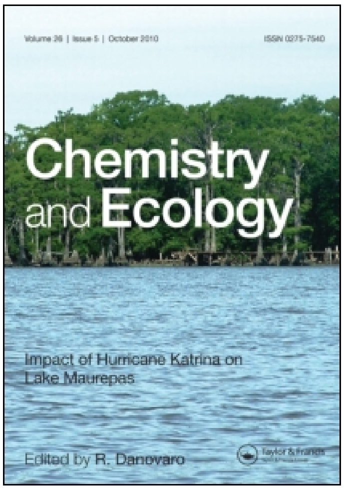

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Contents of heavy metals in marine seaweeds from the Egyptian coast of the Red Sea

A. M. A. Abdallah[a]; M. A. Abdallah[a]; A. I. Beltagy[a]
[a] National Institute of Oceanography & Fisheries, Alexandria, Egypt

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Contents of heavy metals in marine seaweeds from the Egyptian coast of the Red Sea

A. M. A. ABDALLAH*, M. A. ABDALLAH and A. I. BELTAGY

National Institute of Oceanography & Fisheries, Alexandria, Egypt

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Seaweeds belonging to 14 different genera of Chlorophyta, Phaeophyta, and Rhodophyta were analysed to determine the levels of heavy metals in two areas of the Egyptian Red Sea coast. Among the trace metals analysed, Mn and Zn showed the highest mass concentrations in the surface sea waters of the two studied areas. However, algae obtained from the Suez area had higher concentrations of the investigated heavy metals than those collect in the Mars Alam area. Nevertheless, a high variability of the metal levels occurs among the studied algae and also between the investigated areas. Moreover, Zn was the most abundant metal in the seaweeds of the Suez area, while Pb was predominant in the Mars Alam area in red and brown algae. *Liagora* spp. had the highest average concentration factor of Zn in Suez (29 161-fold), while the average concentration factor in *Enteromorpha* spp. at Mars Alam was 20 091-fold. The highest Metal Pollution Index (MPI) value was recorded in *Liagora* spp. (22.0) at Suez. This represents a 4.6-fold higher value than that recorded in *Liagora* spp. at Mars Alam. Among green, brown, and red algae in Suez, the highest values of MPI were recorded in *Cladophora* spp. and *Halimeda* spp. (18.2 and 18.3), *Padina* spp. (16.2), and *Liagora* spp. (22.1), respectively; while at Mars Alam, the highest values of MPI were recorded in *Cladophora* spp. (6.6), *Padina* spp. (3.4) and *Liagora* spp. (4.8), respectively.

Keywords: Heavy metals; Seaweeds; Contamination; Red Sea; Egypt

1. Introduction

Benthic marine algae are one of the most suitable organisms for the study of heavy-metal concentration in aquatic ecosystems [1–3]. Their immobility relates them directly to their surrounding environment as they do not their inner metal concentrations when the ambient concentrations vary suddenly. Among the coastal benthic algae, Chlorophyta (green algae) Phaeophyta (brown algae), and Rhodophyta (Red algae) are especially useful for this type of study as they show a clear tendency to accumulate heavy metals [4–15].

*Corresponding author. Present address: 479 El-Horria, St., Bokly, Alexandria, Egypt.
Email: abdallah@wwwsol.com

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The problems and threats facing the Egyptian Red Sea ecosystem and geosystem include recreation and tourism activities, landfilling, dredging, sea-water pollution, solid-waste disposal, phosphate pollution, and fishing practices. It is also worth mentioning that high heavy-metal concentrations along the Egyptian Red Sea coast are found in areas within or near the harbours of Suez are related to the terrigenous input and the anthropogenic influence. However, Mars Alam, situated about 700 km from Suez city, is probably also far from any human influence.

Before explaining the use of seaweeds in any coastal pollution monitoring program, it is essential to try to define the state of pollutants. Unfortunately, it is impossible to give all details of pollutants levels at the same time with the heterogeneous groups of algae samples and define the pollution state along the Egyptian Red Sea coast. However, the aim of the present study is to determine some of the heavy-metal (Cd, Cu, Co, Cr, Mn, Ni, Pb, and Zn) concentrations in 14 different genera of seaweeds in two different areas of the Egyptian Red Sea coast, from Suez (the polluted area) and Mars Alam (the reference area).

2. Materials and methods

Two areas of the Egyptian Red Sea coast (Suez and Mars Alam) were chosen for the study. In each area, seaweeds and sea-water samples for the metal analysis were collected at depths no more than 5 m during May 2002 (see figure 1). Sea-water samples (2 L) were filtered through a 0.45 μm Sartorius membrane filter within 1 h of sample collection. Each filtered sample

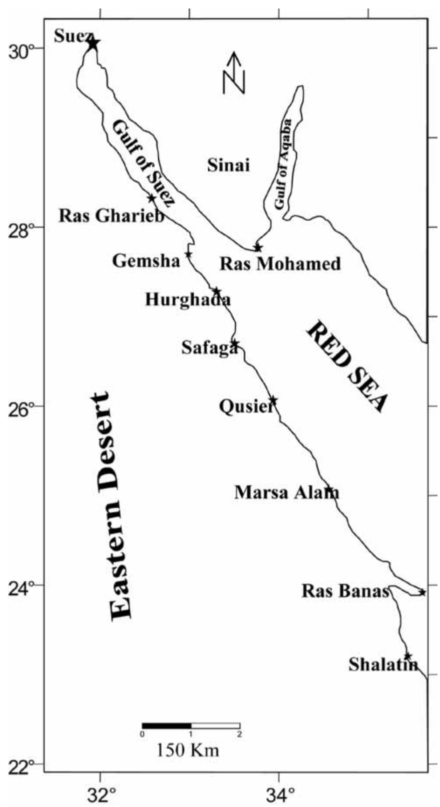

Figure 1. The Egyptian Red Sea coast.

was adjusted to pH 3.5 by adding 6 N HCl. Ammonium pyrolidine dithiocarbamate (APDC, 10 ml, 1%) was added while stirring to complete the metal chelation. Methylene isobutyl ketone (MIBK, 50 ml) was added to the sample in a separating funnel to extract the metals. Three replicates of each sea-water sample were analysed.

