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Uptake of Heavy Metals by Marine Aquatic Macrophytes

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Abstract

The potential of algae to accumulate heavy metals in marine environments was studied. The aim is to study the accumulation of Cd, Pb, Cu, Zn, Mn, Fe, and Mg in algal biomass that grows in the Little Bitter Lake, Egypt. Consequently, the level of metals in twelve different algal species was studied extensively. The investigated algae belong to Green, Brown, and Red algae. The investigation includes the influence of seasonal variation on the rate of heavy metals accumulation by algae. Meanwhile, levels of metals in the Lake water were also assessed. The results indicated differences between the metal concentration and the different algal species. Furthermore, differences were also found in the levels of different metals within the studied algae. The overall results showed that the highest accumulation rate was exhibited by Red algae followed by Green and then Brown algal species. Correlation between the level of metals in the Lake Water and the studied algal species was conducted to determine the concentration factors for each metal. It was concluded that the bioaccumulation of heavy metals by aquatic algae is an indication of the availability of those metals within the aquatic environment.

Keywords: environmental contamination, removal, accumulation, algae, micro-pollutants, aquatic, bio-indicator

1. Introduction

The release of heavy metals into the aquatic environments has been recently investigated by several investigators aiming at the protection of waterways (1) Metals occur in the natural aquatic ecosystems at very low concentrations within the nano-gram to microgram per/Liter. During the last decade metals occurrence as contaminants has presented a problem of serious concern (2). Such problems have arisen because of the expansion of industrial activities, urbanization, rapid growth of population, exploration as well as exploitation of natural resources. In addition, the application of pesticides in agriculture activities and other modern agricultural practices is an additional source of heavy metals in the waterways (3, 4).

Heavy metals are unlike other pollutants such as petroleum, agriculture drainage water, and/or litter, they are non-degradable, persist, and can be accumulated by organisms in the environment up toxic levels (3, 5). Problems associated with contamination and accumulation of heavy metal was first highlighted in Japan and Sweden due to the discharge of industrial wastewater into the marine ecosystems particularly pollution with mercury and cadmium (5, 6). Despite the low industrial activity in the under-developed zones, there is an amount awareness of the necessity of rational management of aquatic resources, including the control of waste discharge into the environment (7). This is more significant given the increasing industrial, urban, and agriculture activities all over the world (8).

Existing information regarding different environmental issues has been reviewed earlier (9). While accumulation of heavy metals by plants as affected sewage was also studied by several investigators (6, 7, 10). For effective water pollution control and management, there should be clear understanding of the loads (inputs), distribution and fate of pollutants, and of trace metals in aquatic ecosystems as well as the effects on biota (10).

Heavy metals accumulation by macro-algae represents one of the reliable tools as bio-indicator of aquatic contamination (8). Recently, environmental pollutants including heavy metals have become one of the severe public concerns that severely endanger the ecological environment and negatively affect human health. Heavy metals are non -degradable and well-known some of them are toxic to Man, plants,

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freshwater, marine invertebrates, fish, algae, earthworms, and other non-target organisms (9).

Due to the toxic properties of such heavy metals, information about their fate as well as sources in the environment are of great concern to the Environmentalists (11). Heavy metals enter the aquatic environment via anthropogenic and natural sources. Direct discharge of heavy metals is a common practice into both marine and freshwater ecosystems via indirect input and land runoff including dry and wet deposition as well as industrial activities (8). Continental weathering, volcanic activity, and forest fires are important natural sources. Volcanic activities contribution occurs generally large quantities through explosive volcano and emissions including magma degassing and geothermal activity (12).

Heavy metals are generally partitioned in the aquatic environment between biota, water, suspended solids (SS) and sediments (13). Similarly, accumulation of heavy metal by fish in the Mediterranean Sea as indication of heavy metals in the sea water was studied by different investigators (14). Metals in the aquatic environment are present in several forms including dissolved, complex and particulate salts or compounds (11, 15).

