*Egypt. J. Aquat. Biol. & Fish., Vol. 11, No.1:191 - 205 (2007) ISSN 1110 –6131*

# LEVELS OF TRACE METALS IN MARINE MACROALGAE FROM BITTER LAKES, SUEZ CANAL, EGYPT.

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**Keywords:** Trace metals, marine macroalgae, Bitter Lakes, Suez Canal

## ABSTRACT

The levels of trace metals (Ni, Co, Cu, Fe, Zn, Cd and Pb) were determined in ten macroalgal species (green algae: *Enteromorpha compressa* and *Cladophora albida;* brown algae:, *Sargassum dentifolium*, *Cystoseira yrica*, *Padina pavonia*; red algae: *Acanthophora najadiformis*, *Laurencia papillosa*, *Ceramium tenuissima*, *Polysiphonia figariana*, *Hypnea cornuta*) collected from six sites along Bitter lakes (Suez Canal, Egypt). The relative abundance of trace metals in algal species decreased in the order (Fe> Zn> Ni> Cu> Pb> Co> Cd). The highest concentration of Co ( 1.17 µg/g dry wt.) and Pb ( 8.00 µg/g dry wt.) were found in brown algae *C. myrica*, while Cd ( 1.00 µg/g ) and Cu ( 16.92 µg/g dry wt ) were recorded in *P. pavonia* and *S. dentifolium*, respectively. In red algae, the highest value of Ni (9.28 µg/g dry wt.), Zn (36.50 µg/g dry wt.) and Fe (502.20 µg/g dry wt.) were observed in *A. najadiformis, P. figariana* and *H. cornuta*, respectively. According to the local variation of metals in the investigated area, the highest values of most metals (Ni, Cu, Fe, Zn and Pb) were recorded in front of Fayed (site III) which is the biggest village in the Bitter Lakes area and receives agricultural and domestaic drains in addition to the effluent from the vessels crossing the Suez Canal. Inter – elemental relationships were studied and showed positive significant correlation ($p < 0.05$) between Ni – Fe ($r = 0.63$), Ni – Zn ($r = 0.47$), Co – Fe ($r = 0.52$), Zn – Cd ($r = 0.41$) and between Zn – Pb ($r = 0.49$).

The present study recommended that the pollution sources at Fayed, which considered as fishing and recreational marine area, must be controlled. As well as, some algal species can be used as a good target for monitoring metals pollution in Bitter Lakes.

# INTRODUCTION

One of the main problems to adequately evaluate natural and anthropogenic contributions of trace metals to the ecosystem, is the inherent variability in their concentrations caused by the continuous change in the conditions of the marine environment, and by dynamics of currents and upwelling processes. An alternative that recently has been explored is the possibility of using macroalgae as bioindicators of metal concentrations in seawater (Denton and Burdon-Jones, 1986; Haritonidis and Malea,1995; Muse *et al.*, 1995). The main advantage of analysing metals in seaweed tissues is that macroalgae can accumulate trace metals in concentrations which are several orders of magnitude higher than their respective concentrations in seawater (Biney, 1991; De Leon-Chavira *et al.*, 2003).

Concentrations of trace metals associated to seaweeds have been studied in different parts of the world (Muse *et al.*, 1995; Rainbow, 1995; El-Sarraf, 1995; Riget *et al.*, 1997).

The area considerd in this study (Bitter Lakes) represents a huge water body of high salinity, and separating Suez Canal into two main parts. The Bitter lakes consists of two parts (Fig. 1);the northern, the Great Bitter Lake, has a maximum width of 13 Km and a length of 22.250 Km., while the southern. the Little Bitter Lake, has a width of 4.5 Km and a length of 15 Km (El-Manawy, 1992). It possesses some complications to flow between Red Sea and Mediterranean. However, there has been a remarkable population development accompanied by intense urbanization, industrial activities, tourism activities and higher exploitation of cultivable land at this area and its surrounding. These activities result in increased quantity of discharged pollutants, including heavy metals. The objective of the present study is to estimate the concentration of heavy metals in different algal species growing in different localities of Bitter lakes (Suez Canal, Egypt).

