RESEARCH ARTICLE

Eurasian Journal of Medical and Biological Sciences
AN INTERNATIONAL JOURNAL
Eurasian J Med Biol Sci **3(1):23-33**

Comparison of heavy metal concentrations in marine macroalgae of the Northern Aegean Sea, Türkiye

Fatma Koçbaş[*1], Saniye Türk Çulha[2], Ayşe Gündoğdu[3], Neslihan Türkçü[4]

[*1]*Department of Biology, Faculty of Arts and Sciences, Manisa Celal Bayar University, Manisa, Türkiye*
[2] *Department of Marine Biology, Faculty of Fisheries, Izmir Katip Celebi University, İzmir, Türkiye*
[3] *Department of Hydrobiology, Faculty of Fisheries, Sinop University, Sinop, Türkiye*
[4] *Department of Hydrobiology, Faculty of Fisheries, Ege University, İzmir, Türkiye*

Received : 16/12/2022 Revised : 31/01/2023 Accepted : 27/02/2023

ABSTRACT: The seven heavy metal levels were determined in marine macroalgae species from 15 stations determined from the North Aegean Sea coast. Considering the metal contents varying according to the species and region, the highest concentration determined in the study was Fe, and the lowest concentration was Cd metal. According to the green algae MPI values at the all stations, the most intense pollution was found in the Alsancak, Inciraltı and Güzelbahçe stations located in the inner and middle parts of Izmir Bay. In addition, the present results were compared with the maximum allowable heavy metal values in seaweed and it was determined that the Pb values were high in some stations. In addition, this study also attempted to compare the measured values with international standards for food.

Keywords: Aegean Sea, bioindicator, heavy metal, Macroalgae, MPI, Türkiye.

INTRODUCTION

The most important problem in the world is water pollution, which is the end point of all pollution. Because of bioaccumulation, biomagnification in food chains and toxicity of the heavy metal pollution in the aquatic environment has become a worldwide, ecological, economic and health problem (Naw et al., 2020). Natural events and anthropogenic activities are the main cause of heavy metals in seawater, sediments and marine organisms worldwide (Mazur et al., 2018; Bibak et al., 2020; Corrias et al., 2020; Costa et al., 2020). Heavy metals are transported long distances by hydrological cycle and atmospheric processes (M´endez et al., 2021). The hydrological cycle of water can bring to significant pollution and exposing the aquatic ecosystems to heavy metals causing contamination of marine organisms (Corrias et al., 2020). The productive coastal zones are especially devastated by the release of innumerable contaminants through a wide range of anthropogenic activities such as unplanned urbanization, municipal wastewaters, industrialization, petrochemical complexes, mining ores, petroleum industry activities, port and shipping activity, agricultural chemicals, fish farms, heavy metals, radioactivity, tourism activities and atmospheric sources e.g. burning of fossil fuels (Naggar et al., 2018; Corrias et al., 2020; Rakib, et al., 2021; M´endez et al., 2021; Ameen et al., 2022). Aquatic ecosystems and the productive coastal zones are especially affected by heavy metals, which has become an emerging issue (Kostopoulou et al., 2013; Robin et al., 2017; Bibak et al., 2020; Arisekar et al., 2021). The distribution of heavy metal in freshwater and marine environment, macroalgae or seaweeds are used as biomonitors in water and sediment (Malea and Kevrekidis, 2014; Chakraborty et al., 2014; Naw et al., 2020; Ho and Bantoto-Kinamot, 2021). Biomonitoring with marine macroalgae has found to be a useful technique for environmental monitoring since it was first used in the early 1950s (García-Seoane et al., 2018; García-Seoane et al., 2019; García-Seoane et al., 2020; Rajaram et.al., 2020). Algae and molluscs are currently among the taxonomical groups most evaluated for the use of marine organisms as biomonitoring tools (Rybak et al., 2012; Malea et al., 2015; Bonanno and Orlando-Bonaca, 2018; Corales-Ultra et al., 2019; Anbazhagan et al., 2021; Orlando-Bonaca et al., 2021). Macroalgae have the basic conditions as the most suitable bioindicator of nutrients and heavy metal accumulation in aquatic environment (Corales-Ultra et al., 2019; Anbazhagan et al., 2021; Ho and Bantoto-Kinamot, 2021).

Another usage area of algae is water filtration applications. It is also used in the removal of nutrients, organic pollutants and heavy metals from wastewater (Yalçın et al., 2012; Yılmaz et al., 2016). The most dominant polysaccharides found in the cell wall of brown algae as cellulose, alginic acid and fucoidone are alginic acid and alginates (alginic acid salts) (Dodson et al., 2015; Sahoo and Seckbach, 2015; Manev and Petkova, 2021). This alginic acid and carboxylic acid abundant in alginates are directly related to metal binding capacity and are abundant in brown algae (brown algae > green algae > red algae) (Dodson et al., 2015; Ali et al., 2020; Manev and Petkova, 2021). Moreover, the chemical composition of brown algae varies according to species, habitat and season (Ko and Wan, 2014). It contains compounds with biological activity such as laminarin, which is a product of metabolism. In addition to cellulose and alginic acid, sulfated polysaccharides are also present in the cell wall. These substances in algae offer functional groups such as hydroxyl, carboxyl, sulfate and amino. These functional groups serve as the

*Corresponding author : fatma.kocbas@cbu.edu.tr

binding site responsible for biosorption (Sun et al., 2016). The bonding of the functional groups in the algal cell wall with metal ions varies according to the algae species and metal species (Ramakrishna et al., 2005).

