

HUSSEIN I. ABDEL-SHAFY*,
MOH. EL-SAID FARGHALY**

ACCUMULATION OF HEAVY METALS BY THE BENTHIC ALGAE IN THE SUEZ CANAL

The present investigation was undertaken to study the accumulation of metals by different benthic macro-algae that exist in the Suez Canal pathway. The algae were successively collected from eight different locations along the canal for a period of 12 months. The variation in the metal uptake by the different algal species in terms of locations was considered. The metals investigated are as follows: cadmium, chromium, zinc, manganese, magnesium and iron. The algae studied belong to green, brown and red seaweeds.

Correlation between the level of metals in the Suez Canal water and algae was carefully investigated in order to determine the concentration factor. The effect of seasonal variation in metal concentrations on accumulation of these metals by algae was considered. The results obtained showed that average metal concentrations in the Suez Canal water were the following: 0.3, 3.5, 7.7, 4.1, 1299 and 32.4 $\mu\text{g}/\text{dm}^3$ for cadmium, chromium, zinc, manganese, magnesium and iron, respectively. The level of metals in sub-surface sediments was also investigated. General distribution pattern of metals accumulated by the algae studied reflected the abundance of metals in both sediments and water. However, there were remarkable variations in metal concentrations accumulated by various species. The paper describes a correlation between the concentration factors of the metals accumulated by the algae and their levels in water and sediments. The present study revealed that the concentration of metals in algae can be considered equal or lower than that previously reported in some other areas.

1. INTRODUCTION

Two groups of substances connected with a development of technology have a long-term effect on the natural balance of aquatic systems. These two groups are: nutrients which promote oxygen depletion and sparingly degradable synthetic chemicals and other waste substances which often produce multiple effects on aquatic ecosystem. Substances such as polycyclic aromatics, pesticides, radio-active

* Water Research & Pollution Control Department, National Research Centre, Tahreer Street, Dokki, Cairo, Egypt.

** Marine Science Department, Faculty of Science, Suez Canal University, Ismailia, Egypt.

matter and trace metals directly endanger the aquatic systems [1]. The latter group of pollutants is important because of two reasons: firstly, in contrast to most organic pollutants, trace metals are not usually eliminated from the aquatic ecosystem by natural processes and secondly, most metal pollutants are in minerals and aquatic creatures [2].

The metal contaminants introduced into aquatic system come from various sources, including smelting processes and fuel combustion via atmospheric fallout, pollution from leaks, effluents and dumping activities, etc. Wide use of metals of all kinds in the last 50 years has caused an increase in their concentration in oceans. However, in marine water, heavy metals are usually found in very low concentrations which are of order of mg/dm^3 [1], [3].

Almost all metals are bioaccumulated on one or more trophic levels of a marine food chain. Being the most persistent substances in environment, they cannot be degraded or destroyed, although they can form various compounds and complexes. Some metals are extremely toxic to marine organisms, whereas others are relatively innocuous. Moreover, many metals such as sodium, calcium, iron, magnesium and even zinc are vital for certain marine organisms. The mechanism and cause of bioaccumulation of metals by these marine organisms are still not understood, but there is little evidence that high concentrations of these elements are seriously harmful to the organisms containing them. On the other hand, algae are suspended in marine as well as surface water, occupying large surface areas. These large surface areas are liable for the uptake of surrounding micropollutants [2], [4]. Algae with high metal content can serve as the indicators of metal pollution [5], [6]. The accumulation of metals by macro-algae has been attributed to their ability to bind metals to molecular groups present in their tissues [4]. In addition, algae are considered as primary producers and metal-concentrating agents in marine water [5], [7], [8], [9].