The present investigation aims to through light on trace metals in marine algae as well as the level of trace elements in fresh water and marine ecosystems of little Bitter Lake. The study included the heavy metals accumulation by different marine algae of the Little Bitter Lake, Suez Canal. The purpose is to determine the effect of several human activities on the contamination of marine water by detecting any contamination of the studied area by metals. The variation of metal up taken by various algal species is considered concerning localities. The role of seasonal change in the accumulation of metals via algae was accounted for. The concentration factor in terms of the level of metals (Cd, Pb, Cu, Zn, Mn, Fe, and Mg) in the Bitter Lake water and the studied algal species was also determined.

2. Materials and Methods

2.1. The study zone

The Great Little Bitter Lakes consisted of two lakes, namely the small and the large Bitter Lakes connected as part of the Suez Canal passway (Figure 1). They were originally dry depressions and valleys before digging the Suez Canal in 1869. During that time these two depressions were then flooded to connect between the Mediterranean Sea in the North and the Red Sea in the South of the Canal in Egypt. The average depth of the canals at that time was 18 m (59 ft), the average Surface area was 194 km^2 (75 sq mi), and the Maximum depth was 28 m (92 ft). The average salinity is 41‰. The potential sources of heavy metals in the Little Bitter Lake are shipping activities, discharge of domestic sewage, beaching activities, and littering.

Figure 1: The sampling points along the Great Bitter Lake, the Suez Canal pathway, Egypt. (G.B.L: Great Bitter Lake; L.B.L: Little Bitter Lake)

2.2 Accumulation of Metals by Different Algae

An extensive sampling program in the current investigation was designed for the study of the accumulation of heavy metals through different marine algal species from three different intertidal localities along the Little Bitter by Suez Canal pathway. The sampling points are indicated in the map (Figure 1). Within this respect, twelve different algal species as well as lake water samples were monthly collected during a period of successive 12 months. The lake water samples were collected from the algal habitats. These collected samples were passed through 0.45 um Millipore filters for the elimination of any suspended particles. The filtered waters were preserved, stored, and analyzed according to the Standard Methods (16). All algae samples were thoroughly washed with double distilled water and dried at 105^0 C till a constant weight followed by grounding to powder. Determination of metal concentration was detected using the atomic absorption spectrophotometer Model (551) with the Heated Graphite Atomizer Model (651), and deuterium arc background modification was employed to determine the level of metal in this study.

The detected metals were Cd, Pb, Cu, Zn, Mn, Fe, and Mg in all the twelve different marine algal species and the digested lake water sample. The algae are Green, Brown, and Red algae. The Green algal species are *Chaetomorpha Linum*, *Enteromorpha Intestinalis*, *Ulva Lactuca*, and *Cladophora Albida*. The Brown algal species are: *Sargassum Dentifolium*, *Padina Pavonica*, *Colpomenia Sinuosa* and *Cystoseira Myrica*. The Red algal species are

Laurencia Papillosa, *Jania Adherens*, *Laurencia Obtusa*, and *Sarconema Furcatum*.
Determination of the concentration factor was calculated according to the level of metal in the algae in correlation to the level of metal in the aquatic environment.

Results

The obtained results are presented in Tables (1) and (2). These results indicated that there are remarked differences in the concentrations of metals but at lesser degree compared to red algae. Such variation in the ability of metal accumulation can be attributed to the tendency of each algal biomass towards metal uptake. Also, the correlation between the levels of metal accumulation in the investigated algal groups showed that the red algae group exhibited the highest rate of metal accumulation followed by the brown, then the green algae. Metals including Mn, Zn, Cu, and Pb were highest accumulated by the red algal species, namely *L. Obtusa*. On the other hand, Cd and Fe were the highest accumulated by the brown algae (Fig. 2). Nevertheless, Mg was mostly concentrated by green algal species (Fig. 3).