# MATERIALS AND METHODS

Five species of red macroalgae ((*Acanthophora najadiformis* (Delile) Papenfuss, *Laurencia papillosa* (C. Agardh) Greville, *Ceramium tenuissima*, *Polysiphonia figariana* (Zanardini) and *Hypnea cornuta* (Kutzing) J. Agardh)), three species of brown algae ((*Sargassum dentifolium* (Turner) C. Agardh, *Cystoseira myrica* (Gmelin) C. Agardh and *Padina pavonia* (Linnaeus) Jaillon)) and two species of green algae ((*Enteromorpha compressa* (Linnaeus) Nees and *Cladophora albida*

(Hudson) Kutzing)) were collected from six sites at the Bitter Lakes Suez Canal (Fig. 1). Algal samples were harvested haphazardly from the seafloor by hand or by SCUBA diving according to the depth.

Samples were rinsed with clean seawater and particulate material was removed as far as possible. Air drying of algal samples, followed by grinding process. Between 0.5 and 1.5 g of dried sample of each separate sample was weighed into a 100 ml Erlenmeyer glass flask, digested with 10 ml of nitric acid at 110-135 °C. The solution was then evaporated to dryness and the digestion completed by addition of 2 ml of 1:1 mixture of nitric and perchloric acids as dicribed by Denton and Burdon-Jones (1986). The residue was dissolved in 2N nitric acid and analysed by Atomic Absorption Spectrophotometer (AAS), Concentrations of metals in seawater were extracted by APDC (ammonium pyrollidine dithiocarbamate) and MIBK (methyl isobutyl ketone) treatment as described by APHA (1989); All glassware was cleaned with dilute nitric acid and thoroughly rinsed with double-distilled water before use. Correlation matrix was calculated using Statistical program (Stat 5).

## RESULTS AND DISCUSSION

The red algae were represented through all the investigated sites, while the brown and green algae were found at some sites. Figures (2-7) shows the concentrations of trace metals in the different separate algal species along the investigated sites. At site III (Fayed), the highest values of Ni (9.28 µg/g dry wt.), Zn (36.50 µg/g dry wt.), Fe (502.20 µg/g dry wt.) were recorded in the red algae *A. najadiformis*, *P. figariana* and *H. cornuta*, Pb (8.00 µg/g dry wt.) and Cu (16.92 µg/g dry wt.) were in the brown algae *C. myrica* and *S. dentifolium*, respectively. Deversoir characterized by the highest concentrations of Cd (1.00 µg/g dry wt.) and Co (1.70 µg/g dry wt.) which found in the brown algae *P. pavonia* and *C. myrica.* The lowest concentrations of Cu (1.40 µg/g dry wt.), Ni (2.88 µg/g dry wt.), Pb (1.17 µg/g dry wt.) and Zn (4.40 µg/g dry wt.) were recognized at site IV in the three algal groups, while the red algae had the lowest values of Co (0.512 µg/g dry wt.), Fe (213.50 µg/g dry wt.) and Cd (0.24 µg/g dry wt.) at the sites II, V and VI, respectively.

The significant high metal concentrations recorded in brown and red seaweed in site III may be attributed to the effect of Fayed sewage outlet, activities of ships waiting transit at this site along Suez Canal and agriculture run off. Fayed drain comprised high levels of most determined metals ( Abd El-Azim, 2002). Ho (1987) and El-Sarraf (1995) stated that high seawater metal concentrations led to high bioaccumulation of these metals in macrophytes. In contrast, site IV which showed the lowest concentrations effluents where are far from any pollution sources. Haritonidis and Malea (1995) concluded that the variation of metal concentration in algae bioavailability from site to site reflects the metal concentration in different environment and physico-chemical factors (such as temperature, pH, salinity, wave exposure, light, etc.) which affect the bio-availability of algae to accumulate metals, beside the sources of pollution invaded these stations. The increase of metal concentration in algae at site III may be affected by the low value of salinity than other site in Bitter Lakes due to the invaded lower saline water (5.83 ‰) from Fayed drain (Abd El-Azim, 2002). Accumulation of metals in algae was enhanced by decreasing salinity of the surrounding media, presumbly owing to competition with chloride ions for binding sites (Munda, 1984; Moore, 1991).

Range and average concentrations of trace metals in the studied algal species are listed in Table (1). In the red algae, *A. najadiformis* the minimum concentrations of Ni, Co, Cu, Zn and Pb and the maximum of Ni, Cu and Cd were recorded, while *H. cornuta* had the highest values of Co and Fe. The brown alga *C. myrica* had the lowest concentrations of all measured trace metals at site IV. while *P. pavonia* showed the highest Fe, Cd and Zn levels. *Enteromorpha compressa*, found at site III was characterized by the maximum levels of trace metals among the other estimated green algae. Regarding these results, it is clear that different species have different affinities for certain metals. Thus, inter-locational differences in ambient metal levels should be investigated using a species or group of species common to all sites of interest. The red algae *A. najadiformis* and *L. papillosa*, were common in most stations. By comparing with *L. papillosa,* the distribution of metals in *A. najadiformis* along most stations was changed. showing that, 1) the different uptake from different populations of the species, 2) the stage of development and 3) the presence of different metallic contaminants are other important factors modifying metal bioaccumulation by algae (Karez *et al.,* 1994).