The present investigations were undertaken to study the accumulation of metals by some of the benthic macro-algae that exist in the Suez Canal international pathway. Sources of micropollutants introducing metals to the Canal are shipping activities, beaching activities and littering. The variations in the concentrations of the metals uptaken (cadmium, chromium, zinc, manganese, magnesium and iron) by various algal species, depending on their localities, are considered. The studied algae are: green algae, brown algae and red algae. Green algae belong to the following genera: *Enteromorpha*, *Chaetomorpha*, *Cladophoropsis* and *Ulva*, while brown algae to: *Sargassum*, *Cystoseira* and *Padina*. The red algae are represented by: *Jania*, *Laurencia* and *Sarconema*. Correlation between the level of the metals investigated in the Suez Canal water and the algae studied was carefully established in order to determine the concentration factor.

2. MATERIALS AND METHODS

Samples of different algal species were collected from 8 different intertidal locations along the Suez Canal marine pathway during an intensive sampling programme. The sampling locations are shown in figure 1. This sampling area is located between the

entrance to the Suez Canal from the Mediterranean Sea, Port Said city ($32^{\circ}20' E$, $31^{\circ}15' N$), and Deversoir ($32^{\circ}19' E$, $30^{\circ}25' N$). The maximum draught wetcross sectional area at the present time is around 3600 m^2 . The Suez Canal authority has been working to increase as soon as possible this wetcross sectional area to 5000 m^2 .

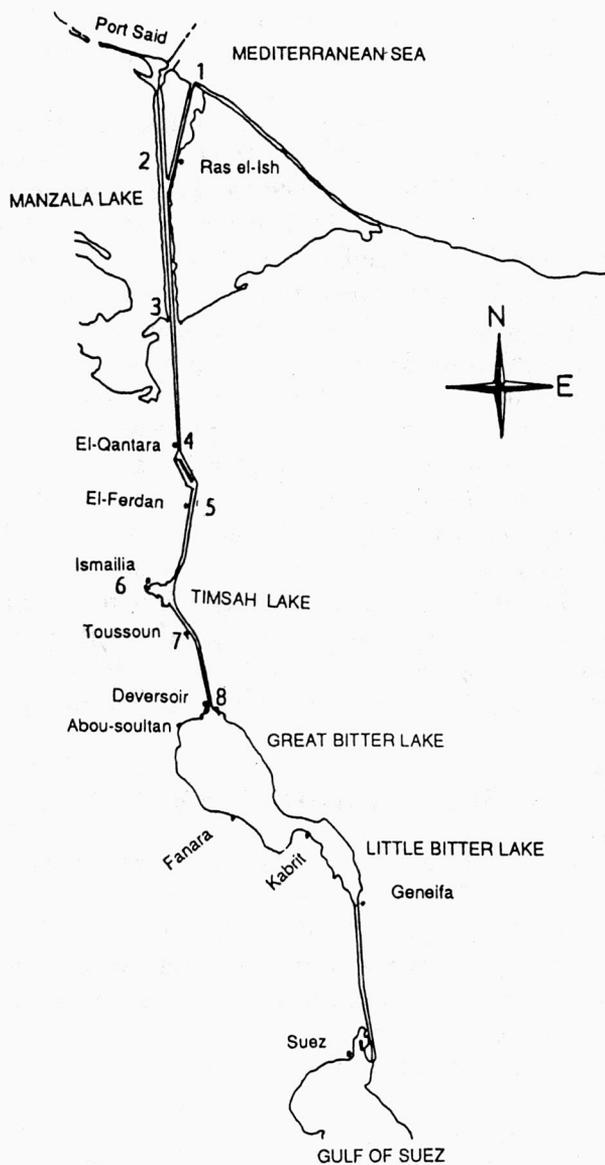


Fig. 1. The sampling locations along the Suez Canal

The collected algal species were moderately dense and were found in the depth of approximately 2 m. Twelve different algal species along with water and sediment samples from the same locations were collected successively over a period of 12 months. The algal samples were washed with redistilled water, oven-dried at 80 °C to a constant weight, then ashed in a muffle furnace (450 °C, 24 h) and ground into powder. Sediment samples were oven-dried for 24 h at 105 °C and sieved to separate the fraction smaller than 100 μ m. This fraction was then subject to acid digestion.

