



The Role of Marine Algae as a Bioindicator in Assessing Environmental Pollution

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Abstract:

The potential ecological effects of rising levels of heavy metal concentrations in the aquatic environment are of great concern caused by their highly bio-accumulative nature and higher toxicity, which leads to the destroy of several habitats for marine organisms. The purpose of this research are presented analyses, for both the concentration of heavy metals in marine water and algae tissue, in an effort to gain some insight into the level of metal contamination which might exist in the coastal marine environment along the Libya beaches. Assessed by measuring pollution indicating parameters of marine water (TC^O, S ‰, pH, Do), and concentration of heavy metals. This study also determined indices of pollution as a bioaccumulation factor (BAF) and metal pollution index (MPI), from six different sites in two seasons (Spring and summer), 2016. The results indicate the slightly higher level of temperature and pH on the summer season, while salinity and dissolved oxygen were slightly higher level in spring. A Positive correlation was found between dissolved oxygen and salinity ($r^2= 0.897^*$) and, a negative correlation was found between other parameters. The results show that there is a statistically significant difference in averages of concentration of (Pb), (Mn) and (Zn) between algae species and stations overall. The highest concentration of (Pb) was recorded in the *Enteromorpha sp.*, 1.228 $\mu\text{g g}^{-1}$. The highest concentration of (Mn) was recorded in the *U. lactuca*, *Corallina sp.*, and *Chaetomorpha sp.* The present study recorded higher concentrations of Zinc (Zn) 0.867 $\mu\text{g g}^{-1}$, in the *Enteromorpha sp.*, and *Laurencia sp.* 0.861 $\mu\text{g g}^{-1}$. In general, Cadmium recorded low values irrespective of sites and algal species. The region of S6(Libya station) can be identified as a place with higher Pb and Zn contents while the region of S1(Libya harbor), shows higher contents of Mn. As well the region of S2(Libya company), shows higher contents of Cd. The metals concentrations recorded for the different tissues and sites of the present study confirm the occurrence of significant seasonal variability, with maximum concentrations usually observed in summer. The data demonstrate a positive correlation between all the metals, except the negative correlation between Zn and Mn. The concentration of the metals in seawater in the six sampling sites followed the order of Mn>Zn>Pb>Cd. A somewhat, BAF of the different heavy metals showed a common pattern of peaking at S2(Libya company), with moderate reduction at S6 (Libya station), S3(Libya station), S4(Libya station) and S1(Libya harbor), and a relatively greater reduction at S5(Libya station). The ability to accumulate heavy metals MPI was highest in *Laurencia sp.*, which was substantially higher than those of the accompanying species at all species at all stations. The present study emphasizes of control of pollutants such as sewage and industrial effluent discharges into the marine environment without treatment.

Keywords: Marine algae, Bioindicator, Environmental Pollution, bioaccumulation factor, metal pollution index

INTRODUCTION

Increasing human population and coastal expansion facilitate to the rising in anthropogenic pollution burden, which has become the main threat to marine and aquatic environment. In fact that polluted water can reduce water quality thus restricting use of water bodies for many purposes. It is a well-known fact that pollution of heavy metals in aquatic environment is a growing problem worldwide and currently it has reached an alarming rate. There are various sources of heavy metals; some originates from anthropogenic activities like draining of sewerage, dumping of hospital wastes and recreational activities. Pollution levels in marine environments by heavy metals can be estimated by analysis of water and marine organisms (Morillo *et al.*, 2005). In this context, some kinds of algae were studied extensively for their potential use as bioindicators for metallic contamination in the past (Phillips, 1994), because they are able to absorb heavy metals from water and sediment and to disseminate them within their cytoplasm cells (Davis *et al.*, 2003).

Wastes from both industrial and domestic activities usually introduce huge amounts of pollutants discharged into the marine environment, causing significant and permanent disturbances in the marine ecosystem systems and consequently, environmental and ecological deterioration (Buffle *et al.*, 2009; Akcali and Kucuksezgin, 2011). This phenomenon is especially significant in coastal areas, owing to the fact that these are the main drainages of most anthropogenic pollutants. It has long been reported that heavy metals in the marine environment have a particular importance in the eco toxicology, as they are highly persistent and can be very toxic even in very low concentration (Simon *et al.*, 2011). Many toxic pollutants are found in only trace amounts in water, and often at elevated levels in sediments. Therefore, risk assessments based only on data derived from water analyses are usually misleading (Gosavi *et al.*, 2004). The main advantage of bio-monitoring approach using marine organisms compared to direct measurement in water or sediment is to provide a direct and time- integrated assessment of the

metal fraction that is actually available to the organisms (Coteur *et al.*, 2003; Danis *et al.*, 2004; Metian *et al.*, 2008). However, several criteria have been established to ensure appropriate organisms to be used as biomonitors and bioindicators. The organisms should ideally be sedentary, and thus reflect only pollutant specific to a particular site, easy to identify, and cosmopolitan, ensuring wide geographic relevance. Furthermore, bioindicators should be sensitive to contaminants and tolerate high contaminant concentrations and also provide sufficient tissue for analysis (Conti and Cecchetti, 2003). There has been a growing interest in determining the heavy metal levels in marine environment and awareness has been dragged to the cubits of infection levels in public food stores, particularly fish (Abdullah *et al.*, 2007). Marine pollutants effect direct and indirect on almost all marine living creatures, so, heavy metals contain less than one percent of living copulative organisms, and their different density cause to some aberrations (Hylland, 2006).

Though the heavy metal like, Cd, Pb and Ni are not essential for plant growth, they are readily taken up and accumulated by plants in toxic forms. Ingestion of vegetables irrigated with waste water and grown in soils contaminated with heavy metals possess a possible risk to human health and marine environment (Jan, Abbas Ullah *et al.*, 2011). Heavy metal concentration in the marine environment. plays an important role in controlling metal bioavailability to plants. (Jan, Abbas Ullah *et al.*, 2011).

Algae are the main primary producers in all kinds of water bodies and they are involved in water pollution in a number of significant ways. However, certain algae flourished in water polluted with organic wastes play an important part in “self-purification of water bodies”. Some pollution algae may frequently be toxic to fish and also mankind and animals using polluted water (Sigworth, 1957). In fact, algae can play significant part of food chain of aquatic life, thus whatever alters the number and kinds of algae strongly affects all organisms in the chain including fish. Algae are also known to be causes of tastes and odors

in water (Sigworth,1957).

In general, marine algae accumulate heavy metal by two stages, consisting first of rapid and reversible physico-chemical process of adsorption on the surface of the algae and then of a slower metabolically arranged intracellular uptake (Güven *et al.*,1992). Heavy metal concentrations are generally dependent both on the external factors as (pH, salinity, inorganic and organic complex molecules) and on physico-chemical parameters which control the metabolic rate (nutrients, temperature, light and oxygen). The accumulation of heavy metals in the marine algae is a continuous processes their life span after binding on the external wall, older tissues usually contains higher levels of some heavy metals (Barreiro *et al.*, 1993). Determination of heavy metal concentrations in marine algae samples is usually preferred in the seawater and sediment samples. Heavy metal concentrations in seawater are very low and show wide fluctuation. At the same time, heavy metal levels in the sediment samples can be changed by organic matter content, grain size composition, pH and oxidation-reduction potential, etc. (Förstner,1985). On the other hand, marine organisms can be used as monitors to give information on concentrations of heavy metals in the surrounding environment. Especially, marine algae species are usually used to indicate heavy metal levels in coastal waters throughout the world (Fowler,1979).

Government agencies throughout the world now use algae to monitor and assess ecological conditions in many types of aquatic ecosystems (Weber,1973; Dixit and Smol, 1994; Dixit *et al.*,1992; Bahls,1993; Whitton and Rott, 1996; Biggs *et al.*, 1998; Kelly *et al.*,1998 ; Stevenson and Bahls,1999). Macro algae have been used extensively to measure heavy metal pollution in freshwater and marine environments throughout the world. They are used as bio indicators because of their distribution, size, longevity, presence at pollution sites, ability to accumulate metals to a satisfactory degree and ease of identification. It is preferred to measure heavy metal levels in bioindicators organisms rather than measuring the concentrations in water and/or sediment

samples (Palmer,1980).

Libya is located in North Africa. To the north of it lies the Mediterranean Sea, it is ranked 124th out of 142 countries on an Environmental Sustainability Index, which places the country well down the list signifying a country with serious environmental degradation (Environmental Sustainability Index, 2002). The Jabal Akhdar region is located between latitude 32° and 33° North and 20° to 23° East; it is about 360 km long and 60 km in width on the Mediterranean coast (Azzawam,1984). This region is very important, due to it having distinct environmental characteristics associated. Also it has an environment similar to other regions in Southern Europe such as Italy, the Greek islands and Turkey (Azzawam,1984). The study area is located along the Derna coast, in Jabal Akhdar region the north east part of Libya at latitude 32° North and 22° East and this area is exposed to different degrees of pollution.

The aim of present study is to assessing the environmental conditions in the aquatic habitats of Derna coast, through determination of some physicals and chemicals factors (temperature, salinity, pH and DO) in the water, quantify the concentration of several heavy metals in dry weight of red, brown, green algae and sea water. The use of algae in environmental assessments, through obtaining metal pollution indices (MPI) of studied metals and evaluating their BAF which reveals the interactions between metals in water and some algae species.

Materials and methods

1. Study area and selection of sites:

The study area is located along the Derna coast, the north east part of Libya at latitude 32° North and 22° East. This area included six sites, which are exposed to different degrees of pollution. In addition, it describes the methods used to collect and analyses the data for different measurements which include the heavy metal concentration in water and algae tissue, as well as the certain environmental parameters such as temperature, salinity, hydrogen-ion concentration (pH) and dissolved oxygen (DO). The location of the six sites is shown in Fig.1, and their characteristics are presented in Table 1.



Fig 1: Locations of the six study sites, which are located along Derna coast. The inset map shows the location of the study area in Libya (Source: Google Earth).

Table 1: The locations of the study sites with latitude and longitude, the nature of substratum and pollution status. The terms ‘S1 to S6 refer to the stations.

Site	Latitude	Longitude	the nature of substratum	pollution status	
S1	Derna Harbor	32°46'0.79	22°39'9.48	Rocky	sewer pipes
S2	Shahat company	32°46'18.98	22°38'45.57	Rocky	sea water
S3	Post station	32°46'28.48	22°38'27..83	Rocky	sewer pipes
S4	Republic station	32°46'23.75	22°37'46.25	Rocky	sewer pipes
S5	Algarod station	32°46'27.55	22°36'27.55	Sandy	sea water
S6	Desalination station	32°47'4.30	22°35'12.02	Rocky	fuel and oil

2. Algae:

1. *U. lactuca* . Kingdom:

Protista **Phylum :**

Chlorophyta **Class:**

Ulvophyceae **Order:**

Ulvales **Family :**

Ulvaceae **Genus :*Ulva***

Species: *U. lactuca*



Fig 2: *Ulva lactuca*

Ulva lactuca, also known by the common name sea lettuce, is an edible green alga in the division Chlorophyta. It is the type species of the genus *Ulva*. The distribution is worldwide: Europe, North America (west and east coasts), Central America, Caribbean Islands, South America, Africa, Indian Ocean Islands, South-west Asia, China, Pacific Islands, Australia and New Zealand (Mattox and Stewart, 1984).

2. *Laurencia. sp.*

Kingdom : Protista

Phylum: Rhodophyta

Class: Florideophyceae

Order : Ceramiales

Family : Rhodomelace

Genus : *Laurencia* (Mattox and Stewart, 1984).



Fig 3: *Laurencia. sp*

3. *Amphiroa anceps*.

Kingdom : Protista

Phylum: Rhodophyta

Class: Florideophyceae

Order : Corallinales

Family : Corallinaceae

Genus: *Amphiroa* *anceps*.

Amphiroa is a genus of thalloid red algae comprising 111 species. Specimens can reach around 30 cm in size. The thalli take a crustose form; dichotomous branches are formed. The organisms possess secondary pit connections.



Fig 4: *Amphiroa anceps*.

Amphiroa reproduces by means of conceptacles; it produces tetra spores. Its pore canals are lined with parallel filaments; the morphology of the pore canal is a key trait used to delineate species within the genus.

4. *Cystoseira asmundaceae*.

Kingdom : Protista

Phylum: Ochrophyt

Class: Phaeophyceae.

Order: Fucales .

Family : Fucaceae

Genus: *Cystoseira*

Species: *Cystoseira asmundaceae* .

Cystoseira is one of the most widely distributed genera of the Fucales order and provides an essential habitat for many epiphytes, invertebrates, and fish. *Cystoseira* is found mostly in temperate regions of the Northern Hemisphere, such as the Mediterranean, Indian, and Pacific Oceans. *Cystoseira* (as well as sargassum) are the largest algae in the Eastern Mediterranean. The *Cystoseira* has a developed holdfast that connects it to the substrate, and cylindrical or flattened branches that sometimes contain a central vein. *Cystoseira* resemble a branched bush. The division of holdfast, stipe (a thick ended stem like structure) and branch containing a central axis and leaf-like branches indicates the algal high level of development, although not as high as that of the Sargassum.



Fig 5: *Cystoseira asmundaceae*.

Most *Cystoseira* have air vesicles, which are a part of the stalk-like thallus and not to be found in separate organs, as in Sargassum. Many *Cystoseira* plants reach a length of 20 cm; an examination of an entire colony showed larger individuals reaching even 50 cm.

Cystoseira are shades of light brown and cream. Sometimes the color is uniform, and sometimes spots are evident. In water, they seem greener than outside, a result of return radiation by chlorophyll-a. Upon dehydration, the thallus gains a darker shade. Most *Cystoseira* plants are encountered in the upper regions of the intertidal zone, usually in places that are not exposed to the air during low tide. A small number of species are deep sea algae. *Cystoseira* depend on good water quality, and can be used for bioindication. This was

discovered in a study of *Cystoseira* species undertaken on Menorca (Yamaguchi *et al.*,

1997).

5. *Enteromorpha .sp.*

Kingdom: Protista

Phylum: Chlorophyta

Class: Ulvophyceae

Order :Ulvales

Family :Ulvaceae

Genus: *Enteromorpha*

Species: *Enteromorpha intestinalis*

(Mattox and Stewart, 1984).

Enteromorpha sp., within the genus *Enteromorpha* are very difficult to identify as differences between species are small and hard to spot. They are green seaweeds, with tubular and elongate fronds that may be branched, flattened or inflated. They are bright green in color and may occasionally be bleached white,



Fig 6: *Enteromorpha intestinalis*

particularly around rock pools. They attach to the substrate by means of a minute disc-like holdfast. The fronds of a species may vary in appearance due to changes in environmental conditions, which further confuses identification, and microscopic examination (Mattox, *et al.*, 1984).

6. *Chaetomorpha. Sp.* Kingdom: Protista

Phylum :Chlorophyta

Class: Ulvophyceae

Order: Ulvales

Family: Ulvaceae

Genus: *Chaetomorpha*

Species: *Chaetomorpha linum*

(Mattox and Stewart, 1984).

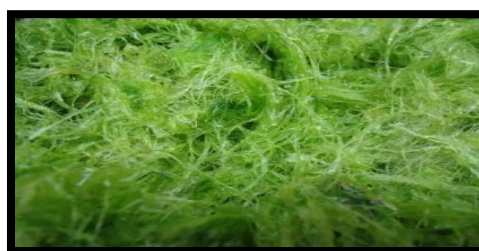


Fig 7: *Chaetomorpha linum*

its un branched filaments, making it distinctive; its closest relatives are branching species of the genus *Cladophora*.

Chaetomorpha is a genus of green algae in the family *Cladophora aceae*, Algae of this genus are made up of macroscopic filaments of cylindrical cells. The genus is characterized by

7. *Corallina. Sp*

Kingdom: Protista.

Division: Rhodophyta.

Class: Florideophyceae

Order: Corallinales..

Family: Corallinaceae.

Genus: *Corallina*.



Fig 8: *Corallina. Sp*

Corallina is a calcareous red seaweed which grows in the lower and mid- littoral zones on rocky shores. It is primarily found growing around the rims of tide pools, but can be found in shallow crevices anywhere on the rocky shore that are regularly refreshed with sea

water. It predominantly grows on the lower shore, especially where fucoids algae are absent, but is also found further up shore on exposed coasts. It forms calcium carbonate deposits within its cells which serve to strengthen the thallus.

2. Sample preparation:

1. Water Samples

Sea water samples were collected from each stations and stored in polyethylene bottles (1L), during two seasons: spring season 2016 (season 1), and summer seasons 2016 (season 2), The polyethylene bottles were previously cleaned with detergent, rinsed several times with distilled water.

2. Algae Samples

The algae were collected by manually, randomly, at several places on each beach, to a total of approximately 200 g of each alga, the samples were placed in separate plastic bags. Upon arrival at the laboratory, the algae were washed twice distilled water to remove remaining salts, sand, and epiphytes, then washed twice with NaCl (3.5%, w/v), blotted dry to remove excess water using laboratory blotting paper towel, then dried at air and milled using blender to produce analysis following.