A comprehensive number of seaweed species belonging to Chlorophyta (*Enteromorpha intestinalis, Enteromorpha compressa, Enteromorpha flexuosa, Ulva lactuca, Cladophora crystalline, Cladophora serica, Cladophora coelothrix, Cladophora ramulosa, Caulerpa racemosa, Caulerpa serrulata, Caulerpa sertularioides*, and *Halimeda tuna*), Phaeophyta (*Sargassum dentifolium, Sargassum lattifolium, Turbinaria triquetra, Dictyota* spp., *Padina pavonia*, and *Padina pavonia*), and Rhodophyta (*Laurencia papillosa, Chondria seticulosa, Galaxaura oblongata, Galaxaura cylindrical, Galaxaura rugosa, Hypnea comuta, Hypnea esperi, and Liagora farinose*) were sampled.

Random seaweed samples were collected from the inter-tidal zones at low tide in each area ($200\,m^2$) and washed three times in sea water, then in distilled water and sea water again. Samples were then scrubbed in sea water using a nylon brush and rinsed in distilled water to remove traces of salt. After air-drying at room temperature for 3–4 days, the samples were stored in polythene bags until analysis. Dried samples were crushed and homogenised before digestion with nitric acid (10 ml, 69%) and perchloric acid (5 ml 1:1, 72%) in Teflon® bombs (C.E.M.) in a microwave oven. The extracts were made up to 50 ml with distilled water. Three replicates of each algae sample were analysed.

Metal content was determined using a GBC 932 atomic absorption spectrophotometer, and the analytical quality control was determined using BCR certified reference materials CRM 279 (sea lettuce) and CRM 403 for sea water.

3. Results

The average recoveries of all analysed metals in reference materials were 97 ± 5% and 99.5 ± 6% for CRM 279 (nine replicates) and CRM 403 (10 replicates), respectively. The mean concentrations ± SD of the metals (Cd, Cu, Ni, Pb, Mn, Co, Cr, and Zn) in the sea water are listed in table 1. However, for comparison purposes, the descending order of studied metals in sea water was Mn > Zn > Pb > Ni > Cu > Cd > Co > Cr for Suez and Mn > Zn > Ni > Pb > Cr > Co > Cu > Cd for Mars Alam. Although anthropogenic impact is very rare in Mars Alam, it seems that Mn and Zn were the dominant elements in Suez (4.0 and 1.1 $ng\,ml^{-1}$) and Mars Alam (3.1 and 1.1 $ng\,ml^{-1}$). Sea-water temperatures varied between 20.3 ± 1.2 °C in Suez and 23.6 ± 1.7 °C in Mars Alam during the sampling period. The dissolved oxygen shows that the content varied between 6.2 $mg\,l^{-1}$ in Suez and 7.1 $mg\,l^{-1}$ in Mars Alam. The sea-water salinity was 41.3‰ in the Suez and decreased in the southern portion, reaching 38.5‰ in Mars Alam. Moreover, tables 2 and 3 illustrate the concentrations ($mg\,kg^{-1}$ on dry weight basis) ± SD of the heavy metals analysed for the algae. Algae collected from the Suez area had higher concentrations of investigated heavy metals than those from the Mars Alam area. Nevertheless, there was a great fluctuation of metal levels among the sampled

Table 1. Mean ± SD concentrations ($ng\,ml^{-1}$) of heavy metals in sea water collected from Suez and Mars Alam.

	Cd	Cu	Ni	Pb	Mn	Co	Cr	Zn	MPI
Suez	1.2 ± 0.7	1.6 ± 0.8	2.2 ± 0.7	3.0 ± 1.1	4.0 ± 1.2	1.1 ± 0.4	1.0 ± 0.3	3.1 ± 0.9	1.9
Mars Alam	0.25 ± 0.1	0.35 ± 0.1	0.7 ± 0.2	0.6 ± 0.2	1.1 ± 0.4	0.4 ± 0.1	0.5 ± 0.1	1.1 ± 0.4	0.6

Table 2. Mean ± SD concentrations (mg kg^{-1}, dry weight) of heavy metals in algae species collected from Suez.