Algae and sediment samples were digested with nitric acid followed by H₂O₂ treatment under reflux according to ABDEL-SHAIFY et al. [9]. This acidic treatment allows us to break weak bonds of metals which can pass to sediments where they are potentially available to plants [10], [11]. The canal water samples were filtered through 0.45 μ m Millipore filters to separate particles acidified by concentrated nitric acid to pH lower than 2.0, preserved, stored and then analysed according to the U.S. EPA analytical procedure [13]. Concentrations of metals were determined by means of instrumental laboratories (IL) atomic absorption spectrophotometer, Model (551), equipped with a Heated Graphite Atomizer Model (651) and deuterium arc back ground correction. Each result presented here is an average of the sequence of the 10 readings for each sample on the atomic absorption (A.A.) spectrophotometer. These readings were compared with the standards determined by the A.A. manufacturer, i.e. instrumental laboratory. As a control, a blank was made for each metal determined. Each blank was redistilled water, which was subjected to all chemical treatments and digested according to the same procedures as the samples tested. The values of the metal concentrations that are given are the average values for the whole period of study. The concentration factors of the metals typical of various algal species were calculated according to [12].

3. RESULTS AND DISCUSSION

Levels of metals in the canal water and surface sediments along the Suez Canal pathway are given in table 1. The results showed that the concentrations of the metals studied are within the range of "non-contaminated" marine sediment [6], [14], [15]. Therefore, they allow comparison with other algal species studied in non-contaminated areas. The level of metals in the sediments studied can be arranged according to the following descending order: Mg > Fe > Zn > Cr > Cd.

The levels of metals accumulated by algae collected from eight different locations along the Suez Canal pathway are presented in figure 2. The results obtained indicated that the levels of metals in algae reflected their relative abundance in both sediments and water (table 2 and figure 2). However, different metals present different within-plant distribution patterns in the algae studied.

Table 1

Levels of heavy metals in water and surface sediments along the Suez Canal pathway presented as mean values

Metals	Water ($\mu\text{g}/\text{dm}^3$)		Sediments ($\mu\text{g}/\text{kg}$)*	
	Range	Average	Range	Average
Cd	0.0-0.7	0.3	0.05-0.17	0.1
Cr	0.8-7.8	3.5	0.511-1.854	0.9
Zn	2.1-10.6	7.7	6.52-26.87	13.2
Mn	1.9-6.9	4.1	7289-18416	151
Mg $\times 10^3$ **	894-2907	1299	831-2790	1638
Fe	21.7-58.1	32.4	8531-2117	1386

* As dry weight.

** Those results are multiplied by ($\times 10^3$).

Table 2

The distribution and abundance of the algae studied along the Suez Canal area

Algal species	Sampling site numbers							
	1	2	3	4	5	6	7	8
Green algae								
<i>Enteromorpha flexusa</i>	C	C	C	C	C	A	O	O
<i>Enteromorpha intestinalis</i>	D	C	C	C	C	A	O	O
<i>Chaetomorpha linum</i>	C	O	O	C	C	R	A	A
<i>Cladophoropsis</i> sp.	C	C	C	C	C	C	C	C
<i>Ulva lactuca</i>	C	C	C	C	C	A	C	C
Brown algae								
<i>Cystoseira sinuosa</i>	C	C	C	A	C	R	R	C
<i>Sargassum subrepandum</i>	R	R	R	R	C	R	D	D
<i>Cystoseria myrica</i>	R	R	R	R	C	R	D	D
<i>Padina pavonica</i>	O	O	O	O	O	R	O	O
Red algae								
<i>Laurencia obtusa</i>	C	C	C	C	C	R	C	C
<i>Jania rebens</i>	C	C	C	C	C	R	C	C
<i>Sarconema furciculatum</i>	C	C	C	C	C	R	C	C

C - common, A - abundant, D - dominant, R - rare, O - occasional.

Certain amount of these metals settles and thus is adsorbed by sediment. In both canal water and sediments, magnesium occurred in the highest concentration, while cadmium - in the lowest.