Concentrations of heavy metals in macroalgae of the Northern Aegean Sea were investigated to evaluate an environmental risk assessment from metals contamination in May and July 2009. This study was conducted to assess the status of 7 heavy metals (Co, Cu, Fe, Ni, Cd, Pb and Zn) in marine macroalgae in the Aegean Sea. In the present work the main aimes of the study were as follows:

- to determine the concentration of Co, Cu, Fe, Ni, Cd, Pb and Zn in macroalgae (*Ulva lactuca, Ulva intestinalis, Ulva linza, Codium fragile, Cystoseira barbata, Padina pavonica, Colpomenia sinuosa, Corallina elongata*), samples collected from different stations of the Aegean Sea, at 15 station in 2009,
- to know the class of studied macroalgae which have the ability to accumulate more the heavy metals than the other classes,
- to compare the present results with maximal level of heavy metals authorized in seaweeds (mg kg^{-1} dry weight)

to compare the present results with the similar studies have been carried out in the same region of the Aegean Sea.

MATERIALS AND METHODS

Study area and sampling stations

This study was carried out in fifteen stations (Akcay, Oren, Ayvalık Cunda Port, Ayvalık, Dikili Port, Çandarlı Port, Çandarlı, Aliağa Port, Aliağa PETKIM, Izmir Karşıyaka, Izmir Turan, Izmir Alsancak, Izmir Inciraltı, Izmir Güzelbahce, Izmir Çeşme Ilıca) of the Aegean Sea (Türkiye) (Figure1). The sampling sites in this study were selected the four bays (Izmir, Çandarlı, Dikili and Edremit Bay) within the Aegean Sea. Sampling stations within the study area present different degree of trace element inputs of anthropogenic origin such as industrial activities, tourism, shipping, shipbreaking area, and fishing activities (Table 1).

Sampling materials

Macroalgae were collected from May to July 2009 from the fifteen sampling stations on coastal zone of North Aegean Sea. The sampling marine algae species were; green algae (*Ulva lactuca, Ulva intestinalis, Ulva linza, Codium fragile,*), brown algae (*Cystoseira barbata, Padina pavonica, Colpomenia sinuosa*), red algae (*Corallina elongata*).

Chemical analyses

The macroalgae were collected by hand directly. About 500 g of the fresh weight were harvested at low tide. The samples were rinsed to remove sand, mud and epiphyte in the sea water and then with top water and distilled water. Then they were dried at 60ºC to a constant weight and homogenized manually in porcelain mortar into powder. 0.5 g of dried macroalgae samples was digested in Teflon vessels with 10 mL analytical ultrapure HNO_3 (Merck) using a microwave oven (MARS5 Microwave Digestion System-CEM Corporation). The microwave was programmed on a 20 min ramp, for macroalgae samples 15 min at 200ºC and potency of 1200 W. Tree replicate subsamples of each sample were processed. All procedure of the method (Method 3051A) was similar to that previously described (USEPA, 2007, UNEP, 1984). Macrolagae samples were diluted with ultrapure Milli-Q water to a final volume of 25 mL and analyzed via ICP-MS. The concentration of the heavy metals were determined by ICP-MS. Standard solutions were prepared from stock solutions (Merck, multi-element standard). Certified Reference Material BCR-279 sea lactuca (*Ulva lactuca*) (powder) was used for calibration. The results showed good agreement between certified and analytical values (recovery rates 90-110%).

The heavy metal content of algae at fifteen stations investigated in this study was compared on a regional and algae basis using the Metal Pollution Index (MPI) calculated with the formula for algae (Usero et al., 1997).

$$MPI = (C1 \times C2 \times \ldots \times Cn)^{1/n}$$

Where: Cn are the average concentration of trace metals (n) in algae

If this combined index is above 1 the concentrations of trace metals would be considered elevated and ecosystem could be regarded as "polluted" (Teodorovic et al., 2000).

Figure 1. *Sampling stations*

Table 1. *Coordinates and characteristics of sampling stations*

Sampling stations	Coordinates	Pollution sources of sampling stations
Akçay	**N**39° 34.990′ **E** 026° 55.395′	Tourism, fishing activities
Oren	**N**39° 29.057′ **E** 026° 55.742′	Tourism, fishing activities
Ayvalık Cunda Port	**N**39° 19.591′ **E** 026° 37.168′	Tourism, fishing activities, shipping
Ayvalık	**N**39° 16.481′ **E** 026° 39.469′	Tourism, fishing activities, shipping
Dikili Port	**N**39° 04.246′ **E** 026° 53.180′	Tourism, fishing activities, shipping
Çandarlı Port	**N**38° 55.762′ **E** 026° 55.933′	Tourism, fishing activities, shipping
Çandarlı	**N**38° 56.404′ **E** 026° 56.152′	Tourism, fishing activities, shipping
Aliağa Port	**N**38° 48.359′ **E** 026° 58.393′	Industrial activities, refinery, shipping, shipbreaking area, fishing activities
Aliağa PETKIM	**N**38° 48.455′ **E** 026° 57.766′	Industrial activities, refinery, shipping, shipbreaking area, fishing activities
Izmir Karşıyaka	**N**38° 28.960′ **E** 027° 04.856′	Urbanization, shipping
Izmir Turan	**N**38° 28.070′ **E** 027° 09.522′	Urbanization, shipping
Izmir Alsancak	**N**38° 25.248′ **E** 027° 07.511′	Urbanization, shipping
Izmir İnciraltı	**N**38° 24.712′ **E** 027° 01.968′	Urbanization, shipping, fishing activities
Izmir Güzelbahçe	**N**38° 21.382′ **E** 026° 18.521′	Urbanization, shipping, fishing activities
Izmir Çeşme Ilıca	**N**38° 19.382′ **E** 026° 18.077′	Tourism, Fishing activities

RESULTS AND DISCUSSION

The eight species of North Aegean Sea coast algae were examined for their accumulation ability in the uptake of different metals from the Turkish aquatic environment. A wide range of metal retention capacity among the different species was observed. The collected seaweed genera are listed as per sampling station, and the concentration values of the metals are summarized in Table 2.