	Species name	Cd	Cu	Ni	Pb	Mn	Co	Cr	Zn	MPI
Green	*Ent. flexuosa*	4.7 ± 1.2	9.9 ± 2.7	16.4 ± 3.1	33.2 ± 4.1	23.1 ± 2.9	9.1 ± 0.9	8.8 ± 1.2	55.1 ± 5.8	15.0
	Ent. intestinalis									
	Ent. compressa									
	Ulva lactuca	5.3 ± 1.6	8.3 ± 2.4	11.5 ± 3.1	37.2 ± 4.8	16.9 ± 1.4	6.8 ± 1.7	9.2 ± 1.1	40.7 ± 4.4	13.0
	Cladophora crystallina	4.4 ± 1.8	17.3 ± 4.1	15.3 ± 2.8	38.1 ± 4.2	37.1 ± 3.1	9.1 ± 0.7	11.7 ± 1.4	69.7 ± 5.7	18.2
	Cladophora serica									
	Cladophora coelothrix									
	Caulerpa serrulata	6.1 ± 2.2	6.3 ± 1.9	10.3 ± 2.5	29.7 ± 3.3	15.5 ± 1.8	10.4 ± 0.7	7.0 ± 1.1	53.9 ± 4.8	12.8
	Caulerpa sertularioides									
	Halimeda tuna	10.4 ± 3.1	7.4 ± 1.7	16.7 ± 2.9	49.8 ± 4.1	27.7 ± 1.7	14.5 ± 1.4	13.4 ± 3.3	37.3 ± 3.7	18.3
	Average	6.2	9.8	14.1	37.6	24.1	9.9	10	51.3	
Brown	*Sargassum dentifolium*	2.1 ± 0.4	5.2 ± 1.4	8.7 ± 2.4	25.8 ± 2.9	27.1 ± 1.8	3.5 ± 0.4	1.2 ± 0.2	55.3 ± 2.8	7.9
	Turbinaria triquetra	2.3 ± 0.6	2.3 ± 0.9	6.3 ± 1.1	19.4 ± 1.6	8.3 ± 0.8	2.7 ± 0.3	0.6 ± 0.2	23.4 ± 2.4	4.6
	Dictyota spp.	3.6 ± 1.1	5.4 ± 1.4	9.1 ± 1.8	22.1 ± 1.7	36.4 ± 4.5	5.6 ± 0.4	4.5 ± 1.4	67.5 ± 5.5	11.2
	Padina pavonia	6.6 ± 1.9	10.7 ± 3.1	13 ± 2.9	38.9 ± 3.1	40.9 ± 4.1	7.4 ± 0.8	5.9 ± 1.6	74.8 ± 5.9	16.2
	Average	3.7	5.9	9.3	26.6	28.2	4.8	3.1	55.3	
Red	*Laurencia papillosa*	4.1 ± 1.5	7.2 ± 2.2	16.2 ± 4.1	28.7 ± 3.1	13.4 ± 2.2	7.7 ± 0.9	3.1 ± 1.1	51.3 ± 5.7	11.1
	Chondria seticulosa	3.8 ± 1.2	6.9 ± 2.1	11.1 ± 2.2	29.5 ± 3.3	40.6 ± 4.4	7.1 ± 0.5	4.6 ± 0.5	81.3 ± 8.6	13.2
	Galaxaura oblongata	6.9 ± 0.9	9.9 ± 2.4	13.3 ± 2.8	45.6 ± 3.7	45.9 ± 4.8	12.4 ± 0.7	5.3 ± 1.4	63.1 ± 4.8	17.3
	Galaxaura rugosa									
	Hypnea comuta	4.7 ± 2.4	8.8 ± 1.7	10.3 ± 2.1	19.8 ± 1.8	35.7 ± 4.7	4.6 ± 0.7	4.7 ± 0.4	55.1 ± 4.7	11.7
	Liagora farinosa	8.6 ± 1.9	11.4 ± 2.7	17.1 ± 3.4	50.5 ± 4.4	66.8 ± 5.1	16.6 ± 2.2	6.6 ± 1.7	90.4 ± 6.3	22.1
	Average	5.6	8.8	13.6	34.8	40.5	9.7	4.9	68.2	
	Average	5.3	8.4	12.5	33.5	31.1	8.4	6.2	58.5	
	Minimum	2.1	2.3	6.3	19.4	8.3	2.7	0.6	23.4	
	Maximum	10.4	17.3	17.1	50.5	66.8	16.6	13.4	90.4	
	SD	2.3	3.5	3.4	10.4	15.5	4.0	3.7	17.8	

Note: Ent.: Enteromorpha.

Table 3. Mean ± SD concentrations (mg kg^{-1}, dry weight) of heavy metals in algae species collected from Mars Alam.

