



## Spatial and temporal variations of heavy metals accumulation in some macroalgal flora of the Red Sea

Amany G. Madkour\*, Sara H. Rashedey and Mahmoud A. Dar

National Institute of Oceanography and Fisheries, Egypt

\*Corresponding author: [dramanymadkour@yahoo.com](mailto:dramanymadkour@yahoo.com)

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### ABSTRACT

The average contents of Zn, Cd, Cu, Co, Fe, Mn and Ni were measured seasonally in the ashes of *Caulerpa racemosa*, *Cystoseira myrica*, *Digenea simplex*, *Hormophysa cuneiformis*, *Padina pavonica* and *Sargassum cinereum* using Flame Atomic Absorption Spectrometry (AAS). The studied species were collected from three different sites along the northern part of the Red Sea coast during 2017. *Cystoseira myrica* recorded the highest Fe average (575.88 µg/g dry wt.) and Mn (164.12 µg/g dry wt.) in summer at Site II, *Caulerpa racemosa* recorded the highest Cu average (91.10 µg/g dry wt.) at Site I in autumn, meanwhile *Sargassum cinereum* showed the highest averages of Zn and Co (33.88 and 16.56 µg/g dry wt.) in spring at sites II and III respectively. The highest averages Ni and Cd (10.46, 2.05 µg/g dry wt.) were observed in *Padina pavonica* at Site III in summer and spring seasons respectively. The obtained data indicated that the studied macroalgae have significant differential abilities to accumulate a certain heavy metals under the local conditions and it can be used as a good target for monitoring metals pollution in marine waters.

### INTRODUCTION

The contamination of water with heavy metals is quite critical issue causing many problems all over the world. The toxicity of these metals in reducing growth of plants and development of microorganisms, which seriously harm the health of animals and humans.

Macroalgae have the capability of filtering some metals as; zinc, cadmium, copper, nickel and iron and some potential carcinogens from the surrounding seawater. Subsequently; they have the ability to remove the toxic heavy metals and accumulate them in high concentrations within their body cells reach  $4 \times 10^3$  to  $20 \times 10^3$  times higher than the surrounding seawater (Torres et al., 2008). Several works have demonstrated that macroalgae can be used to partly strip heavy metal in the marine waters (El-Manawy et al., 2005; Mohamed and Mohamed, 2007; Ginneken and de Vries, 2018).

Accumulation of heavy metals by macroalgae has been shown to occur in two phases (Murphy, 2007). The first is a rapid surface reaction where physical and chemical interaction takes place among the metal and the surface polysaccharides of the algae, complexation, adsorption and ion-exchange occur. The second phase is described by a much slower heavy metal uptake over a period of hours. Some factors affecting on bio-sorbents such as the physiological state of the algae, the availability

of micronutrients throughout their growth, the age of the cells and finally the environmental conditions during uptake as temperature, light intensity and pH (Murphy, 2007). Because of the bio-monitors like seaweeds are efficient in reporting measurable bioavailable concentrations of the contaminants, the present work aims to measure the differential abilities of macroalgal to accumulate certain heavy metals under the local conditions.

## MATERIALS AND METHODS

### Study Area

The study area included three sites along the northern part of the Red Sea coast under different natural and anthropogenic effluents. Site (I) is located in front of the National Institute of oceanography and Fisheries (NIOF). It is characterized by the widely distributed reef flats that extended for about 5km seaward and including many diving sites and many coastal lagoons with depth variation between 1.5 and 6m. The inshore zone of this site suffers from extensively high sedimentation rates throughout the year and underground wastewater seepage. Site (II) is located about 77 km to the south of Hurghada City at 17km south of Safaga in the mangrove forest. This site is distinguished by mangrove trees and shrubs of *Avicenna marina* and extended tidal zone (400m) formed from the raised Quaternary terrace disrupted by sand patches overlying by the mangrove trees near the coastline. This site is highly affected by; the landfilling from the phosphate shipment, the effect of shipyard and many other human activities from Safaga harbor, fishing and other coastal activities. Site (III) is located in the downstream of Wadi Gasus (Magic Life Kalawy Resort) at about 40km northern Qusier City. Tidal zone is rocky formed from the raised coral terrace with small sand zone near the coastline. The tidal flat has kidney shape extended for 100 to 150m with water depth ranged between 0.50 and 5.00m., this site is impacted by the temporary flashfloods and tourist activities (Figure 1).