3. Method of Digestion

Wet digestion procedure which described by Jones and Case (1990), was used, where 0.5 g of sample was placed in a 250 ml digestion tube and 3.5 ml of concentrated H₂SO₄ was added. The mixture was allowed to stand for 30 min at room temperature. About 10 ml of 30 % H₂O₂, was added to the digestion tube and the sample was then heated at 250° C for 30 min. Thereafter, the digestion tube was removed from the digestion block and cooled down, 1 ml of 30 % H₂O₂ was added until the digest was clear upon cooling, When the solution was clear following cooling, 42 filter paper and <0.45µm Millipore filter paper and transferred quantitatively to a 25 ml volumetric flask by adding distilled water (Zeng,2004).

4. Chemical Analysis:

4.1. Hydrographical Parameters Analysis

Some parameters were totally or partially measured in the field as soon as the sample was collected. (Fritioff, 2005).

4.2. Temperature Measurements (°C)

In situ, at each station, water temperatures were measured at the time of water sampling to the nearest 0.1 °C by using an ordinary

thermometer.

4.3 Salinity(S ‰)

Salinity was determined by measuring the electrical conductivity using an inductive Salinometer (Beckman; model RS-10).

4.4 Hydrogen-ion concentration (pH)

The pH-value of water sample was measured in the site immediately after collection using Bench type (JEN WAY, 3410 Electrochemistry Analyzer pH-meter).

4.5 Dissolved Oxygen (DO)

It was determined by using DO (MI/L) meter in the site.

4.6 Heavy Metal Analysis

The concentrations of (Pb ,Mn, Zn and Cd) in the final solutions were determined by an atomic absorption spectrometer (AAS) (Hitachi Z-8100,Japan).(Zeng, 2004).

5. Calculated variables Indices of pollution:

1. Bioaccumulation factor (BAF)

BAF of the studied metals was calculated according to the following formula of (El- Adl *et al.*, 2017).

BAF= Metal concentration (µg g⁻¹) in algal biomass / Metal concentration (µg l⁻¹) in sea water.

2. Metal pollution index (MPI)

It was used to compare the total content of heavy metals in algal biomass at different sites (El-Adl *et al.*, 2017).

MPI = (Cf1 × Cf2 × Cf3 ... × Cfn)^{1/n}

Where Cf1, Cf2, Cf3, ... Cfn are the concentrations of metal 1, metal 2 and metal (n) in the sample respectively.

3. Statistical analysis

The experiment was designed as completely randomized design with three replicates Analysis of variance was carried out using genstat software. Means were separated with Duncan's multiple range test at 5% level of significance.

Results & Discussion

Over many years the untreated sewage or wastewater discharges into the Derna coast area. The concentration of heavy metals in marine water and algae tissue are presented, in

an effort to gain some insight into the level of metal pollution which might exist in the coastal marine environment along the Derna beaches. Assessed by measuring some parameters of marine water as temperature, salinity, DO and pH, heavy metals as lead (Pb), zinc (Zn), manganese (Mn) and cadmium (Cd) concentration. Also, was determination of indices of pollution as bioaccumulation factor (BAF) and metal pollution index (MPI). These analyses are aimed at identifying the extent of the environmental pollution in Derna coast. This intertidal region is relatively uniform in character in some sites, consisting of a rocky substrate composed of large and numerous rocks, but sandy at other sites, which are exposed to different degrees of pollution.

1. Water Parameters Analyses

Temperature (°C): The absolute as well as the seasonal average values of surface water temperature at the different sites during the period from April 2016 to June 2016 shown graphically in Fig. (9). The water temperature (°C) measured in situ exhibited wide variations, which attains its maximum value of 32.1 °C in summer at S1 area and its minimum value of 21.2 °C in Spring 2016 at S5. The seasonal average values for the studied station (S1, S2, S3, S4, S5 and S6), fluctuated between (24.1°, 22.5°, 24.3°, 24.6°, 21.2°, 23.4°C) in spring 2016, and (32.1°, 27.4°, 31.6°, 27.5°, 27.5°, 28.3°C) in summer, Fig. (9).

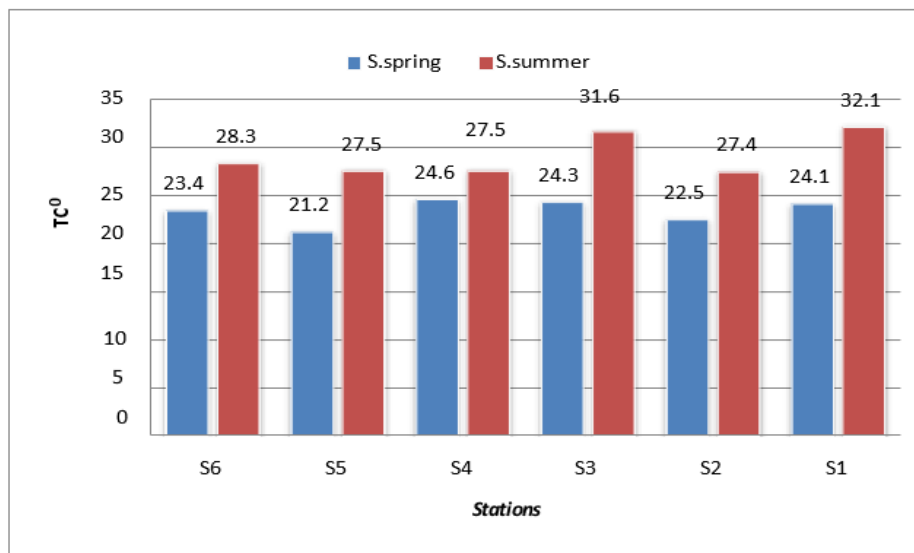


Fig 9: Average values of (TC°) of Derna coast in spring and summer seasons

Water temperature plays a substantial role in the aquatic system and can determine where aquatic life is found and the quality of the habitat. For example, water temperature can influence the metabolic rates of fish and the rate of photosynthesis of aquatic plants (and algae). Water temperature also plays a significant role in ocean circulation patterns and influences the distribution and mixing of nutrients (Castonguay et al.,1999). Water temperature is affected by: sunlight (solar radiation), atmospheric heat transfer, turbidity (water cloudiness), confluence of water bodies (rivers, streams, storm drains, etc.) depth, anthropogenic (human-induced) factors as you may have noticed by now, the water quality indicators we are attempting to collect data on are all linked in one way or another. Water temperature, however, has a major effect on

nearly every other water quality parameter we are attempting to observe and measure and is critical to any water monitoring program (Arnold and Peterson,1989; Avery,1994; Litzgus and Brooks,1998a).

1. Salinity (S ‰)

The absolute, as well as the seasonal and regional averages of salinity in the surface water during the seasons of study are reported graphically in fig.(10). Salinity of coast water showed wide variations, which directly reflects the influence of dilution with domestic, industrial and fresh water discharge. The seasonal average values for the studied station in spring and summer respectively, fluctuated between (37.8–34.5), (38.4–36.2), (38.4–35.9), (38.2–38.2), (37.7–36.7), and (38.4–35.6) ‰ from study site S1 to S2 respectively. Salinity,

as temperature, is one of the most important limiting factors of biological distribution in

aquatic environment.

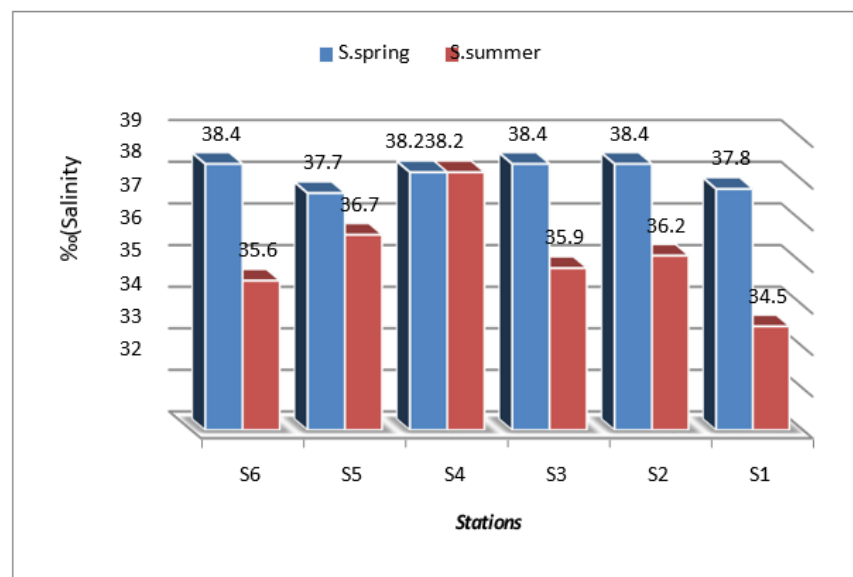


Fig 10: Average values of salinity (S ‰) of Derna coast in spring and summer seasons

In the present investigation, salinity was used as indicator to reflect changes resulting from mixing of fresh and seawaters. The levels of salinity ranged between 38.4‰ during spring in S2, S3, and S6, this is resulted of mixing surface water with deeper and higher saline waters as an effect of the wind system while recorded 34.5‰ during summer in S1, may be due to the high amounts of drainage water enter in the water coast Derna. It is noticed that variation in salinity during the period of investigation at each station is relatively limited. Salinity is simply the measure of dissolved salts in water. Salinity is usually expressed in parts per thousand (ppt) or ‰. The average salinity of ocean water is 35 ppt. Plants and animals are often sensitive to changes in salinity and salinity levels control local species composition. Abear, (2014) reported that, salinity of surface water is markedly fluctuated and depending mainly upon ionic influences of drainage, exchange with the surrounding land, atmospheric sources, as well as the equilibrium and exchange with sediment inside the water body, natural water's salinity is influenced further by depth, latitude and the mode of water percolation, as salinity increases at the surface by evaporation, water becomes denser and tends to sink to a level where equilibrium can be achieved. These events can change the condition of the water as the concentration of dissolved mineral salts typically increases with these types of events (which tend to decrease

general water quality).

2. Hydrogen Ion Concentration (pH)

Hydrogen ion concentration (pH) values of the surface water at the Derna coast, these data are reported graphically in fig (11). The pH-values ranged between a minimum of (7.10) and a maximum of (8.32) the pH-values tended to increase at some locations during summer season. It is obvious that the values of pH showed slight local variations. The hydrogen ion concentration is not only a measure of potential pollutant but also it is related to the concentrations of many other substances, particularly the weakly dissociated acids and bases, it may be considered as a highly significant factor in determining the concentration of un-dissociated and ionic compounds, since the un-dissociated compounds are frequently more toxic than the ionic forms, pH may be a highly significant factor in determining or limiting the threshold concentration. It reflects the position of many equilibriums in aquatic environments, such as the carbon dioxide system, the iron and sulphur cycles. These in turn are linked to important biological processes such as photosynthesis, respiration and bacterial activity (Abdel-Halim, 2004). Various authors have observed that solution pH is an important parameter affecting heavy metal bio sorption by seaweed species (Chen *et al.*, 2002).

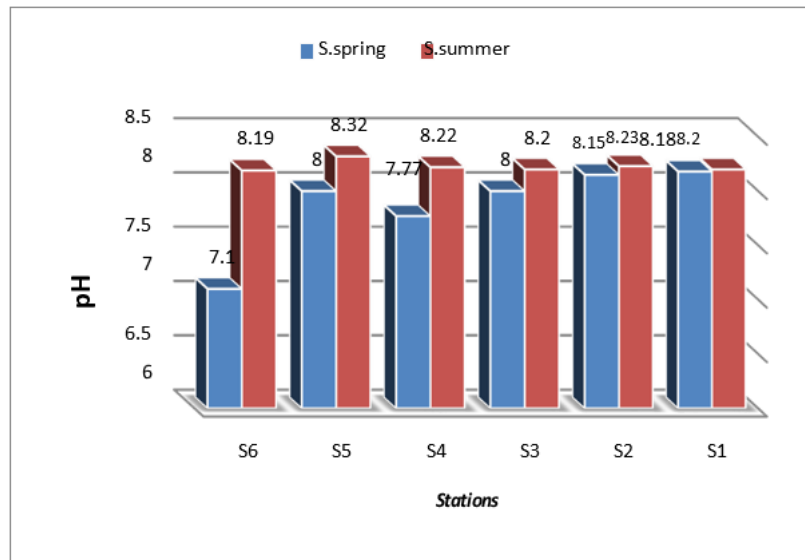


Fig 11: Average values of (pH) of Derna coast in spring and summer seasons

The pH is measured on a 14 point scale. A pH of 7 (pure water) is neutral; a pH higher than 7 is basic (alkaline); and less than 7 is acidic. pH is measured on a logarithmic scale. This means that each 1.0 change in pH (positive or negative) is a difference of a factor of 10. Thus a pH of 8.0 is 10 times more basic than 7.0 and 100 times more basic than 6.0. The average pH for sea water is 8.2 but can range between 7.5 and 8.5 depending on the local conditions. The pH of water in coastal areas and enclosed seas normally ranges from 7.9 to 8.2. Human activities such as sewage overflows or runoff, can cause significant short-term fluctuations in pH and long-term impacts can be extremely harmful to plants and animals. Extreme changes in pH, can stress local organisms and may ultimately lead many species to leave the area or die (Dromgoole, 1978).

Peckol *et al.*, (1994); Beijer, (1979), reported that sewage is discharged into the oceans all over the world mostly from urban settlement, sewage adds to the amount of small particles suspended in the water column and contributes large amounts of nutrients, so affecting directly pH for sea water and all marine organisms. Peterson *et al.*, (1984) reported that, pH potential affects the bioavailability of metals in

solution; at high pH elements are present as cations, while at low pH the bioavailability of metals ions is enhanced. Stokes, (1983) said that, it is known, however, that metals in seawater may exist in either particulate, or dissolved form mainly determined by the properties of a particular metal and other factors, such as pH, salinity, redox potential, ionic strength, alkalinity, persistent organic and particulate organic matter, and biological activity.

3. Dissolved Oxygen (DO)

The average of dissolved oxygen, (ml/L) in the Derna coast, during the year of study are given in illustrated graphically in fig.(12). In the present investigation, most of seawater was well oxygenated at all stations, The distribution pattern of DO at the different stations varied according to season from a minimum of (3.61 ml/L) at S1 in summer to a maximum of (11.43 ml/L) at S3 in spring, with respect to seasonal averages, spring and summer represent moderate oxygenated condition (4.25, 3.61 ml/L respectively) at S1, (8.37, 5.44 ml/L) at S2, (11.43, 8.32 ml/L) at S3, (7.43, 5.65 ml/L) at S4, (5.22, 6.78 ml/L) at S5 and (9.32, 8.11 ml/L) at S6.

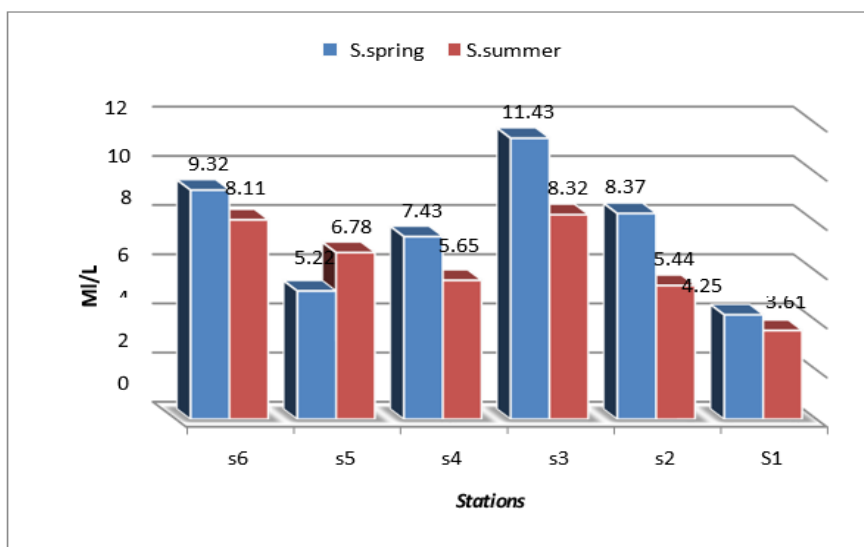


Fig 12 : Average values of (DO) of Derna coast in spring and summer seasons.

Abear, (2014) reported that the dissolved oxygen (DO) is an important and useful parameter for identification of different water masses. It has been used as basic water criteria in assessing the degree of pollution in any aquatic environment. DO is a fundamental requirement for the aquatic organisms, it affects their biological processes and is needed in the aerobic oxidation of the organic matter in water. In the latter process, complex organic

substances are converted to simple dissolved inorganic salts, which could be utilized by micro and macrophyta. A positive correlation was found between dissolved oxygen (DO) and salinity (S‰) ($r^2= 0.897^*$) and, a negative correlation was found between other parameters. A negative correlation was found between PH with salinity, also between PH and dissolved oxygen (DO) table 2.