Figure (8) shows the average values of trace metals concentrations for the different algal groups. Brown algae had the lower average values of Ni, Fe, Zn and Cd, and the highest of Co, Cu and Pb. Green algae had the highest average of Fe, Zn and Cd, while the highest of Ni was found in red algae.

The accumulation of metals in the body of macroalgae showed a wide variation specially between highest abundant metal (Fe) and the lowest one (Cd) (El-Moselhy *et al.*, 2006). The relative abundance of trace metals in red algal species decreased in the order Fe > Zn > Ni > Cu> Pb> Co> Cd, also the order of metals concentrations in the other two groups was slightly different recording the following regime: Brown algae Fe > Zn> Cu > Ni> Pb> Co> Cd, green algae Fe> Zn> Ni > Pb> Cu> Co> Cd. Abdallah *et al.*, (2005) stated Zn was the most abundant metal in the seaweeds of the Suez area The relative abundance of metals in algal species are largely influenced by the abundance of metals dissolved in seawater . This order should also depend on the affinity of each element for plant's components (Haritonidis and Malea,1995).

Correlation matrix for inter-elemental relationships in the macroalgal tissues is presented in Table (2). The obtained data showed in-significant correlation at $p < 0.05$ between most of the studied metals. The positive significant correlation were found between Ni – Fe ($r = 0.63$), Ni -- Zn ($r = 0.47$), Co – Fe ($r = 0.53$), Zn – Cd ($r = 0.41$) and between Zn – Pb ($r = 0.49$). El Sayed and Dorgham (1994) indicated that the metals which showed significant relationships were existed at almost regular proportions in the plant tissue, as a result of a controlled processes.

Taking into account that the collection sites are fairly distant and influenced by different marine environment, it was important to determine algal bio-concentration of heavy metals from the surrounding seawater ( Table 1 ), and the mean concentration factor (CF)* [The ratio of the metal concentration in the plant (µg/g dry wt) to its concentration in seawater (µg/l)]. Accumulation of Ni, Zn and Pb in green algae *E. compressa* had 5372, 6286 and 1498 times the concentration in seawater; red algae *H. cornuta* accumulate 5851 and 22883 times of Co and Fe than in seawater; brown algae *S. dentifolium* had 5697 times of Cu concentration that of seawater and in *P. pavonia* 2949 times of Cd. These variations in conentration factors were depending on the algal species studied and collection site. Brown algae showed a tendency to incorporate higher concentrations of elements than red and green algae ( Sanchez-Rodriguez, *et al.*, 2001) The values of metals concentration in seawater were submitted by Abd El-Azim (2002).

The metal concentrations in seaweed from Bitter Lakes were compared with levels found in studies of (Table 3). Comparisons of element concentrations from different areas should be done taking into account that, 1) metal concentrations may be affected by the use of different analytical procedures, 2) use of different parts of the plant, 3) sampling at different times of the year (Haritonidis and Malea,1995). The available obtained data showed that, in *S. dentifolium*, all the metal concentrations in the studied algae, except for Cu were lower than that found by El-Moselhy *et al.* (2006) and Abd El-Azim (2002). Abdallah *et al.* (2006) found that algae obtained from Suez area had the highest concentrations of the investigated heavy metals than those collected from Mars Alam area (Table 4). The concentration of Cu in *S. dentifolium*, Zn in *E. compressa* and Co in most studied algae exceeded the typical metal concentrations listed by Moore ( 1991 ).

## CONCLUSIONS

From the obtained data in the present study, it can be stated that, among the Bitter Lakes area at Suez Canal, Fayed is the most polluted site. It receives different drains and is considered as waiting area for the vessels crossing the Suez Canal and, so had the highest metals concentrations in the investigated algal species. Shaat El-Wozaraa site is considered as the most clean area, far away from pollution sources and so it could be used as control sampling site for monitoring programms El- ( Abd El-Azim 2002; Moselhy *et al.*, 2006 ).