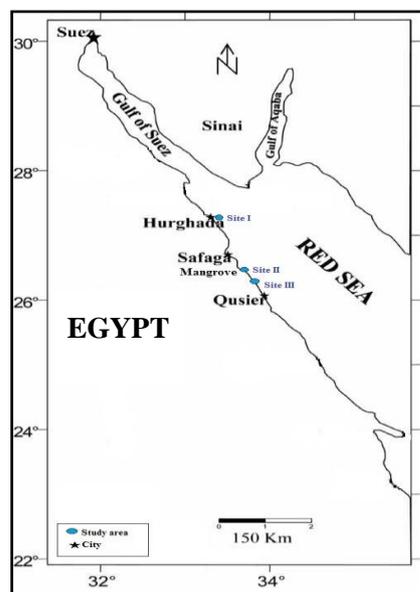


Fig. 1: Positions of the sampling sites

### Samples Collection and preparation

Six species of macroalgae belonging to three families were collected seasonally from the selected sites in period between autumn 2016 and summer 2017 including;

*Caulerpa racemosa* var. *gracilis* (Zanardini) Weber-van Bosse belongs Chlorophyta, *Cystoseira myrica* (Gmelin) C. Agardh, *Hormophysa cuneiformis* (Gmelin) Silva, *Padina pavonica* Alender & Kraft, and *Sargassum cinereum* (Turner) C. Agardh belonging Phaeophyta and *Digenea simplex* (Wulfen) C. Agardh from Rhodophyta (plate1). The algae were identified by morphological characters using taxonomic references (Aleem, 1978; Coppejans and Beeckman, 1990 and Sahoo, 2001). The collected samples were cleaned in the field as possible with seawater then the samples were packed in polyethylene bags containing seawater from the local environment and transferred to the laboratory after a few hours. At the laboratory, the samples were cleaned again by tap water followed by distilled water to remove any agglutinated materials as; the epiphytes, sand or mud particles. The selected specimens were oven dried at 105°C for 48 h to remove excess water and moisture, cooled, weighted, and then ashed at 475°C in a muffle furnace for 24 h (Fuge and James, 1973).

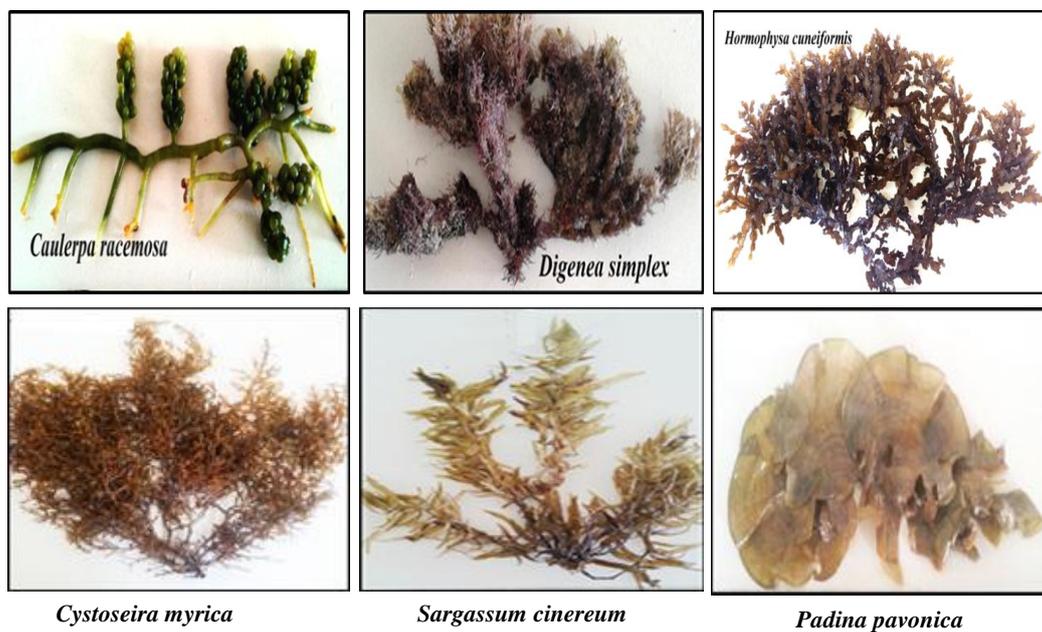


plate1: The six selected macroalgae species during survey.

### Heavy metals determination

Accurately, 10 ml of aqua regia (2.5 ml of 16 M HNO<sub>3</sub> and 7.5ml of 16 M HCl) were added to 0.5 g of each ashed sample in the conical flask and kept at room temperature overnight. Then the solution was digested on a hotplate (80°C), evaporated to near dryness and allowed to cool at room temperature. The digested samples were diluted with distilled water, filtered with Whatman filter paper to remove the solid residuals and diluted again accurately to 25 ml. Finally; the heavy metals; Fe, Mn, Cu, Zn, Co, Ni and Cd in the extracts were analyzed using atomic absorption spectrophotometer (GBC-932AA) at the National Institute of Oceanography and Fisheries, Red Sea Branch. Three technical replicates of each measurement were applied with differences less than 3% to obtain the maximum accuracies.

