



## Heavy metal concentrations in three species of green algae from the Saudi coast of the Arabian Gulf

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### Abstract

Several species of green algae have been used as indicators of heavy metal contamination in coastal areas. The concentrations of Cu, Zn, Fe, Cd, Pb and Ni were determined in the green algae *Chaetomorpha aerea* (Dillwyn) Kützinger, *Enteromorpha clathrata* (Roth) Greville and *Ulva lactuca* Linnaeus collected from three sites on the Saudi coast of the Arabian Gulf. The algal samples were dry digested using hot concentrated nitric acid and the metals were analyzed by atomic absorption spectrophotometry. Levels of heavy metals similar to those of polluted coastal areas were detected for all elements except Cd. The mean concentrations of metals in the examined algae were as follows: Cu 8.41-48.52, Zn 34.16-68.18, Fe 812-2,335, Pb 13.90-30.50 and Ni 25.51-44.51  $\mu\text{g g}^{-1}$  dry weight. The levels of Cu, Zn, Fe, Cd and Ni in *C. aerea* were significantly higher than in the other two algae, and this species could serve as bioindicator for heavy metal pollution in this part of the world. No significant differences were detected for the heavy metal levels in the three areas studied indicating a high degree of pollution at all sites. High levels of industrialization and urbanization and oil spillages, which are taken place in the Arabian Gulf region, are probably responsible for the elevated levels of pollutants in this area.

**Key words:** Heavy metals, accumulation, green algae, Saudi coastal waters, Arabian Gulf.

### Introduction

Anthropogenic activities around coastal areas may have an adverse impact on coastal ecosystems and human health due to the discharge of industrial waste and domestic sewage<sup>1</sup>. These effluents usually contain elevated levels of heavy metals that are known to accumulate in macro-algae which form the basis of many food chains<sup>2,3</sup>. Several species of the green algae *Chaetomorpha*, *Enteromorpha* and *Ulva* have been widely used as indicators of heavy metal pollution in the coastal areas of several countries around the world, including Argentina<sup>4</sup>, Australia<sup>5</sup>, Canada<sup>6</sup>, Egypt<sup>7</sup>, Greece<sup>8</sup>, Hong Kong<sup>9</sup>, Ireland<sup>10</sup>, Italy<sup>11</sup>, Lebanon<sup>12</sup>, New Zealand<sup>13</sup>, Poland<sup>14</sup>, Spain<sup>15</sup>, Turkey<sup>16</sup> and UK<sup>17</sup>.

In the Arabian Gulf region, a very limited number of studies have been published about the accumulation of heavy metals by marine algae. The levels of numerous metals were determined in several species of macro-algae collected from the coastal areas of Saudi Arabia, Qatar and Kuwait<sup>18-20</sup>. In a recent study<sup>21</sup>, the levels of Cd, Cu, Fe, Pb and Zn in four species of brown algae collected from the Saudi coast of the Arabian Gulf were investigated. The objective of this work was to measure the concentrations of Cu, Fe, Zn, Cd, Pb and Ni and in *C. aerea*, *E. clathrata* and *U. lactuca* and to assess if these species can be used as bioindicators of heavy metal pollution in this part of the world.

### Materials and Methods

**Study area and sampling sites:** The Arabian Gulf is a semi-enclosed sea, 990 km long and 200-300 km wide, covering an area of approximately 230,000 km<sup>2</sup> (Fig. 1). Its south-eastern end is connected to the Gulf of Oman by the Strait of Hormuz. The north-western end of the Gulf receives waters from the delta of Shatt Al-Arab which carries the waters of the Euphrates and the Tigris rivers. The Arabian Gulf is a shallow sea and has a maximum depth of 90 m and an average depth of 50 m. Large parts of the Arabian Gulf experience extremes of temperature and salinity. Water temperatures usually varied between 15 and 33°C and greater extremes may occur in shallow waters in winter (10°C) and summer (40°C). The Arabian Gulf is characterized by high evaporation rates, which create high salinity values. The salinity values of the study areas ranged between 41 and 47‰.

The algal samples were collected from the beach areas of Dammam, Khobar and Qateef (Fig. 1). Dammam is the largest city in the Eastern province of Saudi Arabia with a population of more than 850,000 and its port is one of the largest on the Arabian Gulf. Khobar is located about 15 km south of Dammam and it has a population of more than 500,000 inhabitants. Qateef is a coastal agricultural oasis north of Dammam with a population of more than 470,000. The population of these areas increases significantly during summer months and holiday breaks.