The general distribution pattern of metals within plants follows the same descending order than that of the metals in the canal water. However, there are

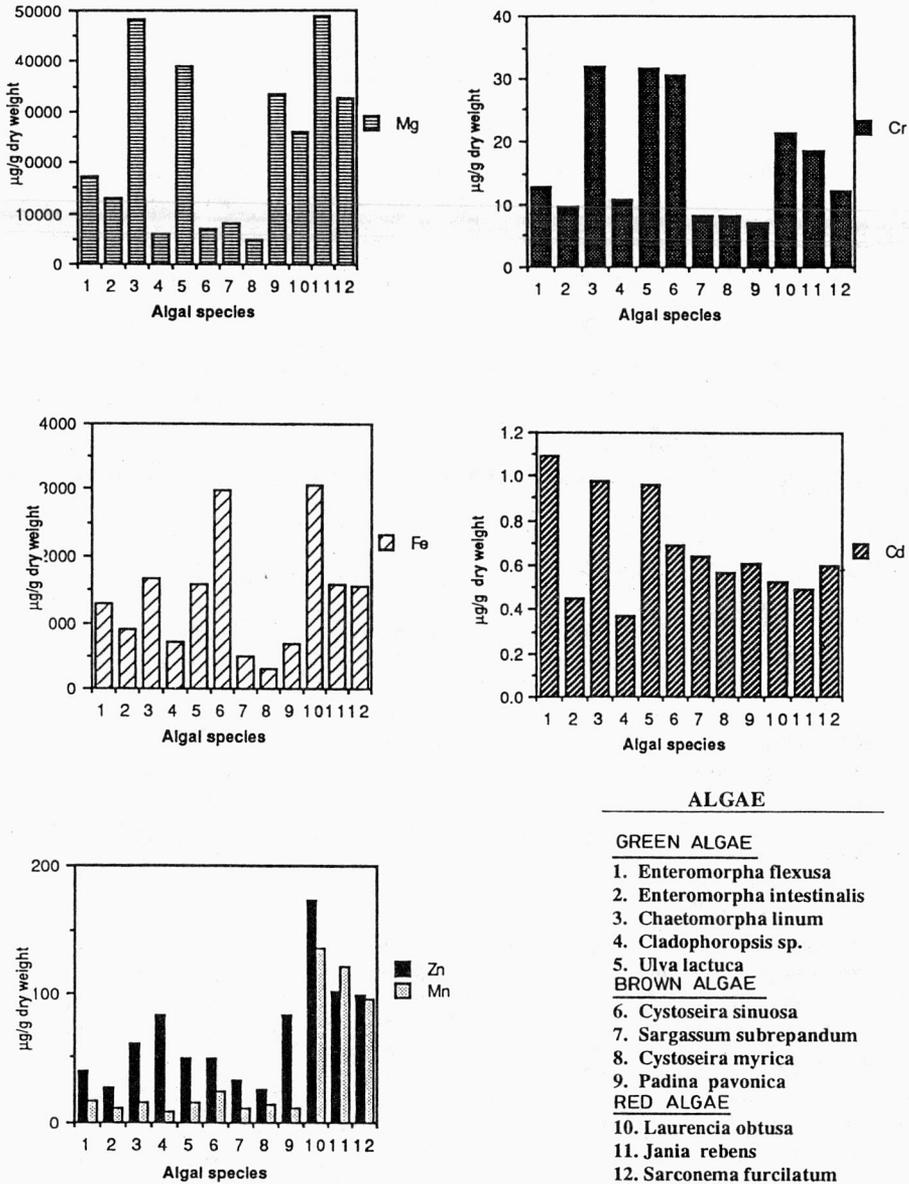


Fig. 2. Levels of metals in various algal species collected from the Suez Canal

remarkable variations in the metal concentrations in different species. General correlation between the levels of the metals in the studied algal species indicates that the accumulation abilities of algae may be arranged according to the following descending order: red algae, green algae and brown algae. Cadmium and chromium

were highly accumulated by green algae. On the other hand, zinc, magnesium and iron were mostly accumulated by red algae followed by green, and next by brown algae. On the contrary, the level of manganese in brown algae was slightly higher than that in green algae.