### Analysis of physico-chemical parameters

Water temperature (°C), salinity (ppt), pH value and dissolved oxygen (mg/L) were determined from the average of three readings at each site by the multiparameter instrument (YSI ProODO Instrument). Turbidity (NTU) was measured by turbidity-

meter (LaMotte 2020e). Sedimentation rate ( $\text{gm.cm}^{-2}.\text{day}^{-1}$ ) was determined by the method of Gardner, 1980.

### Statistical analysis

The spatial and temporal variability are illustrated by Boxplots graph and the statistical significance of these variations is illustrated by two-way ANOVA. All statistical tests were performed using Minitab<sup>®</sup> (Version 16) software.

## RESULTS AND DISCUSSION

### Heavy metal concentration in the selected macroalgae

As shown in Table 1, *Sargassum cinereum* showed the highest averages of Zn (33.88  $\mu\text{g/g}$  dry wt.) in spring and the highest average of Cu (91.1  $\mu\text{g/g}$  dry wt.) in summer at site II. Also it recorded the highest average of Co (16.56  $\mu\text{g/g}$  dry wt.) at site III in spring. The highest average of Fe was recorded in *Cystoseira myrica* (557.88  $\mu\text{g/g}$  dry wt.) at Site II in summer, while the highest annual mean (439.81  $\mu\text{g/g}$  dry wt.) was in *Digenea simplex*. *Padina pavonica* recorded the highest averages of Cd, Ni and Mn (2.05, 10.46, 164.12  $\mu\text{g/g}$  dry wt.) at site III in spring and summer and the highest annual mean of Cd (1.22  $\mu\text{g/g}$  dry wt.), while *Digenea simplex* recorded the highest annual mean of Ni (5.01  $\mu\text{g/g}$  dry wt.), *Digenea simplex*, *Caulerpa racemosa* and *Padina pavonica* recorded the highest annual means of Zn, Cu, Co and Mn (9.38, 22.80 and 4.55, 47.89  $\mu\text{g/g}$  dry wt. respectively). The concentration of Zn may be attributed or controlled by activators of dehydrogenases and protein-synthesis enzymes in these species (Besada *et al.*, 2009). Foster, 1976 found that macroalgae tend to accumulate Zn within their tissues much more than Cd due to the competition for binding sites. The competition between metals for algal sites could decrease the accumulation of those elements which exhibited lower concentration levels in environment (water or sediment) or which are present in less available forms (e.g. Cd). The accumulation of Co in macroalgae tissue might be due to the physiological participation of Co in the certain enzymes.

The highest concentrations of Cu in marine plants can be attributed to the fact that it is important micronutrient for various metabolic functions of the plants (Donat and Dryden 2001). The levels of the accumulated copper in the algal tissues indicated the lipid body of the plant cell. The high concentrations of Cu are causing a great danger to the marine organisms including; fish, crustaceans, phytoplankton and zooplankton, algae and filter feeders. Zn enhances the catalytic, structural and regulatory functions, stabilizes membranes, hormones and nucleic acids (Norziah and Ching, 2000). Cu and Zn accumulations in the studied species at the different sites and seasons are much more than Cd that may be attributed the species ability to assimilate both metals within their tissues much more Cd.

Fe showed the highest concentrations followed by Mn in the different species relative to the other metals may attribute to the high bio-availability in both fine particulate sediments and the surrounding aquatic environment. Several factors such as human activities, natural inputs and abilities of algal species to biomagnifying Fe from the surrounding environment lead to the bio-availability of Fe and Mn in high levels. Occurrence of higher concentration of Mn in plants is a common feature for maintaining osmotic balance, ion regulation and for enzyme catalysis (Clarkson and Hanson, 1980). The heavy metal accumulations in the sampled macroalgae species showed significant variation from species to another indicating to the differential capability of these species to accumulate the heavy metals from the surrounding aquatic environment.

Table 1: Average and annual concentration of heavy metals ( $\mu\text{g/g}$  dry wt.) in macroalgal species at different sites and seasons