Table 2: Correlation coefficients between Hydrographical Parameters.

Environmental parameters	TC°	S (‰)	DO (mg/l)	pH
TC°	1			
(S ‰)	0.388	1		
DO (mg/l)	0.319	0.897*	1	
pH	0.257	-0.551	-0.640	1

*<0.05.

4. Heavy Metals

The value of algae as bio-indicators has already been recognized in the mid of 19th century (Naicheng, 2014). Sea grass or macroalgae can be used as bio-monitors to give information on concentrations of heavy metal or changes in metal availabilities in the surrounding environment, besides their abundance in various environmental systems (Capiomont *et al.*,2000; Campanella ,2001). In general, algae are widely distributed in the aquatic environment and are sedentary, easy to collect, identify, and the bioaccumulation of trace metals occur in high degrees; satisfying all the fundamental requirements for bio indicators (Campanella *et al.*, 2001). These algae were chosen to conduct the investigation as bio-indicators for heavy metals pollution of Derna city coastal area at the east of Libya. Because

they were almost available in all sites during field study. Due to their short life cycle, algae respond quickly to environmental changes and are thus a valuable indicator of water pollution (Domingues, 2007).

Many of the chemicals tested are basic parts of components of domestic and sewage sludge. The nature of any potentially toxic substances depends mainly on the types of wastes entering the sewage system. Heavy metals are common types of toxic substance present in sewage sludge that affect aquatic life. The concentrations of four heavy metals examined in seven algae samples collected from six stations from Derna coast in the year of 2016 are shown in tables 3 and 4 and represented graphically in figures (13) and (14). The concentrations of various toxic heavy metals

were determined in all of the collected algal samples, including Pb, Mn, Zn and Cd are important to mention here all sites have different characteristics and peculiarities that are of great important effect on the levels of

heavy metals found in algae, were some of sites contains pollutants such as sewage and waste from local activities, while other sites, were selected free from contaminants.

Table 3: Average heavy metals concentrations ($\mu\text{g g}^{-1}$ dry weight) in the selected marine macroalgae collecting during two seasons 2016, along stations of Derna coast.

Algae	Pb	Mn	Zn	Cd
<i>Chaetomorpha sp.</i>	1.104 ^C	1.876 ^A	0.747 ^C	0.01AB
<i>Corallina sp.</i>	1.068 ^C	1.883 ^A	0.818 ^B	0.01 AB
<i>U. lactuca</i>	0.961 ^D	1.961 ^A	0.694 ^D	0.01 B
<i>Laurencia sp</i>	1.182 ^B	1.675 ^B	0.861 ^A	0.02C
<i>Amphiroa anceps</i>	0.754 ^F	0.709 ^D	0.695 ^D	0.01 C
<i>Cystoseria asmundaceace</i>	0.839 ^E	0.869 ^D	0.721 ^{CD}	0.01 C
<i>Enteromorpha sp.</i>	1.228 ^A	1.167 ^C	0.867 ^A	0.01A

^{a - d}.means followed by same letters are not significantly different according to Duncan's multiple range test at 5% significance level.

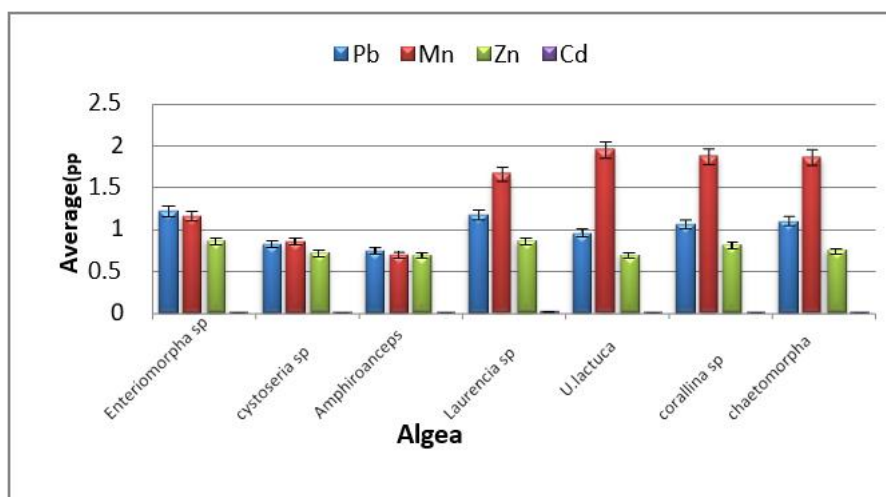


Fig. 13: Average heavy metals concentrations ($\mu\text{g g}^{-1}$) in the selected marine macroalgae collecting during 2016, along stations of Derna coast.

i) Lead (Pb)

When these data were analyzed by using genstat software (Table3) and subsequent Duncan test for comparison of averages, the results show that there is a statistically significant difference for averages of concentration of (Pb) between algae species overall. It can be realized from the results gained that *Enteromorpha sp.*, was superior to other species tested as it showed the highest concentration $1.228 \mu\text{g g}^{-1}$, (regardless of sampling site or seasons). Among the seven species studied *Enteromorpha sp.*, had the highest capacity for metal accumulation of Pb and Zn, were similar to those found by Astorga-España *et al.*, (2008), and could therefore be considered as a biomonitor for

future studies in the area. Followed by *Laurencia sp.*, $1.182 \mu\text{g g}^{-1}$. Comparison of the averages indicated a statistically significant differences among them, and with other species. On the other hand, there was no significant differences between *Chaetomorpha sp.*, and *Corallina sp.* However, the species (*U. lactuca*, *Cystoseria sp.*, and *Amphiroa anceps*) showed significant differences among each other and the previously mentioned species, with the *Amphiroa anceps*, showed the lowest concentration $0.754 \mu\text{g g}^{-1}$ (regardless of sampling site or seasons). According to Shiber and Shatila, (1979), the metals levels, particularly of lead seem to be rather high and may, in part, be due to untreated domestic sewage, industrial effluent, automobile

exhaust, and outdoor incinerator. It must be taken into account that the variation in data in the literature, as well as being due to different amounts of contaminants in the environment, may also be related to factors such as the different analytical methods used, seasonal variations, salinity in the sampling area, etc.

The highest rate of lead (Pb) was recorded in S6 $1.396 \mu\text{g g}^{-1}$ (regardless of algae or seasons), which have significant differences with other stations, regardless of their averages. Followed by the S5 $1.026 \mu\text{g g}^{-1}$, which show that there is a statistically significant difference for averages of concentration of metals with other stations: S2, S3, S4 and S1 (0.945 , 0.921 , 0.898 and $0.927 \mu\text{g g}^{-1}$), respectively. The rate of (Pb) was recorded in both S1, and S3 0.927 and $0.921 \mu\text{g g}^{-1}$, respectively, (they no significant differences between them) but have significant differences with other stations, regardless of their averages (Table 4).

ii) Manganese (Mn)

The highest concentration of (Mn) was recorded in the *U. lactuca*, *Corallina sp.*, and *Chaetomorpha sp.*, (regardless of sampling site or seasons). Comparison of the average indicated statistically no significant differences between *U. lactuca*, *Corallina sp.*, and *Chaetomorpha sp.*, while there is showed a statistically significant difference with other species. The results show that there is a statistically significant difference for averages of concentration of (Mn) between *Laurencia sp.*, and *Enteromorpha sp.*, as well both with other species. While, scored the lowest rate of (Mn) in *Amphiroa anceps sp.*, and *Cystoseria sp.*, which there is showed a statistically no significant difference among them. Chakraborty *et al.*, (2014) reported that the Mn concentration in the algae revealed major spatial differences which might be due to differential background Mn concentrations resulting from selective anthropogenic sources.

The highest rate of manganese metal (Mn) was recorded in both S1, and S3 1.799 and $1.718 \mu\text{g g}^{-1}$, respectively, (they no significant differences between them.) but have significant differences with other stations, regardless of their averages. Followed by the S2, S6 and S4, which they no significant

differences between them, but have significant differences with other stations, regardless of their averages. For S5, they recorded the lowest rate of manganese $0.977 \mu\text{g g}^{-1}$, which have a significant difference with other stations (Table 4).

iii) Zinc (Zn)

In the present study (regardless of sampling site or seasons) recorded higher concentrations of $0.867 \mu\text{g g}^{-1}$ dry weights, in the *Enteromorpha sp.*, and *Laurencia sp.* $0.861 \mu\text{g g}^{-1}$, which have no significant differences between them, regardless of their averages. Brown *et al.*, (1999) reported a significantly higher levels of Zn in *E. sp.*, than in *U. lactuca*. The average of concentrations in *Corallina sp.* $0.818 \mu\text{g g}^{-1}$, *Chaetomorpha sp.*, $0.747 \mu\text{g g}^{-1}$ and *Cystoseria sp.* $0.721 \mu\text{g g}^{-1}$ respectively. In addition, there are no significant differences between the *U. lactuca* $0.694 \mu\text{g g}^{-1}$ and *Amphiroa anceps* $0.695 \mu\text{g g}^{-1}$, which recorded the lowest value of zinc concentration.

The highest rate of Zinc (Zn) was recorded in S6 $1.037 \mu\text{g g}^{-1}$ (regardless of algae or seasons), which have significant differences with other stations, regardless of their averages. Followed by the S5 $0.796 \mu\text{g g}^{-1}$, which show that there is a statistically significant difference for average of concentration of metals with other stations: S2, S3, S4 and S1 (0.638 , 0.749 , 0.664 and $0.748 \mu\text{g g}^{-1}$), respectively. The rate of (Zn) was recorded between S1, and S3 they no significant differences between them but have significant differences with other stations, regardless of their averages. As well as, between S2, and S4 they no significant differences between them) but have significant differences with other stations, regardless of their averages.

iv) Cadmium (Cd)

In general, Cadmium recorded low values irrespective of sites and algal species. According to El-Adl *et al.*, (2017) (Cd) was the least accumulated heavy metal along Al-Hanyaa Coastline, Libya. The (Cd) is exceptionally toxic even at very low concentrations which necessitates the study of (Cd) contamination sources as well as its distribution in marine ecosystems. The (Pb), (Mn) and (Zn) concentration is several times higher than the (Cd) concentration, but both

elements are present in the macroalgae in concentrations that should not substantially affect the algal life cycle (Strezov and Nonova,

2003). The cadmium recorded very low values in all station (Table 4).

Table 4: Average heavy metals concentrations ($\mu\text{g g}^{-1}$ dry weight), during seasons 2016, along stations of Derna coast.

Station	Pb	Mn	Zn	Cd
S1	0.927 ^{CD}	1.799 ^A	0.748 ^C	0.01B
S2	0.945 ^C	1.484 ^B	0.638 ^D	0.02A
S3	0.921 ^{CD}	1.718 ^A	0.749 ^C	0.01 B
S4	0.898 ^D	1.326 ^B	0.664 ^D	ND c
S5	1.026 ^B	0.977 ^C	0.796 ^B	ND c
S6	1.396 ^A	1.387 ^B	1.037 ^A	ND c

^{a - d}. means followed by same letters are not significantly different according to Duncan's multiple range test at 5% significance level.

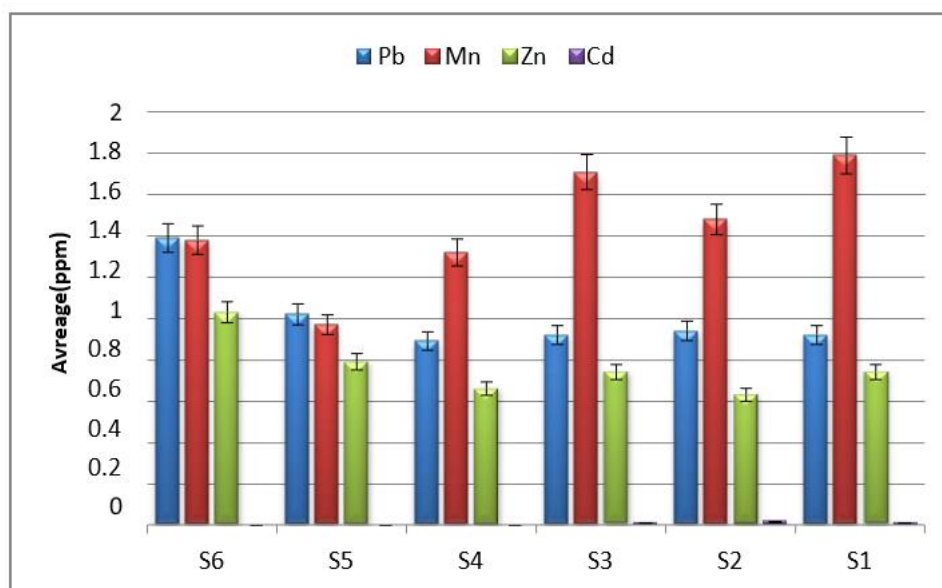


Fig 14: Average heavy metals concentrations ($\mu\text{g g}^{-1}$ dry weight), during 2016, along stations of Derna coast.

The fact that the most macro algae are proven bio-monitors gives us a reason to assess the contamination of the marine ecosystem at the observed six locations. The region of S6 can be identified as a place with higher Pb and Zn contents while the region of S1 shows higher contents of Mn. As well the region of S2 shows higher contents of Cd. The investigated heavy metals, however, are present in the macroalgae in concentrations that should not significantly affect their development and spreading. The different of metal contents in most species and the comparatively similar values in the different regions suggest an absence of specific geographically dependent contamination (Table 4).

There are several possible explanations for these findings including: These results may be

explained by the natural ability of certain species to evolve adaptive mechanisms of decontamination, including the extra cellular release of certain compounds. Another possibility is that metals was not present in a bio-available form and also very dependent on the species evaluated. (Strezov and Nonova, 2003). Different factors, such as turbidity, nutrient availability, light intensity, salt content and temperature can, among others, alter growth rates of macro algae. These factors contribute to the variability of the results obtained and make difficult the inter-site comparison of metal levels in the different species evaluated (Merz, Sinclair Knight 2013). Even when these factors have been minimized in the present study, as all the species were collected under the same conditions, a wide variation in metal content

was observed in the different species.

5. Heavy metals during two seasons:

The metals concentrations recorded for the different tissues and sites of the present study confirm the occurrence of significant seasonal variability, with maximum concentrations usually observed in summer. Such seasonal variability in metal concentrations have been reported by other authors for Pb and Cu in *Posidonia oceanica* (Malea *et al.*, 1994), for Cd, Cu, Pb and Zn in *Posidonia australis* (Ward, 1987), and for Cd, Cu, Pb and Zn in *Zostera marina* L. (Lyngby and Brix, 1982). The latter authors found that maximum concentrations of heavy metals were recorded when the growth has ceased, and decline of these metals occurred at the beginning of the growth season.

In this study, the concentrations of zinc, lead and manganese in algae varied seasonally, the concentrations collected in summer show exhibiting significantly higher metals levels than those of individuals collected during the spring. Except the concentration of cadmium in algae in spring exhibiting significantly higher metals levels than those of individuals collected during the summer, as reported in table (7).

The all species used in the present study have different capacities for metal concentration as reported in table 7. The average of concentrations of Lead in algae showed that the summer season recorded the highest value at $1.16 \mu\text{g g}^{-1}$ dry weights, while spring showed the lowest at $0.82 \mu\text{g g}^{-1}$ dry weights, also the seasonal variations of manganese in algae showed that the summer season recorded the highest value at $1.62 \mu\text{g g}^{-1}$ dry weights, while spring showed the lowest at $1.27 \mu\text{g g}^{-1}$ dry weights, as well the concentration of Zinc in algae showed that the summer season recorded the highest value at $0.90 \mu\text{g g}^{-1}$ dry weights, while spring showed the lowest at $0.61 \mu\text{g g}^{-1}$ dry weights, in contrast to other metals, the average concentrations of Cd was slightly higher in spring, with $0.009 \mu\text{g g}^{-1}$ dry weights, Compared with the summer at $0.002 \mu\text{g g}^{-1}$ dry weights.

Generally, as previously reported by many

authors as (Akcali and Kucuksezgin, 2011; Brown *et al.*, 1999), there may be a number of reasons for the seasonal differences found, including: environmental factors, such as variations in metal concentrations in solution, interactions between metals and other elements, salinity, pH etc., metabolic factors, such as dilution of metal contents due to growth; or they may be due to interactions between both kinds of factors, different genetic capacities for metals concentration.

Table 5: Average heavy metals concentrations ($\mu\text{g g}^{-1}$ dry weight), during spring and summer seasons 2016, along stations of Derna coast (regardless of sampling algae and stations).

Seasons	Metals			
	Pb	Mn	Zn	Cd
Spring	0.82	1.27	0.61	0.009
Summer	1.16	1.62	0.90	0.002

7. Heavy Metals Concentration in Algae:

1. *U. lactuca*.