The heavy metals accumulated in different algal taxa were: in green algae (*U. intestinalis, U. linza, U. lactuca, C. fragile*), Fe > Zn > Cu > Ni > Co > Pb > Cd; in brown algae (*P. pavonica, C. barbata, C. sinuosa*), Fe > Cu > Zn > Ni > Co > Pb > Cd;

in red algae (*C. elongata*) Fe > Zn > Cu > Ni > Co > Pb = Cd. The Cd concentrations in tested macro algae samples were found to be below the lower limit detection (<0.01). In this study, high levels of Fe were detected in almost all the specimens tested, especially, *U. intestinalis and U. linza* in green algae, reaching a concentration higher than the other species. Algae belonging to the Chlorophyceae (*U. intestinalis and U. linza*) from the North Aegean Sea generally accumulated most elements.

The biomass concentration is another important variable during metal uptake. At a given equilibrium concentration, the biomass takes up more metal ions at lower than at higher cell densities (Mehta and Gaur, 2001). It has been suggested that electrostatic interactions between cells can be a significant factor in the relationship between biomass concentration and metal sorption. In this connection, at a given metal concentration, the lower the biomass concentration in suspension, the higher will be the metal/biosorbent ratio and the metal retained by sorbent unit, unless the biomass reaches saturation. High biomass concentrations can exert a shell effect, protecting the active sites from being occupied by metal. The result of this is a lower specific metal uptake, that is, a smaller amount of metal uptake per biomass unit (Romera et al., 2007). The highest uptake in macroalgae species at the sampling sites were as follows: **Cu** in C. *sinuosa*, *U. linza*, *U. intestinalis*, *P. pavonica*, **Co** in *U. lactuca*, U. *linza*, *P. pavonica*, **Zn** in *U. linza*, *U. lactuca*, *U. intestinalis*, **Fe** in C. *sinuosa*, *U. intestinalis*, Ni in *U. intestinalis*, C. *sinuosa*, *U. lactuca*, **Pb** in *U. linza*, and *P. pavonica*. Heavy metal levels of C. s*inuosa, U. intestinalis* and *U. linza* were significantly higher than those in other marine algae species. The highest levels of heavy elements were found in *C. sinuosa* collected from Ören, with concentrations up to 5667.3 μg g^{-1} for Fe. Studies performed in other Aegean Sea Coast revealed that the concentration of heavy metals in macroalgae is at high levels of Fe (Tunçer, 1989; Türkan et al., 1989; Uysal, 1992; Çetingül and Aysel, 1998; Akçalı and Küçüksezgin, 2009).

The information acquired in this preliminary investigation supports of the assumption on the selective ability of macroalgae to accumulate inorganic contaminants from seawater. The concentration of trace elements in macro algae samples range widely, from <0.01 μg g^{-1} (Cd) to 5667.3 μg g^{-1} (Fe). This situation is supported by the results of other studies (Farias et al., 2002). Compared to metals accumulation; high levels of Fe and Cu were found in *C. sinuosa* collected from Oren, high levels of Co were found in *U. lactuca* collected from Turan, high levels of Ni were found in U. *intestinalis* collected from Akçay, high levels of Zn were found in *U. linza* collected from Güzelbahçe (Table 2). Biological, physical and chemical conditions affect both the distribution and the role of the elements, compounds and residues in a system. Furthermore, seaweeds have a high potential capacity for storing trace metals, depending on the species of alga and the metal. Previous studies have shown that members of the macroalgae have the high capacity for storing metals (Rodriguez-Castaneda et al., 2006). This study shows that concentrations of elements in the macroalgae collected in the Aegean Sea and the world vary depending on species and sampling area (Table 3), probably because many variables affect the accumulation of elements in algae including the abundance of these elements in the local environmental conditions, and by a species particular metabolic processes (Försberg et al., 1988; Rodriguez-Castaneda et al., 2006).

The green macroalgae *U. lactuca* was the most widespread in the area of the sample, being found in 10 stations. Therefore, *U. lactuca* is selected that compare levels of heavy metal accumulation is thought to be appropriate. The variations in the concentrations of these elements in the *U. lactuca* can be related to the influence of territorial factors such as naturally resulting higher contents of heavy metals in the water and sediments of certain parts of the Aegean Sea. The area has been subject to very high levels of pollution due to industrial activity, municipal wastewaters, agricultural chemicals, oil pollution and airborne particles. The macroalgae species are usually used to indicate heavy metal levels in both estuarine and coastal waters throughout the world. In benthic food webs, macroalgae are key links and they act as time-integrators of pollutants (Türk Çulha et al., 2010). This study compared the amount of the metals. The relative abundance of the heavy metals was always the following Fe > Zn > Cu (5667.3, 93.52, 51.18 μg g^{-1}, respectively). An analogous sequence is reported in other paper concerning metal distribution in seaweeds (Türkan et al., 1989; Ganesan et al., 1991; Uysal, 1992; Rajendran et al., 1993; Çetingül and Aysel, 1998; Malea and Haritonidis, 1999; Caliceti et al., 2002). In algae species collected from all stations, while the lowest level of Pb and Cd were also measured.

The MPI was calculated to compare the total metal concentrations in the algae of fifteen different stations (Table 2, Figure 2). The MPI values determined according to the seven metals detected in all algae sampled from each station are as follows; Oren (6.89) > Akçay (6.18) > Ayvalık Cunda (4.73) > Alsancak (3.49). MPI values in the green algae seaweed species are summarized in Figure 3. The MPI values determined according to the green algae species found in other stations except Çeşme Ilıca station are as follows; Alsancak (3.49) > Güzelbahçe (2.69) > Inciraltı (2.63). According to the data obtained from the study, it was determined that the metal distributions in the stations differed. The higher metal content in the algae species sampled from these 4 stations is related to the amount of metal in the water, the form of the metal (ion, compound, dissolved, etc.) and the presence of the metal. It differs in metal concentrations in sampling stations compared to green algae. It has been determined that MPI values are high because the sampling stations with the highest metal concentrations are located in Izmir Inner and Middle Bay. Studies have shown that algae is a good indicator species for detecting heavy metals in the environment (Rakib et al., 2021).