Species	Season	Site	Cd	Zn	Cu	Ni	Co	Mn	Fe	
<i>Hormophysa cuneiformis</i>	summer	I	ND	1.7	13.26	2.28	1.39	3.88	95.71	
		II	0.4	<b>0.21</b>	<b>49.92</b>	3.33	<b>0.56</b>	58.75	436.14	
		III	0.54	1.15	41.98	4.18	3.67	<b>154.8</b>	53.9	
	spring	I	0.41	9.64	18.02	<b>8.68</b>	2.67	5.89	138.15	
		II	0.85	<b>20.54</b>	13.4	4.63	3.8	4.57	318.52	
		I	<b>2.03</b>	11.5	4.09	3.34	2.53	9.63	74.42	
	winter	II	0.43	6.42	3.26	3.97	2.9	13.5	431.28	
		III	0.44	2.52	2.32	3.59	2.63	35.96	64.45	
		I	0.09	2.16	1.9	<b>1.49</b>	2.14	<b>3.54</b>	57.92	
	autumn	II	0.86	1.54	3.69	3.68	3.01	61.64	<b>451.74</b>	
		III	1.25	2.94	<b>1.57</b>	2.69	<b>4.44</b>	86.17	<b>39.83</b>	
		Ann. Mean		<b>0.66</b>	<b>5.48</b>	<b>13.95</b>	<b>3.81</b>	<b>2.70</b>	<b>39.85</b>	<b>196.55</b>
<i>Cystoseira myrica</i>	summer	I	0.48	1.41	6.86	<b>0.98</b>	1.88	25.71	381.63	
		II	0.58	<b>0.6</b>	<b>29.57</b>	5.94	2.37	<b>147.29</b>	<b>557.88</b>	
		III	0.73	0.65	10.74	<b>10.28</b>	1.25	143.54	142.33	
	spring	I	0.68	14.69	10.07	7.5	1.42	5.4	404.22	
		II	1.1	<b>25.75</b>	9.94	4.99	9.03	13.64	483.92	
		III	<b>1.94</b>	6.7	4.9	4.28	<b>13.78</b>	71.26	179.29	
	winter	I	<b>0.36</b>	7.75	3.36	3.04	6.04	<b>4.7</b>	306.04	
		II	0.5	6.8	3.6	3.1	1.89	18.45	471.9	
		III	0.55	2.22	2.78	3.2	1.61	36.25	113.27	
	autumn	I	0.45	2.99	18.09	1.9	<b>1</b>	8.79	320.42	
		II	1.06	10.12	3.13	4.01	1.47	15.2	485	
		III	1.47	2.92	<b>1.53</b>	1.99	3.02	35.93	<b>77.33</b>	
Ann. Mean		<b>0.83</b>	<b>6.88</b>	<b>8.71</b>	<b>4.27</b>	<b>3.73</b>	<b>43.85</b>	<b>326.94</b>		
<i>Padina pavonica</i>	summer	I	0.76	1.97	5.75	<b>1.82</b>	1.29	27.08	351.41	
		II	0.74	<b>0.41</b>	28.95	6.41	3.12	<b>164.12</b>	<b>533.55</b>	
		III	0.83	0.75	4.5	<b>10.46</b>	2.12	40.75	126.84	
	spring	I	0.88	7.88	4.34	5.96	3.9	4.25	361.08	
		II	1.7	<b>22.49</b>	8.87	6.43	<b>12.93</b>	26.13	519.44	
		III	<b>2.05</b>	4.69	3.8	3.69	<b>12.15</b>	73.36	142.68	
	autumn	I	<b>0.72</b>	5.19	<b>51.65</b>	3.27	1.86	<b>2.48</b>	366.52	
		II	1.58	14.95	4.16	5.04	2.98	77.39	530.06	
		III	1.76	2.55	<b>1.27</b>	1.84	<b>0.64</b>	15.41	<b>53.24</b>	
	Ann. Mean		<b>1.22</b>	<b>6.76</b>	<b>12.59</b>	<b>4.99</b>	<b>4.55</b>	<b>47.89</b>	<b>331.65</b>	
	<i>Sargassum cinereum</i>	summer	I	<b>0.26</b>	2	24.44	<b>0.57</b>	ND	6.59	54.85
			II	0.72	<b>1.25</b>	<b>66.56</b>	5.3	3.33	<b>53.41</b>	<b>538.88</b>
III			0.58	1.58	19.19	<b>8.85</b>	3.51	<b>2.22</b>	72.79	
spring		I	0.8	2.75	5.74	<b>8.68</b>	2.96	6.99	166.42	
		II	0.88	<b>33.88</b>	27.21	5.26	2.28	17.05	469.39	
		III	1.74	24.45	14.85	5.72	<b>16.56</b>	42.54	463.89	
winter		I	<b>1.86</b>	9.13	5.16	3.52	8.42	7.77	75.98	
		II	0.45	2.96	2.81	4.46	0.72	4.4	152.82	
		III	0.62	2.6	3.49	3.19	2.6	5.2	60.27	
autumn		I	0.47	4.09	60.91	2.08	0.95	11.78	<b>29.4</b>	
		II	0.95	10.52	3.03	4.3	4.36	36.81	470.85	
		III	1.8	3.63	<b>1.73</b>	1.79	2.69	3.68	56.9	
Ann. Mean		<b>0.93</b>	<b>8.24</b>	<b>19.59</b>	<b>4.48</b>	<b>4.40</b>	<b>16.54</b>	<b>217.70</b>		
<i>Digenea simplex</i>	summer	I	0.53	2.49	15.88	<b>1.71</b>	1.33	17.26	434.57	
		II	0.83	<b>0.41</b>	13.9	5.74	3.11	<b>137.02</b>	<b>540.68</b>	
		I	0.93	<b>22.38</b>	7.77	6.12	<b>0.7</b>	22.31	405.84	
	spring	II	<b>1.74</b>	<b>22.74</b>	9.88	<b>7.06</b>	<b>12.92</b>	14.23	483.85	
		I	0.53	7.32	<b>3.03</b>	4.19	1.78	<b>4.15</b>	<b>350.81</b>	
		II	<b>0.27</b>	10.29	9.19	6.55	2.36	41.76	504.86	
	autumn	I	0.9	2.84	<b>30.56</b>	3.71	1.13	9.43	364.62	
		II	1.45	6.53	<b>3.38</b>	4.99	5.25	87.28	433.24	
		Ann. Mean		<b>0.90</b>	<b>9.38</b>	<b>11.70</b>	<b>5.01</b>	<b>3.57</b>	<b>41.68</b>	<b>439.81</b>
	<i>Caulerpa racemosa</i>	summer	I	0.33	<b>0.19</b>	41.41	3.17	<b>0.72</b>	4.32	186.94
			III	0.79	1.7	27.78	<b>8.43</b>	2.83	7.62	97.85
			I	0.58	5.05	10.04	4.24	3.18	4.51	183.79
spring		III	<b>1.86</b>	<b>6.18</b>	5.21	2.7	<b>9.43</b>	44.91	104.54	
		I	0.55	1.25	2.8	3.74	3.29	<b>3.75</b>	<b>82.98</b>	
		III	<b>0.23</b>	1.62	2.74	<b>1.56</b>	2.84	<b>48.71</b>	<b>276.53</b>	
autumn		I	0.6	5.06	<b>91.1</b>	3.54	2.18	27.25	93.36	
		III	1.8	2.53	<b>1.34</b>	1.87	1.31	9.53	88.5	
		Ann. Mean		<b>0.84</b>	<b>2.95</b>	<b>22.80</b>	<b>3.66</b>	<b>3.22</b>	<b>18.83</b>	<b>139.31</b>