Table 1: Concentrations (ug/g of dry wt) of Trace Metals Cd, Cu, Pb and Zn accumulated by Green Algae, Brown Algae and Red Algae Collected from Three Localities in the Little Bitter Lake, (Lake Water are in ug/1)

Algae	Cd		Cu		Pb		Zn	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Green Algae								
C. Linum	0.53	0.42-0.59	32.8	28.2-38.1	1.81	1.52-1.92	69.2	48.1-79.9
E. Intestinalis	0.62	0.51-0.82	30.6	25.7-39.4	1.73	1.49-1.86	30.2	25.8-40.3
U. Lactuca	0.51	0.49-0.77	35.2	24.1-41.8	1.69	1.41-1.83	39.7	35.3-48.7
C. Albida	0.73	0.44-0.81	44.5	32.6-49.8	0.74	0.67-0.86	79.7	59.4-88.5
Average accumulation (ug/g dry wt)	0.6		35.78		1.49		54.7	
Brown Algae								
S. Dentifolium	0.77	0.53-0.84	27.4	23.4-35.2	0.85	0.71-0.98	33.7	25.8-39.3
P. Pavonica	0.59	0.48-0.65	30.6	27.1-33.8	1.12	0.81-1.23	75.7	59.3-92.4
C. Sinusa	0.66	0.58-0.79	25.7	20.6-29.1	1.38	1.08-1.52	45.8	34.6-49.1
C. Myrica	0.59	0.55-0.69	17.5	11.4-22.6	0.97	0.75-1.14	25.6	20.1-31.4
Average accumulation (ug/g dry wt)	0.65		25.3		1.08		45.2	
Red Algae								
L. Papillose	0.95	0.71-1.13	50.4	44.3-53.7	2.34	2.09-2.67	131.5	112.4-151.6
J. Adherens	0.42	0.38-0.51	38.5	35.9-44.6	1.71	1.60-1.93	96.2	25.2-107.3
L. Obtusa	0.31	0.22-0.40	35.4	30.8-39.7	2.16	1.84-2.38	169.7	145.2-189.3
S. Futcelatum	0.39	0.35-0.49	37.4	34.1-45.2	1.88	0.11-0.24	100.1	85.2-116.8
Average accumulation (ug/g dry wt)	0.52		40.43		2.02		124.38	
Lake Water (ug/1)	0.26	0.01-0.32	3.71	2.89-4.41	3.28	2.91-3.53	6.11	5.81-7.69

Table 2: Concentrations (ug/g of dry wt) of Trace Metals Mg, Mn, and Fe accumulated by Green Algae, Brown Algae and Red Algae Collected from Three Localities in the Little Bitter Lake, (Lake Water are in ug/1)

Algae	Mg		Mn		Fe	
	Mean	Range	Mean	Range	Mean	Range
Green Alga						
C. Linum	17,183.6	12,518.8-18,781.2	12.5	10.1-14.9	622.4	481.7-785.3
E. Intestinalis	15,173.8	12,341.5-16,811.7	14.8	12.8-15.8	1,147.3	919.9-1,341.7
U. Lactuca	18,133.5	1,226.8-2,168.5	13.9	11.8-15.2	598.4	405.4-773.8
C. Albida	5,361.2	4,901.2-6,172.5	8.8	7.9-10.5	669.2	606.1-789.4
Average accumulation (ug/g dry wt)	13,963.03		12.5		759.33	
Brown Algae						
S. Dentifolium	7,439.2	6,557.3-8,622.4	10.9	8.8-12.9	458.2	373.4-551.6
P. Pavonica	30,857.6	27,118.7-32,281.3	11.0	9.5-12.8	696.3	641.4-753.6
C. Sinusa	6,531.7	4,978.6-7,512.4	13.8	12.7-14.6	1,715.3	1,523.6-1,811.4
C. myrica	5,172.1	4,517.3-5,637.9	14.7	12.9-16.6	319.8	302.5-393.6
Average accumulation (ug/g dry wt)	12,500.15		12.6		797.4	
Red Algae						
L. Papillose	3,369.1	2,981.7-3,718.6	100.7	59.3-113.1	339.2	218.3-411.2
J. Adherens	45,210.1	4,0210.1-49,781.2	114.2	96.3-123.6	1,723.6	1,276.1-1,977.6
L. Obtusa	24,139.2	23,693.7-29,781.2	119.8	103.8-136.4	2,919.2	2,721.7-3,136.6
S. Futcelatum	35,181.3	30,924.1-40,193.2	109.8	93.2-118.5	1,607.5	1,431.7-1,798.3
Avergae accumulation (ug/g dry wt)	26,974.93		111.13		1,647.38	
Lake Water (ug/1)	$1.293X10^6$	$1.191-1.385) X10^3$	3.95	3.11-4.27	29.17	25.78-33.49