Table 2. *Average heavy metal concentrations (mg kg^{-1} dry weight) in marine algae samples of all sampling stations in the North Aegean Sea*

Stations	Species	Cd	Pb	Co	Cu	Ni	Zn	Fe	MPI
Akçay	*U. lactuca*	<0.01	<0.01	1.31	34.34	13.71	1.63	467.54	
	C. barbata	<0.01	<0.01	1.44	22.85	6.24	10.28	340.73	**6.18**
	P. pavonica	<0.01	2.34	2.90	11.98	10.10	41.20	2380.74	
	U. intestinalis	<0.01	**6.30**	0.40	31.26	17.97	21.36	4146.66	
Oren	*C. barbata*	<0.01	<0.01	1.50	32.36	3.18	10.22	640.32	
	P. pavonica	<0.01	1.94	1.64	34.50	3.73	18.77	1034.46	
	C. sinuosa	<0.01	**9.31**	5.68	60.70	16.86	54.77	5667.30	**6.89**
	U. linza	<0.01	**14.01**	2.45	39.12	1.93	10.81	280.84	
	U. lactuca	<0.01	<0.01	<0.01	26.12	1.34	1.67	330.37	
Ayvalık-Cunda Port	*C. barbata*	<0.01	1.52	<0.01	18.33	<0.01	13.21	528.41	
	U. lactuca	<0.01	<0.01	1.72	34.53	1.76	11.25	457.07	
	U.intestinalis	<0.01	<0.01	1.17	24.27	2.83	11.51	972.30	4.73
	P. pavonica	<0.01	**11.4**	0.19	31.50	1.51	44.68	1699.32	
	U. linza	<0.01	1.89	1.00	51.18	3.22	75.97	2132.94	
Ayvalık	*C. barbata*	<0.01	<0.01	1.76	23.82	2.32	45.60	838.74	
	U.intestinalis	<0.01	<0.01	0.98	42.53	2.32	10.53	924.42	2.00
	P. pavonica	<0.01	<0.01	<0.01	44.22	0.66	35.93	1738.08	
	U. lactuca	<0.01	<0.01	1.57	23.95	<0.01	0.35	1140.54	
Izmir/Dikili Port	*U.intestinalis*	<0.01	<0.01	2.82	34.87	<0.01	36.43	647.58	1.78
	C. barbata	<0.01	<0.01	<0.01	14.96	2.77	2.71	519.64	
Izmir/Çandarlı Port	*U. lactuca*	<0.01	<0.01	1.97	9.14	0.24	0.53	739.74	0.85
	U. linza	<0.01	<0.01	1.54	7.11	2.69	0.12	221.38	
Izmir/Çandarlı	*U. lactuca*	<0.01	<0.01	1.42	9.26	0.34	4.37	546.18	1.37
	U.intestinalis	<0.01	<0.01	<0.01	7.77	2.96	22.46	768.72	
Izmir/Aliağa Port	*U.intestinalis*	<0.01	<0.01	<0.01	4.44	2.37	61.10	539.32	0.83
	C. elongata	<0.01	<0.01	<0.01	8.54	7.43	11.51	299.46	
Izmir/Aliağa PETKIM	*U. lactuca*	<0.01	<0.01	0.49	7.93	6.36	12.69	304.76	
	C.elongata	<0.01	<0.01	2.16	37.94	9.69	71.97	2297.52	2.26
	C. fragile	<0.01	<0.01	<0.01	2.93	1.64	16.14	526.57	
Izmir/Karşıyaka	*U. linza*	<0.01	<0.01	14.38	10.26	1.67	39.83	77.50	1.86
Izmir/Turan	*U. lactuca*	<0.01	<0.01	15.96	10.76	<0.01	29.46	885.72	1.24
Izmir/Alsancak	*U.intestinalis*	<0.01	<0.01	8.91	19.42	8.19	72.04	608.16	3.49
Izmir/Inciraltı	*U. lactuca*	<0.01	<0.01	12.69	15.49	2.72	19.30	827.04	2.63
Izmir/Güzelbahçe	*U.intestinalis*	<0.01	<0.01	4.52	6.66	3.83	32.20	454.89	
	U. lactuca	<0.01	<0.01	10.48	11.48	2.85	81.34	364.91	2.15
	U. linza	<0.01	<0.01	1.93	1.57	<0.01	93.52	295.28	
Izmir/Çeşme-Ilıca	*P. pavonica*	<0.01	<0.01	12.32	18.16	<0.01	20.82	1450.80	1.31

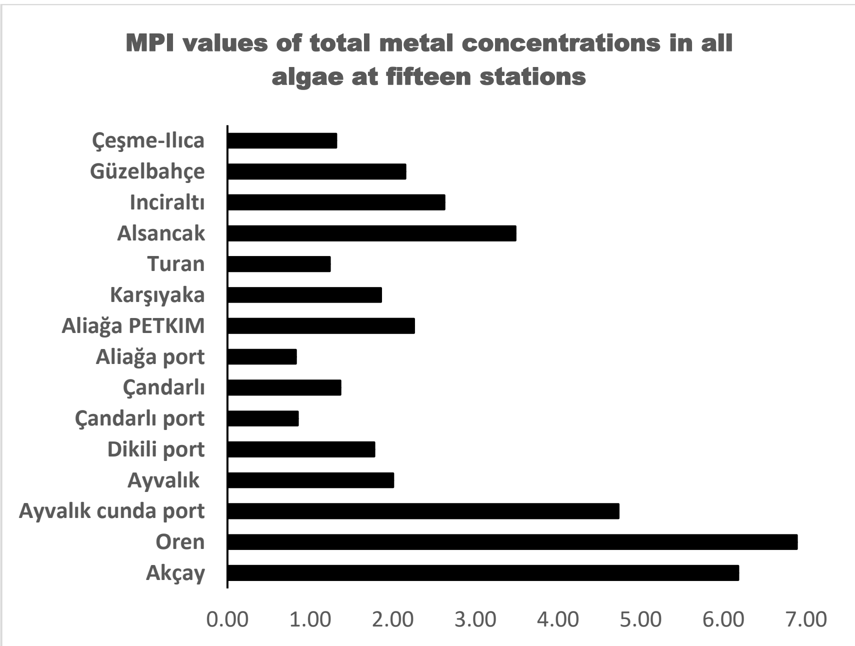

Figure 2. *MPI values of total metal concentrations in all algae at fifteen stations*