ND: Not Detected

Vymazal (1995) suggested that the accumulation of metals depend on the type of polysaccharides in the algae and since various elements have different

electronegativity (tends to accept electrons) probably this may effects on the metals uptake in algae at different levels. He attributed the variations in the metals contents in the seaweeds to the different metals electronegativity (e.g. Fe, Ni and Cu). Billah *et al.* (2017) documented that the concentrations of heavy metals in algal tissues are varied among macroalgal species, probably due to of the differences of structure, age, and growth of thallus among macroalgal species. Levels of heavy metals in Red Sea macroalgae and other tropical locations worldwide comparing to background concentrations are listed in Table 2.

Table 2: Levels of heavy metals ( $\mu\text{g/g}$  dry wt.) in Red Sea macroalgae and other tropical locations worldwide comparing to background concentrations

Species	Co	Cd	Cu	Ni	Zn	Mn	Fe	Reference
<i>P. pavonica</i>	-	5.02	16.87	46.5	48.65		8304	Ali et al, 2011
	0.56	0.97	2.78	-	12.35		98.97	Mohamed, 2005
	0.05	0.57	2.50	2.38	31.34	21.5	520	Sayhan et al., 2010
<i>C. myrica</i>	-	5.1 $\pm$ 1.3	7.6 $\pm$ 2.9	34.8 $\pm$ 28.3	-		-	Dadolahi-Sohrab <i>et al.</i> , 2011
	0.291	0.07	-	0.49	-		-	2011
	-	0.18	6	-	51.25		271.42	El-naggar and Al-Amoudi, 1989
	-	1.72	1.80	-	52.4		-	1989
	-	0.1	7.21	-	14.37		-	Akcali and Kucuksezgin, 2011
	0.53	0.53	14.1	4.73	-	7.9	15.1	Schintu et al., 2010
<i>C. racemosa.</i>	0.8	0.93	20.5	5.3	7.9	13.7	90.1	Al-Masri et al., 2003
<i>D. simplex</i>	0.361	0.07	-	0.65	-	-	-	Al-shwafi and Rushdi, 2008
<i>S. cinereum</i>	-	-	-	8.1	18.1	55.2	-	El-naggar and Al-Amoudi, 1989
<i>H. Cuneiformis</i>	2.70	0.66	13.95	3.81	5.48	39.85	196.55	Mohamed, 2005
<i>C. myrica</i>	3.73	0.83	8.71	4.27	6.88	43.85	326.94	Our study
<i>P. pavonica</i>	4.55	1.22	12.59	4.99	6.76	47.89	331.65	Our study
<i>S. cinereum</i>	4.40	0.93	19.59	4.48	8.24	16.54	217.70	Our study
<i>D. simplex</i>	3.57	0.90	11.70	5.01	9.38	41.68	439.81	Our study
<i>C. racemosa</i>	3.22	0.84	22.80	3.66	2.95	18.83	139.31	Our study