The variation in the metal uptake by algae is mainly controlled by the availability of these metals in the aquatic environment, the ability of algae to accumulate them, the concentrations of these metals in the environment and the time at which the algae are in contact with these available metals [6], [16], [17]. However, a failure of metal accumulation from water by seaweeds could be expected due to the toxicity which is referred to plant exposure to high metal concentration. It was reported previously that the metabolic activity and the surface area of algae are important factors responsible for metal accumulation [4], [18]. In addition, efficiencies of binding the metal inside the tissues may be considered as another important factor that affects the rate of metal accumulation [4], [19]. By considering the level of metals in each group of seaweeds separately, it can be noticed that this level is in agreement with the law of homological series which states that closely related plant species have similar chemical composition [8], [9], [18]. Meanwhile, each species of algae within the same group exhibits variable levels of metals.

Among red algae *Laurencia* exhibited the highest level of chromium, zinc, manganese and iron. *Jania* showed the highest concentration of manganese. The lowest concentrations of chromium, zinc, manganese and iron and the highest level of cadmium were typical of *Sarconema*. As for green algae, the highest concentrations of chromium, magnesium and iron were stated in *Chaetomorpha linum*. Meanwhile, the lowest level of cadmium, manganese, magnesium and iron was shown by *Cladophoropsis* which had the highest concentration of zinc. In the case of brown algae, *Cystoseira sinuosa* showed the highest level of cadmium, chromium, manganese and iron. Meanwhile, the highest concentrations of zinc and magnesium were determined in *Padina pavonica*, which had the lowest level of chromium and manganese. The lowest concentrations of cadmium, zinc, magnesium and iron were stated in *Cystoseira myrica*.

Concentration factors of metals accumulated by various algal species, calculated as dry weight, are given in table 3. These factors ranged from 3.8 for magnesium in *C. myrica* to 95×10^3 for iron in *Laurencia*. Correlation between these different concentration factors showed that the rate of metal accumulation can be arranged according to the following descending order: Fe > Mn > Cr > Cd > Mg.

Iron concentrations are substantially higher than any of the remaining metals. It is worth pointing out here that the concentration factors of the algae investigated are similar to those reported by other researchers [6], [18], [20]. On the other hand, concentration factors of cadmium, chromium, zinc and manganese in the present study are lower than those recorded in previous papers [4], [5], [9], [21]. The importance of iron, copper and manganese in photosynthetic reactions is well known [22]. Some trace metals are necessary for growth of marine algae [23].

Table 3

Concentration factors of metals accumulated by various algal species and sediments collected from the Suez Canal area

Algae	Cd × 1000	Cr × 1000	Zn × 1000	Mn × 1000	Mg × 10	Fe × 10 000
Green algae						
<i>Enteromorpha flexusa</i>	3.6	3.7	5.2	4.1	13.2	4.0
<i>Enteromorpha intestinalis</i>	1.5	2.7	3.5	2.9	10.0	2.8
<i>Chaetomorpha linum</i>	3.3	9.1	7.9	3.9	37.0	5.2
<i>Cladophoropsis</i> sp.	1.2	3.1	10.7	2.2	4.6	2.2
<i>Ulva lactuca</i>	3.2	9.1	6.5	3.9	30.1	4.9
Brown algae						
<i>Cystoseira sinuosa</i>	2.3	3.9	6.3	6.0	5.3	9.2
<i>Sargassum subrepandum</i>	2.1	2.3	4.1	2.8	6.2	1.6
<i>Cystoseira myrica</i>	1.9	2.4	3.2	3.5	3.8	1.0
<i>Padina pavonica</i>	2.0	2.1	10.8	2.7	25.8	2.1
Red algae						
<i>Laurencia obtusa</i>	1.8	6.1	22.4	33.7	20.0	9.5
<i>Jania rebens</i>	1.6	5.3	13.2	30.2	37.7	4.9
<i>Sarconema furcilatam</i>	2.0	3.5	12.8	24.0	25.3	4.8
Canal sediments	0.3	0.3	1.7	3.8	1.3	0.4