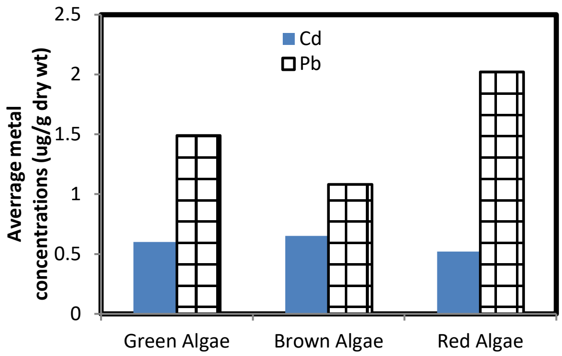

Figure 2: Correlation between the accumulation of Cd, and Pb by the three algal groups namely: green, brown and red algae

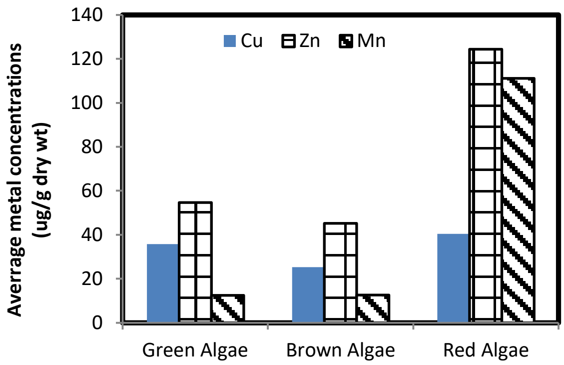

Figure 3: Correlation between the accumulation of Cu, Zn, and Mn by the three algal groups namely: green, brown and red algae

It is worth mentioning that the differences in metal accumulation between the red, brown, and green algae may be attributed to the highest ability of red algae to concentrate various metals. Meanwhile, both brown and green algae have a similar tendency to concentrate metals but at lesser degree compared to red algae. Such variation in the ability of metal accumulation can be attributed to the tendency of each alga towards metal uptake. Meanwhile, the efficiency of binding a metal inside the tissues is also a significant factor affecting the metal accumulation rates by the given algae (1, 15).

By considering each group of algae individually, it can be depicted that the available results are in good agreement with the homological series law. This law indicates that closely related species of the plant possess similar chemical compositions (3, 17). However, certain algal species exhibited variable levels of metal accumulation (Tables 1 and 2).

It was noticed that the red algae recorded the highest levels of Zn, Fe, and Mn by Laurancia obtuse. Meanwhile, Cu, Pb, and Cd were highest accumulated by *Laurencia Papillosa*. On the other hand, the lowest Mg concentration was recorded by the red algae group.

Brown algae, namely *Padina Pavonica*, they exhibited the highest accumulation of Mg, Cu and Zn. However, *Cystoseira Myrica* demonstrated the highest concentration of manganese. Furthermore, the *Colpomenia Sinuosa* exhibited the highest concentration of Fe and Pb as shown in Table (1 and 2). These results agree with those reported by other researchers (18, 19).