### Physico-chemical parameters

Physico-chemical parameters of the Red Sea influence the composition and the structure of the existing macroalgal communities including surface water temperature, light intensity and salinity (Osman and Mohammed, 2016). At the same time Murphy, 2007 reported that, environmental conditions like temperature, salinity and pH are one of the factors that effect on metal uptake by macroalgae.

As shown in Table 3, the costal water temperature varied between a minimum of 17.7  $^{\circ}\text{C}$  in winter at St. II and a maximum of 31.8 $^{\circ}\text{C}$  in summer at the same station. The pH values were found on the alkaline side with a maximum of 8.2 at St. II in summer and autumn and a minimum of 7.7 at St. III in spring. Water turbidity was varied between sites and seasons, the highest average was 38.3 NTU recoded in autumn at site II, while the lowest average was 0.6 NTU recorded in summer at site III. Like turbidity, mangrove area (site II) had the highest average of sedimentation

rate ( $0.010 \text{ g.cm}^{-2}.\text{day}^{-1}$ ) in autumn, while the lowest average  $0.002 \text{ g.cm}^{-2}.\text{day}^{-1}$  was recorded in summer at site III.

Dissolved oxygen of seawater was varied among  $5.1 \text{ mg/L}$  in summer at site I and  $7.3 \text{ mg/L}$  in winter at the same site. Salinity was varied between sites and seasons, where the highest average ( $44.2 \text{ ppt}$ ) was recorded in summer at site II and the lowest average ( $40.5 \text{ ppt}$ ) was recorded in autumn at site II.

Table 3: Seasonal fluctuations of the physico-chemical parameters in the studied area during 2016- 2017

site	Season	Temperature ( $^{\circ}\text{C}$ )	Turbidity (NTU)	Salinity (ppt)	DO (mg/L)	pH	Sed. rate ( $\text{gm.cm}^{-2}.\text{day}^{-1}$ )
I	Autumn	$21.3 \pm 0.1$	$3.7 \pm 0.38$	$41.1 \pm 0.13$	$6.5 \pm 0.2$	$7.9 \pm 0.008$	$0.004 \pm 0.001$
	Winter	$20.9 \pm 0.02$	$8.9 \pm 1.4$	$42.3 \pm 0.3$	$7.3 \pm 0.1$	$7.9 \pm 0.008$	$0.005 \pm 0.001$
	Spring	$29.03 \pm 0.2$	$5.5 \pm 0.3$	$41.1 \pm 0.01$	$6.8 \pm 0.1$	$7.9 \pm 0.01$	$0.003 \pm 0.002$
	Summer	$30.4 \pm 0.09$	$2.3 \pm 0.04$	$43.2 \pm 0.04$	$5.1 \pm 0.04$	$7.89 \pm 0.01$	$0.003 \pm 0.002$
II	Autumn	$24.5 \pm 0.07$	$38.3 \pm 9.5$	$40.5 \pm 0.08$	$5.5 \pm 0.1$	$8.2 \pm 0.03$	$0.010 \pm 0.001$
	Winter	$17.7 \pm 0.1$	$7.2 \pm 1.5$	$41.7 \pm 0.08$	$7.2 \pm 0.1$	$7.9 \pm 0.01$	$0.008 \pm 0.001$
	Spring	$27.3 \pm 0.1$	$5.1 \pm 0.5$	$41.3 \pm 0.1$	$5.2 \pm 0.2$	$8.0 \pm 0.1$	$0.007 \pm 0.001$
	Summer	$31.8 \pm 0.2$	$3.9 \pm 1.3$	$44.2 \pm 0.08$	$5.7 \pm 0.04$	$8.2 \pm 0.01$	$0.005 \pm 0.002$
III	Autumn	$23.6 \pm 0.1$	$6.1 \pm 1.4$	$41.2 \pm 0.1$	$5.5 \pm 0.2$	$8.1 \pm 0.02$	$0.003 \pm 0.001$
	Winter	$20.3 \pm 0.1$	$8.7 \pm 2$	$42.4 \pm 0.05$	$6.7 \pm 0.1$	$7.8 \pm 0.01$	$0.007 \pm 0.001$
	Spring	$29.3 \pm 1$	$4.6 \pm 1$	$41.5 \pm 0.1$	$6.7 \pm 0.1$	$7.7 \pm 0.1$	$0.005 \pm 0.001$
	Summer	$30.4 \pm 0.08$	$0.6 \pm 0.2$	$42.7 \pm 0.08$	$5.5 \pm 0.4$	$7.9 \pm 0.1$	$0.002 \pm 0.001$

Each value is the average  $\pm$  SD

### Spatial and seasonal variation of heavy metals in the tested seaweed

The spatial and temporal variability of heavy metals in the investigated algae are illustrated by boxplots (Fig.2) and the statistical significance of these variations is assembled in Table 4.