Table 3. *Comparison of heavy metal distribution in marine algae of Türkiye and in the world (µg g^{-1} dry weight).*

Species	Sites	Fe	Zn	Cu	Pb	Cd	Ref.
U. lactuca	Izmir and Çandarlı Bay (Türkiye)	34.30-583.80	3.20-37.13	0.39-6.22	0.29-8.40	0.01-0.60	1
Ulva sp.	Izmir Bay (Türkiye)	458-1300	32-80	39 67	31-132	0.56-1.06	2
Ulva sp.	Izmir Bay (Türkiye)	--	8.02	1.82	3.31	0.13	3
Ulva sp.	Aegean Sea (Türkiye)	223-1331	9.10-29.50	1.30-15.34	0.54–3.07	0.42- 3.00	4
C. barbata	Izmir Bay (Türkiye)	258-15060	31.2-150	4.60-56.50	0.0-30.0	0.30-2.40	5
P. pavonina	Izmir and Çandarlı Bay (Türkiye)	40.70- 345.20	3.7-35.40	0.50-2.60	1.50-9.86	0.06-0.72	1
Cystoseira sp.	Izmir/Foça (Türkiye)	97.62	10.81	3.78	0.01	0,0052	6
Cystoseira sp.	Izmir/Urla (Türkiye)	212.14	27.17	2.25	0.01	0.19	7
Codium sp.	Izmir Bay (Türkiye)	--	4.89	0.92	3.13	0.14	8
Codium bursa	Izmir Bay (Türkiye)	--	1.98	0.63	1.64	0.18	8
C.barbata	Ayvalık (Türkiye)	--	4.36-7.95	3.12-7.87	20.7-67.44	<0.001	9
P. pavonica	Ayvalık (Türkiye)	--	0.28-3.09	6.95-10.85	24.20-45.35	<0.001	9
Ulva sp.	Coast of Istanbul (Türkiye)	88.74	6.92	4.92	0.26	0.05	10
U. intestinalis	Kadin Creek (Gokova Bay/Türkiye).	--	7.20-68.22	1.50-38.95	2.49-8.02	0.01-0.19	11
C. fragile	Thessaloniki Gulf, Aegean Sea (Greece)	--	105.96	5.07	3.89	0.046	12
U. lactuca	Iskenderun and Mersin Bay (Turkey)	5828.50	129.0	29.56	12.09	0.24	13
P. pavonica	Iskenderun and Mersin Bay (Turkey)	777.90	25.48	8.01	5.89	0.24	13
Cystoseira corniculata	Iskenderun and Mersin Bay (Turkey)	236.23	31.03	10.79	5.83	0.24	13
U. lactuca	Black Sea (Turkey)	1754	--	--	0.08-1.90	0.09-0.66	14
U. linza	Black Sea (Turkey)	--	7	--	--	--	14
C. barbata	Black Sea (Turkey)	327	65	5-37	--	--	14
U. intestinalis	Sürmene Bay (Turkey)	--	351.50	493.00	15.80	--	15
Corallina officinalis	Aegean Sea (Greece)	--	37.50	0.85	0.02	2.90	16
U. lactuca	Gulf of Gaeta (Italy)	--	37-54	4.9-6.4	1.67-2.28	0.13-0.21	17
U. intestinalis	Thessaloniki Gulf, (Greece)	--	122.8	9.15	4.62	0.03	12
P. pavonica	Gulf of Gaeta (Italy)	--	45-56	11.8-13.2	0.34-4.82	0.39-0.66	17
U. lactuca	Suez Gulf (Egypt)	464.10	22.35	5.70	8.69	0.66	18
U. lactuca	Suez Canal (Egypt)	628.00	13.90	8.92	7.19	0.59	18
Ulva sp.	Alexandria region (Egypt)	687.60	12.63	11.71	4.96	0.31	19

*Ref: 1. Tunçer, 1989; 2. Türkan et.al., 1989; 3. Küçüksezgin and Balcı, 1994; 4. Uysal, 1992; 5. Çetingül and Aysel, 1998; 6. Akçalı and Küçüksezgin, 2009; 7. Akçalı and Küçüksezgin, 2009; 8. Küçüksezgin and Balcı, 1994; 9. Koçbaş et al., 2018; 10. Özden et al., 2019; 11. Yozokmaz et al., 2018; 12. Malea et al., 2015; 13. Erguden et al., 2021; 14. Arici and Bat, 2016; 15. Alkan et al., 2020; 16. Sawadis et al., 2001; 17. Conti and Cecchetti, 2003; 18. Mourad and El-Azim, 2019; 19. Saeed and Moustafa, 2013.

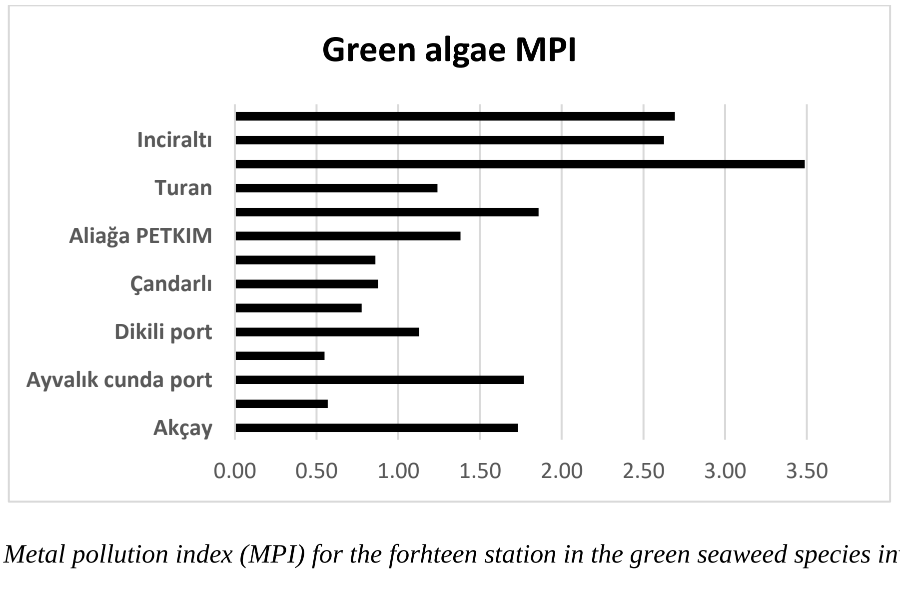

Figure 3. *Metal pollution index (MPI) for the forhteen station in the green seaweed species investigated*