In these areas, there are several major industrial activities including major complexes of primary and secondary industry, power plants, desalination and seawater treatment plants, major sewage treatment plants and a fertilizer factory. Parts of domestic

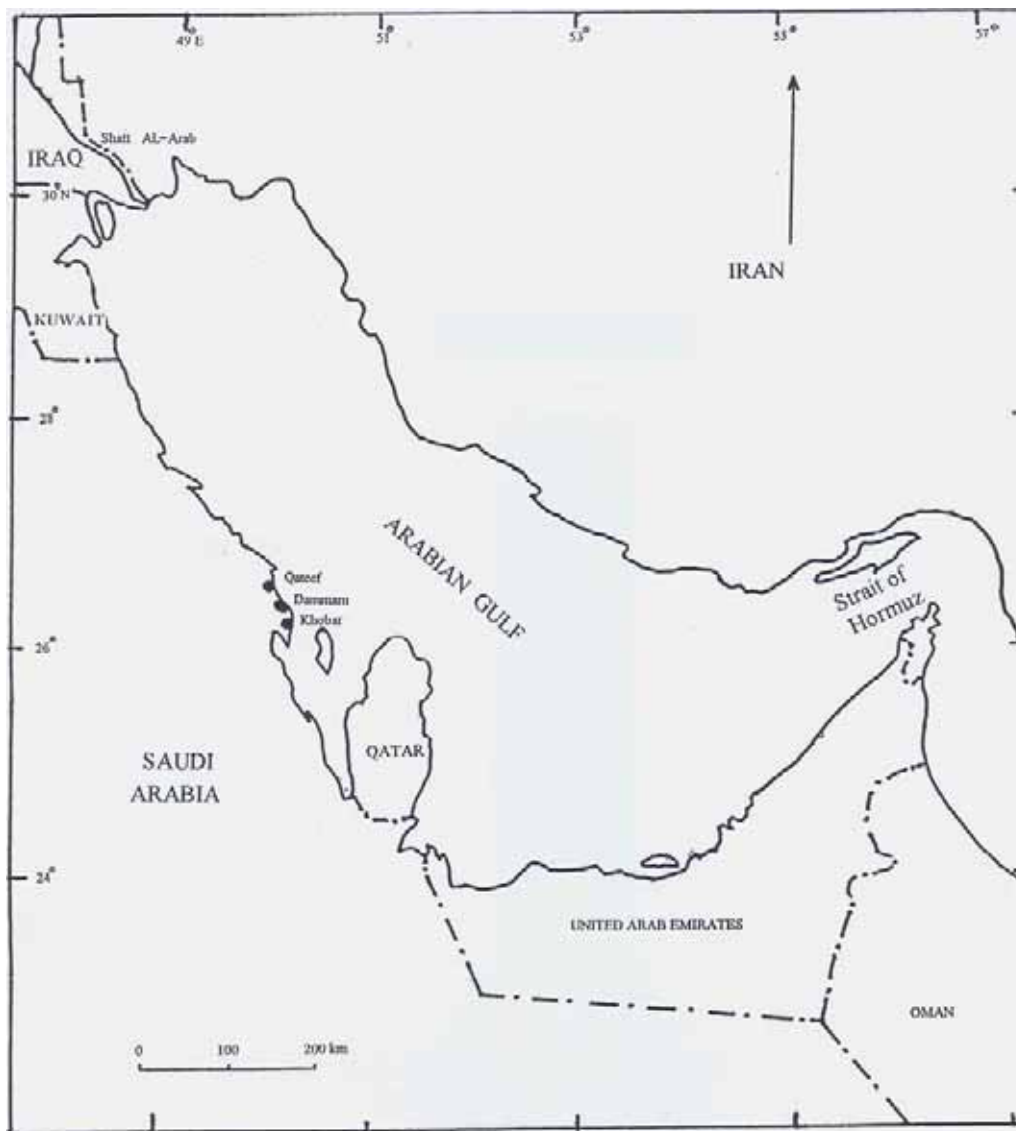


Figure 1. Map of the Arabian Gulf.

sewage and industrial wastewater are discharged to the Gulf without proper treatment<sup>1</sup>.