The concentration of Pb in the *U. lactuca* fluctuated between 0.70 ± 0.2 ($\mu\text{g/g}$); dry weight in Spring at the S5 to 1.58 ± 0.01 ($\mu\text{g/g}$); dry weight and in summer at the S6. S5 also recorded high values in summer 1.49 ± 0.03 ($\mu\text{g/g}$) dry weight. The highest Mn concentration level 3.03 ± 0.03 ($\mu\text{g/g}$) in *U. lactuca*, was recorded in summer for three samples collected from S1, S2 and S3 Average while the S3 recorded relatively high Mn concentration in the spring 2.47 ± 0.02 ($\mu\text{g/g}$) dry weight. While the lowest values were detected in both spring and summer for the S5 and S6 (1.14 ± 0.03 and 0.61 ± 0.1 ($\mu\text{g/g}$) dry weight, respectively). In *U. lactuca*, maximum values of Zn were found at stations S2 in summer, and S1 in spring, with 1.12 ± 0.03 and 0.77 ± 0.008 ($\mu\text{g g}^{-1}$), respectively. Minimum levels of Zn were found at S6 in spring and S3 in summer, with 0.32 ± 0.01 and 0.72 ± 0.04 ($\mu\text{g/g}$), respectively.

U. lactuca which are the indicator of heavy metal pollution, were studied on the north west coast of Spain (Villares *et al.*, 2001; Akcali and Kucuksezgin, 2011) detected recorded lower values for Pb than that

reported in the present study. On the other hand, *U. lactuca* recorded a lower value of Pb than that recorded by Ramírez *et al.*, (1990) for algae collected from the Northern Littoral, Cuba, Strezov and Nonova ,(2003) in the Tyrrhenian Sea, Atlantic Ocean, and Black Sea, Caliceti *et al.*, (2002) in the *U. lactuca*, of the Venice lagoon in Italy.

The present data, show the *U. lactuca* recorded a lower value of (Mn) than that recorded by Ramírez *et al.*, (1990); Villares *et al.*, (2001); Strezov and Nonova (2003). Average while, our values of (Zn) for *U. lactuca* were very lower to those obtained by Catsiki & Papatthanassiou (1993); Villares *et al.*, (2001); Ramírez *et al.*, (1990); Strezov and Nonova (2003). The value of average concentration for (Cd) was in this study, lower than to those found by Strezov and Nonova (2003) for *U.*

lactuca, collected in the Tyrrhenian Sea, Atlantic Ocean, and Black Sea. Also Caliceti *et al.*, (2002),in the *U. lactuca* of the Venice lagoon in Italy.

In some instances, the value of average concentrations of (Zn) registered for a metal was in this study, comparable to those found by some authors in different species of algae, as reported by Muse *et al.*, (1999) for *U. lactuca*. While, the value of average concentration for (Zn) was in this study, higher than to those found by Culha *et al.*, (2013) for *U. lactuca*, in marine algae in Ordu station in Black Sea. Also, the value of average concentration for (Pb) was in this study, higher to those found by Culha *et al.*, (2013) for *U. lactuca*, in marine algae samples of all sampling stations in Black Sea, Marmara Sea and Mediterranean Sea. Also by Sawidis *et al.*, (2001) in the Aegean Sea, Greece.

Table 6: Average concentrations ($\mu\text{g g}^{-1}$ dry weight) with standard error of metals in *U. lactuca*, collecting during spring and summer seasons 2016, along stations of Derna coast.

tations	Metals							
	Pb		Mn		Zn		Cd	
	Spring	Summer	Spring	Summer	Spring	Summer	Spring	Summer
S1	0.90±0.005	0.91±0.01	1.79±0.01	3.01±0.03	0.77±0.008	0.91±0.07	0.006±0.01	0.003±0.01
BAF	1.91	1.68	4.83	7.16	4.52	4.33	0	1.5
S2	0.77±0.02	0.93±0.02	1.75±0.02	3.03±0.06	0.44±0.02	1.12±0.03	0.01±0.06	0.05±0.01
BAF	5.13	4.65	7.29	9.77	4	6.58	0	50
S3	0.71±0.01	0.95±0.008	2.47±0.02	3.03±0.03	0.52±0.01	0.72±0.04	0.006±0.002	0.008±0.00
BAF	4.43	4.52	6.86	7.39	1.85	2.05	0	4
S4	0.80±0.017	0.99±0.01	1.85±0.04	1.91±0.06	0.53±0.03	0.78±0.008	0.003±0.01	0.004±0.02
BAF	6.66	4.95	4.51	3.67	1.82	2.51	0	1
S5	0.70±0.2	1.49±0.03	1.14±0.03	1.99±0.07	0.61±0.01	0.79±0.003	0.008±0.01	0.005±0.02
BAF	1.89	3.63	3.16	4.42	2.17	2.19	0	1
S6	0.76±0.03	1.58±0.01	1.28±0.04	1.61±0.1	0.32±0.01	0.86±0.02	0.004±0.00	0.004±0.01
BAF	6.33	7.52	4.57	5.19	0.78	1.65	2	1

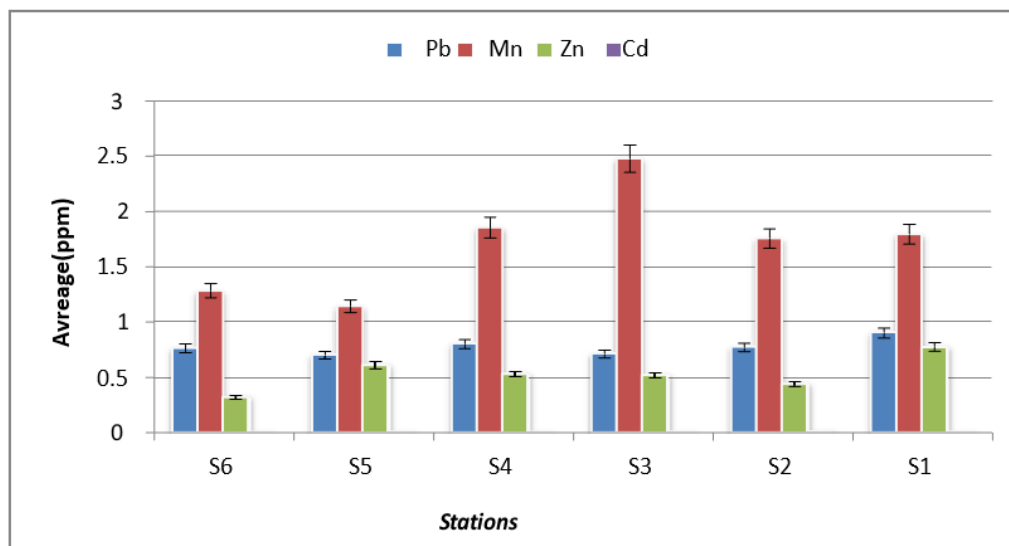


Fig 15: Average concentrations ($\mu\text{g g}^{-1}$ dry weight) in *U. lactuca*, collecting during spring season

2016, along stations of Derna coast.

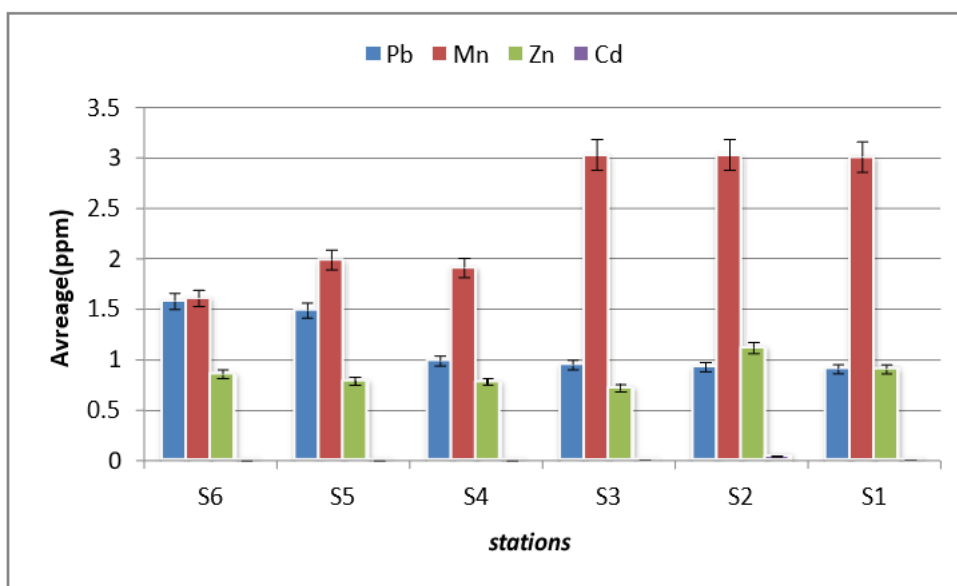


Fig 16: Average concentrations(µg g⁻¹ dry weight) in *U. lactuca*, collecting during summer season 2016, along stations of Derna coast.

2. *Laurencia sp.*

The present data revealed of *laurencia sp.*, the S6 recorded the highest concentration of Pb (1.95±0.01 and 1.50±0.03 (µg/g) dry weight) in summer and spring. On the other hand, the *laurencia sp.*, recorded the lowest Pb values at both the S5 0.55±0.2 (µg/g) and S3 0.85±0.06 (µg/g) in spring and summer, respectively (Table7). For *laurencia sp.*, the S3 recorded the highest concentration of Mn (2.14±0.03 and 2.96±0.02 (µg/g dry weight) in summer and Spring, respectively. On the other hand, the *laurencia sp.*, recorded the lowest Mn values at the S5 0.52±0.03 and 0.86±0.07 (µg/g) in

spring and summer, respectively (Table7). To compare the present study with those previously studied by many authors revealed that *Laurencia sp* recorded Pb, Zn, Cd and Mn concentrations lower than that recorded in the literature by Ramírez *et al.*, (1990) for algae collected from the Northern Littoral, Cuba, Khaled *et al.*, (2014) for algae collected from the Marsa-Matrouh beaches, Egyptian in Mediterranean Sea. While, the value of average concentration for (Pb) was in this study, higher to those found by Sawidis *et al.*, (2001) for *Laurencia obtusa*, in the Aegean Sea, Greece.

Table7: Average concentrations (µg g⁻¹ dry weight) with standard error of metals in *Laurencia sp.*

Stations	Metals							
	Pb		Mn		Zn		Cd	
	Spring	Summer	Spring	Summer	Spring	Summer	Spring	Summer
S1	0.8±0.03	1.58±0.01	1.89±0.01	1.61±0.03	0.41±0.008	0.86±0.07	0.002±0.01	0.004±0.01
BAF	1.70	2.92	5.10	3.83	2.41	4.09	0	2
S2	1.42±0.04	1.56±0.01	1.09±0.02	2.03±0.06	0.78±0.02	0.92±0.03	0.005±0.06	0.00±0.01
BAF	9.46	7.8	4.54	6.54	7.09	5.41	0	0
S3	0.90±0.01	0.85±0.06	2.96±0.02	2.14±0.03	1.09±0.01	0.87±0.04	0.006±0.002	0.02±0.00
BAF	5.62	4.04	8.22	5.21	3.89	2.48	0	10
S4	1.16±0.03	0.92±0.01	2.16±0.04	1.86±0.06	0.72±0.03	0.84±0.008	0.007±0.01	0.005±0.02
BAF	9.66	4.6	5.26	3.57	2.48	2.70	0	1.25
S5	0.55±0.2	0.93±0.03	0.52±0.03	0.86±0.07	0.26±0.01	0.70±0.003	ND	0.00±0.02
BAF	1.48	2.26	1.44	1.91	0.92	1.94	0	0
S6	1.50±0.03	1.95±0.01	1.12±0.04	1.82±0.1	0.92±0.01	1.93±0.02	ND	0.000±0.01
BAF	12.5	9.28	4	5.87	2.24	3.71	0	0

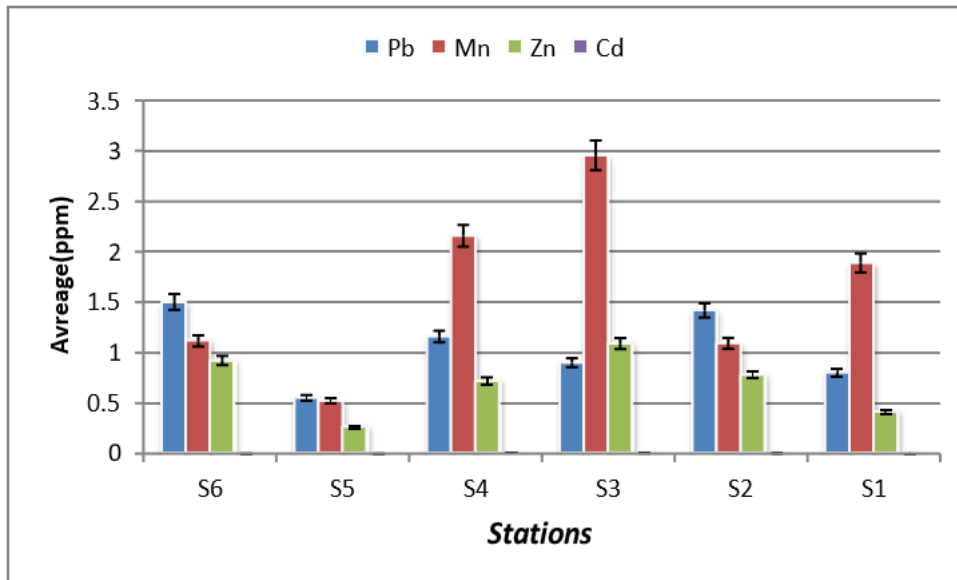


Fig 17: Average concentrations ($\mu\text{g g}^{-1}$ dry weight) in *laurenica sp.*, collecting during spring season 2016, along stations of Derna coast.

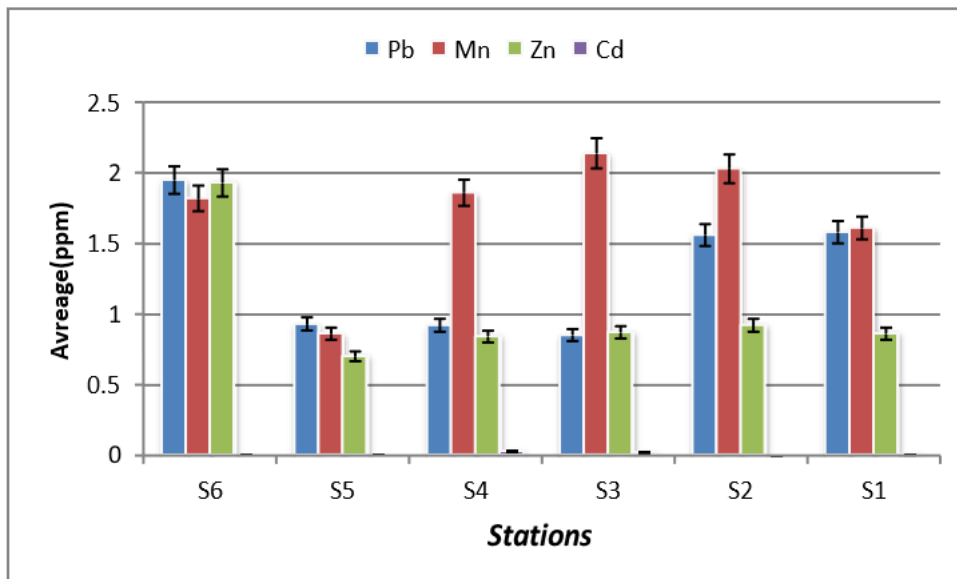


Fig 18: Average concentrations ($\mu\text{g g}^{-1}$ dry weight) in *laurenica sp.*, collecting during summer season 2016, along coastal .

3. *Amphiro anceps*

The *Amphiro anceps* algae collected from the S6 at summer recorded the highest concentration of Pb level 1.27 ± 0.3 ($\mu\text{g/g}$) dry weight) followed by that collected from the both S4 and S5 at the same season (0.92 ± 0.03 ($\mu\text{g/g}$) dry weight). *Amphiro sp* algae, collected from the S6 recorded the highest concentration of Mn (1.18 ± 0.09 and 0.79 ± 0.09 ($\mu\text{g/g}$) dry weight) in summer and Spring, respectively. On the other hand, the *Amphiro sp.*, recorded the lowest Mn values at the S4 0.32 ± 0.06 ($\mu\text{g/g}$) in spring (Table8). *Amphiro sp* algae recorded a relatively

high Zn concentration in summer at the S6 (1.19 ± 0.06 and 0.91 ± 0.01 ($\mu\text{g/g}$) dry weight) in summer and spring, respectively. While recorded their lowest values in spring at the S4 (0.21 ± 0.01 and S2 0.61 ± 0.04 ($\mu\text{g/g}$) dry weight) in spring and summer, respectively. In the natural aquatic environment, heavy metals occur at low concentrations (nano gram to micrograms per litre). Occurrence of heavy metals in excess of the mentioned natural loads indicates the presence of additional external sources (Lobban and Harrisson, 1994).