As shown by boxplots (Fig. 2-a), Zn in studied species was varied from  $33.88 \mu\text{g/g}$  dry wt. at site II in spring to  $0.19 \mu\text{g/g}$  dry wt. at site II in summer. Plots of spring showed long tails with a large box area above median indicating to that the data configuration is skewed towards the high values during this season. Co in the tested algae ( $16.56 \mu\text{g/g}$  dry wt.) was recorded at site III during spring, while it was reached  $0.56 \mu\text{g/g}$  dry wt. at site I in summer. Site II showed the highest variability (large box length) in spring and site III recorded the lowest variability in winter. All plots of the studied sites and seasons showed long tails with a large box area under the median indicating to that the values of Co in the selected species skewed towards low concentration during all seasons except at sites I, III in spring and site I in winter (Fig. 2-b). Cu in the investigated species was largely varied between  $91.10 \mu\text{g/g}$  dry wt. at site I and  $1.27 \mu\text{g/g}$  dry wt. at site III with the highest variability at site I and the lowest variability at site III during autumn. (Fig. 2-c).

The investigated macroalgae species showed Cd values between  $2.05 \mu\text{g/g}$  dry wt. at site III in spring and undetected at site I in autumn. The highest median of Cd ( $0.94 \mu\text{g/g}$  dry wt.) was illustrated by line (in center of box) meanwhile highest variability was observed in autumn at site III compared with other sites (Fig. 2-d). Ni was varied between  $10.46 \mu\text{g/g}$  dry wt. in the tested species at site III and  $0.57 \mu\text{g/g}$  dry wt. at site I in summer. Site II in the same season, plots of site II in winter and autumn have a long tail with a large box area above the median, which means that the studied macroalgae in this sites have high concentrations of nickel (Fig. 2-e).

The highest Fe ( $557.88 \mu\text{g/g}$  dry wt.) in the studied species was recorded at site II in summer and the lowest one ( $29.40 \mu\text{g/g}$  dry wt.) was showed at site I in autumn.

The highest variability of Fe in tested algae was found at site I during summer, while the lowest fluctuation was occurred at site III during autumn. Plots of winter showed longer tails than other seasons with large box area above the median indicating to that the Fe distribution is skewed toward high concentration during this season (Fig. 2-f). Mn in the studied species was varied between 164.12  $\mu\text{g/g}$  dry wt. at site II during summer and 2.22  $\mu\text{g/g}$  dry wt. at site I during autumn. Summer season showed long tails with large box area above the median at sites I and III, this indicate that the underlying distribution is skewed towards high values during this season (Fig. 2-g).