On the basis of our results we conclude that the Aegean Sea has suffered seriously from human impacts, and that the characteristics of this region encourage a natural increase in certain elements in the sediments and water, which is then reflected in the macroalgae. During each algal genera assorted in its ability to uptake and accumulate individual metals, general accumulation trendencies were still evident across all genera of algae. On the basis of the levels of heavy metals observed its wide distribution in the North Aegean Sea, this organism achieves a number of preconditions to be considered as an adequate biomonitor for future studies. Results obtained so far from macroalgae collected in the coastal waters of Aegean Sea demonstrate that there is localized variation in each of the different areas, and that the accumulation of some elements is probably identified by their relative concentration in the surrounding water and sediments, by a species' particular metabolic processes, and by local environmental conditions.

Moreover, maximum allowed levels of heavy metal have been defined for edible seaweed (Table 4). According to CEVA (Centre d'Étude et de Valorisation des Algues) (2014)' s maximum limit in consumable algae, values; *U. intestinalis* from Green algae at Akçay station, *U. linza* from Green algae at Oren station, *C. sinuosa* from Brown algae and pavonica from Brown algae sampled from Ayvalık-Cunda Port station were found to be well above the limit values for Pb consumption. Since these algae are not consumed as food in Türkiye, they do not effect any health risk.

Table 4. *Maximal level of heavy metals and iodine authorized in seaweeds (mg kg^{-1} dry weight) (CEVA, 2014)*

Elements	Max. Level (mg kg^{-1} dry weight)
Inorganic Arsenic (As)	3
Cadmium (Cd)	0.5
Mercury (Hg)	0.1
Lead (Pb)	5
Tin (Sn)	5
Iodine (I)	2000

CONCLUSION

Our results showed that Fe, Ni, Cu, Co and Zn concentrations are higher, but Pb and Cd levels are lower than in the same macroalgae species collected from the Aegean Sea in 2009. A comparison of the present results with data reported for similar macroalgae species from other Turkish marine environment, suggest that the heavy metal levels are higher in the Aegean macroalgae than Bosphorus and Marmara Sea, Mediterranean and Black Sea macroalgae. It has been determined that the macroalgae species examined in this study in the North Aegean Sea are good indicator species in determining environmental pollution. Compared to other seas, heavy metal concentrations determined in Aegean Sea macroalgae are quite high. Since these marine macroalgae are not consumed as food in Turkey, they do not pose any health risk. In future research, it is necessary to examine in more detail the exportable and consumable marine macroalgae in terms of heavy metal accumulation and to determine the maximum consumable limit values for Türkiye.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

Akçalı, İ., Küçüksezgin, F. (2009). Bioaccumulation of heavy metals by the brown algae *Cystoseira* sp. along the Aegean Sea. E.U. Journal of Fisheries & Aquatic Sciences, 26(3), 159-163.

Alkan, N., Alkan, A., Demirak, A., Bahloul, M. (2020). Metals/metalloid in marine sediments, bioaccumulating in macroalgae and a mussel, soil and sediment contamination. An International Journal, 29(5), 569-594. doi:10.1080/15320383.2020.1751061.

Ali, H.S., Kandil, N.F.E.S., Ibraheem, I.B.M. (2020). Biosorption of Pb^{2+} and Cr^{3+} ions from aqueous solution by two brown marine macroalgae: An equilibrium and kinetic study. Desalination and Water Treatment, 206, 250–262.

Ameen, F., Al-Homaidan, A. A., Almahasheer, H., Dawoud, T., Alwakeel, S., AlMaarofi, S. (2022). Biomonitoring coastal pollution on the Arabian Gulf and the Gulf of Aden using macroalgae: A review. Marine Pollution Bulletin. 175, 113156. doi: 10.1016/j.marpolbul.2021.113156.

Anbazhagan, V., Partheeban, E.C., Arumugam, G., Arumugam, A., Rajendran, R., Paray, B. A., Al-Sadoon, M.K., Al-Mfarij, A.R. (2021). Health risk assessment and bioaccumulation of metals in brown and red seaweeds collected from a tropical marine biosphere reserve. Marine Pollution Bulletin, 164, 112029. doi: 10.1016/j.marpolbul.2021.112029.

Arici, E., Bat, L. (2016). Using marine macroalgae as biomonitors: heavy metal pollutıon along the Turkish west coasts of the Black Sea. 41st CIESM Congress, Kiel (Germany), 12-16 September 2016. Rapp. Comm. Int. Mer Medit.At: Kiel (Germany) Vol. 41, 238.

Arisekar, U., Shakila, R.J., Shalini, R., Jeyasekaran, G., Sivaraman, B., Surya, T. 2021. Heavy metal concentrations in the macroalgae, seagrasses, mangroves, and crabs collected from the Tuticorin coast (Hare Island), Gulf of Mannar, South India. Marine Pollution Bulletin, 163, 111971.

Bibak, M., Sattari, M., Tahmasebi, S., Agharokh, A., Nami, J.I. (2020). Marine macro-algae as a bio-indicator of heavy metal pollution in the marine environments, Persian Gulf. Indian Journal of Geo Marine Sciences, 49 (03), 357-363.