The red (15 samples) and brown algae (7 samples) are the most dominant algal groups found in Bitter Lakes. The green algae: *E. compressa* is a specific to the metals Ni, Zn and Pb, The red alga: *H. cornuta* is specific to the metals Co and Fe, while the Brown algae: *S. dentifolium* and *P. pavonia* are specific for Cu and Cd, respectively. These algae can be considered as good target for monitoring contamination in Bitter Lakes.

Bitter Lakes area is still lower in most metals levels compared to the Southern part of Suez Canal and Suez Bay area (Table 3). The present study recommended that the pollution sources at Fayed, which considered as fishing and recreational marine area, must be controlled. As well as, some algal species can be used as good indicators for monitoring contamination in Bitter Lakes.

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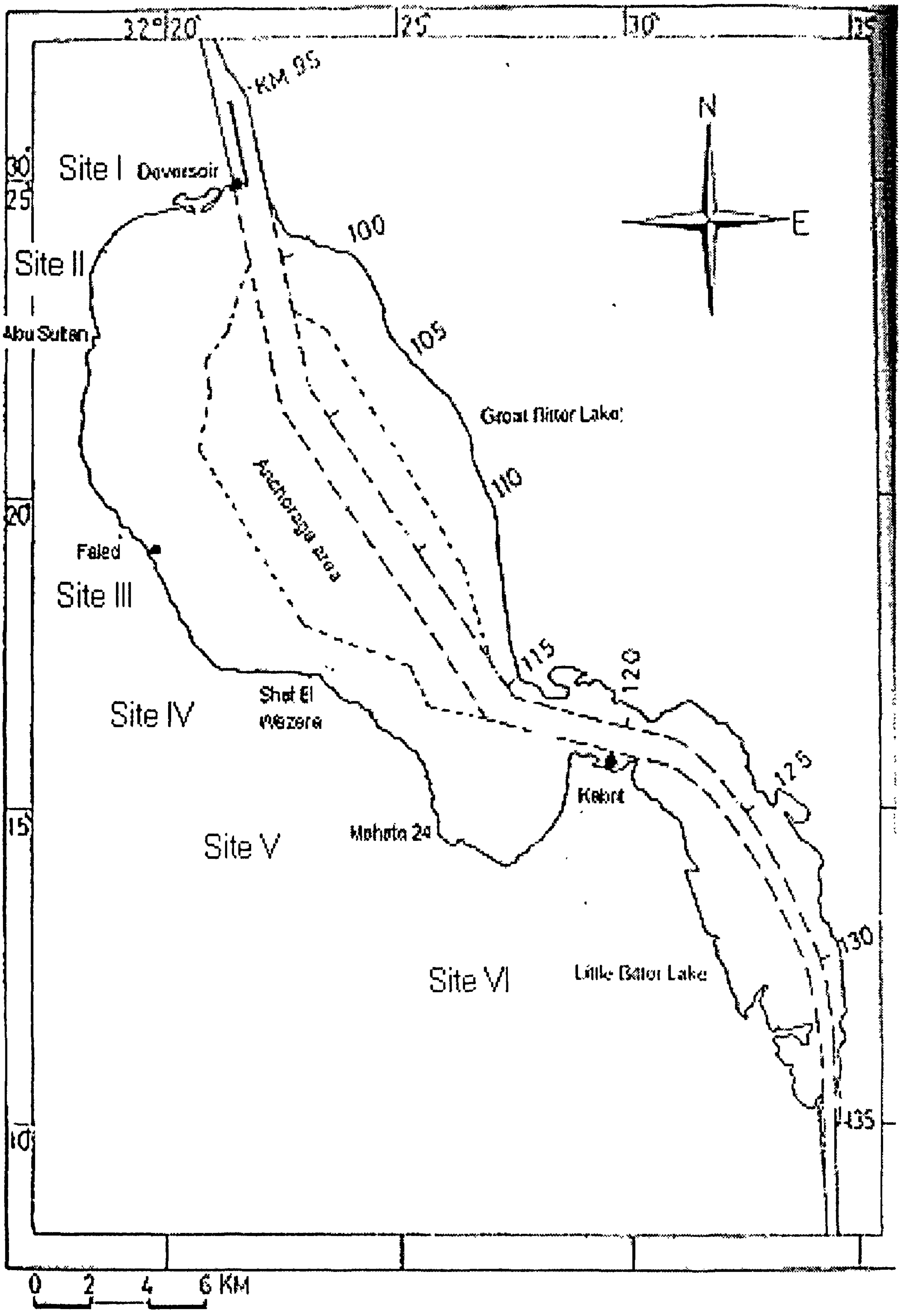

Fig. (1). Bitter Lakes and location of the six investigated sites.