	Species name	Cd	Cu	Ni	Pb	Mn	Co	Cr	Zn	MPI
Green	*Ent. flexuosa*	0.9 ± 0.1	3.1 ± 1.1	4.3 ± 1.2	13.3 ± 3.3	15.1 ± 3.1	6.3 ± 1.1	5.6 ± 2.1	22.1 ± 3.7	6.1
	Ent. intestinalis									
	Ent. compressa									
	Ulva lactuca	0.8 ± 0.1	3.5 ± 1.2	2.9 ± 0.9	11.3 ± 3.1	12.5 ± 2.9	4.5 ± 1.2	6.8 ± 2.2	12.4 ± 6.5	5.1
	Cladophora crystallina	0.9 ± 0.1	3.9 ± 0.9	4.7 ± 1.9	11.4 ± 2.9	22.2 ± 1.4	9.6 ± 1.4	4.9 ± 1.7	17.6 ± 3.1	6.6
	Cladophora serica									
	Cladophora coelothrix									
	Cladophora ramulosa									
	Caulerpa racemosa	0.4 ± 0.08	3.1 ± 0.8	2.1 ± 0.4	5.7 ± 1.7	4.7 ± 0.7	4.7 ± 1.4	1.5 ± 0.7	4.6 ± 3.4	2.7
	Caulerpa serrulata									
	Caulerpa sertularioides									
	Halimeda tuna	2.4 ± 1.0	3.8 ± 1.0	5.7 ± 1.4	8.9 ± 1.4	7.3 ± 2.1	4.1 ± 1.3	3.8 ± 1.8	6.3 ± 2.1	4.9
	Average	1.1	3.5	3.9	10.1	12.4	5.8	4.5	12.6	
Brown	*Sargassum dentifolium*	0.98 ± 0.3	1.5 ± 0.4	2.1 ± 0.4	4.5 ± 1.1	6.7 ± 2.7	1.8 ± 0.4	0.6 ± 0.2	4.5 ± 1.9	2.1
	Sargassum lattifolium									
	Turbinaria triquetra	0.8 ± 0.3	0.6 ± 0.1	1.1 ± 0.2	3.1 ± 1.1	6.2 ± 2.4	2.9 ± 0.7	0.10	1.9 ± 0.9	1.2
	Dictyota spp.	0.98 ± 0.3	1.3 ± 0.4	2.2 ± 0.6	19.2 ± 5.5	5.2 ± 2.1	4.3 ± 1.2	1.1 ± 0.3	4.9 ± 1.2	3.0
	Padina pavonia	1.1 ± 0.3	2.9 ± 0.9	4.9 ± 1.2	7.4 ± 2.1	5.5 ± 2.1	4.6 ± 1.1	1.0 ± 0.3	5.7 ± 1.7	3.4
	Average	1	1.6	2.6	8.5	5.9	3.4	0.7	4.3	
Red	*Laurencia papillosa*	0.6 ± 0.2	0.7 ± 0.1	0.98 ± 0.2	12.7 ± 4.4	4.6 ± 1.9	4.1 ± 1.7	1.3 ± 0.4	4.3 ± 1.4	2.2
	Chondria seticulosa	0.8 ± 0.3	1.5 ± 0.3	5.5 ± 1.4	5.8 ± 1.7	3.5 ± 1.1	4.3 ± 1.4	1.7 ± 0.6	6.2 ± 2.1	3.0
	Galaxaura cylindrical	1.0 ± 0.09	3.4 ± 1.2	7.1 ± 1.9	10.8 ± 2.7	7.8 ± 2.3	5.3 ± 1.4	3.6 ± 1.4	2.4 ± 0.7	4.2
	Galaxaura oblongata									
	Galaxaura rugosa									
	Hypnea comuta	0.4 ± 0.1	1.8 ± 0.4	2.2 ± 0.7	3.2 ± 0.8	7.3 ± 2.2	4.9 ± 1.2	3.2 ± 1.2	4.1 ± 1.2	2.7
	Hypnea esperi									
	Liagora farinosa	1.8 ± 0.1	4.3 ± 2.1	6.9 ± 2.1	7.3 ± 1.9	5.2 ± 1.8	7.3 ± 1.9	2.9 ± 1.1	6.9 ± 2.2	4.8
	Average	0.9	2.4	4.5	8.0	5.7	5.2	2.5	4.8	
	Average	1.0	2.5	3.8	8.9	8.1	4.9	2.7	7.4	
	Minimum	0.4	0.6	1.0	3.1	3.5	1.8	0.1	2.0	
	Maximum	2.4	4.3	7.1	19.2	22.2	9.6	6.8	22.1	
	SD	0.5	1.3	2.1	4.5	5.1	1.9	2.0	5.9	

Note: Ent.: Enteromorpha.

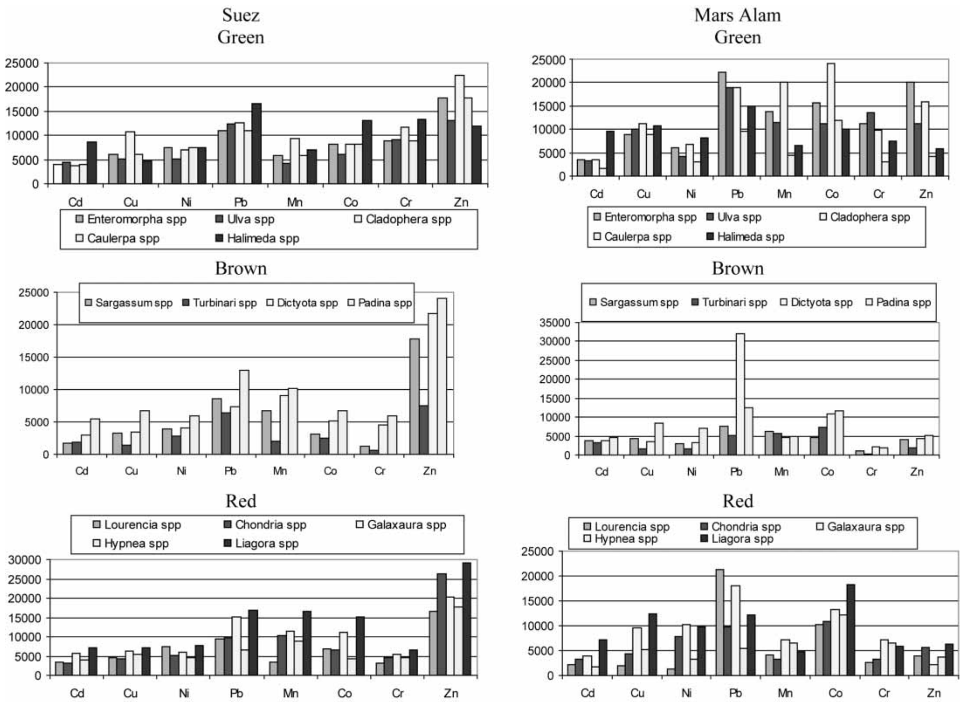

Figure 2. Concentration factors of metals between water and algae in Suez and Mars Alam. Concentration factors were the ratio of the element concentrations (per gram) divided by the same element in sea water (ml).

seaweeds and also between the investigated areas. Moreover, Zn was the most predominant metal in the algae from Suez area, while in the Mars Alam area Pb was the most predominant except for green algae. The concentration factors were the ratio of the element concentrations (per gram) divided by the same element in sea water (ml); see figure 2.

