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Contents of Trace Metals in Water and Macroalgae along the Mediterranean Coast of Tunisia

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Marine macroalgae are able to accumulate trace metals up to concentration values many times larger than those found in the surrounding waters (Cardwell et al., 2002). Moreover, these species are sedentary, widespread, satisfactory in dimension, and easy to sample and to identify (Conti, 2002). For these reasons, these species have been widely used as biomonitors of metal contamination in coastal environments that are the main sinks of almost all industrial and urban inputs of pollutants (Campanella et al., 2001; Stengel et al., 2004).

In the last decades, the Tunisian country is subjected to important urban and industrial extension that may affect the exploitation of its maritime resources and contaminate its coastal environments. In order to evaluate the environmental quality of the Tunisian coast, the brown algae *Fucus vesiculosus* and the green algae *Enteromorpha* spp. were selected as cosmopolitan biomonitors of pollution by two micronutrient metals (Zn, Cu) and a nonessential trace element (Cr). To quantify the extent of bioaccumulation in the two aquatic plants, soluble metal concentrations were assessed in seawater samples collected at the experimental stations.

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Materials and Methods

Samples of algae and seawater were collected during March 2002 from 12 sampling stations located in the Tunisian Mediterranean coast (Fig. 1). Samples of *Enteromorpha* and *Fucus vesiculosus* were handpicked in the subtidal zone at a depth of about 2 m. In order to obtain more reliable results, samples of algae were collected from five points in each station within an area of approximately 15 m in diameter. The samples were then homogenized to form a representative sample from each station and then the samples were transferred to the laboratory in polyethylene bags. Seaweed samples were initially washed under a jet of tap water, were then rinsed in metal-free double distilled water, and were finally frozen at –20°C to await the heavy metals analysis. Water samples were collected with precleaned polyethylene bottles of 1 L at a depth of 2 m. The samples were filtered through a 0.45-μm membrane filter and were acidified to master the adsorption of certain elements on internal walls of the sampling flasks. Neutralization was made by the addition of concentrated hydrochloric acid to lower the pH from about 8.5 to 2. After acidification, water samples were stored at 4°C for soluble metal analysis.

Samples of algae were dried in an oven at 105°C to constant weight. Digestion was carried out in triplicate on the dried algal material: 10 mL of ultrapure concentrated HNO_3 (Merck, Darmstadt, Germany) were added to 1 g of ground sample and left for 12 h. After