Bonanno, G., Orlando-Bonaca, M. (2018). Trace elements in Mediterranean seagrasses and macroalgae. A review. Science of the Total Environment, 618, 1152–1159. doi: 10.1016/j.scitotenv.2017.09.192.

Caliceti, M., Argese, E., Sfriso, A., Pavoni, B. (2002). Heavy metal contamination in the seaweeds of the Venice lagoon. Chemosphere, 47, 443 – 454.

CEVA (Centre d'Étude et de Valorisation des Algues) 2014. Edible seaweed and French regulation-Synthesis made by CEVA, 3 pp.: www.ceva.fr/. Available 09.11.2021.

Chakraborty, S., Bhattacharya, T., Singh, G., Maity, J.P. (2014). Benthic macroalgae as biological indicators of heavy metal pollution in the marine environments: A biomonitoring approach for pollution assessment. Ecotoxicology and Environmental Safety, 100, 61–68. doi: 10.1016/j.ecoenv.2013.12.003.

Conti, M.E., Cecchetti, G. (2003). A biomonitoring study: trace metals in algae and molluscs from Tyrrhenian coastal areas. Environmental Research, 93, 99–112. doi:10.1016/S0013-9351(03)00012-4.

Corales-Ultra, O.G., Peja Jr, R.P., Casas Jr, E.V. (2019). Baseline study on the levels of heavy metals in seawater and macroalgae near an abandoned mine in Manicani, Guiuan, Eastern Samar, Philippines. Marine Pollution Bulletin, 149, 110549. doi: 10.1016/j.marpolbul.2019.110549.

Corrias, F., Atzei, A., Addis, P., Secci, M., Russo, M., Angioni, A. (2020). Integrated environmental evaluation of heavy metals and metalloids bioaccumulation in invertebrates and seaweeds from different marine coastal areas of Sardinia, Mediterranean Sea. Environmental Pollution, 266, 115048. doi: 10.1016/j.envpol.2020.115048.

Costa, G.B., Koerich, G., de Ramos, B., Ramlov, F., Martínez-Crego, B., Costa, M.M., Jesus, D., Santos, R.O.P., Horta Jr, P.A. (2020). A review of common parameters and descriptors used in studies of the impacts of heavy metal pollution on marine macroalgae: identification of knowledge gaps and future needs. Acta Botanica Brasilica, 34(3), 460-477. doi: 10.1590/0102-33062020abb0072.

Çetingül, V., Aysel, V. (1998). Heavy metal accumulation of some Brown and red algae which has economical importance. E. U. Journal of Fisheries & Aquatic Sciences, 15 (1-2), 63-76.

Dodson, J.R., Parker, H.L., García, A.M., Hicken, A., Asemave, K., Farmer, T.J., He, H., Clark, J.H., Hunt, A.J. (2015). Bio-derived materials as a green route for precious & critical metal recovery and re-use. Green Chemist, 17(4),1951–65. doi:10.1039/C4GC02483

Erguden, S.A., Erguden, D., Ciftci, N., Akbora, H.D., Ayas, D. (2021). Metal levels of macroalgae from Iskenderun and Mersin Bay Turkey Eastern Mediterranean. Fresenius Environmental Bulletin, 30(07), 8365-8371.

Farias, S., Arisnabarretab, S.P., Vodopivezc, C., Smichowskia, P. (2002). Levels of essential and potentially toxic trace metals in Antarctic macro algae. Spectrochimica Acta Part B, 57, 2133–2140.

Försberg, A., Söderlund, S., Frank, A., Petersson, L. R., Pedersén M. (1988). Studies on metal content in the brown seaweed *Fucus vesiculosus*, from the Archipelago of Stockholm. Env. Pollut, 49, 245 – 263.

Ganesan, M., Kannan, R., Rajendran, K., Govindasamy, C., Sampathkumar, P., Kannan, L. (1991). Trace metal distribution in seaweeds of the Gulf of Mannar, Bay of Bengal. Marine Pollution Bulletin, 22 (4), 205–207.

García-Seoane, R., Aboal, J.R., Boquete, M.T., Fernández, J.A. (2018). Biomonitoring coastal environments with transplanted macroalgae: A methodological review. Marine Pollution Bulletin, 135, 988–999. doi: 10.1016/j.marpolbul.2018.08.027.

García-Seoane, R., Fernandez, J.A., Varela, Z., Real, C., Boquete, M.T., Aboal, J.R. (2019). Sampling optimization for biomonitoring metal contamination with marine macroalgae. Environmental Pollution, 255, 113349. doi: 10.1016/j.envpol.2019.113349.

García-Seoane, R., Aboal, J.R., Boquete, M.T., Fernández, J.A. (2020). Phenotypic differences in heavy metal accumulation in populations of the brown macroalgae *Fucus vesiculosus*: A transplantation experiment. Ecological Indicators, 111, 105978. doi: 10.1016/j.ecolind.2019.105978.

Ho, M.T.G., Bantoto-Kinamot, V. (2021). *Sargassum, Padina* and *Turbinaria* as bioindicators of cadmium in Bais Bay, Negros Oriental. The Palawan Scientist, 13(1), 90-98.

Ko, F.K., Wan, Y. (2014). Introduction to nanofiber materials. Cambridge University Press. doi:10.1017/CBO9781139021333

Koçbaş, F., Ay, G., Kılıç, M., Kılıç, F. (2018). Investigation of the pollution ın the Ayvalık saltern with green and brown macroalgae. Agriculture, Environment and Health Congress, Aydın (Turkey).

Kostopoulou, M., Guida, M., Nikolau, A., Oral, R., Trifuoggi, M., Borriello, I., Vagi, M., D'Ambra, Meriç, S., Pagano, G. (2013). Inorganic and organic contamination in sediment from Izmir Bay (Turkey) and Mytilene Harbor (Greece). Global NEST Journal, 15(1), 57-68.