The overall metal contents of algae at the sites investigated in this study were compared on a regional basis using the metal pollution index (MPI) calculated using the formula for mussel [16]:

$$\mathrm{MPI} = (M_1 \times M_2 \times \cdots M_n)^{1/n},$$

where M_n is the concentration of metal *n*.

The metal MPI was calculated in the two studied areas for both sea water and algae. For sea-water samples, the highest MPI values in Suez and Mars Alam were 1.9 and 0.6, respectively. Presumably, the greater the MPI ratio, the more variable the relative concentrations of the metals found in the two investigated areas (Suez and Mars Alam). Considering the algal groups, the highest MPI values were recorded in *Halimeda* spp., *Padina* spp., and *Liagora* spp. for green, brown, and red algae: these values in Suez (18.3, 16.2, and 22.1) were higher than those found in Mars Alam (4.9, 3.4, and 4.8), respectively. These variations in MPI values of seaweeds from the two areas obtained may reflect the anthropogenic effects on marine algae and emphasise the ability of the algae to accumulate heavy metals.

3.1 *Cadmium*

Concerning sea-water samples (table 1), the concentrations of Cd in sea water from Suez (1.2 ng ml^{-1}) were fivefold higher than those found in Mars Alam (0.25 ng ml^{-1}). Tables 2 and 3 show the mean Cd concentrations in the investigated seaweeds. The highest cadmium concentrations in algae from Suez area were found in *Halimeda* spp. (10.4 mg kg^{-1}) for green algae, *Padina* spp. (6.6 mg kg^{-1}) for brown algae, and *Liagora* spp. (8.6 mg kg^{-1}) for red algae. The same trend is observed in algae from Mars Alam for *Halimeda* spp. (2.4 mg kg^{-1}), *Padina* spp. (1.1 mg kg^{-1}), and *Liagora* spp. (1.8 mg kg^{-1}). *Halimeda* spp. had the highest concentration factors of Cd (8667-fold) in Suez along studied species, while this value was calculated for *Cladophora* spp. in Mars Alam (9520-fold) with an average value of 4298 and 3983 for Suez and Mars Alam, respectively (figure 2).

3.2 *Copper*

The concentration of Cu in sea water was higher in Suez (1.6 ng ml^{-1}) than in Mars Alam (0.35 ng ml^{-1}) (table 1). In Suez, the highest concentrations were found in *Cladophora* spp. (17.3 mg kg^{-1}) for green algae, *Padina* spp. (10.7 mg kg^{-1}) for brown algae, and *Liagora* spp. (11.4 mg kg^{-1}) for red algae. At Mars Alam, a similar trend was recorded for *Cladophora* spp. and *Halimeda* spp. (3.8 and 3.9 mg kg^{-1}) for Chlorophyta, *Padina* spp. (2.9 mg kg^{-1}) for Phaeophyta, and *Liagora* spp. (4.3 mg kg^{-1}) for Rhodophyta. At Suez, *Cladophora* spp. (10 813-fold), *Padina* spp. (6688-fold), and *Liagora* spp. (7125-fold) had the highest concentration factor for Chlorophyta, Phaeophyta and Rhodophyta, respectively, with an average concentration factor of 5384. Moreover, at Mars Alam, the highest concentration factors were recorded in *Cladophora* spp. (11 143-fold) *Padina* spp. (8400-fold), and *Liagora* spp. (12 400-fold), which belong to green, brown, and red algae, respectively, with an average concentration factor of 7229 (figure 2).

3.3 *Nickel*

The concentration of Ni in sea water was higher in Suez (2.2 ng ml^{-1}) than in Mars Alam (0.7 ng ml^{-1}) (table 1). Tables 2 and 3 show the mean concentrations of Ni in chlorophyta species in which *Enteromorpha* spp. and *Halimeda* spp. had the highest concentrations (16.4 and 16.7 mg kg^{-1}) in Suez, while in Mars Alam, *Halimeda* spp. had the highest concentration (5.7 mg kg^{-1}). The average concentrations of green, brown, and red algae were 14.1, 9.3, and 13.6 mg kg^{-1}, respectively, at Suez, while at Mars Alam, these concentrations were 3.9, 2.6, and 4.5 mg kg^{-1}, respectively. Figure 2 shows the concentration factor for Ni in green algae and shows that *Halimeda* spp. and *Enteromorpha* spp. had higher values (7591- and 7455-fold) in Suez, while in Mars Alam, *Halimeda* spp. and *Cladophora* spp. had higher values (8200- and 6714-fold, respectively). The highest concentration factors in brown algae were observed in *Padina* spp. collected from Suez (5909-fold) and Mars Alam (7000-fold). Among red algae, *Galaxaura* spp. collected from Mars Alam had the highest concentration factor, 10 200-fold, followed by *Liagora* spp. (9800-fold) while at Suez, the highest concentration factor was found for *Liagora* spp., 7773-fold (figure 2).

3.4 *Zinc*

These results reveal that the highest accumulation of Zn is in Suez. The highest concentrations of Zn recorded in sea water (table 1) from Suez and Mars Alam were 3.1 and 1.1 ng ml^{-1}. The descending order of Zn average concentrations in seaweeds were red (68 mg kg^{-1}) $>$ brown (55.3 mg kg^{-1}) $>$ green algae (51.3 mg kg^{-1}). The highest mean concentrations in Suez were 69.7, 74.8, and 90.4 mg kg^{-1} for *Cladophora* spp., *Padina* spp., and *Liagora* spp., respectively. Moreover, the highest mean concentrations of Zn in Mars Alam were 22.1, 5.7, and 6.8 mg kg^{-1} for *Enteromorpha* spp., *Padina* spp., and *Liagora* spp., respectively. On the other hand, *Liagora* spp. had the highest concentration factor among red algae in both Suez and Mars Alam areas (29 161- and 6236-fold), while for green algae the highest values were observed in *Enteromorpha* spp. from Mars Alam (20 091-fold), and in *Cladophora* spp. (22 484-fold) at Suez (figure 2).

