, 1975; Talbot and Chegwidden, 1982).

Cladophoropsis membranacea presented not only a high variability between months for each element but also between stations, and did not reflect a definite pattern for sampling locations. Denton and Burdon-Jones (1986) reported the same behaviour for the green algae studied by them, which showed interspecific and intraspecific variations (based on differences between sites). They suggested in the event of the use of these species as monitors, that consideration be given to the factors which influence these levels, such as growth on the shore, age, etc.

The two Chlorophyceae species coincided in the order of concentration of the elements: $Fe > Zn > Mn \approx Cu > Pb$. Reports on these species are scarce (Table 3). Eisler (1981) in his extensive review, gave only a brief description of other species. For *Ulva lactuca,* Pulich (1980) finds higher values of iron, manganese and zinc, and comparable levels of copper; Wahbeh *et al.* (1985), studying a

Table 3 Selected values for trace metal levels in *Ulva lactuca* ($\mu g.g^{-1}$ dry weight)

Fe	*Mn*	*Zn*	*Cu*	*Pb*	*Locations*	*References*
102.2	20.0	57.0	12.5		Port Aransas, Texas	Pulich, W. M., 1980
1800.0	28.0	55.0	8.5		Corpus Christi Bay, Texas	Pulich, W. M., 1980
833.0 ± 105.0	24.5 ± 2.4	51.0 ± 4.1	42.1 ± 1.8		Coast of Aqaba, Jordan	Wahbeh, M. I. *et al.*, 1985
415.0	10.6	44.4	6.5	1.7	Cockburn Sound, West. Australia	Talbot, V. & Chegwidden, A., 1982
		19.2 – 162.1	4.8 – 38.7	0.90–3.3	Slightly affected area	Hagerhall, B., 1973
3380.0 – 8890.0	210.0 – 1630.0	55.0 – 136.0	12.0 – 34.0	16.0 – 66.0	Poole Harbour, England	Boyden, C. R., 1975

zone influenced by different anthropogenic activities, determined higher values of zinc, manganese, copper and iron in *Laurenica obtusa* and *Turbinaria elatensis* than we did. They found in *Padina pavonica,* a pattern (Fe > Zn > Cu > Mn) similar to *Padina vickersiae* at the bay's mouth. For the other species the order of metal contents coincided with the report of this work.

Saenko *et al.* (1976) found lower values of zinc and higher levels of manganese, iron and copper in *Ulva fenestrata* and *Ulvaria splendens* then those reported for *Ulva lactuca* presented in this paper.

In the Australian Great Barrier Reef (Denton and Burdon-Jones, 1986), at zones considered not to be contaminated, for species of the genera *Padina, Turbinaria* and *Laurencia,* metal values were reported similar to those found in our reference zone.

CONCLUSIONS

The metal contents found may serve as a basis for future investigations of these species. Only two species showed extended distribution in the study area; this enabled us to compare the levels between sites with different degrees of contamination. However, one of them, *Cladophoropsis membranacea,* was not favoured due to the high variability between months and also between sites; this fact did not allow us to obtain a definite pattern. The other species, *Padina vickersiae,* showed the potential to bioconcentrate the heavy metals studied, and, as a consequence, was proposed as a suitable candidate for chemical monitoring.

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