Comparison between the different concentration factors (C.F.) of the metals studied in the canal sediments showed that the rate of metal accumulation decreases according to the following order: Fe > Mn > Zn > Cr = Cd > Mg. The correlation between the level of metals in the water of the area studied and the level of metals in the water of some other areas proves that the waters of the Suez Canal pathway are not polluted [6], [10], [15], [17]. Meanwhile, the concentrations of metals in the algae studied can be considered equal or lower than those previously reported in some other areas [4], [6], [9], [11], [21].

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AKUMULACJA METALI CIĘŻKICH PRZEZ GLONY ŻYJĄCE W BENTOSIE KANAŁU SUESKIEGO

Zbadano proces akumulacji metali przez różne gatunki glonów występujących w bentosie Kanału Sueskiego. Glony były pobierane kolejno w ośmiu różnych miejscach kanału przez okres 12 miesięcy. Przeanalizowano zmiany w poborze metali przez różne ich gatunki w zależności od miejsca kanału. Określano stężenie następujących metali: kadmu, chromu, cynku, manganu, magnezu i żelaza. Badane glony były zielenicami, brunatnicami i krasnorostami.

Określono współczynniki akumulacji metali przez glony. W tym celu oznaczano poziom metali w wodzie Kanału Sueskiego i w glonach. Przeanalizowano wpływ sezonowych zmian w stężeniu metali na proces ich akumulacji przez glony. Średnie stężenie kadmu, chromu, cynku, manganu, magnezu i żelaza w wodzie Kanału Sueskiego wynosiło 0,3; 3,5; 7,7; 4,1 1299 i 32,4 $\mu\text{g}/\text{dm}^3$. Zbadano również poziom

metali w osadach. Ogólny rozkład metali zakumulowanych przez glony odzwierciedla stężenia tych pierwiastków zarówno w osadach, jak i w wodzie. Zaobserwowano jednak znaczące różnice w stężeniu metali pobranych przez różne gatunki glonów. W pracy przedstawiono korelację między współczynnikami załężania metali zakumulowanych przez glony a stężeniem metali w wodzie i osadach.

АККУМУЛЯЦИЯ ТЯЖЕЛЫХ МЕТАЛЛОВ ВОДОРОСЛЯМИ, ВЫСТУПАЮЩИМИ В БЕНТОСЕ СУЭЗСКОГО КАНАЛА

Исследован процесс аккумуляции металлов разными породами водорослей, выступающих в бентосе Суэзского канала. Водоросли подбирали в восьми разных местах канала в течение 12 месяцев. Проведен анализ изменений в аккумуляции металлов их разными породами в зависимости от места канала. Определена концентрация следующих металлов: кадмия, хрома, цинка, марганца, магния и железа. К исследуемым водорослям принадлежали: зеленые водоросли, бурые водоросли и багрянки.

Определены коэффициенты аккумуляции металлов водорослями. Для этого был определен уровень металлов в воде Суэзского канала и в водорослях. Проведен анализ влияния сезонных изменений концентрации металлов на процесс их аккумуляции водорослями. Средняя концентрация кадмия, хрома, цинка, марганца, магния и железа в воде Суэзского канала составляла 0,3; 3,5; 7,7; 4,1; 1299 и 32,4 $\mu\text{г}/\text{дм}^3$. Исследован также уровень металлов в осадениях. Общее распределение металлов, аккумулируемых водорослями отождествляет концентрации этих элементов как в осадениях, так и в воде. Наблюдались однако значительные различия в концентрациях металлов, аккумулируемых разными породами водорослей. В настоящей работе представлена корреляция между коэффициентами концентрирования металлов, аккумулируемых водорослями и концентрацией металлов в воде и осадениях.