3.5 *Manganese*

Regarding the average concentrations of Mn in sea water (table 1) in the two investigated areas, it seems that manganese is the dominant metal in Suez and Mars Alam (3.2 and 1.1 ng ml^{-1}). However, tables 2 and 3 show the average concentrations of Mn in the investigated green seaweeds, which are 24 and 12.4 mg kg^{-1} in Suez and Mars Alam. *Cladophora* spp. had the highest concentrations (37.1 and 22.2 mg kg^{-1}), with an average concentration of 24 and 12.4 mg kg^{-1} in Suez and Mars Alam, respectively. Brown algae had the lowest ability to bioaccumulation the Mn in both studied areas compared with green and red algae. Figure 2 shows the concentration factor of Mn in studied seaweeds. *Cladophora* spp. had the highest value (9275- and 20 182-fold) in Suez and Mars Alam, respectively. The highest concentration of Mn in Phaeophyta was recorded in Suez in *Padina* spp. (40.9 mg kg^{-1}), while in Mars Alam, the average concentration was 5.7 mg kg^{-1} with SD 0.7 for brown algae. Figure 2 shows that the highest concentration factors were found in *Padina* spp. in Suez (10 225-fold) and *Sargassum* spp. in Mars Alam (6109-fold). *Liagora* spp. had the highest concentrations in Suez (66.8 mg kg^{-1}). *Liagora* spp. had the highest concentration factor in Suez (16 700-fold) followed by *Galaxaura* spp. (11 475-fold).

3.6 *Cobalt*

The mean concentration of cobalt in sea water from Suez and Mars Alam was 1.1 and 0.4 ng ml^{-1}, respectively. The highest concentrations of Co in Suez for each algal group were found in *Halimeda* spp., *Padina* spp., and *Liagora* spp. (14.5, 7.4, and 16.6 mg kg^{-1}) respectively, while in Mars Alam these concentrations were recorded in *Cladophora* spp. (9.6 mg kg^{-1}), *Padina* spp. (4.6 mg kg^{-1}), and *Liagora* spp. (7.3 mg kg^{-1}), respectively, for green, brown, and red algae. Figure 2 shows that the highest concentration factor was found in the red algae for *Liagora* spp. (15 019-fold), in Suez and (18 200-fold) in Mars Alam, while in green algae, different genera had the highest concentration factors: in Suez, this was *Halimeda* spp. (13 182-fold), and in Mars Alamm this was *Cladophora* spp. (24 000-fold). Brown algae generally had the lowest ability to accumulate the Co in both studied areas.

3.7 *Chromium*

For more detailed handling and further comparative purposes, the highest mean concentrations of Cr for each algae group in Suez were found in *Halimeda* spp., *Padina* spp., and *Liagora* spp. (13.4, 5.9, and 6.6 mg kg^{-1}), while in Mars Alam the highest concentrations were in *Ulva* spp., *Dictyota* spp., and *Galaxaura* spp. (6.8, 1.1, and 3.6 mg kg^{-1}), respectively, for green, brown, and red algae. The mean concentrations of Cr in sea water were 1.0 and 0.5 ng ml^{-1} in Suez and Mars Alam (table 1). Based on the present data, in general, Suez had the highest concentrations of Cr and Co in different algae species. In this respect, *Halimeda* spp. had the highest concentration factor in Suez (13 400-fold), while in Mars Alam, *Ulva* spp. had the highest value (13 600-fold) (figure 2).

3.8 *Lead*

The abundance of Pb in the marine environment is due to the lubricating oil from diesel- and gasoline-powered motors and engines from boats and ships. In this study, the mean concentrations of Pb found in sea water were 2.1 and 0.6 $ng\ ml^{-1}$ in Suez and Mars Alam, respectively (table 1). Generally, the average Pb concentrations in the investigated algae species were in the descending order *Liagora* spp. > *Halimeda* spp. > *Padina* spp. collected from Suez, while this descending order was *Enteromorpha* spp. > *Laurencia* spp. > *Sargassum* spp. for Mars Alam with a median value of 31.5 $mg\ kg^{-1}$. However, figure 2 shows the concentration factor of Pb in studied species in Suez; the highest values were found in green algae (*Halimeda* spp. from obtained values, 16 600-fold), while in Mars Alam, the highest value was recorded in brown algae (*Dictyota* spp., 31 967-fold).

4. Discussion

4.1 *Statistical results*

One way of demonstrating the existence of relationships between different metals while removing the source of variability due to genera differentiation is to carry out a correlation analysis of average concentrations for each sampling site. The results of this analysis (table 4) show that there are significant positive correlations between Pb and Cd, Co and Cd, Ni and Co, and Pb and Co in all algae obtained from Suez, while the only significant correlation is between Ni and Mn in algae in Mars Alam. Brown and red algae showed many significant correlations compared with green algae in the both studied areas. However, the significant correlations among these metals in studied algae may be due to their common origin or anthropogenic effects.

The significant correlations between Ni, Cd (except with Mn), and Cu with all metals other than Mn in brown algae in Suez may indicate contamination by particulate material [17], which is favoured by the morphology of these algae. Moreover, these correlations can be explained by a common source of these metals or by synergetic interactions between them [18]. It is difficult to know whether an area is in fact contaminated and if the contamination is natural or not. This problem is even more pronounced in developed countries where truly pristine areas are scarce or even non-existent. These results emphasised the direct anthropogenic impact in the Suez area.