Table 8: Average concentrations ($\mu\text{g g}^{-1}$ dry weight) with standard error of metals in *Amphiro sp.*

Stations	Metals							
	Pb		Mn		Zn		Cd	
	Spring	Summer	Spring	Summer	Spring	Summer	Spring	Summer
S1	0.57±0.01	0.85±0.03	0.44±0.02	0.82±0.1	0.54±0.007	0.78±0.008	0.001±0.01	0.003±0.01
BAF	1.21	1.57	1.18	1.95	3.17	3.71	0	1.5
S2	0.33±0.02	0.73±0.03	0.60±0.02	0.94±0.02	0.26±0.02	0.61±0.04	0.002±0.06	0.003±0.01
BAF	2.2	3.65	2.5	3.03	2.36	3.58	0	3
S3	0.71±0.05	0.85±0.02	0.49±0.03	0.74±0.02	0.57±0.06	0.92±0.03	0.002±0.002	0.001±0.00
BAF	4.43	4.04	1.36	1.80	2.03	2.62	0	0.5
S4	0.59±0.1	0.92±0.03	0.32±0.06	0.81±0.03	0.21±0.01	0.70±0.03	0.003±0.01	0.005±0.02
BAF	4.91	4.6	0.78	1.55	0.72	2.25	0	1.2
S5	0.43±0.08	0.92±0.03	0.59±0.03	0.74±0.03	0.71±0.03	0.90±0.01	0.00±0.0	0.00±0.0
BAF	1.16	2.24	1.63	1.64	2.53	2.5	0	0
S6	0.85±0.03	1.27±0.3	0.79±0.09	1.18±0.09	0.91±0.01	1.19±0.06	0.00±0.00	0.00±0.0
BAF	7.08	6.04	2.82	3.80	2.2	2.28	0	0

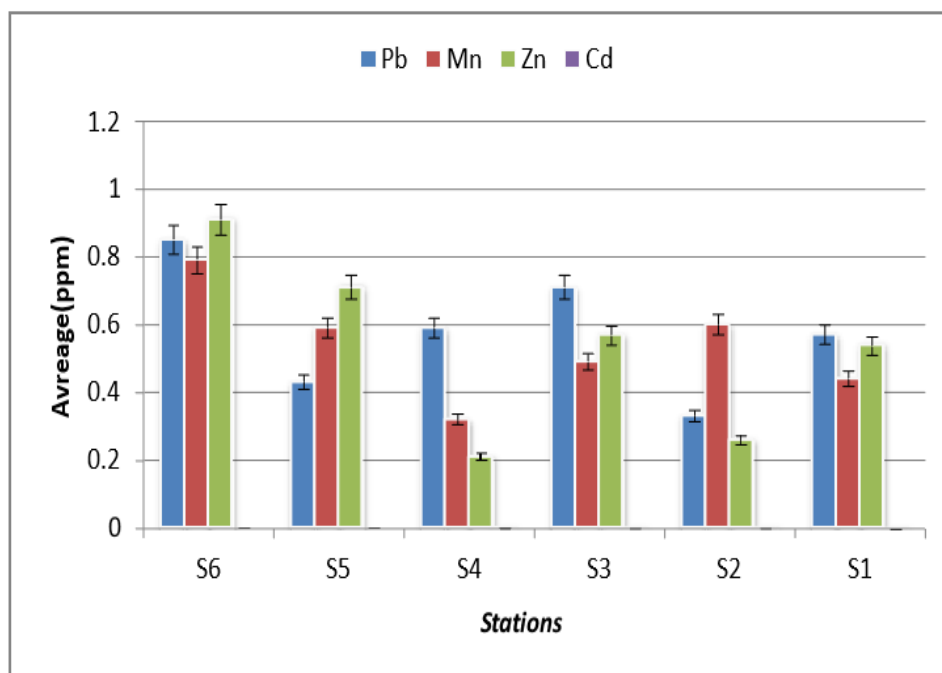


Fig 19: Average concentrations($\mu\text{g g}^{-1}$ dry weight) in *Amphiro sp.*, collecting during spring season 2016, along stations of Derna coast.

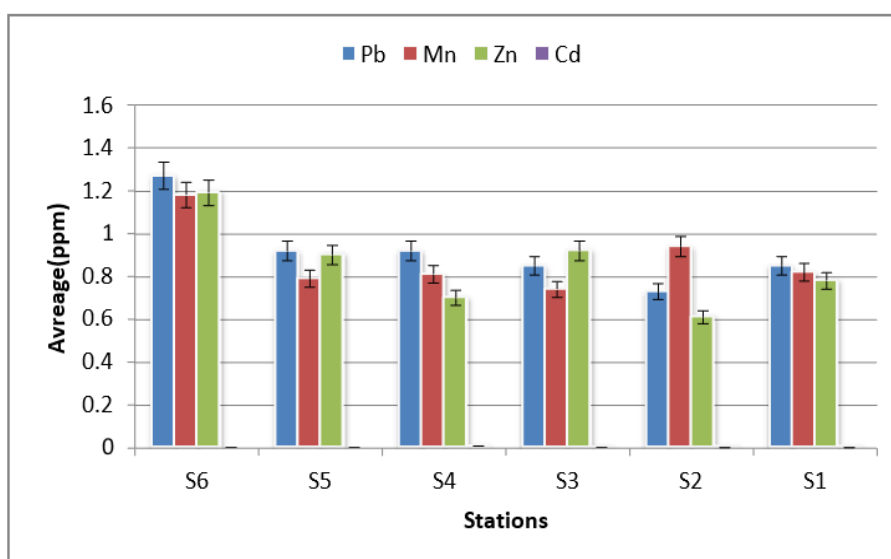


Fig 20: Average concentrations ($\mu\text{g g}^{-1}$ dry weight) in *Amphiroanceap sp.*, collecting during summer season 2016, along stations of Derna coast.

4. *Cystoseria sp.*

The present data revealed of *Cystoseria sp.* (Brown algae) recorded a relatively high Pb concentration in summer at the S6 (1.50 ± 0.3 ($\mu\text{g/g}$) dry weight). while recorded their lowest values in summer and spring at the S3, S5 (0.78 ± 0.02 and 0.40 ± 0.08 ($\mu\text{g/g}$) dry weight) respectively. The *Cystoseria sp.*, recorded a relatively high Mn concentration in summer and spring at the S1 (1.74 ± 0.1 and 1.16 ± 0.02 ($\mu\text{g/g}$) dry weight), while recorded their lowest values in summer and spring at the S2 (0.72 ± 0.02 and 0.36 ± 0.02 ($\mu\text{g/g}$) dry weight) respectively. The *Cystoseria sp.* (brown algae) collected from the S6 in both summer and spring recorded the highest concentration of Zn level 1.15 ± 0.06 and 0.81 ± 0.01 ($\mu\text{g/g}$), respectively. Whereas the lowest levels were found at S3 0.69 ± 0.03 ($\mu\text{g/g}$) in summer, followed by at site S1 0.27 ± 0.007 ($\mu\text{g/g}$) in spring. Some brown algae species can accumulate high concentrations of heavy metals in contaminated ecosystems, and as a result, they are chosen as metal bio monitors in coastal areas (Astorga-España *et al.*, 2008; Karez *et al.*, 1994; Villares *et al.*, 2002; Andrade *et al.*, 2010).

This results are in good agreement with those found by (Strezov and Nonova, 2003) who reported concentrations of Pb level between in two *Cystoseira sp.* (brown macroalgae) in most stations from the Bulgarian Black Sea coast. On the other hand, the *Cystoseira sp.* (brown algae) in the present study, recorded lower values for Pb compared than that reported by many authors as; Al-Masri *et al.*, (2003), also as reported by Schintu *et al.*, (2010) for algae collected from the south-western Sardinia, Italy, as well, reported by Khaled *et al.*, (2014) for *Cystoseira sp.* algae collected from the Marsa-Matrouh beaches, Egyptian in

Mediterranean Sea. Also by Strezov and Nonova (2003) for *Cystoseira sp.*, collected in the Tyrrhenian Sea, Atlantic Ocean, and Black Sea. Average while, the present data revealed a lower value of (Mn) than that recorded by Strezov and Nonova (2003) for the *Cystoseira sp.*, collected in the Tyrrhenian Sea, Atlantic Ocean, and Black Sea.

To compare the present data with those previously studied by many authors revealed that *Cystoseira sp.*, (brown algae), recorded lower values for (Zn) compared than that reported by many authors as; (Akcali and Kucuksezgin, 2011; Al-Masri *et al.*, 2003), also as reported by Schintu *et al.*, (2010), (Khaled *et al.*, 2014), (Strezov and Nonova, 2003). Also, by Culha *et al.*, (2013) in marine algae sample of Kastamonu station in Black Sea. In the present study recorded lower values of (Cd) compared than that reported by many authors as; Akcali and Kucuksezgin (2011), Al-Masri *et al.*, (2003), Schintu *et al.*, (2010), Khaled *et al.*, (2014) and Strezov and Nonova (2003) for *Cystoseira sp.* On the other hand, the value of average concentration for (Pb) was in this study, higher to those found by Culha *et al.*, (2013) for *Cystoseira sp.*, in marine algae samples of all sampling stations in Black Sea, Marmara Sea and Mediterranean Sea. Also by Sawidis *et al.*, (2001) for *Cystoseira sp.*, in the Aegean Sea, Greece. As well, the value of average concentration for (Zn) was in this study, higher than to those found by Culha *et al.*, (2013) for *Cystoseira sp.*, in marine algae sample of Samsun station in Black Sea.

While, the value of average concentration for (Cd) was in this study, comparable to those found by Culha *et al.*, (2013) for *Cystoseira sp.*, in marine algae samples of all sampling stations in Black Sea, Marmara Sea and Mediterranean Sea.

Table 9: Average concentrations ($\mu\text{g g}^{-1}$ dry weight) with standard error of metals in *Cystoseira sp.*

Stations	Metals							
	Pb		Mn		Zn		Cd	
	Spring	Summer	Spring	Summer	Spring	Summer	Spring	Summer
S1	0.61±0.01	1.20±0.03	1.16±0.02	1.74±0.1	0.27±0.007	0.75±0.008	0.007±0.01	0.007±0.01
BAF	1.29	2.22	3.13	4.14	1.58	3.57	0	3.5
S2	0.41±0.02	0.85±0.03	0.36±0.02	0.72±0.02	0.41±0.02	0.71±0.04	ND	ND
BAF	2.73	4.25	1.5	2.32	3.72	4.17	0	0
S3	0.60±0.05	0.78±0.02	0.58±0.03	0.93±0.02	0.59±0.06	0.69±0.03	0.001±0.002	0.001±0.001
BAF	3.75	3.71	1.61	2.26	2.10	1.97	0	0.5
S4	0.69±0.1	0.96±0.03	0.59±0.06	0.81±0.03	0.77±0.01	0.93±0.03	ND	ND
BAF	5.75	4.8	1.43	1.55	2.65	3	0	0
S5	0.40±0.08	0.84±0.03	0.57±0.03	0.89±0.03	0.68±0.03	0.86±0.01	ND	ND
BAF	1.08	2.04	1.58	1.97	2.42	2.38	0	0
S6	1.13±0.03	1.50±0.3	0.95±0.09	1.12±0.09	0.81±0.01	1.15±0.06	ND	ND
BAF	9.41	7.14	3.39	3.61	1.97	2.21	0	0

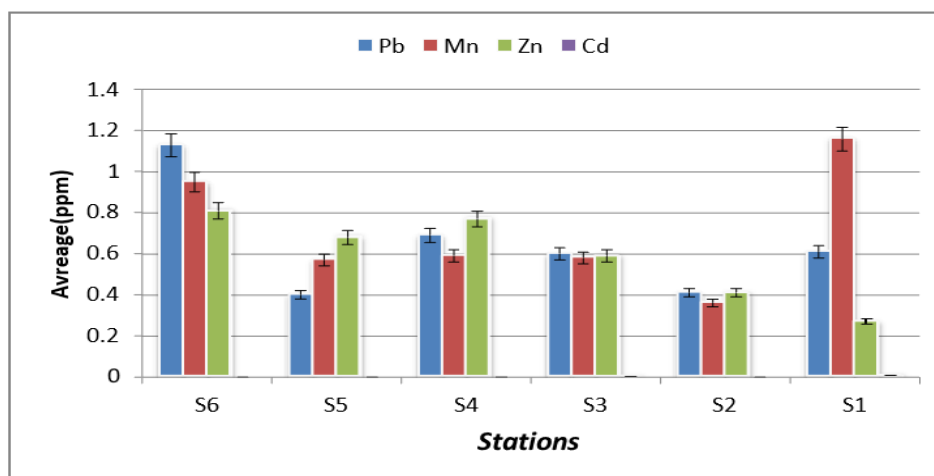


Fig 21: Average concentrations(µg g⁻¹ dry weight) in *Cystoseria sp.*, collecting during spring season 2016, along stations of Derna coast.

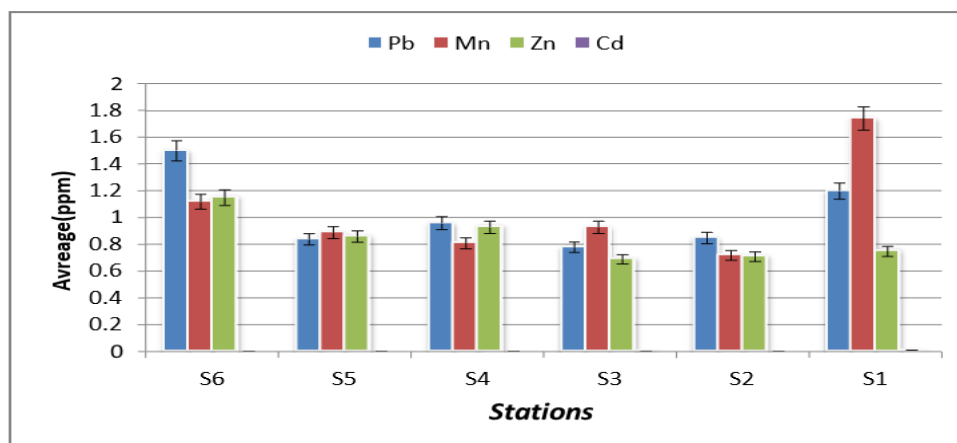


Fig 22: Average concentrations (µg g⁻¹ dry weight) in *Cystoseria sp.*, collecting during summer season 2016, along stations of Derna coast.

5. Enteromorpha sp.

The present data revealed of *Enteromorpha sp.*, recorded a relatively high Pb concentration in summer and spring at the S6 (1.92±0.3 and 1.63±0.03 (µg/g) dry weight) respectively. while recorded their lowest values in summer and spring at the S4 (0.96±0.03 and 0.69±0.1 (µg/g) dry weight) respectively. While, *Enteromorpha sp.*, recorded a relatively high Mn concentration in summer and spring at the

S4 (1.91±0.03 and 1.85±0.06 (µg/g) dry weight), while recorded their lowest values in summer and spring at the S3 (1.12±0.02 and 0.88±0.03 (µg/g) dry weight) respectively. In *Enteromorpha sp.*, we also have data for Zn, which was at a maximum at S6, 1.82±0.06 µg/g in summer. Minimum levels of Zn in this alga (only 0.05±0.01 µg/g) in spring, were found at S4.

Comparison of the present data with those

previously studied by many authors revealed that the concentrations of Zn, Pb and Cd for *Enteromorpha sp.*, lower than that recorded by Schintu *et al.*, (2010) along the south-western Sardinia, Italy, also as reported by Khaled *et al.*, (2014) for *Enteromorpha sp.*, collected from the Marsa- Matrouh beaches, Egyptian in Mediterranean Sea. As well reported by Strezov and Nonova (2003) for *Enteromorpha sp.*, in the Tyrrhenian Sea, Atlantic Ocean, and Black Sea.

The present data revealed a lower values of Mn and Zn for the *E. compressa* than that recorded by (Villares *et al.*, 2001), also for Zn with those previously studied by many authors as (Say *et al.*, 1990; Culha *et al.*, 2013). While, the value of average concentration for (Pb) was in this study, higher to those found by Culha *et al.*, (2013) for *Enteromorpha sp.* in marine algae samples of all sampling stations in Black Sea, Marmara Sea and Mediterranean Sea. Also by Sawidis *et al.*, (2001) for *Enteromorpha sp.* in the Aegean Sea, Greece.