**Sampling procedures:** Entire thalli of algae, a minimum of three samples of each species, were collected from the beach area (Corniche) of each site during the months of March and April of 2006. They were thoroughly cleaned with seawater at sampling sites, followed by running distilled water in the laboratory. The samples were air-dried at 90°C, then used in the analysis.

**Analytical methods:** Exact weights of each species (500 mg dry weight) were placed into acid washed digestion tubes. Twenty-five ml of concentrated nitric acid (AnalaR Grade, BDH) was added to each tube and the contents of each tube were evaporated to near dryness. After cooling, 20 ml of double distilled deionised water was added to each tube and the content was filtered through 0.45 µm Millipore filters. The solutions were then transferred to 25 ml volumetric flasks and the volumes were adjusted to 25 ml with double distilled deionised water<sup>8,13,22</sup>. The resulting solutions were analyzed for Cu, Fe, Zn, Cd, Pb and Ni using a Shimadzu AA 6650 atomic absorption spectrophotometer with deuterium background correction.

**Statistical analysis:** One-way analysis of variance (ANOVA) was used to evaluate the inter-specific significance in algal metal accumulation with  $p=0.05$ .

### Results and Discussion

The concentrations of Cu, Zn, Fe, Cd, Pb and Ni in *C. aerea*, *E. clathrata* and *U. lactuca* are presented in Table 1. All results of this work and other studies are expressed in µg g<sup>-1</sup> dry weight throughout the text. The average concentrations of the essential elements were in the order Fe > Zn > Cu. A similar sequence has been reported by other scientists from different coastal areas in the world<sup>5,11,23</sup>.

The mean mean concentrations of Cu were in *C. aerea*, *E. clathrata* and *U. lactuca* 40.51-48.52, 20.36-30.52 and 8.41-18.50 µg g<sup>-1</sup>, respectively. Copper concentrations in *Enteromorpha* spp. from uncontaminated sites ranged from 6 to 12 µg g<sup>-1</sup> whereas concentrations from contaminated areas varied between 20 and 70 µg g<sup>-1</sup><sup>8,13,24</sup>. The values for Cu in *U. lactuca* collected from uncontaminated sites ranged from 0.1 to 3 mg g<sup>-1</sup>, and values from highly contaminated areas fluctuated between 14 and 134 mg g<sup>-1</sup><sup>13,25</sup>. A very limited number of reports has been published about

**Table 1.** Concentration of heavy metals ( $\mu\text{g g}^{-1}$  dry weight) in thalli of *C. aerea*, *E. clathrata* and *U. lactuca*.

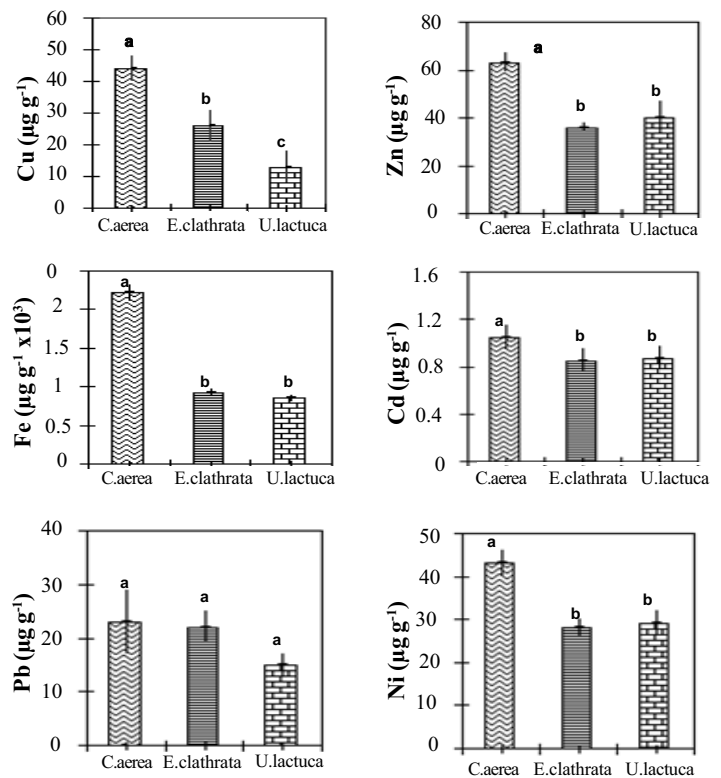
Species and sampling site	Cu	Zn	Fe	Cd	Pb	Ni
<i>C. aerea</i>						
Dammam	42.53	60.51	2,335	1.12	30.50	44.13
Khobar	40.51	61.13	2,190	0.98	18.15	44.51
Qateef	48.52	68.18	2,130	1.05	22.31	39.78
<i>E. clathrata</i>						
Dammam	30.52	34.16	975	0.84	24.92	25.51
Khobar	28.12	37.22	898	0.91	21.34	29.84
Qateef	20.36	35.27	912	0.79	20.19	27.15
<i>U. lactuca</i>						
Dammam	18.50	48.17	848	0.81	13.90	28.71
Khobar	12.71	36.82	812	0.85	17.67	32.37
Qateef	8.41	35.46	894	0.95	14.62	26.31