4.2 *Comparison between trace-metal concentrations in the present study and in the literature*

The relative abundance of metals in *Ulva rigida* collected from the Thermaikos Gulf (Greece) decreased in the order: Mg > Na > K > Ca > Pb > Fe > Mn > Zn > Cr > Cu > Ni > Co > Cd [3]; this consecutive order agreed partially with results obtained from this study. In order to avoid repetitive reasoning and arguments leading to closely related interpretation, a comparison of reviews for trace-metal concentrations ($mg\ kg^{-1}$) in algae from various locations around the world and the present study is given in table 5. However, this table shows that the concentrations of Cd, Co, and Ni are comparable with most published results. Higher levels of Cu and Zn were reported in *E. intestinalis* than in *U. lactuca* [19]. The concentrations of Cd in Chlorophyta for this study were higher than those reported in Lebanon [20], Alexandria, Egypt [21], and Argentina [22]. However, the same concentrations occur in Aqaba and Malaysia, respectively [23, 24]. Moreover, the concentrations of Cd in brown algae observed in this study were

Table 4. Correlation coefficients between metal concentrations in algae samples.

	Suez								Mars Alam						
Correlation coefficients between metal levels in all algae samples ($n = 112$)															
	Cu	Ni	Pb	Mn	Co	Cr	Zn		Cu	Ni	Pb	Mn	Co	Cr	Zn
Cd	0.34	0.65	**0.85**	−0.07	**0.88**	0.67	0.17	Cd	0.50	0.61	0.09	0.41	0.10	0.14	0.02
Cu		0.66	0.55	0.69	0.46	0.62	0.53	Cu		0.72	0.11	0.46	0.66	0.67	0.46
Ni			0.75	0.32	**0.77**	0.65	0.33	Ni			0.06	**0.77**	0.50	0.37	0.19
Pb				0.19	**0.89**	0.66	0.31	Pb				0.04	0.30	0.32	0.39
Mn					0.04	0.58	−0.07	Mn					0.48	0.07	−0.03
Co						0.62	0.36	Co						0.56	0.63
Cr							0.04	Cr							0.74
Correlation coefficients between metal levels in green algae samples ($n = 40$)															
	Cu	Ni	Pb	Mn	Co	Cr	Zn		Cu	Ni	Pb	Mn	Co	Cr	Zn
Cd	−0.5	0.28	**0.78**	−0.63	**0.89**	0.57	−0.70	Cd	0.58	**0.83**	0.02	0.38	−0.3	0.02	−0.25
Cu		0.39	0.02	**0.94**	−0.3	0.37	**0.79**	Cu		0.66	0.15	0.76	0.37	0.24	−0.04
Ni			0.60	0.42	0.46	0.73	0.08	Ni			0.41	**0.78**	0.27	0.22	0.26
Pb				−0.04	0.65	**0.93**	−0.50	Pb				0.38	0.45	**0.89**	0.92
Mn					−0.48	0.28	0.68	Mn					**0.77**	0.15	0.40
Co						0.56	−0.33	Co						0.20	0.65
Cr							−0.15	Cr							0.68
Correlation coefficients between metal levels in brown algae samples ($n = 32$)															
	Cu	Ni	Pb	Mn	Co	Cr	Zn		Cu	Ni	Pb	Mn	Co	Cr	Zn
Cd	**0.92**	**0.92**	**0.88**	−0.66	**0.94**	**0.91**	0.71	Cd	**0.94**	**0.90**	0.31	**0.95**	0.49	**0.85**	**0.98**
Cu		**1.00**	**0.97**	−0.45	**0.92**	**0.86**	**0.85**	Cu		**0.99**	0.06	**0.82**	0.52	0.67	**0.84**
Ni			0.95	−0.48	**0.94**	**0.88**	**0.88**	Ni			0.09	**0.80**	0.62	0.67	**0.81**
Pb				−0.26	**0.81**	0.72	0.70	Pb				0.59	0.61	0.76	0.47
Mn					−0.76	**−0.84**	−0.56	Mn					0.61	**0.97**	**0.99**
Co						**0.99**	**0.88**	Co						0.67	0.48
Cr							**0.87**	Cr							**0.93**
Correlation coefficients between metal levels in red algae samples ($n = 40$)															
	Cu	Ni	Pb	Mn	Co	Cr	Zn		Cu	Ni	Pb	Mn	Co	Cr	Zn
Cd	**0.97**	0.55	**0.89**	0.36	**0.92**	**0.87**	0.53	Cd	**0.85**	0.75	0.10	**0.84**	**0.90**	0.26	0.52
Cu		0.41	**0.75**	0.51	**0.81**	**0.87**	0.43	Cu		**0.83**	−0.07	**0.92**	**0.92**	0.72	0.15
Ni			0.64	−0.23	0.72	0.17	0.22	Ni			−0.05	**0.86**	0.63	0.51	0.18
Pb				0.10	**0.98**	0.72	0.60	Pb				−0.37	−0.15	−0.29	−0.37
Mn					0.06	0.25	−0.43	Mn					**0.88**	0.60	0.43
Co						**0.75**	0.63	Co						0.55	0.40
Cr							0.76	Cr							−0.39

Note: $P < 0.05$, bold values are those with significant correlation.

lower than those reported in similar genera from Malaysia, Lebanon, Gulf of Aqaba, Jeddah coast (Red Sea), and Antikya Gulf (Greece) [20, 23–26], in sequence. These studies reported an average concentration of 2.2–24 in *Padina* spp. Generally, the concentrations of copper were lower than those reported in similar species from Goa coast India [27], Penang island, Malaysia [24], Gulf of Aqaba [23], Alexandria, Egypt [21], Thermikos Bay, Greece [18], Arabian Gulf [28], Antikya Gulf [25], and Turkish Coast [12]. Unfortunately, according to the literature, data on the levels of heavy metals in algae in the Red Sea are very rare.

