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RESEARCH ARTICLE

Determination of Heavy Metals, Mn, Fe, Co, Cu, Zn, Cd and Pb in Sargassum vulgar and Pterocladia capillacea Marine Algae in Libyan Coast of Al-Khoms.

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Abstract

The present study determined the concentration of seven heavy metals (Mn, Fe, Co, Cu, Zn, Cd, and Pb) in brown and red marine algae, *Sargassum vulgar* and *Pterocladia capillacea* respectively, collected from the coast of Al-Khums, Libya. Concentration of Fe showed high concentration in *Sargassum vulgar* and *Pterocladia capillacea*, 367.5 and 850.0 µg/g respectively where concentration of Co was the lowest in species, 2.5 and 7.5 µg/g. It was concluded that and according to strong ability of these algae to accumulate heavy metals and the diversity of marine algae that live in the Libyan coastal areas make them a promising biomonitor of metal contamination in the coast.

INTRODUCTION

Coastal areas are often considered as receptacles for pollutants from industrial and urban activities [1], [2]. Benthic marine algae are of major importance as primary producers and metal concentrating agents in coastal waters. The concentrating ability of macroalgae has been attributed to their property of binding metals to molecular groups in their tissues [1]. Metals are one of the toxic pollutants of great concern because of their potential detrimental effects on aquatic ecosystems. Meanwhile, metals are readily accumulated by aquatic organisms and subsequently transferred along food chains, ultimately posing a risk to human health through seafood consumption [2]. Metals such as Zn, Mn, Cu, Mg and Fe are of physiological importance as they are present in active enzymes, proteins and vitamins [1]. The ability of aquatic plants to take up heavy metals from water, producing an internal concentration greater than in their surroundings has been shown for many species. It is clear from the literature that, in general, the higher the level of metal in water, the higher the level in algae. Thus, analysis of heavy metals composition of aquatic plants gives a better indication of the fraction of the metals in the environment which is likely to affect the aquatic ecosystem than most types of direct chemical analysis [3]. The study of metal concentration in the tissues of aquatic macrophytes has recently received increasing interest [1]. Several activities can contribute to heavy metal pollution in the marine environment, for example, seafloor and bedrock dredging, shipping activities, industrial and urban effluents, mining, agricultural fertilizer use, and burning of fossil fuels [4], [5]. The increasing significance of heavy metals disturbing the environment is especially evident in aquatic systems. Although most of the investigations have been made on microalgae and macrophytic algae and they are considered as valuable indicators because of their accumulation capacity [4].

Brown algae (Phaeophyceae), often dominating seaweed communities in the littoral and sub-littoral, are frequently employed for coastal monitoring Pollution assessment studies have also used red algae (Rodophyceae) which often make up the major biomass in subtidal communities [6]. A few species of marine macroalgae, which commonly known as brown algae, exhibit high metal binding capacities. Brown algae contain high concentrations of alginic acid and sulfated polysaccharides. It has been postulated that the function of these polysaccharides, which are absent in terrestrial plants, is to enable marine algae to selectively absorb metallic ions in a saline medium through ion exchange [3].

Page Sargassum vulgar and Pterocladia capillacea:
Taxonomy:

The term algae refer to a large and diverse assemblage of organisms that contain chlorophyll and carry out oxygenic photosynthesis. The algae are included in the plant kingdom and are distinguished from other chlorophyllous plants on the basis of sexual reproduction. Brown algae derive their characteristic colour from the large amounts of the carotenoid fucoxanthin (which yields a brown colour) contained in their chloroplasts and the presence of various pheophycean tannins. They occur mainly in the marine environment, where they appear as an intertidal component [7], [8]. Table (1) represent taxonomy of the two kind of brown and red marine algae under the study.