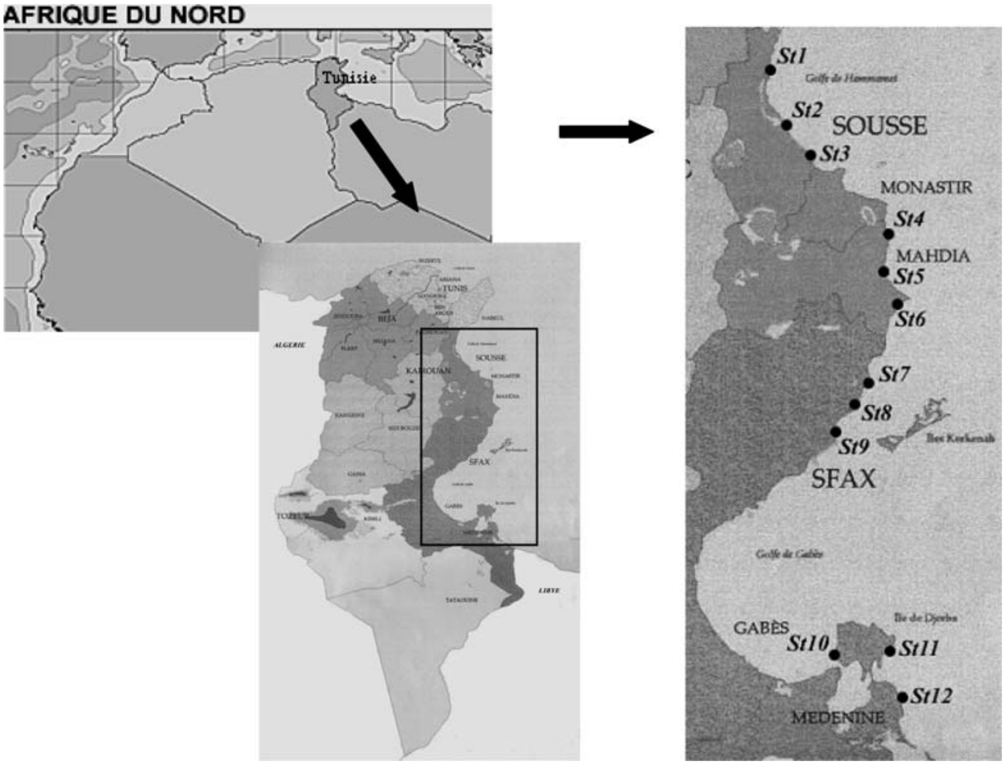

Fig. 1 Location of sampling sites on the Tunisian coast. (St1) Plage hotel Asdrubal; (St2) Plage hotel Salam; (St3) Plage Gaied; (St4) Plage hotel Thapsus; (St5) Plage Mahdia centre; (St6) Plage Corniche Rejich; (St7) Plage hotel Farhat; (St8) Ancien club de natation; (St9) Face Ancien casino Chaffar; (St10) Plage El Grine; (St11) Port Zarzis; (St12) Plage Guellala

drying the ashes by heating on a hotplate at 80°C, 3 to 5 mL of H_2O_2 (50% v/v) (Merck, Darmstadt, Germany) were added until a completely colorless solution was obtained. The mixture was dried again and the residue was extracted three times with 3 mL of 5% HNO_3. The extract was raised to 10 mL and was put in glass tubes. Reagent blanks were also prepared. Soluble metals in water samples were extracted by using the APDC-MIBK procedure (APHA, 1989). The procedure is described elsewhere (El Moselhy and Gabal, 2004).

The analyses were performed with a Shimadzu model AA680 Atomic Absorption Spectrophotometer, equipped with a deuterium background corrector. Zinc (Zn), copper (Cu), and chromium (Cr) were determined by graphite furnace (GF-AAS). Flame atomic absorption spectrometry (FAAS) was used for the analysis of Zn in biota because of the high recorded levels. The precision of the procedure expressed as standard deviation percentage ($n = 5$) was less than 11% for all metals. A recovery test was performed by spiking standard solution of the selected metals to the plant samples before digestion. The average recoveries ($n = 3$) ranged from 95% to 103%. The blank values were below the detection limits: that is, 1.2 μg/L (Zn), 1.0 μg/L (Cu), and 0.5 μg/L (Cr).

The one-way ANOVA (log-transformed data) was done to compare the concentrations of metals in the different sampling sites. Concentration factors (CFs) between macroalgae and seawater samples were calculated. A Pearson correlation analysis was carried out to associate the heavy metal contents in algae with those in coastal water.

Results and Discussion

Metal concentrations determined in water and in the two macroalgal species, at the different sampling stations, are given in Figs. 2 to 4. The mean Zn concentrations in the coastal water samples ranged from 13.1 to 33.7 μg/L, Cu was in the range 1.2 and 5.0 μg/L, whereas Cr ranged between 0.6 and 1.5 μg/L. In regard to macroalgae, metal concentrations were in the descending order Zn > Cr ≥ Cu. The mean concentrations of Zn, Cr, and Cu at the different sampling locations varied from 27 to 327, 2.2 to 17, and 1.3 to 8.2 μg/g dry weight, respectively.

Figures 2 to 4 show large differences in the metal concentrations of the two macroalgal species from one site to another. Some locations indicated higher metal

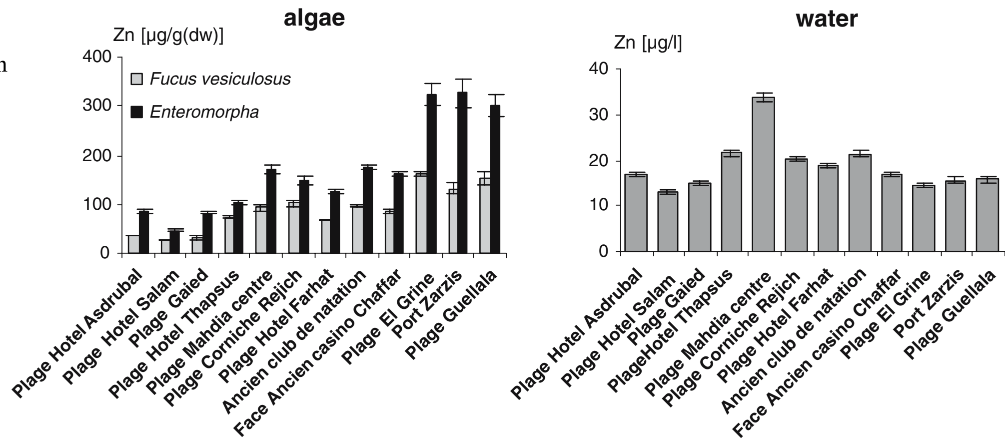

Fig. 2 Concentrations of Zn in algae and water from the Tunisian coast; values are mean (n = 3) ± standard deviation (S.D.).