Table (1). Range and average concentrations of trace metals (µg/g dry wt.) in the algal species collected from the different sites along Bitter Lakes.

| Metal<br>Species | Ni | Co | Cu | Fe | Zn | Cd | Pb |
|---|---|---|---|---|---|---|---|
| Red algae: | | | | | | | |
| 1- *A.najadiformis* | (3.20-9.28)<br>4.99 | (0.51-1.21)<br>0.82 | (1.75-9.42)<br>4.77 | (224.90-431.90)<br>306.06 | (4.90-29.92)<br>15.86 | (0.42-0.96)<br>0.64 | (1.17-4.40)<br>2.71 |
| 2- *L. papillosa* | (3.66-5.76)<br>5.16 | (0.62-1.58)<br>1.00 | (3.27-8.92)<br>5.08 | (213.50-442.20)<br>330.68 | (5.94-28.00)<br>12.65 | (0 36-0.96)<br>0.62 | (2.28-6.40)<br>3.79 |
| 3- *C. tenuissima* | (5.58-8.64)<br>7.11 | (1.10-1.17)<br>1.13 | (3.00-3.61)<br>3.31 | (341.20-457 10)<br>399.15 | (5.67-10.62)<br>8.15 | (0.24-0.798)<br>0.52 | (3.21-4.45)<br>3.83 |
| 4- *P. figariana* | (4.75-8.10)<br>6.43 | (0.86-0.92)<br>0.89 | (3.43-3.51)<br>3.47 | (314.60-430.00)<br>372.30 | (5.57-36.50)<br>21.04 | (0.63-0.68)<br>0.66 | (1.65-4.30)<br>2.98 |
| 5- *H. cornuta* | 6.62 | 1.65 | 3.03 | 502.2 | 5.52 | 0.59 | 2.30 |
| Brown algae: | | | | | | | |
| 1-*C. myrica* | (2.88-4.66)<br>3.60 | (0.73-1.70)<br>1.14 | (1.40-3.42)<br>2.64 | (230.00-321 30)<br>287.05 | (4.68-14.40)<br>9.17 | (0 28-0.84)<br>0.49 | (2.18-8.00)<br>3.94 |
| 2-*S. dentifolium* | (4.39-6.10)<br>5.25 | (0.86-1.40)<br>1.13 | (3.90-16 92)<br>10.41 | (356.5-364 4)<br>360.45 | (5.79-6.24)<br>6.02 | (0 57-0.74)<br>0 66 | (3.31-3.58)<br>3.45 |
| 3- *p. pavonia* | 6.10 | 1.34 | 4 77 | 431.90 | 16.33 | 1.00 | 3.52 |
| Green algae: | | | | | | | |
| 1- *C. albida* | (3.34-4.12)<br>3.73 | (0.76-0.87)<br>0.82 | (1.58-2.67)<br>2.13 | (313.80-341.20)<br>327.50 | (4.21-7.98)<br>6.10 | (0 34-0.83)<br>0.59 | (2.85-3.49)<br>3.17 |
| 2- *E. compressa* | 7.14 | 1.36 | 4.48 | 437.90 | 36.40 | 0 83 | 4.10 |
| Seawater µg/l Abd El-Azim (2002) | 1.33 | 0.28 | 1.83 | 21.94 | 5.79 | 0 34 | 2.74 |

Table (2): Correlation matrix: metal aganist metal in the studied species of macroalgae.

| Metal | Ni $^{(2+)}$ | Co $^{(2+)}$ | Cu $^{(2+)}$ | Fe $^{(2+)}$ | Zn $^{(2+)}$ | Cd $^{(2+)}$ | Pb $^{(2+)}$ |
|---|---|---|---|---|---|---|---|
| Ni | 1.000 | | | | | | |
| Co | 0.247 | 1.000 | | | | | |
| Cu | 0.215 | -0.087 | 1.000 | | | | |
| Fe | 0.629 * | 0.522 * | 0.228 | 1.000 | | | |
| Zn | 0.472 * | -0.084 | 0.218 | 0.330 | 1.000 | | |
| Cd | 0.249 | 0.378 | 0.167 | 0.339 | 0.410 * | 1.000 | |
| Pb | 0.184 | -0.140 | 0.179 | 0.046 | 0.492 * | 0.284 | 1.000 |