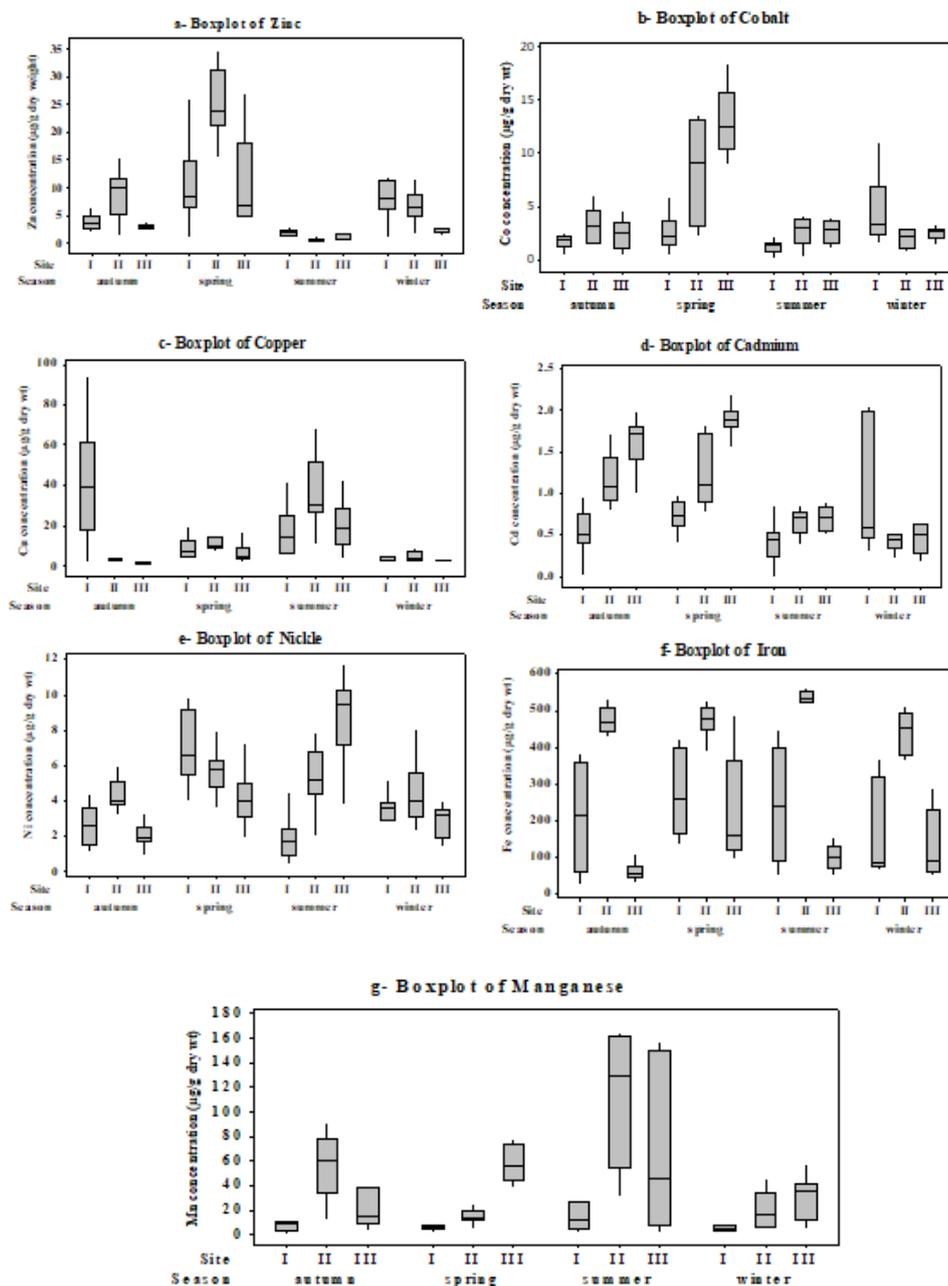


Fig. 2: Boxplot graph for spatial and temporal variation in heavy metals of investigated macroalgae at different sites and seasons.

In general boxplot showed high variation in heavy metal concentrations of selected macroalgae among the studied sites and seasons which was supported by the statistical using Two-Way ANOVA ( $P < 0.001$ ) for sites and seasons (Table 4).

Obvious spatial variations in heavy metal contents of the investigated algal species were observed during this study. Mangrove (Site II) had the highest level of most heavy metals followed by Magic (Site III). Site II was highly affected by the anthropogenic activities from the northern shipment operations in addition to natural inputs from the temporary flashfloods. Abdallah and Abdallah (2008) found significant variation in the heavy metal contents from species to another and from site to another according to the local conditions as; anthropogenic and natural inputs, tidal range, seawater temperature, salinity regimes, dissolved nutrients, type of tissue, age of plant, its nutritional history and the morphological structure of the studied areas. Clear seasonal fluctuations in the heavy metal contents of tested macroalgae were observed. The obtained results indicated that the highest levels of studied metals in algal tissues were occurred in spring and summer while lowest levels were observed in winter that may attributed to the rates of growth for the different species, whereas the highest flourishing of the studied species at the investigated sites were observed in summer.

Table 4: Two way ANOVA showing variations in metals between sites and seasons

Metals	F		P	
	Site	Season	Site	Season
<b>Cd</b>	21.75	23.61	<0.0001	<0.0001
<b>Zn</b>	23.17	66.11	<0.0001	<0.0001
<b>Cu</b>	6.93	14.30	0.002	<0.0001
<b>Ni</b>	6.17	16.08	0.003	<0.0001
<b>Co</b>	15.42	34.07	<0.0001	<0.0001
<b>Mn</b>	30.96	15.77	<0.0001	<0.0001
<b>Fe</b>	129.52	4.88	<0.0001	0.003

## CONCLUSIONS

The present outcomes demonstrated exceptionally variety in substantial metal concentrations of chose macroalgae among the examined location and seasons. Iron, manganese and zinc recorded the highest accumulation in the studied species. Mangrove (Site II) had the largest accumulation of most substantial metals pursued by Magic (Site III). The macroalgae in studied area contribute competently for removal of heavy metals from the water. Many species have high capacity for absorption of certain metals, making them good bioremediators.

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