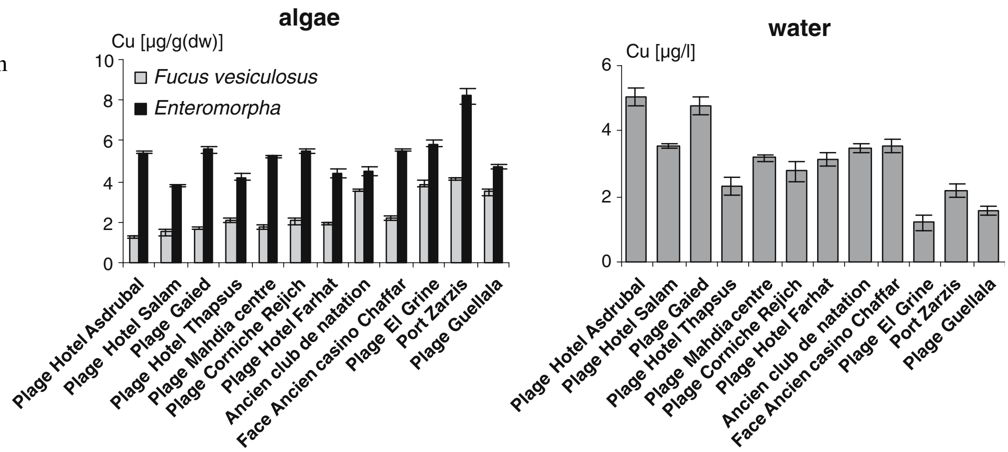

Fig. 3 Concentrations of Cu in algae and water from the Tunisian coast; values are mean (n = 3) ± standard deviation (S.D.).

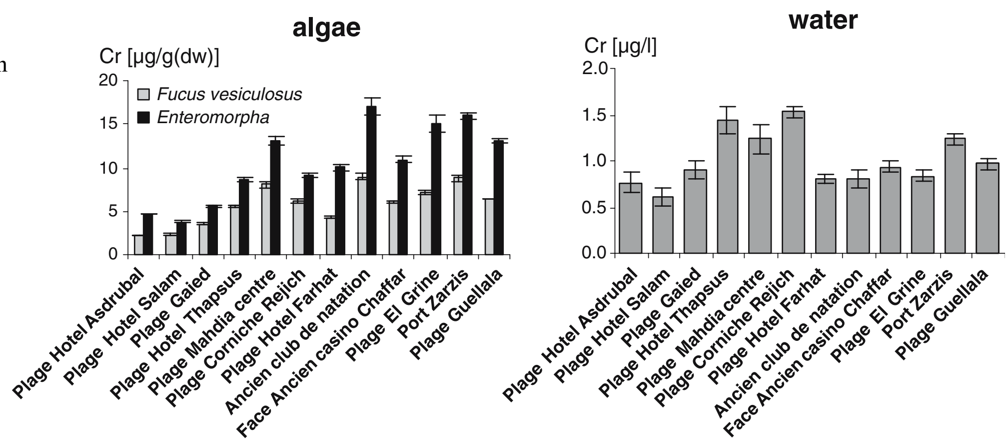

Fig. 4 Concentrations of Cr in algae and water from the Tunisian coast; values are mean (n = 3) ± standard deviation S.D.).

levels, reflecting a contamination in these sites. This is especially evident for the P. Zarzis site, where significant differences were observed as compared with the majority of the other stations.

To evaluate the bioaccumulation extent in the *Enteromorpha* spp. and *F. vesiculosus* tissues, concentration factors (CFs) of Zn, Cu, and Cr were calculated (Table 1). It can be noticed that the green species (*Enteromorpha*) accumulated almost two times more heavy metals than the brown one (*F. vesiculosus*). For the two macroalgal species, Cr gave the highest accumulation rate with CF values ranging between 5.89×10^3 and 10.93×10^3.

The Pearson correlation coefficients between heavy metals in algae and in water are shown in Table 2. Significant positive correlations are recorded in the two

Table 1 Concentration factors × 10^3 calculated with reference to soluble metal concentrations in coastal water

Species	Zn	Cu	Cr
Enteromorpha spp.	9.83	2.06	10.93
Fucus vesiculosus	4.98	1.07	5.89

Table 2 Pearson correlation coefficients between the metal concentrations in algae and in water

Species	Zn	Cu	Cr
Enteromorpha spp.	0.112	–0.177	0.359[a]
Fucus vesiculosus	0.230	–0.739[b]	0.490[b]

[a] $p < 0.05$
[b] $p < 0.01$

investigated species for Cr. A negative significant correlation is observed between Cu contents in the brown species and in water.