By considering the green algae, the highest concentration of Zn, Cu, and Cd was exhibited by *Cladophora Albida* which has the lowest concentration of Pb. Furthermore, *Enteromorpha Intestinalis* recorded the highest accumulation of Fe, Mn, and the lowest of Zn and Cu among this green algae group.

On the other hand, the concentration factors (CF) of metals by the studied algal species were determined on a dry weight basis and are shown in Table (3). The CF was in the range of 2.61 for magnesium as accumulated by *L. Papillosa* to 10.0 x 10^4 for iron accumulated by L. obtuse. Correlation between this calculated C.F. indicated that the metal accumulation rates can be sorted as per the following decreasing order:

Iron>Zinc> Copper > Manganese > Cadmium > Lead > Magnesium

Table 3: The C.F. of metals accumulated by the investigated Algal Species extracted from the Little Bitter Lake

Algae	Cd	Cu	Pb	Zn	Mg	Mn	Fe
Green Algae	10^3	10^4	10^2	10^4		10^3	10^4
C. Linum	2.04	0.88	5.52	1.13	13.29	3.16	2.13
E. Intestinalis	2.38	0.83	5.27	0.49	11.74	3.75	3.93
U. Lactuca	1.96	0.95	5.15	0.65	14.02	3.52	2.05
C.Albida	2.81	1.20	2.27	1.30	4.15	2.23	2.29
Average	2.3	0.97	4.55	0.89	10.8	3.17	2.6
Brown Algae							
S. Dentifolium	2.96	0.74	2.59	0.55	5.75	2.76	1.72
P. Pavonica	2.27	0.82	3.41	1.24	23.87	2.78	2.39
C. Sinusa	2.54	0.69	4.21	0.70	5.05	3.49	5.89
C. myrica	2.27	0.47	2.95	0.42	4.00	3.72	1.10
Average	2.51	0.68	3.29	0.73	9.67	3.19	2.78
Red Algae							
L. Papillose	3.65	1.36	7.13	2.15	2.61	25.49	1.16
J. adherens	1.62	1.04	5.21	1.97	34.97	28.91	5.91
L. Obtusa	1.19	0.95	6.59	2.78	18.67	30.33	10.01
S. Futcelatum	1.50	1.01	5.73	1.64	27.21	27.80	5.51
Average	1.99	1.09	6.17	2.14	20.87	28.13	5.65

It is important to notice that both Fe and Zn were the highest accumulated metals by the studied algae among the others. This may be attributed to the fact that these two metals are considered essential nutrient elements for algal growth (18, 20). Nevertheless, all metals, including those considered micronutrients (i.e., iron, zinc, and copper) are toxic to the algae especially when their concentrations are high (17, 21).

Nevertheless, the CF of iron (Table 3) was similar to those reported previously by other algal species (2, 15). The calculated CF of Cu, Zn, Cd, Pb, and Mn in this study (Table 3) are less than those previously mentioned by other investigators (8, 10). This may be attributed to the fact that the previous studies were concerned with the accumulation of heavy metals by other algal species (4, 22, 23). The importance of Fe and Mn for the photosynthetic reactions by algae is well-established and documented (8, 18).

Heavy metal's toxic nature is a characteristic feature that causes poisoning and in-activation of enzyme systems. Many biochemical and physiological processes are affected by Hg, Cd, and Pb. (2, 3, 11, 18). The accumulation rates of the metals (Cr, Ni, Ag, & Sr) in algae from India’s southwest coast were studied (20). In this study, the marine algae were studied as biological indicators regarding heavy metal contamination in these coastal waters, where six marine algal species were sampled and analyzed. Interspecies as well as interclass variations were calculated on both spatial and temporal scales. Metal levels were recorded as follows: Ni: 0.20–21.06 µg g (mean = 10.13 µg g), Cr: non-detectable level (ND)–37.18 µg g (mean = 13.86 µg g), Sr: 2.19–103.90 µg g (mean = 29.40 µg g), and Ag: ND–6.39 µg g (mean = 1.80 µg g). The contents of Ni and Cr were at similar levels to that determined for algae from contaminated regions (20).