Table (1) Taxonomy of *Sargassum vulgar* and *Pterocladia capillacea*

Algae	*Sargassum vulgar*	*Pterocladia capillacea*
Kingdom	Chromalveolata	Protista
Phylum	Heterokontophyta	Phylum Rhodophyta
Class	Phaeophyceae	Rhodophyceae
Order	Fucales	Gelidiales
Family	Sargassaceae	Gelidiaceae
Genus	Sargassum	Gelidium

Sargassum vulgare is large plant-like group seaweed which classified as *Phaeophyceae* It has an olive brown to dark brown colouration and long ‘stems’ to 1m or longer with leaf-shaped blades that may be narrow, broad or very small (1-5cm long) attached to it.Sargassum seaweeds can be utilized as human food, animal feed, fertilizer, and insect repellent. Various species are used as medicine for ailments ranging from children's fever, cholesterol problems, cleansing the blood, skin ailments. The red colour that most of the Rhodophyta display is due to the accessory pigment phycoerythrin. The major distinguishing characteristic of the Rhodophyta is the lack of any flagellated stage in the life cycle. It has been suggested that the triphasic life cycle found in many species of the Rhodophyta evolved to compensate for the lack of flagellated cells [9].

The noticeable point which should be considered in use of algae as a nutrient is that the algae are one the most important biosorption of heavy metals which may poison animals and human. The algae catch heavy metals from the surrounding environment and accumulate them in their cell wall which their concentration may be 20000-40000 times higher than the surrounding water [10], [11], [13]. Therefore, the algae are very good biosorption [14], [15]. Heavy metals are one of the major pollutants of seas and rivers environment which can ultimately poison animals and humans and cause various diseases [12], [16], [17].

Sargassum vulgar and *Pterocladia capillacea* alga are dominant algae of coastal waters of Al-Khums area which is noteworthy for ranchers to be utilized as animal nutrition because of their high growth speed, large size and their ease to collect.

Materials and Methods

The study area

The study area was located in Al-Khoms coast of the Mediterranean sea is located in the north part of Libya, Fig.(1)

Figure (1)

Experimental

The samples of marine algae (*Sargassum vulgar* and *Pterocladiacapillacea*) was handpicked in the subtidal zone at a depth of about 2-3 m. Care was taken to choose the sample to ensure that all were at a similar stage of development. The samples were washed in seawater at the sampling site and transferred to the laboratory in pre-cleaned polyethylene bags. Upon arrival at the laboratory, they were thoroughly cleaned and any sediment was carefully removed with nylon brushes under tap water for a few seconds. Algal material was rapidly rinsed in deionised water to minimise any possible metal loss during the procedure and was then pulverised. Finally, the samples were dried using the sun and they were transferred to incubator device and were completely dried at temperature of 65 ºC for 24 hours and they were ground to a fine powder.
A 1 g of each dried marine algae were placed in 250 ml beaker; concentrated nitric (HNO_3) and hydrogen peroxide (H_2O_2) were added and the mixture was allowed to stand overnight. The sample was heated until the production of brown NO_2 fumes had ceased. The resultant solutions were diluted to the mark with 0.01 mol L^{-1}HCl.
For each analytical batch of samples processed, blanks and standard solution were carried throughout the entire samples analytical process using Microwave Plasma – Atomic Emission Spectrometer.

Statistical Analysis

One way ANOVA was employed for better understanding of relationship between the concentrations of various metals with respect to *Sargassum vulgar* and*Pterocladia capillacea*.

Results andDiscussion

Concentration of heavy metals, Mn, Fe, Co, Cu, Zn, Cd, and Pb in *Sargassum vulgar* and*Pterocladia capillacea* algae of the study area as determined by AAS analysis in brown and red marine algae and its descriptive statistics of the samples were summarized in Table (2). Concentration of Co and Cd showed less concentration at all species, where accumulation of Fe was the highest in brown algae under the study.

Table (2) Heavy metals content (µg/g) in *Sargassum vulgar* and *Pterocladia capillacea*

Heavy metal	*Sargassum vulgar*	*Pterocladiacapillacea*	Mean ± STD
Mn	107.5	35.0	71.25±51.27
Fe	367.5	850.0	608.75±341.18
Co	2.5	7.5	5±3.54
Cu	10.0	20.0	15±7.07
Zn	52.5	62.5	57.5±7.07
Cd	7.5	10.0	8.75±1.77
Pb	42.5	30.0	36.25±8.84

Except for the concentration of Co and Cd which did not show any significant difference in algae species, other metals showed significant variations in concentration with respect to each species in this study. Considering the sampling areas, no clear trend was observed about the concentration changes of all elements in *Sargassum vulgar* and *Pterocladia capillacea*, but in the case of individual elements, Fe showed highest level concentration for the two species, where Co concentration is the lowest, Fig.(2)

The heavy metals content at*Sargassum vulgar* was in the order: Fe >Mn> Zn >Pb> Cu > Cd > Co, where the order of heavy metals concentration in *Pterocladia capillacea* as follows: Fe > Zn >Mn>Pb> Cu > Cd > Co.