* Significant at $p < 0.05$ . N = 25

Table (3): Comparison of trace metal concentrations (µg/g dry wt.) of some algal species in the present study and previous studies at and near Suez Canal.

| Study | Species \ Metal | Ni $^{(2+)}$ | Co $^{(2+)}$ | Cu $^{(2+)}$ | Fe $^{(2+)}$ | Zn $^{(2+)}$ | Cd $^{(2+)}$ | Pb $^{(2+)}$ |
|---|---|---|---|---|---|---|---|---|
| Present study | *S. dentifolium* | 4 39-6 10<br>(5 25) | 0 86-1 40<br>(1 13) | 3 90-16 92<br>(10 41) | 356 50-364 40<br>(360.45) | 5.79-6 24<br>(6.02) | 0 57-0.74<br>(0 66) | 3 31-3.58<br>(3.45) |
| | *p. pavonia* | 6.10 | 1 34 | 4 77 | 431 90 | 16.33 | 1.00 | 3 52 |
| | *E. compressa* | 7 14 | 1 36 | 4 48 | 437 90 | 36.40 | 0 83 | 4.10 |
| | *L. papillosa* | 3.66-5 76<br>(5 16) | 0 06-0.58<br>(1 00) | 3 27-8.92<br>(5 08) | 213 50-442 20<br>(330.68) | 5 94-28 00<br>(12.65) | 0 36-0.96<br>(0 62) | 2 28-6 40<br>(3 79) |
| | *C. myrica* | 2.88-4 66<br>(3 60) | 0 73-1 70<br>(1.14) | 1 40-3.42<br>(2 64) | 230 00-321.30<br>(287.05) | 4 68-14.40<br>(9.17) | 0.28-0.84<br>(0.49) | 2.18-8.00<br>(3.94) |
| El-Moselhy *et al*., (2006) | *S. dentifolium* | 6 41-9 96<br>(7 60) | 3 11-4.77<br>(3 71) | 2 70-3.90<br>(3 46) | 170 50-625 00<br>(398 00) | 14 78-16 32<br>(15.40) | 2.19-2.52<br>(2.39) | 3.41-5.59<br>(4.70) |
| | *p. pavonia* | 9 00 | 4.37 | 8 35 | 916 20 | 25.75 | 2 57 | 5.30 |
| | *E. compressa* | 6 89-11 82<br>(9 48) | 4 01-5 28<br>(4 55) | 5 38-10.12<br>(7 54) | 582 40-1255 70<br>(937 90) | 25 35-35.25<br>(29 82) | 1 73-2 32<br>(2 01) | 4 26-9 95<br>(6.34) |
| Abd El-Azim (2002) | *S. dentifolium* | 7.33 | 0.87 | 4 47 | 667.74 | 88.22 | 2 75 | 11.00 |
| | *L. papillosa* | 11 55-12 50<br>(12 03) | 3 55-3.83<br>(3 69) | 9 28-16.90<br>(12 64) | 911 84-1075 80<br>(993 82) | 65 55-71 07<br>(68.31) | 2 70-2 86<br>(2 78) | 15 43-11 88<br>(13 66) |
| | *C. myrica* | 13 88 | 4 93 | 6 51 | 1138 40 | 129 10 | 5 21 | 19 34 |
| Moore (1991) | | < 150 | 0 1 - 1 00 | < 10 | * | 5 - 35 | < 5 | * |

* Not listed

Table (4): Comparison of concentration factors (CF) and range of trace metal concentrations (µg/g dry wt.) of some algal species in the present study and previous studies.

| Species | Ni | Zn | Pb | Fe |
|---|---|---|---|---|
| Concentration factor (CF) | | | | |
| *E. compressa*<br>(Present study) | 5372 | 6286 | 1498 | |
| *Enteromorpha spp.* (Mars Alam area)<br>(2005) | | 20091 | | |
| *Liagora farinosa*<br>(Suez area)<br>(2006) | | 29161 | | |
| Range of trace metal concentrations | | | | |
| (Species of present study)<br>(µg/g) | | 4.21-36.5 | | 213.5-457.1 |
| *Gelidium abbottiorum*<br>Misheer, *et al.*, (2006) (South Africa) (µg/g) | | 0.1-0.4 | | 3-8 ppm |