Concerning heavy metals in the marine ecosystem, they are often existent in marine water at low concentrations; within the range of $ug.L.^{-1}$ (22). Such metals have gained great concern from marine biologists due to their refractory nature. Meanwhile, algae are suspended in marine and surface water (1, 8), where they provide a big surface area that is liable for uptake of surrounding micro-pollutants (13). Therefore, algae with high levels of metals can act as an indication of metal contamination (2, 4). Accumulation of heavy metals by macro-algae and/or other aquatic plants is attributed to their ability to uptake absorbing and binding metals to their tissues (8, 22). Moreover, algae represent the primary metal concentration agents within marine environments (5, 15). Studies by many investigators confirmed that algae and aquatic plants are considered an indicator of contamination of a given area (6, 13).

Several studies aimed to investigate the elimination of heavy metals from polluted water (18). The toxicity of metals released into the marine environment was studied by several investigators (2, 10). It was noticed that the accumulation of heavy metals by algae is one of the most efficient methods as indicator of aquatic contamination by metals (12). These studies indicated that some micro-organisms, such as micro-algae, yeast and bacteria were able to absorb and / or accumulate heavy metals. Therefore, the usage of algae for accumulation and /or adsorption of heavy metals are advantageous in terms of low-cost of raw material, high adsorption capacity, as well as no secondary contamination (2, 19). Therefore, algae can be regarded as a promising primary treatment tool regarding the uptake of pollutants such as heavy metals from wastewater.

Conclusions

The mechanism of metal uptake and accumulation by algae was explained by the tendency of each given algae for binding metals to their polysaccharides (4, 22, 24). It was reported that the difference in metal accumulation by algae is seemingly due to the competition between the available metals for bonding with the polysaccharides (4, 8). It was therefore, suggested that this binding affinity is a preferential phenomenon (13).

It is worth noting that the ability of each algal species to accumulate metals varies remarkably according to the available metal, the concentration of this metal, and the time duration at which the algae are contacted with this metal (3, 6, 15, 25).

The present investigation confirmed that the sea water at the coastal area of Port Said the Mediterranean Sea is not polluted as compared with other coastal areas. Meanwhile, the level of metals in the investigated algal species is obviously less than that reported by other investigators (15).

The major processes that govern the presence, partition, and distribution of metals in the environment are dilution, dispersion, advection, adsorption/desorption and sedimentation. However, certain chemical processes may also take place. Meanwhile, instability constants are important factors that govern the speciation of these metals in the environment including various soluble and various complexes forms. The physico-chemical properties of water such as pH, temperature, dissolved ions, and suspended solids are also important factors.

Adsorption and precipitation are important processes for the removal of metals from water and aquatic environment. Storage of metals in the sediments takes place in the forms of distribution, dissociation, permanent or temporary in freshwater as well as marine environments. Redox and microbial activity (aerobic or anaerobic) processes can alter the metals form and the sediments composition; thus, affecting the properties of interstitial water. For example, manganese and iron oxides may be converted to carbonates or sulfides in the sediments as a result of chemical, redox or microbial activity. Such new conversion forms of metals lead to a reduction in the adsorbing capacity of the given sediments. Reforming metal forms in the sediments by microbial activities could also bring sediments to the water surface. Thus, different forms of metals in significant fractions will be released.

Given the advantages of low-cost raw material, high adsorption capacity, and the near zero secondary contamination, etc., algae is considered promising regarding the purification of wastewater with heavy metals content. Years ago, such accumulation of heavy metals by algae had been investigated for biomonitoring or bioremediation (22). Further research should address the adsorption mechanism, including the relation between the binding ability and alginate components, as well as the biosorption characteristics of each of the alginate components. This will result in more efficient algae use, and consequently accelerating the development of highly efficient biosorbents.

Declaration of Interest

The authors declare that they have no conflict of interest.

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