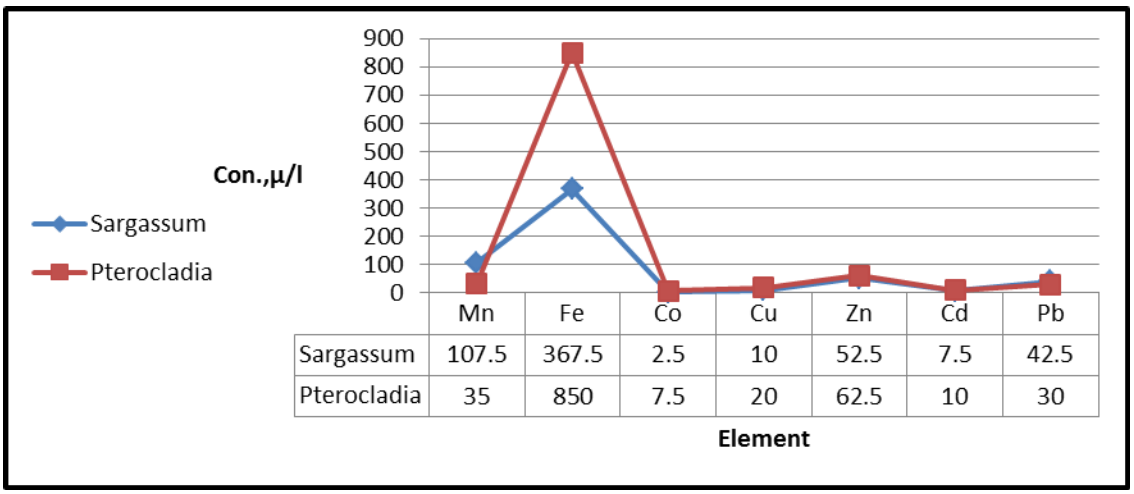

Table (3) One way ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	577198.214	6	96199.702	5.648	.019
Within Groups	119225.000	7	17032.143		
Total	**696423.214**	**13**			

According to One way ANOVA, Table (3), the metals were revealed that the concentration of metals was significantly varied with respect to different species ($P < 0.05$).
Comparison of brown algae in this study (Mean ± STD) with some reported literature is shown in Table (3).Comparison of heavy metals content in samples under study is relatively more than in reported literature but for Mn content in this study it nearly agrees with the reported data of literature.

Table (4) Comparison of this study with some reported literature (expt. Fe & Co)

Reference	algae	Mn	Cu	Zn	Cd	Pb
This study	*Sargassum*	107.5	10.0	52.5	7.5	42.5
	Pterocladia	35.0	20.0	62.5	10.0	30.0
9		27.17-172.53	2.69-8.33	6.49-19.13	0.05-0.11	1.03-1.93
11		53.50	-	18.85	5.00	-
13		16.99	2.64	11.83	0.43	-

The existence of alginate in the cell wall of brown and red marine algae, exceed the ability to absorb heavy metals. Furthermore, the environmental status of an area, temperature, pH, the level of salinity, the waves of the sea, sun light, the algae grow step and its age, season changes and laboratory sample analysis method, all affect the level of heavy metals concentration [7], [14].
According to the result obtained, *Sargassum vulgar* and *Pterocladia capillacea* algae can be used effectively as anbiosorbent in contaminated regions [7], furthermore it can be used as biomarkers for heavy metals pollution in sea environment.

Conclusion

The need for an understanding of the accumulation of the heavy metal in brown algae species provides information on the time of period, reflected in the integrated measurement presented by the accumulated metal concentration. The study reveals that the level of Mn, Fe, Co, Cu, Zn, Cd, and Pb in *Sargassum vulgar* and *Pterocladia capillacea* are moderate in Libyan Coast. In the present study we suggested that red algae have more capacity to uptake of heavy metals even when compared to brown and green algae [8].

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