Concerning the foregoing discussion, the concentrations of Ni in this study were lower than those reported in Lebanon [20] and India [27]. However, some literature records show that the concentrations are similar to or higher than those in the Antikya Gulf [26] and Arabian Sea [29]. These concentrations were lower than those reported in similar genera from India [27], Greece [30], and Lebanon [20]. Comparable zinc levels in algae had been reported by previous studies [18, 21, 23, 24, 26–28, 31]. These studies reported levels of 2246–8519 mg kg^{-1} in *Cladophora* spp. On the other hand, the concentrations of Mn in this study were comparable with those reported in other studies [20, 26, 29, 30, 32] (table 5).

Table 5. Concentration (mg kg^{-1}) ranges of heavy metals in present study and literatures.

	Algae	Present study	Reported in the literature	References
Mn	Green	4.8–37	20–1721	[2, 5, 9, 11, 15, 16]
	Brown	5.2–41	40–554	[2, 6, 7, 11]
	Red	3.5–66	63–344	[2, 4, 9]
Cd	Green	0.4–10	0.8–11	[2, 3, 4, 9, 12, 15,16]
	Brown	0.8–6.6	2.2–24.5	[2, 3, 4, 6–8, 10, 12]
	Red	0.4–10.4	0.8–1.4	[2, 4, 9, 13]
Co	Green	4.1–14.5	4–40	[1, 8, 15]
	Brown	1.8–7.4	0.1–9	[8]
	Red	4.1–16.6	1–13.5	[1, 2, 4]
Cr	Green	1.5–13.4	2.6–4	[10, 12, 14]
	Brown	0.1–5.9	6–25	[1, 3, 7]
	Red	1.3–6.6	15–22	[2]
Ni	Green	2.1–16.7	17–53	[1, 3, 10, 11, 16]
	Brown	1.1–13	14–60	[3, 7, 8, 11,17]
	Red	1.0–17		
Pb	Green	5.7–49.8	0.14–24	[1, 3, 10, 11]
	Brown	3.1–38.9	0.4–18	[3, 7, 8, 11, 17]
	Red	3.2–50.5	6–17	[2, 3, 9]
Zn	Green	4.6–69.7	4–26	[1, 9–12]
	Brown	2.0–74.8	6–610	[2, 4, 6, 7, 10, 11,17]
	Red	2.4–90.4	10–277	[2, 4, 9, 13]
Cu	Green	3.1–17.3	12–120	[1, 2, 4, 9, 10, 11]
	Brown	0.6–10.7	3–515	[4, 7, 10, 11, 17]
	Red	0.7–11.4	7–80	[1, 2, 4, 9]

Note: 1: Agadi *et al.* [27], India; 2: Sivalingam [24], Malaysia; 3: Shiber [20], Lebanon; 4: Wahbeh [23], Aqaba; 5: Ho [37], Hong Kong; 6: Khalil [25], Jeddah; 7: Diapoulis *et al.* [30], Greece; 8: Jaleel *et al.* [29], Arabian Sea; 9: El-Sarraf [21], Alexandria; 10: Malea *et al.* (1995), Greece; 11: Buo: Olayan and Subrahmanyan [21], Kuwait; 12: Muse [22], Argentina; 13: Kut *et al.* [31], Bosphorus; 14: Paez-Osuna *et al.* [32], Greece; 15: Campanella *et al.* [38], Italy; 16: Villares *et al.* [9]; 17: Giusti [8].

5. Conclusions

The present results show a wide variation in the concentration of all eight trace metals analysed in different algae, perhaps due to anthropogenic effects in the Suez rather than Mars Alam, which is longer than 700 km on the North-South axis. The above-mentioned data seriously underline the relevant advanced state of pollution by heavy metals in Suez more than that in Mars Alam in both sea water and algae. All heavy metals studied were detected in all sea-water and algae samples. Observations on the exact relationship between concentrations of metals in the sea water and in the algae seem difficult because of such parameters as tides, salinity, daylight, and darkness.

Considering the results obtained in this current investigation, it is worth while pointing out that certain algae species (*Cladophora* spp., *Padina* spp., and *Liagora* spp.) were efficient bio-accumulators from the surrounding environment reflecting suspected or known localisation increases in metal abundance.

Regarding the concentration factors, Zn is the most bioaccumulated element by all algae studied in Suez, while in Mars Alam, Pb (brown and red algae) and Co (green algae) showed the highest values of bioaccumulation from the surrounding environment. Seaweeds can be excellent indicators of natural and/or artificial changes in biodiversity (in terms of both abundance and composition) due to changes in abiotic, biotic, and anthropogenic factors, and hence are excellent monitors of environmental changes; however, more experimental and field studies with longer sample periods for algae are obviously needed.

For short-time investigation, natural processes at different stages of the life history of a species, diversity of that species and environmental conditions are affected differently by heavy-metal uptake. Large accumulations of metals can occur within the apparent free space between cells, without reaching the cellular compartments of plants [33]. Also, some metals can be associated with extra-cellular polymers of epiphytic bacteria rather than the seaweed under investigation [34]. Remero-Gonzalez *et al.* suggested that the sorption of cadmium by dealginate is mainly due to an ion-exchange mechanism [35], and another report mentioned that seaweeds offer numerous molecular groups which are known to offer ion-exchange sites; carboxyl, sulphate, phosphate, and amine, could be the main ones [36].

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