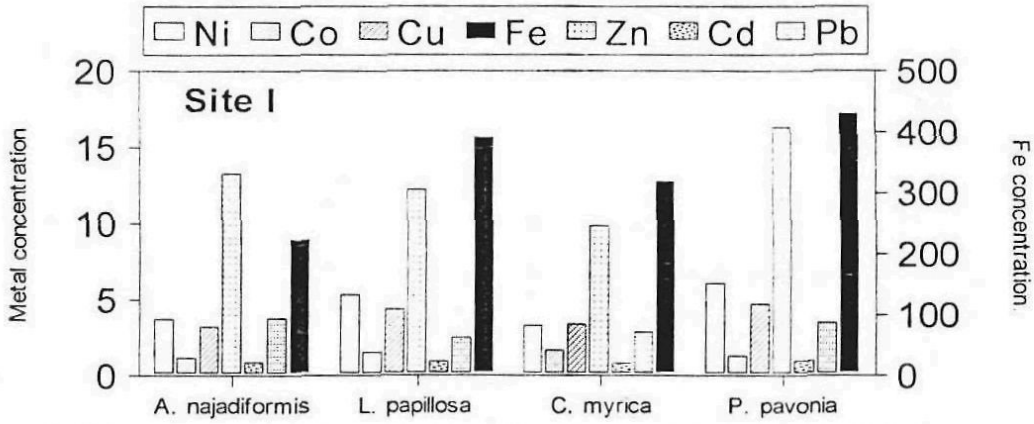

Fig. (2). Metal concentrations (μg/g) in the different algal species collected from site I.

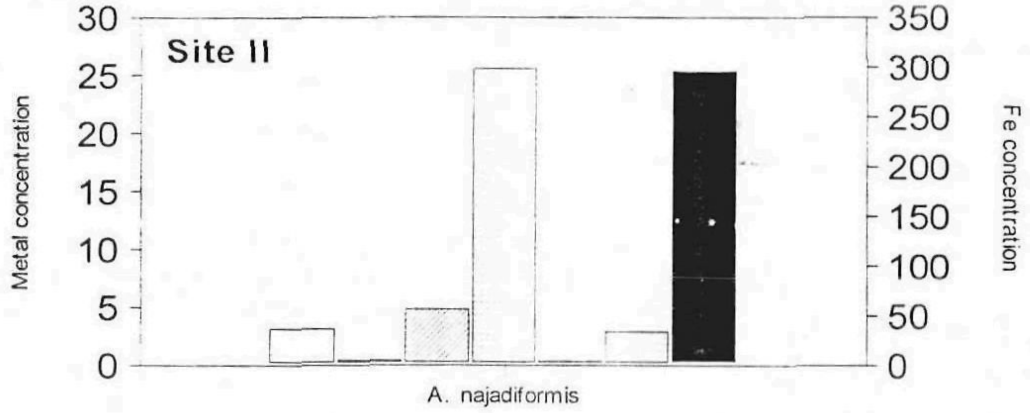

Fig. (3). Metal concentrations (μg/g) in the different algal species collected from site II.

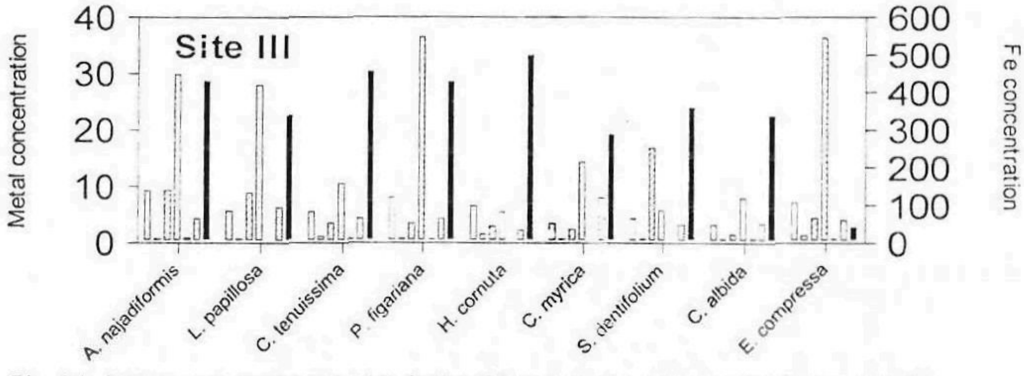

Fig. (4). Metal concentrations (μg/g) in the different algal species collected from site III.