According to the values established by the US Environmental Protection Agency (USEPA) regulations for marine ecosystems (USEPA, 1999), the investigated waters were below the maximum permitted levels for Zn and Cr [81 and 50 μg/L, respectively, for Zn and Cr (VI)].

However, the waters exceeded the upper limit for Cu (3.1 μg/L) in some of the studied stations. When compared to data reported from other trace metal fortified marine environments around the world, our concentrations are close to those found in the Red Sea by Hamed and Emara (2006) ranging between 8.83–21.46 μg/L (Zn), 3.37–4.78 μg/L (Cu), and 0.99–1.21 μg/L (Cr). They are generally lower than the values reported from polluted waters, such as the Mauritius, with highest concentrations (in μg/L) of 310, 352, and 410, respectively, for Zn, Cu, and Cr (Daby, 2006), and the Gulf of Cambey, India, where the Zn, Cu, and Cr levels varied between 4271–-5832 μg/L, 3122–3839 μg/L, and 621–765 μg/L, respectively (Srinivasa Reddy et al., 2005). Compared with background levels (in μg/L) of up to 3.92–10.01 (Zn), 1.15–3.11 (Cu), and 0.123–0.322 (Cr) as recorded by Campanella et al. (2001) in Favignana Island, Sicily, Italy, our metal concentrations were mostly higher than the maximum levels. The data available on metal amounts in the water of this coastal area are scarce. A comparison between the Zn and Cu water concentrations found in the present study with those reported by Rais and Gueddari (1997) in the Gulf of Tunis shows lower metal levels in our study.

The data on the metal concentrations detected in aquatic macrophytes are widely used for evaluating the environmental quality as well as for the comparison between the variously polluted waters (Cardwell et al., 2002). Comparing our data with those of Riget et al. (1995), reported for *F. vesiculosus* collected in unpolluted areas, it could be stated that our metal concentrations correspond to the levels found in the "slightly polluted" areas. Villares et al. (2002) established background levels of Zn (29.9 μg/g), Cu (7.48 μg/g), and Cr (1.18 μg/g) in *Enteromorpha* spp. The majority of our mean Cu concentrations are below the background levels (Fig. 3). However, the mean concentrations obtained for Zn and Cr surpass the natural levels (Figs. 2, 4). From studies undertaken in various parts of the world, the results we obtained are comparable to those reported by Kaimoussi et al. (2004), higher (for Zn and Cr) than those found in uncontaminated sites (Campanella et al., 2001), and lower than data recorded in species from polluted areas (Daka et al., 2003).

Heavy metal concentrations of seaweeds from the Tunisian coast showed significant differences among the investigated locations. The elevated metal levels recorded in the P. Zarzis site could be caused by the influence of the harbor activities and urban discharges.

Table 1 reports the calculation of CFs for the two studied macrophytes. The CF may be used in the monitoring of the environmental state. The results shown in Table 1 confirm the high bioaccumulation extent of the selected species. These species are among the most commonly used genera in the biomonitoring of metal pollution (Topcuoglu et al., 2003). As far as net accumulation is concerned, *Enteromorpha* proved to be a stronger metal accumulator than *F. vesiculosus*. Comparisons with other published works show different accumulation behaviors within taxonomic groups. For example, Phaneuf et al. (1999) found similar Zn concentrations in 16 brown, green, and red algal species from Canada. By contrast, Stengel et al. (2004) reported significant differences between the taxonomic groups in Zn concentrations detected in 19 algal species from western Ireland. Zinc concentrations in red algae were, on average, higher than in those of green and brown algae. Taxa differences in Cr accumulation rates have also been reported. According to De Filippis and Pallaghy (1994), green algae retain more Cr than brown or red algae. However, Conti and Cecchetti (2003) found CFs of Cr almost two times higher for the brown algae *Padina pavonica* than for the green algae *Ulva lactuca*.

Positive significant correlation (Table 2) between Cr in water and in seaweeds shows that these algal species may be used in the chemical monitoring of the environment of the examined coastal waters. The correlation coefficient for Cu is significantly negative in the

F. vesiculosus species. This result can be explained by the source of the metal in the brown algae tissue, which may be derived from the bottom sediment or the particulate matter in the surrounding environment.

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