the heavy metal content of *Chaetomorpha* spp. and these articles indicate that the Zn values of this alga in contaminated areas range from 7 to 31  $\mu\text{g g}^{-1}$ . From these data it is apparent that the three study sites can be considered as contaminated with respect to copper.

The Zn values in *C. aerea*, *E. clathrata* and *U. lactuca* were 60.51-68.18, 34.16-37.22 and 35.46-48.17  $\mu\text{g g}^{-1}$ , respectively. The expected levels of Zn for uncontaminated sites range from 10 to 50  $\mu\text{g g}^{-1}$  for *Enteromorpha* and from 0.5 to 23  $\mu\text{g g}^{-1}$  for *Ulva*<sup>13,24</sup>. For contaminated sites these values vary between 95 and 130  $\mu\text{g g}^{-1}$  for *Enteromorpha* and between 42 and 160  $\mu\text{g g}^{-1}$  for *Ulva*<sup>8,13,24</sup>. The ranges of Zn for *Chaetomorpha* have not been established but concentrations ranging from 21 to 177  $\mu\text{g g}^{-1}$  have been reported for this alga from contaminated sites<sup>5, 16, 24</sup>. The concentrations of Zn found in this work, especially in *C. aerea* and *U. lactuca*, indicate to a moderate degree of Zn contamination in the study area. The high levels of Cu and Zn in this area, especially in Qateef, have been attributed to the discharge of agricultural and municipal wastewater to the coastal area<sup>26</sup>.

High concentrations of Fe in *C. aerea* were found at all sites and they varied between 2,130 and 2,335  $\mu\text{g g}^{-1}$ . Lower values were obtained for *E. clathrata* (898-975  $\mu\text{g g}^{-1}$ ) and for *U. lactuca* (812-894  $\mu\text{g g}^{-1}$ ). Such high levels have been reported from the Saudi coast of the Arabian Gulf for four species of brown algae<sup>21</sup>. High values of Fe ( $> 50 \mu\text{g l}^{-1}$ ) in seawater samples from this area have been reported before<sup>27</sup> and these values are probably responsible for the elevated concentrations of this metal in the algal tissues. High levels of Fe, similar to the findings of the study, have been reported from contaminated coasted waters of various countries, including Australia<sup>5</sup>, Italy<sup>11,23</sup>, Lebanon<sup>12</sup>, Spain<sup>15</sup> and Turkey<sup>16</sup>. The high Fe concentrations encountered in the green algae of the Adriatic Sea have been attributed to: a) industrial contamination, b) the ability of most algae to biomagnifying Fe from the surrounding water and c) the established need of Fe for normal growth<sup>23</sup>.

The relative concentrations of the non-essential elements were in the order Ni>Pb>Cd. Cadmium levels in the three algae varied between 0.79 and 1.12  $\mu\text{g g}^{-1}$ . These values are lower than those previously reported in brown algae from this area<sup>18,21</sup>. Higher levels of this metal have been reported in green algae from contaminated coastal areas throughout the world<sup>5, 7, 12, 14, 17</sup>. The Cd concentrations found in this study are within the expected values for uncontaminated coastal areas. Cadmium values in algae of  $<2 \mu\text{g g}^{-1}$  have been considered as normal levels for unpolluted environments<sup>28</sup>.