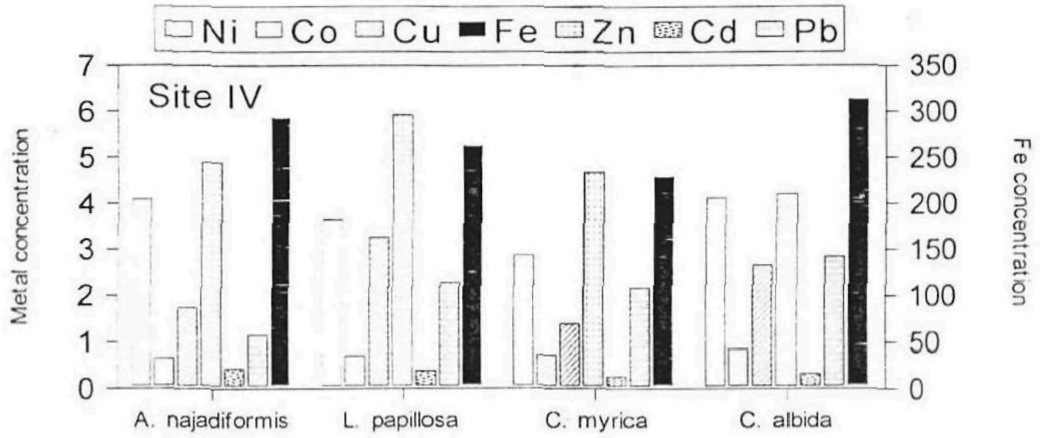

Fig. (5) Metal concentrations (µg/g) in the different algal species collected from site IV.

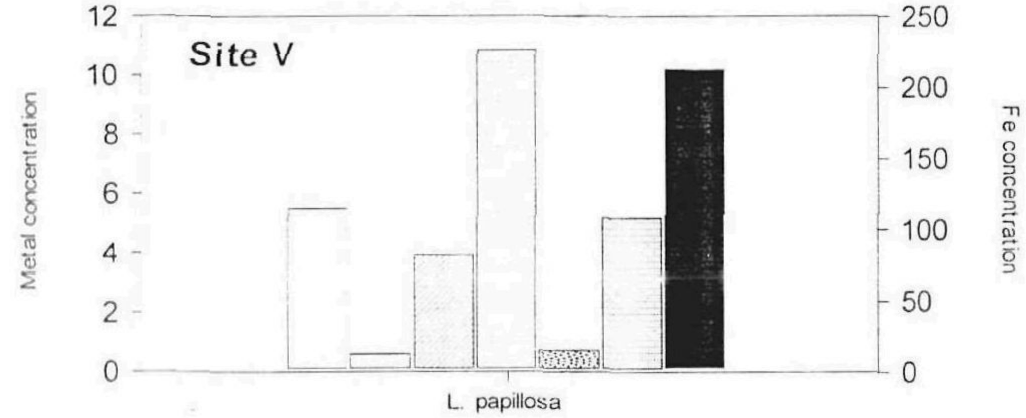

Fig. (6) Metal concentrations (µg/g) in the different algal species collected from site V

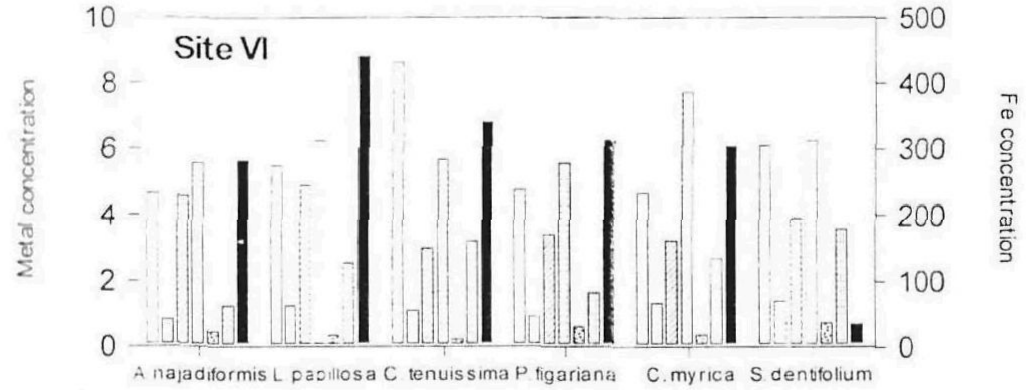

Fig. (7) Metal concentrations (µg/g) in the different algal species collected from site VI