The value of average concentration for (Zn) was in this study, higher than to those found by Culha *et al.*, (2013) for *Enteromorpha sp.*, in

marine algae in Ordu station in Black Sea. As well, the value of average concentration for (Cd) was in this study, comparable to those found by Culha *et al.*, (2013) for *Enteromorpha sp.* In marine algae samples of all sampling stations in Black Sea, Marmara Sea and Mediterranean Sea. Studies in which higher levels of metals are found in *U. lactuca* than in *Enteromorpha sp.* are less frequent; Wahbeh *et al.*, (1985) report higher concentrations of Zn and Mn in *U. lactuca* than in *E. clathrata* and lower levels of only Cd. Many authors reported that the expected levels of zinc in *Enteromorpha sp.* are in the range 10-50 $\mu\text{g g}^{-1}$ and 95-130 $\mu\text{g g}^{-1}$ dry weight, for uncontaminated and contaminated sites respectively (Stenner and Nickless, 1975; Wong *et al.*, 1982; Ho, 1987; Phillips, 1990). Graham *et al.*, (1996) tested the growth of green alga under laboratory conditions at different pH and Zn concentration. Algae grew best at pH 8 and was tolerant to high levels of metals indicating that other factors like competition may be the reason for this species often being observed at low pH in lakes.

Table 10: Average concentrations ($\mu\text{g g}^{-1}$ dry weight) with standard error of metals in *Enteromorpha sp.*

Stations	Metals							
	Pb		Mn		Zn		Cd	
	Spring	Summer	Spring	Summer	Spring	Summer	Spring	Summer
S1	0.86±0.01	1.20±0.03	1.22±0.02	1.72±0.1	1.74±0.007	1.25±0.008	0.001±0.01	0.003±0.01
BAF	1.82	2.22	3.29	4.09	10.2	5.95	0	1.5
S2	0.95±0.02	1.26±0.03	1.21±0.02	1.35±0.02	0.20±0.02	0.39±0.04	0.06±0.01	0.04±0.00
BAF	6.33	6.3	5.04	4.35	1.8	2.29	0	40
S3	1.08±0.05	1.55±0.02	0.88±0.03	1.12±0.02	0.60±0.06	0.88±0.03	0.05±0.002	0.006±0.001
BAF	6.75	7.38	2.44	2.73	2.14	2.51	0	3
S4	0.69±0.1	0.96±0.03	1.85±0.06	1.91±0.03	0.05±0.01	0.19±0.03	0.002±0.0	0.006±0.001
BAF	5.75	4.8	4.51	3.67	0.17	0.61	0	1.5
S5	1.13±0.08	1.55±0.03	0.92±0.03	1.60±0.03	1.07±0.03	1.14±0.01	0.004±0.0	0.007±0.02
BAF	3.05	3.78	2.55	3.55	3.82	3.16	0	1.4
S6	1.63±0.03	1.92±0.3	1.24±0.09	1.56±0.09	1.53±0.01	1.82±0.06	0.007±0.0	0.007±0.0
BAF	13.3	9.14	4.42	5.03	3.73	3.5	3.5	1.7

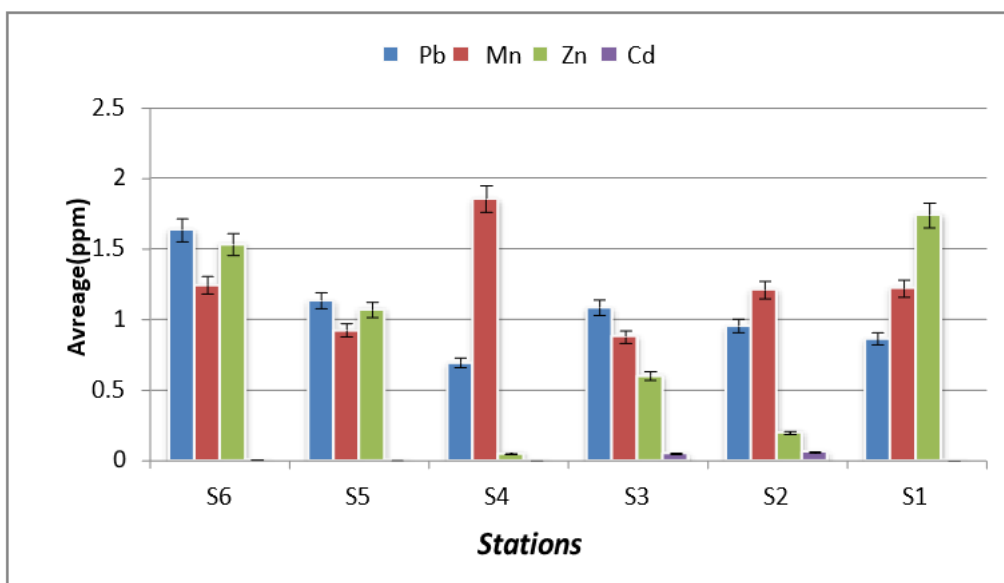


Fig 23: Average concentrations (µg g⁻¹ dry weight) in *Enteromorpha sp.*, collecting during spring season 2016, along stations of Derna coast.

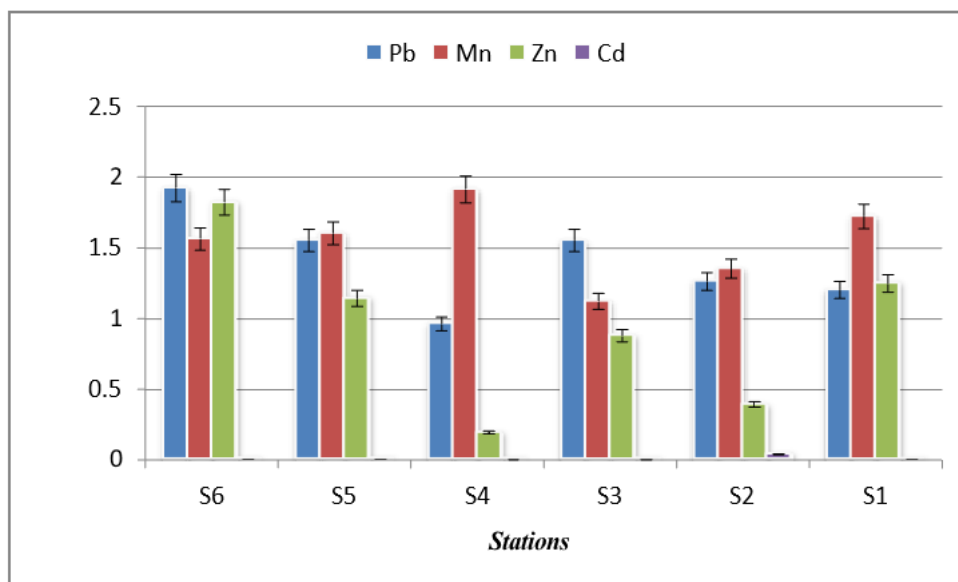


Fig 24: Average concentrations in *Enteromorpha sp.*, collecting during summer season 2016, along stations of Derna coast.

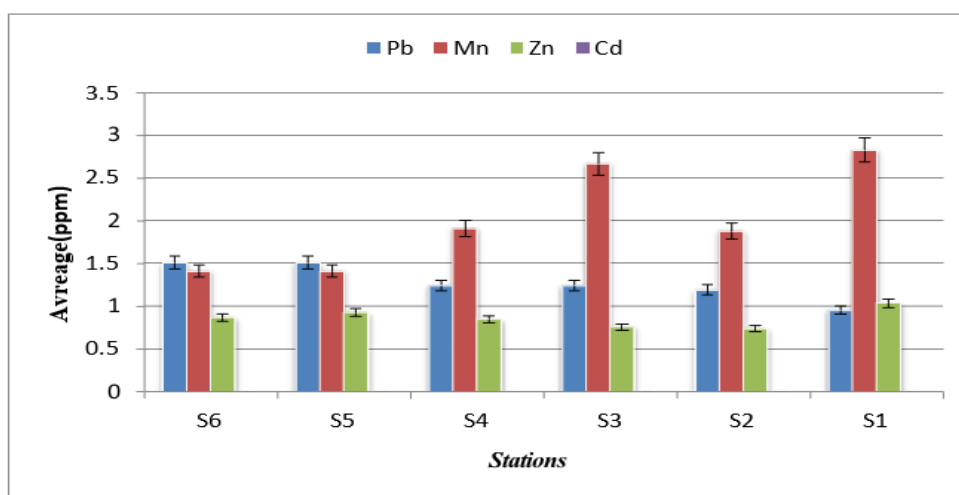
6. Chaetomorpha sp.

The highest Pb level in *Chaetomorpha sp.*, was recorded in spring for samples collected from S4 1.86±0.2 (µg/g dry weight) followed by S6 and S5 (1.51±0.4 (µg/g) dry weight) in summer. The highest Mn level in *Chaetomorpha sp.*, was recorded in summer for samples collected from S1 2.83±0.6 (µg/g), followed by S3 (2.12±0.5 (µg/g) dry weight) in spring. While *Chaetomorpha sp.*, recorded a relatively high Zn concentration in spring at the S2 (1.41±0.1 (µg/g) dry weight). while recorded their lowest values in spring at the S3 (0.51±0.1 (µg/g) dry weight). The present data, show the value of average concentration for (Pb), (Mn), (Zn) and (Cd) was in this study,

lower than to those found by Strezov and Nonova (2007) for *Chaetomorpha sp.*, collected in the Tyrrhenian Sea, Atlantic Ocean, and Black Sea.

Table 11: Average concentrations ($\mu\text{g g}^{-1}$ dry weight) with standard error of metals in *Chaetomorpha sp.*

Stations	Metals							
	Pb		Mn		Zn		Cd	
	Spring	Summer	Spring	Summer	Spring	Summer	Spring	Summer
S1	0.71±0.08	0.95±0.2	1.94±0.4	2.83±0.6	0.82±0.1	1.03±0.3	0.02±0.05	ND
BAF	1.51	1.75	5.24	6.73	4.82	4.90	0	0
S2	0.93±0.1	1.19±0.3	1.43±0.2	1.88±0.6	1.41±0.1	0.73±0.8	0.03±0.1	0.03±0.02
BAF	6.2	5.95	5.95	6.06	12.8	4.29	0	30
S3	0.70±0.08	1.24±0.2	2.12±0.5	2.67±0.3	0.51±0.1	0.75±0.8	ND	ND
BAF	4.37	5.90	5.88	6.51	1.82	2.14	0	0
S4	1.86±0.2	1.24±0.2	1.85±0.3	1.91±0.2	0.64±0.2	0.84±0.9	ND	ND
BAF	15.5	6.2	4.51	3.67	2.20	2.70	0	0
S5	1.13±0.3	1.51±0.4	1.04±0.1	1.41±0.6	0.68±0.4	0.92±0.3	ND	ND
BAF	3.05	3.68	2.88	3.13	2.42	2.55	0	0
S6	1.25±0.4	1.51±0.4	1.97±0.1	1.41±0.6	0.75±0.8	0.86±0.2	ND	ND
BAF	10.4	7.19	7.03	1.1	1.82	1.65	0	0

Fig 25: Average concentrations ($\mu\text{g g}^{-1}$ dry weight) in *Chaetomorpha sp.*, collecting during spring season 2016, along stations of Derna coast.**Fig26:** Average concentrations ($\mu\text{g g}^{-1}$ dry weight) in *Chaetomorpha sp.*, collecting during summer season 2016, along stations of Derna coast.

7. *Corallina. Sp.*

The S6 station recorded relatively high Pb concentration in summer for *Corallina sp.*, algae 1.84 ± 0.4 ($\mu\text{g/g}$), while the lowest values were detected in spring for the S3 (0.67 ± 0.1 ($\mu\text{g/g}$) dry weight). Average while both the S2 and S1 recorded relatively high Mn concentration in summer for *Corallina sp.*, algae 3.06 ± 0.7 and 3.05 ± 0.4 ($\mu\text{g/g}$) respectively, while the lowest values were detected in spring for the S5 (0.84 ± 0.3 ($\mu\text{g/g}$) dry weight).

The value of average concentration for (Pb), (Mn), (Zn) and (Cd) was in this study, Comparable lower than to those found by Strezov and Nonova (2003) for *Corallina. sp.*, collected in the Tyrrhenian Sea, Atlantic Ocean, and Black Sea. The value of average

concentration for (Zn) was in this study, lower than to those found by Culha *et al.*, (2013) for *Corallina sp.*, in marine algae in Yalova station in Marmara Sea. In some instances, the value of average concentration for (Cd) was in this study, comparable to those found by Culha *et al.*, (2013) for *U. lactuca*, *Cystoseira sp.*, *Enteromorpha sp.* and *Corallina sp.*, in marine algae samples of all sampling stations in Black Sea, Marmara Sea and Mediterranean Sea. While, the value of average concentration for (Pb) was in this study, higher to those found by Culha *et al.*, (2013) for *Corallina sp.*, in marine algae samples of all sampling stations in Black Sea, Marmara Sea and Mediterranean Sea. Also by Sawidis *et al.*, (2001) for *Corallina sp.*, in the Aegean Sea, Greece. The variability of these metal concentrations in sea grass

tissues could be due to different metal uptake of different sea grass species. It could also be due to different environmental factors (e.g. temperature variation, pH, and salinity) which requires further detailed studies. In fact, this lack of consistency in the results obtained from

different studies makes it difficult to arrive at a suitable explanation for the processes which account for the measured levels of metals within these sea-weeds. Their appropriateness as cosmopolitan quantitative biomonitors therefore requires closer scrutiny.

Table 12: Average concentrations ($\mu\text{g g}^{-1}$ dry weight) with standard error of metals in *Corallina sp.*

Stations	Metals							
	Pb		Mn		Zn		Cd	
	Spring	Summer	Spring	Summer	Spring	Summer	Spring	Summer
S1	0.92±0.17	0.86±0.28	1.91±0.4	3.05±0.4	0.76±0.2	0.88±0.08	0.05±0.01	0.004±0.02
BAF	1.95	1.59	5.16	7.26	4.47	4.19	0	2
S2	0.92±0.12	0.93±0.28	1.31±0.4	3.06±0.7	0.74±0.2	1.17±0.1	0.002±0.00	0.003±0.00
BAF	6.13	4.6	5.45	9.87	6.72	4.17	0	3
S3	0.67±0.18	1.29±0.63	1.96±0.2	1.92±0.3	0.63±0.1	1.12±0.1	0.04±0.01	0.05±0.00
BAF	4.18	6.14	5.44	4.68	2.2	3.2	0	25
S4	0.90±0.11	0.95±0.14	1.91±0.3	2.01±0.6	0.40±0.5	0.79±0.9	0.008±0.0	0.05±0.00
BAF	7.5	4.7	4.65	3.86	1.37	2.5	0	12.5
S5	1.15±0.33	1.58±0.16	0.84±0.3	1.29±0.3	0.72±0.3	1.14±0.2	0.002±0.00	0.002±0.00
BAF	3.10	3.85	2.33	2.86	2.57	3.1	0	0.4
S6	0.75±0.21	1.84±0.43	1.90±0.005	1.41±0.4	0.51±0.08	0.92±0.1	0.008±0.0	0.002±0.00
BAF	6.2	8.76	6.78	4.54	1.2	1.7	4	0.5

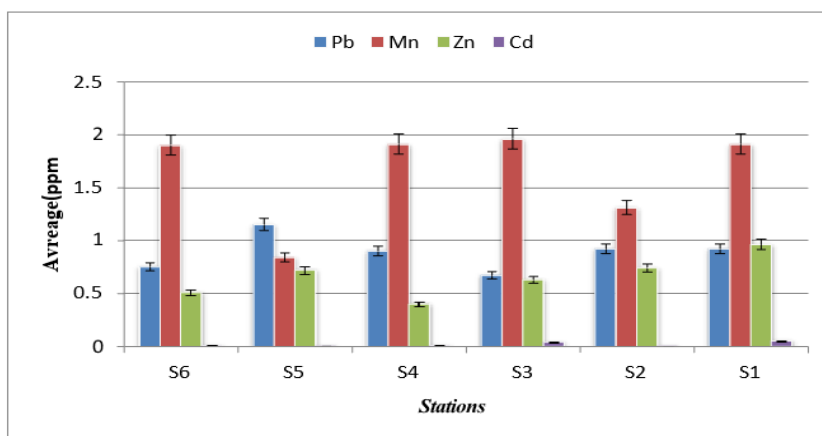


Fig 27: Average concentrations ($\mu\text{g g}^{-1}$ dry weight) in *Corallina sp.*, collecting during spring season 2016, along stations of Derna coast.