**Figure 2.** Concentrations (mean  $\pm$  SD, n = 6) of Cu, Zn, Fe, Cd, Pb and Ni in *C. aerea*, *E. clathrata* and *U. lactuca* from the Saudi coast of the Arabian Gulf. Bars with different letters indicate significantly different results.

High levels of Pb were found in all algae at all sites and they varied between 13.90 and 30.50  $\mu\text{g g}^{-1}$ . These values are higher than those previously recorded in the brown algae of this area<sup>21</sup> and this confirms a high degree of Pb contamination in the study area. Similar high values of Pb have been reported in green algae from many contaminated coastal regions throughout the world<sup>5, 7, 11, 14, 17, 28</sup>. The elevated levels of Pb in this area are probably caused by high consumption of fossil fuels for transportation and other industrial activities. In addition, the discharge of municipal sewage to coastal areas usually leads to an increase in the levels of Pb and other elements such as Cu, Zn, Fe and Cd<sup>2, 29</sup>.

High values were also found for Ni in the three algae at all sites and they ranged between 25.51 and 44.51  $\mu\text{g g}^{-1}$ . The concentration of Ni in *E. clathrata* varied between 25.51 and 29.84  $\mu\text{g g}^{-1}$  and these levels are much higher than those previously reported in *Enteromorpha* from the Arabian Gulf<sup>20</sup> and from the Red Sea<sup>30</sup>. They are also higher than concentrations reported for Ni in green algae from other parts of the world<sup>11, 14-16</sup>. The high levels of Ni in the tested algae are probably caused by oil spills to the marine environment. Substantial amounts of oil are discharged to the Arabian Gulf every day<sup>1</sup> and these oils contain high levels of Ni. The concentrations of Ni in the Saudi and Kuwaiti crude varied between 1 and 29  $\mu\text{g g}^{-1}$  oil<sup>31</sup>. The high levels of Ni in organisms collected from the Kuwaiti coastal areas were attributed to the oil spill that took place during the Gulf War in 1991<sup>32</sup>.

The mean metal concentrations with standard deviations in each alga are represented in Fig. 2. Interspecific comparisons showed that *C. aerea* had the highest levels of all metals, followed by *E. clathrata* with respect to Cu, Fe and Pb. The levels of Zn, Cd and Ni were slightly higher in *U. lactuca* when compared to *E.*

**Table 2.** Concentrations (mean  $\pm$  SD, n = 9) of metals ( $\mu\text{g g}^{-1}$  dry weight) in sampled macroalgae from Dammam, Khobar and Qateef areas.

Location	Cu	Zn	Fe	Cd	Pb	Ni
Dammam	30.52 $\pm$ 12.02	47.61 $\pm$ 13.18	1,386 $\pm$ 824	0.92 $\pm$ 0.17	23.11 $\pm$ 8.45	32.78 $\pm$ 9.96
Khobar	27.11 $\pm$ 13.93	45.06 $\pm$ 13.92	1,300 $\pm$ 772	0.91 $\pm$ 0.07	19.05 $\pm$ 1.99	35.57 $\pm$ 7.84
Qateef	25.76 $\pm$ 20.59	46.30 $\pm$ 18.95	1,312 $\pm$ 708	0.93 $\pm$ 0.13	19.04 $\pm$ 3.97	31.08 $\pm$ 7.55

*clathrata*. Copper, Zn, Fe, Cd and Ni concentrations were significantly greater in *C. aerea* than in the other two algae. The concentration of Cu was significantly higher in *E. clathrata* than in *U. lactuca*. No significant differences in Zn, Fe, Cd, Pb and Ni concentrations were found between *E. clathrata* and *U. lactuca*. Accumulation of Pb was quite similar in all algae. From these findings it is possible to conclude that *C. aerea* could serve as bioindicator for monitoring heavy metal pollution in this part of the world.

Statistical comparison was also carried out between heavy metal levels in the three studied sites (Table 2). No significant differences were found between these sites indicating that these areas are going through a similar degree of pollution.

### Conclusions

High levels of heavy metals were found in the three algae at all sites. These high concentrations are caused by anthropogenic discharges of pollutants into the coastal areas of the Arabian Gulf. Therefore, serious measures should be taken by the governments of the Arabian Gulf countries to reduce the input of pollutants into this area and action must be taken now before it is too late.

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