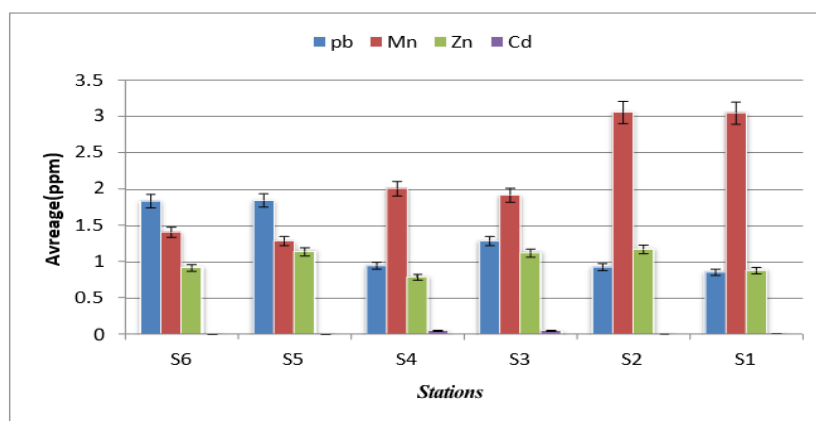


Fig 28: Average concentrations ($\mu\text{g g}^{-1}$ dry weight) in *Corallina sp.*, collecting during summer season 2016, along stations of Derna coast.

8. Heavy Metals in Water:

Determination of heavy metal concentrations in marine algae samples is usually preferred in the seawater and sediment samples. Heavy metal concentrations in seawater are very low and show wide fluctuation. At the same time, heavy metal levels in the sediment samples can be changed by organic matter content, grain size composition, pH and oxidation-reduction potential, etc. (Förstner, 1985; Farias *et al.*, 2002).

In the present study, low metal contamination was found in S1 for Pb, Mn, Cd and Zn in seawater compared with contamination metals accumulated in the tissues of algae. The concentration of the metals in the six sampling sites followed the order of Mn>Zn>Pb>Cd. The average of heavy metals concentrations in sea water were lower at site S2 and relatively higher at site S1 (Table 13). Mn was the most abundant metal, whereas Cd was the least abundant. The other metals exhibited intermediate concentrations and variability among the six sites. Largely, metals contents in seawater, from S1 obtained in this work are intermediary to previous reports worldwide.

For example, site S1 in our study were the most contaminated for Pb in summer and spring seasons. This site is seem heavily affected by human activities and were the closest to the wharf. Pb concentrations from seawater in this study ranged between 0.12 and 0.54 ($\mu\text{g l}^{-1}$), were this result agree with (Chakraborty *et al.*, 2014) for water sea along the coast of the Gulf of Kutch in India. While site S4 were the most contaminated for Mn in both summer and spring seasons, between 0.24 and 0.52 ($\mu\text{g l}^{-1}$). As well, the maximum value of Cd metal were also determined at site S5 in both summer and spring seasons between 0.003-0.05 ($\mu\text{g l}^{-1}$). These were much similar results obtained by (El-Adl *et al.*, 2017., along Al-Hanyaa coastline, Libya, as well as the standard limits of Environmental Protection Agency (EPA) (2014). In addition, results in this study show that the site S6 were the most contaminated for Zn in summer and spring seasons. Despite of the discharge of wastes in sea water, our results were much lower than those reported from along Al-Hanyaa Coastline, Libya 5.4–7.4 ($\mu\text{g l}^{-1}$) ((El-Adl *et al.*, 2017).

Table 13 : Average heavy metals concentrations ($\mu\text{g l}^{-1}$) with standard error of metals in the selected marine water.

Stations	Metals							
	Pb		Mn		Zn		Cd	
	Spring	Summer	Spring	Summer	Spring	Summer	Spring	Summer
S1	0.47±0.01	0.54±0.05	0.37±0.03	0.42±0.08	0.17±0.01	0.21±0.008	ND	0.002±0.0
S2	0.15±0.08	0.20±0.05	0.24±0.03	0.31±0.01	0.11±0.2	0.17±0.05	ND	0.001±0.0
S3	0.16±0.08	0.21±0.05	0.36±0.01	0.41±0.08	0.28±0.2	0.35±0.05	ND	0.002±0.0
S4	0.12±0.01	0.20±0.06	0.41±0.01	0.52±0.01	0.29±0.05	0.31±0.01	ND	0.004±0.0 2
S5	0.37±0.01	0.41±0.01	0.36±0.02	0.45±0.08	0.28±0.01	0.36±0.01	ND	0.005±0.002
S6	0.12±0.01	0.21±0.08	0.28±0.01	0.31±0.08	0.41±0.01	0.52±0.01	0.002±0.0	0.004±0.01

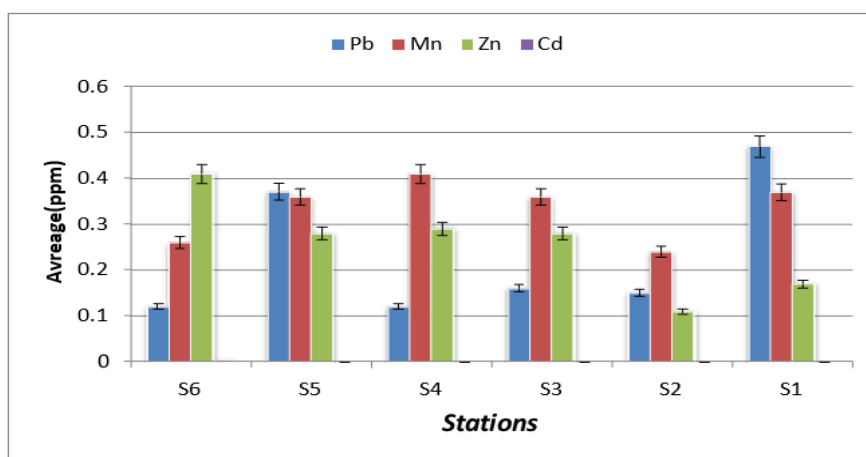


Fig 29: Average concentrations ($\mu\text{g l}^{-1}$) in water collecting during spring season 2016, along stations of Derna coast.

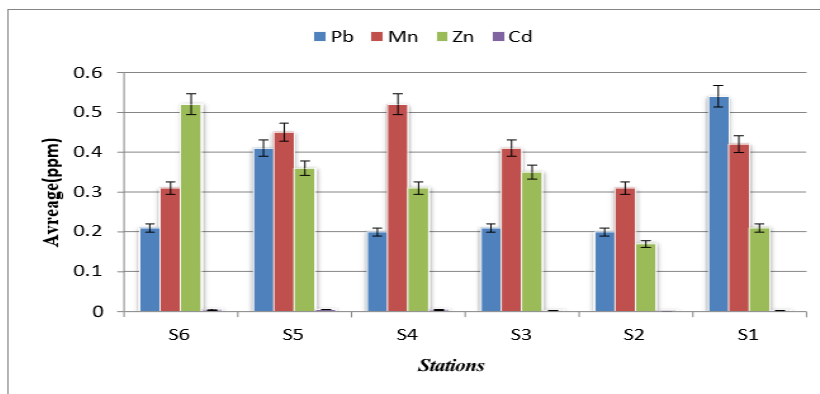


Fig 30: Average concentrations ($\mu\text{g l}^{-1}$) in water collecting during summer season 2016, along stations of Derna coast. .

9. Indices of pollution

i) Bioaccumulation factor (BAF)

Bioaccumulation assessment is important in the scientific evaluation of risks that chemicals may pose to humans and the environment. The bioaccumulation factor of heavy metals (Pb, Mn, Zn and Cd), in different samples was quantified as the ratio of the concentration of a specific heavy metal in the dry tissue of the organism ($\mu\text{g /kg}$) to the concentration of the heavy metal in the water sample ($\mu\text{g /l}$) (El-Adl *et al.*, 2017). Metal accumulation by algae was highly variable. Different algal species showed preferential assimilation towards specific elements. There are several attributing factors for such differences in metal accumulation by different species, including life span, morphology, contact surface area, growth rate and specific affinity for selective metals by particular species (Chakraborty *et al.*, 2014). Figure (31), show that heavy metals were accumulated in the different algal species in stations to different extents. According to Chakraborty *et al.*, (2014), the state of

conservation of an ecosystem or the choice to monitor its state can be evaluated using the bioaccumulation factors (BAF) of the living organisms for heavy metals. A somewhat, BAF of the different heavy metals showed a common pattern of peaking at S2, with moderate reduction at S6, S3, S4 and S1, and a relatively great reduction at S5. The average BAF of the species of S2 attained peaks of Cd, Pb, Mn and Zn respectively, and a lower average of BAF in the S5 by pattern Pb, Mn, Zn and Cd respectively, where its BAF at S2 was about 3 times its value at S5. The BAF was lowest for Cd - the least abundant metal in sea water - and averaged around 0.20, 0.86, 0.91, 1.25, 3.07 and 9.00 at S5, S1, S6, S4, S3 and S2 respectively but the BAF was highest for Pb and averaged around 1.81, 2.59, 4.95, 5.38, 6.46 and 8.59 at S1, S5, S3, S2, S4 and S6 respectively. This reflects the fact that accumulation highly dependent upon the ambient pollution levels (Chakraborty *et al.*, 2014).

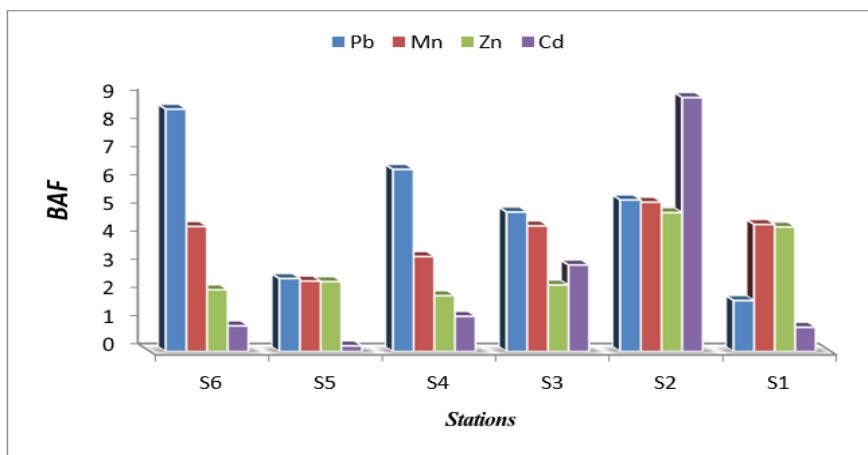


Fig 31: Bioaccumulation factor (BAF) of algae species along the six stations of Derna coast.

ii) Metal pollution index (MPI):

The average MPI was highest (0.86) for the algae species inhabiting S6, intermediate (0.50, 0.58 and 0.59) for the algae species of S2, S5 and S4, and least (0.30 and 0.41) for the algae species of S1 and S3 (Table 14 and Fig. 32). Metal pollution index (MPI) can be used to compare the average heavy metal content of different algal species within the same site or among different sites (El-Adl *et al.*, 017).

The ability to accumulate heavy metals was

highest in *Laurencia sp.*, which was substantially higher than those of the accompanying species at all species at all stations. This points to a marked genotypic variability in heavy metal accumulation and agrees with the findings of (Khan *et al.*, 2015) who reported that some macroalgae can concentrate heavy metals in their tissues to several times higher than those in the ambient water.

Table 14 : MPI of algae species along six stations of Derna coast.

Algae	S1	S2	S3	S4	S5	S6
<i>U. lactuca</i>	0.29	0.46	0.25	0.23	0.31	0.25
<i>Laurencia sp</i>	0.25	1.18	0.38	0.31	0.7	1.63
<i>Amphiroa anceps</i>	0.22	0.21	0.24	1.04	0.68	1.21
<i>Cystoseria asmundaceae</i>	0.26	0.66	0.13	0.83	0.76	1.07
<i>Enteromorpha sp.</i>	0.32	0.37	0.37	0.16	0.31	0.41
<i>Chaetomorpha sp.</i>	0.32	0.36	1.09	1.21	1.06	1.16
<i>Corallina sp.</i>	0.43	0.24	0.42	0.38	0.22	0.29

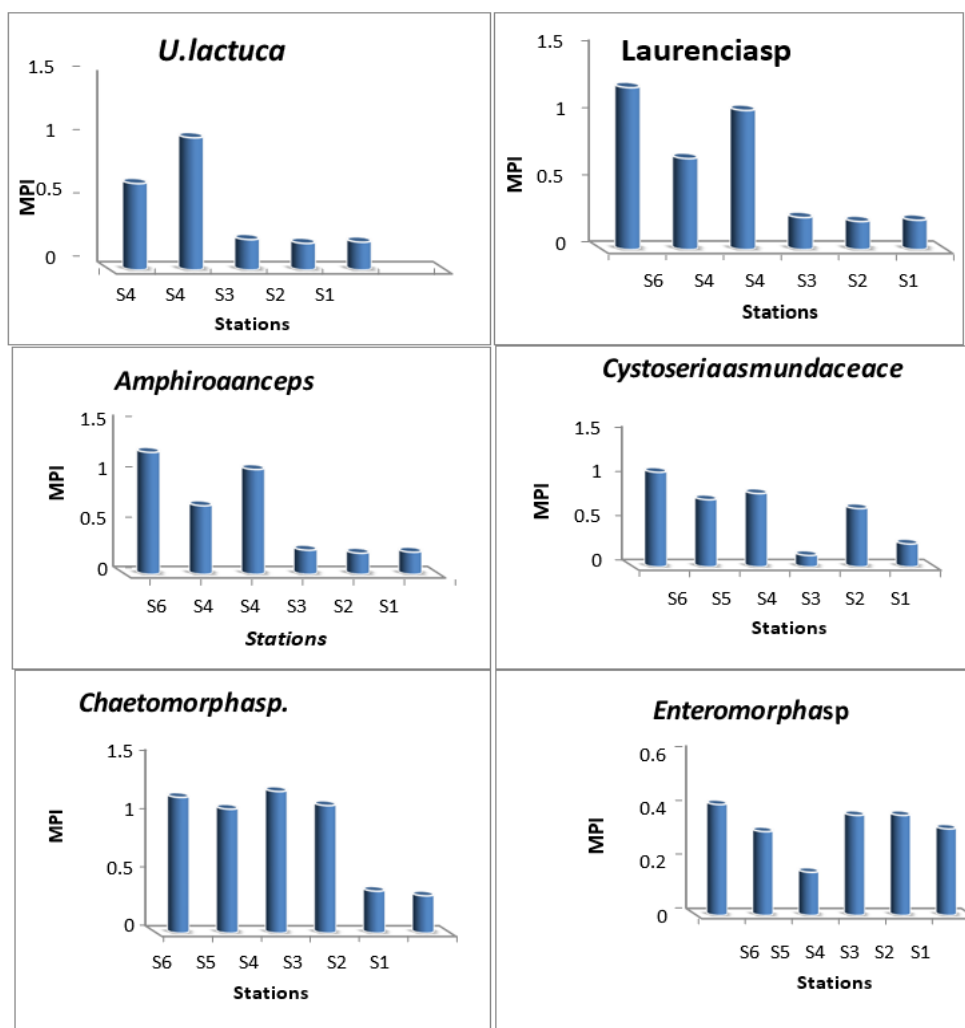


Fig 32: Metal pollution index (MPI) of algae species along the six stations of Derna coast.

Conclusion

The increase of environmental factors in the study that effect on the concentration and accumulations of heavy metals in some marine algae despite of the levels of the heavy metals (Pb,Mn,Zn, and Cd),in sea water and nature study area resulting from discharged wastes and sewage, that removal by no correct method causes unsafe on human life, Mn was the most abundant metal, whereas Cd was the least abundant one. The radical variation in floristic composition among the studied sites along with the limited variation in heavy metal composition of sea water justifies the use of biological indices rather than chemical indices as criteria for assessment of environmental pollution. Dominance of brown and red algae at the sites of study points to their ability to tolerate heavy metal pollution. The expected results and concentrations, which do not appear for the most part, have the potential to have adverse effects on the local environment. However, these minerals should be monitored to ensure their survival at non-harmful levels.

References

1. Abeir,M.M. (2014). Assessment of heavy metals and hydrocarbons in some types of algae as an indicators of contamination at some aljabal alakater Libya coast regions. Thesis, faculty of natural resources. Environ, Sci.(1):60,64 pp.
2. Abbas Ullah Jan. ;Mohammad Jamal Khan. ;Mohammad Tariqjan.; Farhatullah. ; Naqib Ullah Khan . ;Mohammad Arif . ;Sajida Parveen , and Shah Alam. (2011). The Effect of Using Waste Water on Tomato. Pak. J. Bot.,43,1.
3. Abdel-Halim, A.M. (2004). Chemical equilibria studies of some phosphorus compounds under different conditions ,Ph.D. Thesis, faculty of Science, Alexandria University. Egypt 260 pp.
4. Abdulla,A.(2007).The social marketing strategy: Employment skills training project: Final report Ministry of Higher Education, Employment and Social Security, Male', Republic of Maldives.
5. Akcali , I. and Kucuksezgin, F. (2011). A bio monitoring study Heavy metals in macro algae from eastern Aegean coastal areas. Mar. Pollut. Bull. 62:637-645.
6. Andrade, L. R. ; Leal, R. N. ; Nosedá, M.; Duarte, M. E.; Pereira, M.S.; Mourão,pA.;Farina ,M. and Amado,filho.g.m.(2010).Brown algae overproduce cell wall polysaccharides as a protection mechanism against the heavy metal toxicity. Marine pollution Bulletin.60(9):1482-8.
7. Arnold, S.J. and Peterson, C.R.(1989). A test for temperature effects on the ontogeny of shape in the garter snake, *Thamnophis sirtalis*. *Physiol. Zool*,62: 1316– 1333.
8. Astorga. Espaa, M. S.; Calisto-Ulloa,N.C. and Guerrero, S.(2008). Baseline concentrations of trace metals in macro algae from the Strait of Magellan, Chile. *Bull. Environ. Contam. Toxicol*, 80 (2), 97–101.
9. Avery, R.A. (1994). Growth in reptiles. *Gerontology* ,40: 193–199.
10. Azzawam , S. (1984). Al Jabal Al Akhdar: A natural geography study. Garyounis University. Benghazi, Libya.
11. Bahls, L. L. (1993). Periphyton bio assessment methods for Montana streams. Water Quality Bureau, Department of Health and Environmental Sciences, Helena, MT.
12. Barreiro, E.; Real, C. and Carballeira , A. (1993). Heavy-metal accumulation by *Fucus ceranoides* in a small estuary in north-west Spain. *Mar. Environ. Res.* 27: 789-814.
13. Beijer, K. and Jerenlöv, A. (1979). Sources, transport and Transformation of metals in the environment In: Freiberg, L., G.F. Nordberg, and V.B. Vouk (Eds.), *Handbook on Toxicology of Heavy Metals*. Amsterdam: Elsevier, pp. 47–63.
14. Biggs, B. J.; Kilroy, F.C. and Mulcock, C. M. (1998). New Zealand stream health monitoring and assessment kit. Stream monitoring manual, Version 1. Niwa Technical Report, Christchurch, New Zealand. 150 pp.
15. Brown, M. T.; Hodgkinson, W. M. and Hurd, C. L. (1999). Spatial and temporal variations in the copper and zinc concentrations of two green seaweeds from Otago Harbour, New Zealand. *Mar. environ. Res.* 47: 175–184.
16. Buffle, J.; Wilkinson, K.J. and Van Leeuwen ,H.P. (2009). Chemo dynamics

- and bioavailability in natural waters. *Environ. Sci. Technol.* 43:7170-7174.
17. Caliceti, M.; Argeese, E.; Sfriso, A. and Pavoni, B. (2002). Heavy metal contamination in the seaweeds of the Venice lagoon. *Chemosphere*,47. 4436–54.
 18. Capiomont, A.; Piazzzi ,L. and Pergent, G.(2000). Seasonal variations of total mercury levels in foliar tissues of *Posidonia oceanica*. *J.Mar .Biol Assoc.* 80: 1119–1123.
 19. Castonguay, M., Rollet, C.; Fre´chet, A.; Gagnon, P.; Gilbert, D. and Breˆthes,C. (1999). Distribution changes of Atlantic cod (*Gadus morhua* L.)in the northern Gulf of St Lawrence in relation to anoceanic cooling. *ICES Journal of Marine Science*, 56: 333–344.
 20. Chakraborty, S.T.; Bhattacharya, G.; Singh, J.P. and Maity. (2014). Benthic macro algae as biological indicators of heavy metal pollution in the marine environments. A bio monitoring approach for pollution assessment. *Eco toxicology environmental safety*, 100: 61-68.
 21. Chen, J.P.; Hong, L.A.; Wu, S.N. and Wang, L.(2002). Elucidation of interactions between metal ions and Cu alginate-based ion exchange resin by spectroscopic analysis and modeling simulation. *Langmuir* ,18:9413–9421.
 22. Conti, M.,E. and Cecchetti ,G .(2003). A bio monitoring study: trace metals in algae and molluscs from Tyrrhenian coastal areas. *Environ. Res*, 93:99-112.
 23. Coteur,G.; Gosselin, P.; Wantier, P.; Chambost-Manciet, Y.; Danis, B.; Pernet, P. H.; Warnau ,M.and Dubois, P .(2003). Echinoderms as bio indicators bioassays and impact assessment tools of sediment associated metals and PCBs in the North Sea. *Arch. Environ. Contam. Toxicol*, 45:190-202.
 24. Culha, S. T., Kocbas, f., Gundogdu, A. and CULha, M.(2013). Heavy Metal Levels in Marine Algae from the Black Sea, Marmara Sea and Mediterranean Sea. 40th CIESM Congress, 239.D. E. G. irvine and D. M. John, pp 2972. *Systematics Association special vol. no. 27.* Academic Press, London.
 25. Danis ,B.; Wantier ,P.; Flammang, R.; Dutrieux, S.; Dubois ,P. and Warnau ,M (2004). Contaminant levels in sediment and asteroids (*Asteriasrubens*, Echinoderm) from the Belgian coast and Scheldt estuary: polychlorinated biphenyls and metals. *Sci. Total Environ*, 333:149-165.
 26. Davis, T.A.; Volesky, B. and Mucci, A. (2003) .A Review of the Biochemistry of Heavy Metal Bio sorption by Brown Algae. *Water Research*, 37: 4311-4330.
 27. Dixit, S. S.; Smol, J. P.; Kingston, J. C. and Charles, D. F. (1992).A Diatoms: Powerful indicators of environmental change. *Environmental Science & Technology*. 26:22–33.
 28. Dixit, S.S. and Smol, J. P. (1994). Diatoms as environmental indicators in the Environmental Monitoring and Assessment—Surface Waters(EMAP-SW) program.31:206–275.
 29. Domingues , R.and Galvão ,H. (2007). Phytoplankton and environmental variability in a dam regulated temperate estuary. *Hydrobiologia*. 586: 117-134.
 30. Dromgoole, F.I. (1978). The effect of pH and inorganic carbon on photosynthesis and dark respiration of *Carpophyllum* (Fucales, Phaeophyceae). *Aquat. Bot.*, 4: 11–22.
 31. El-Adl, Magda Faiz ; El-Katony, Taha Mohamed, and Bream, Ahmed Saber. (2017). Effect of sewage pollution on macroalgal diversity and heavy metal accumulation along Al-Hanyaa coastline, Libya. *Advances in Environmental Biology*. Feb.2017, Vol. 11 Issue 2, p52, 8 p.
 32. Förstner, U. (1985). Chemical forms and re activities of metals in sediment. In: Leschber,R., Davies, R.D.,H’Hermite, P. (Eds.), *Chemical Methods of Assessing Bioavailable Metals in Sludges and Soil*. Elsevier Press. London, pp. 1-30.
 33. Fowler, S.W. (1979). Use of marine algae as reference material for pollutant monitoring and specimen banking. In: Luepke, N.P. (Ed.), *Monitoring Environmental Materials and Specimen Banking*, Martinus Nijh off, The Hague, pp. 267-347.
 34. Fritioff, Å. L. Kautsky, and Greger, M. (2005). Influence of tempera-ture and

- salinity on heavy metal uptake by submersed plants. *Environ. Pollut.* 133: 265–274.
35. Gosavi, K.; Sammut, J.; Gifford, S. and Jankowski, J. (2004). Macroalgal biomonitors of trace metal contamination in acid sulfate aquaculture ponds. *Sci. Total Environ.* 324:25-39.
 36. Graham, J. M.; Arancibia-Avila, P. and Graham, L. E. (1996): Effects of pH and selected metals on growth of the filamentous green alga *Mougeotia* under acidic conditions. *Limnology and Oceanography* 41, 263-270.
 37. Güven, K.C.; Topcuoğlu, S.; Kut, D.; Esen, N.; Erentürk, N.; Saygı, N.; Cevher, E.; Güvener, B. and Öztürk, B. (1992). Metal pollution of Black Sea algae. *Acta pharmaceutica Turcica* 34:81-89.
 38. Jones, J.B. and Case, V.W. (1990). Sampling, handling and analyzing plant tissue samples. In: Westerman, R.L. (Ed.), *Soil Testing and Plant Analysis*. third ed., Soil Science Society of America, Book Series No. 3, Madison, Wisconsin, pp. 389–427.
 39. Karez, C.S.; Magalhaes, V.F.; Pfeiffer, W.C, Filho, G.M. (1994). Trace metal accumulation by algae in Sepetiba Bay, Brazil. *Environ. Pollut.* 83:351-356.
 40. Kelly, M. G.; Cazaubon, A.; Coring, E.; Dell'Uomo, A.; Ector, L.; Goldsmith, B.; Guasch, H.; Hürlimann, J.; Jarlman, A.; Kawecka, B.; Kwandrans, J.; Laugaste, R.; Lindström, E.; Leitao, M.; Marvan, P.; Padisák, J.; Pipp, E.; Pyrgiel, J.; Rott, S.; Sabater, van Dam, H and vizinet, J. (1998). Recommendations for the routine sampling of diatoms for water quality assessments in Europe. *Journal of Applied Phycology* 10, 215-224.
 41. Khaled, A.; Hessein, A.; Abdel-Halim, A. M. and F. M. Morsy (2014). Distribution of heavy metals in seaweeds collected along Marsa-Matrouh beaches, Egyptian Mediterranean Sea. *The Egyptian Journal of Aquatic Research* 40(4): 363-371.
 42. Khan, N.; Ryu, K.Y.; Choi, J.Y.; Nho, E.Y. Habte, G. ; Choi, H. ; Kim, M.H.; Park, K.S. and Kim, K.S. (2015). Determination of toxic heavy metals and speciation of arsenic in seaweeds from south Korea. *Food Chem.* (169): 464-470.
 43. Litzgus, J.D. and Brooks, R. J. (1998a). Growth in a cold environment: body size and sexual maturity in a northern population of spotted turtles, *Clemmys guttata*. *Can. J. Zool.* 76: 773–782.
 44. Lobban, C.S. and Harrison, P.J. (1994). *Seaweed Ecology and Physiology*, 1st ed. Cambridge University Press, 366 pp.
 45. Mattox, K. R. and Stewart, K. D. (1984). Classification of the green algae : a concept based on comparative cytology. In *Systematics of the Green Algae*, ed. D.E.G. Irvin and D.M. John, pp. 297-316. Systematics Association special vol. no. 27. Academic Press, London.
 46. Merz, Sinclair Knight. (2013). *Characterizing the relationship between water quality and water quantity*, St Leonards NSW 2065, Australia.
 47. Metian, M.; Giron, E.; Borne, V.; Hédouin, L.; Teyssié, J. and Warnau, M. (2008). The brown alga *Lobophora variegata*, a bio indicator species for surveying metal contamination in tropical marine environments. *J. Exp. Mar. Biol. Ecol.* 362:49-54.
 48. Morillo, J.; Usero, J.; and Gracia, I. (2005). Biomonitoring of Trace Metals in a Mine-Polluted Estuarine System (Spain). *Chemosphere*, 58:1421-1430.
 49. Muse, J. O.; Stripeikis, J. D.; Fernández, F. M.; Huicque, L. d' Tudino, M. B. Carducci, C. N. and Troccoli, O. E. (1999). Seaweeds in the assessment of heavy metal pollution in the Gulf San Jorge, Argentina. *Environ. Pollut.* 104: 315–322.
 50. Naicheng, W.u.; Britta; Schmalz; Nicola and Fohrer. (2014). Study progress in river in phytoplankton and its use as bio-indicator – a review. *Austin Journal of Hydrology*, 1(1): 9 p.
 51. Palmer, C. M. (1980). *Algae and water pollution: the identification, significance, and control of algae in water supplies and in polluted water*. Algae and water pollution: the identification, significance, and control of algae in water supplies and in polluted water. Castle House Publications.
 52. Peckol, P.; Demeo Anderson, B. ; Rivers, J. ; Valiela, I. ; Maldonado, M. ; Weiner, J.

- and Yates, J. (1994). Growth nutrient uptake capacities, and tissue constituents of the macroalgae, *Gracilariatik vahiae* and *Cladophora vagabunda*, related to site-specific nitrogen loading rates. *Mar. Bio.* 1, 121: 175-185.
53. Peterson, H.G. Healey, F.P. and Wagemann, R. (1984). Metal toxicity to algae a highly pH dependant phenomenon. *Can. J. Fish. Aquat. Sci.* 41: 974–979.
 54. Phillips, D.J.H. (1994) .Macro phytes as Bio monitors of Trace Metals .Bio monitoring of Coastal Waters and Estuaries, 85-103.
 55. Ramírez;Marta; González ;Humberto, and Ablanedo Nora. (1990). Heavy Metals in Macro algae of Havana's Northern Littoral, Cuba, *Torres Ibis Chemistry and Ecology.* 4(2). p.49.
 56. Sawidis, T.; Brown, M.T.; Zachariadis, G. and Sratis, I. (2001). Trace metal Concentrations in Marine Macro algae from Different Biotopes in the Aegean Sea. *Environment International,* 27: 43-47.
 57. Say, P. J.;Burrows , J. G. and Whitton, B. A. (1990). *Enteromorpha* as a monitor of heavy metals in estuaries. *Hydrobiologia* 195: 119–126.
 58. Schintu, M.;Marras, B.; Durante, L.; Meloni, P. and Conti, A. (2010). Macroalgae and DGT as Indicators of Available Trace Metals in Marine Coastal Waters near a Lead-Zinc Smelter. *Environmental Monitoring and Assessment,* 167.
 59. Shiber, J. G. and Shatila, T. (1979). Certain metals in three coastal algae from Ras Beirut waters. *Hydrobiologia.* 63: 105-112.
 60. Sigworth, E.A. (1957) . Control of odor and taste in water supplies. *J. Amer. Water Wks. Assn.* 49: 1507-1521.
 61. Simon, D .F.; Davis, T .A.; Tercier,Waeber ,M.T. ;England ,R. and Wilkinson,K.J. (2011). In situ evaluate on of cadmium biomarkers in green algae. *Environ. Pollut.* 159:2630-2636.
 62. Stevenson, R. J. and Bahls, L. L.(1999). Periphyton protocols, in: Barbour, M. T., Gerritsen, J., Snyder, B. D., Eds., *Rapid bio assessment protocols for use in wade able streams and rivers :Periphyton,* benthic macro invertebrates, and fish, 2nd Ed., EPA 841-B-99-002. U.S. Environmental Protection Agency, Washington, DC, pp 6–1–6–22.
 63. Stokes, P.M. (1983). Responses of freshwater algae to metals. *Prog. Phycol. Res.* 2: 87–112.
 64. Strezov, A . and Nonova , T.(2003). Monitoring of Fe, Mn, Cu, Pb and Cd levels in two brown macro algae from the Bulgarian Black Sea coast *Intern. J. Environ. Anal. Chem.,* 83, 1045-1054.
 65. UNEP, (1997). Assessment of land-based sources and activities affecting the marine sediment in the Red sea and Gulf of Aden. *UNEP Regional Seas Reports Studies,* No. 166.versus INAA in *Pollution Control of Soil, J. Radioanal. Nucl. Chemistry,* 268 (1), 71.
 66. Villares ,R.; Puente ,X. and Carballeira, A .(2002). Seasonal variation and background levels of heavy metals in two green seaweeds. *Environ Pollut.* 119:79-90.
 67. Villares, R.; Puente, X. and Carballeira, A. (2001). *Ulva* and *Enteromorpha* as indicators of heavy metal pollution. *Hydrobiologia,* 462: 221-232.
 68. Wahbeh, M. I.; Mahasneh , D. M. and Mahasneh, I. (1985). Concentrations of zinc, manganese, copper, cadmium, magnesium and iron in 10 species of algae and sea water from Aqaba, Jordan. *Mar. Envir. Res.* 16: 95–102.
 69. Wang, W.X. and Dei, R.C.H., (1999). Kinetic measurements of metal accumulation in two marine macroalgae. *Marine Biology* 135, 11–23.
 70. Ward, T. J. (1987). Temporal variation of metals in the seagrass *Posidonia australis* and its potential as a sentinel accumulator near a lead smelter. *Marine Biology* 95, 315-332.
 71. Weber, C. I. (1973). Recent developments in the measurement of the response of plankton and periphyton to changes in their environment, in: Glass, G., Ed., *Bioassay techniques and environmental chemistry.* Ann Arbor Science Publishers, Ann Arbor, MI, pp. 119–38.
 72. Whitton, B. A. and Rott, E. (1996). *Use of Algae for Monitoring Rivers II.* Institut fur Botanik, Universita't In nsbruck,Inns

bruck: 196 pp.

73. Yamaguchi, M.; Itakura, S.; Nagasaki, K.; Matsuyama, Y.; Uchida, T. and Imai, (1997). Effects of temperature and salinity on the growth of the red tide flagella *Heterocapsa circularis* quaman (Dinophyceae) and *Chattonella verruculosa* (Raphidophyceae). *J. Plankton Res.* 19:1167–117.
74. Zeng-Yei. Hseu. (2004). Evaluating heavy metal contents in nine composts using four digestion methods, Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, Taiwan, 53–59.