Küçüksezgin, F., Balcı, A. (1994). Heavy metal concentrations in selected organisims from Izmir Bay, Turkey, Marine Pollution Bulletin, 28 (5), 333-335.

M´endez, S., Ruepert, C., Mena, F., Cort´es, J. (2021). Accumulation of heavy metals (Cd, Cr, Cu, Mn, Pb, Ni, Zn) in sediments, macroalgae (*Cryptonemia crenulata*) and sponge (*Cinachyrella kuekenthali*) of a coral reef in Moín, Lim´on, Costa Rica: An ecotoxicological approach. Marine Pollution Bulletin, 173, 113159. doi: 10.1016/j.marpolbul.2021.113159.

Malea, P., Kevrekidis, T. (2014). Trace element patterns in marine macroalgae. Science of the Total Environment, 494–495, 144–157. doi: 10.1016/j.scitotenv.2014.06.134.

Malea, P., Chatziapostolou, A., Kevrekidis, T. (2015). Trace element seasonality in marine macroalgae of different functional-form groups. Marine Environmental Research, 103, 18-26. doi: 10.1016/j.marenvres.2014.11.004.

Malea, P., Haritonidis, S. (1999). Seasonal accumulation of metals by red alga *Gracilaria verrucosa* (Hud.) Papenf. From Thermaikos Gulf, Greece. Journal of Applied Phycology, 11, 503 – 509.

Mazur, L.P., Cechinel, M.A.P., Guelli U. de Souza, S.M.A., Boaventura, R.A.R., Vilar, V.J.P. (2018). Brown marine macroalgae as natural cation exchangers for toxic metal removal from industrial wastewaters: A review. Journal of Environmental Management, 223, 215-253. doi: 10.1016/j.jenvman.2018.05.086.

Manev, Z.K., Petkova, N.T. (2021). Component composition and antioxidant potential of *Cystoseira barbata* from the Black Sea. Bulletin of the Transilvania University of Brasov, Series II: Forestry, Wood Industry, Agricultural Food Engineering, 14–63(1),164–72.

Mehta, S.K., Gaur, J.P. (2001). Characterization and optimization of Ni and Cu sorption from aqueous solution by *Chlorella vulgaris*. Ecological Engineering, 18, 1 – 13.

Mourad, F.A., El-Azim, H.A. (2019). Use of green alga *Ulva lactuca* (L.) as an indicator to heavy metal pollution at intertidal waters in Suez Gulf, Aqaba Gulf and Suez Canal, Egypt. Egyptian Journal of Aquatic Biology & Fisheries, 23(4), 437 – 449.

Naggar, Y.A., Khalil, M.S., Ghorab, M.A. (2018). Environmental pollution by heavy metals in the aquatic ecosystems of Egypt. Open Access Journal of Toxicology, 3(1): doi:10.19080/OAJT.2018.03.555603.

Naw, S.W., Zaw, N.D.K., Aminah, N.S., Alamsjah, M.A., Kristanti, A.N., Nege, A.S., Aung, H.T. (2020). Bioactivities, heavy metal contents and toxicity effect of macroalgae from two sites in Madura, Indonesia. Journal of the Saudi Society of Agricultural Sciences, 19(8), 528-537. doi:10.1016/j.jssas.2020.09.007.

Orlando-Bonaca, M., Pitacco, V., Bajt, O., Falnoga, I., Hudobivnik, M.J., Mazej, D., ˇSlejkovec, Z., Bonanno, G. (2021). Spatial and temporal distribution of trace elements in *Padina pavonica* from the northern Adriatic Sea. Marine Pollution Bulletin, 172, 112874. doi: 10.1016/j.marpolbul.2021.112874.

Özden, Ö., Orhan, Y., Kaplan, M., Parıldar, S., Erkan, N. (2019). Trace toxic mineral levels of sea lettuce (*Ulva* spp.) from coast of Istanbul. *Aquatic Research*, 2(3), 154-160. doi:10.3153/AR19013.

Rajaram, R., Rameshkumar, S., Anandkumar, A. (2020). Health risk assessment and potentiality of green seaweeds on bioaccumulation of trace elements along the Palk Bay coast, Southeastern India. Marine Pollution Bulletin, 154, 111069. doi: 10.1016/j.marpolbul.2020.111069.

Rakib M.R.J., Jolly, Y.N., Dioses-Salinas, D.C., Pizarro-Ortega, C.I., De-la-Torre, G.E., Khandaker, M.U., Alsubaie, A., Almalki, A.S.A., Bradley, D.A. (2021). Macroalgae in biomonitoring of metal pollution in the Bay of Bengal coastal waters of Cox's Bazar and surrounding areas. Scientific Reports, 11(1), 20999. doi: 10.1038/s41598-021-99750-7

Ramakrishna, S., Fujihara, K., Teo, W. E., Lim, T. C., Ma, Z. (2005). An introduction to electrospinning and nanofibers. An Introduction to Electrospinning and Nanofibers. doi: 10.1142/5894.

Rajendran, K., Sampathkumar, P., Govindasamy, C., Ganesan, M., Kannan, R., Kannan, L. (1993). Levels of trace metals (Mn, Fe, Cu and Zn) in some Indian seaweeds. Marine Pollution Bulletin, 26 (5), 283 – 285.

Robin, A., Chavel, P., Chemodanov, A., Israel, A., Golberg, A. (2017). Diversity of monosaccharides in marine macroalgae from the Eastern Mediterranean Sea. Algal Research, 28, 118–127. doi: 10.1016/j.algal.2017.10.005.

Rodríguez-Castaneda, A. P., Sànchez-Rodríguez, I., Shumilin, E. N., Sapozhnikov, D. (2006). Element concentrations in some species of seaweeds from La Paz Bay and La Paz Lagoon, south-western Baja California, Mexico. Journal of Applied Phycology, 18, 399–408.

Romera, E., Gonzalez, F., Ballester, A., Blazquez, M. L., Munoz, J. A. (2007). Comparative study of biosorption of heavy metals using different types of algae. Bioresource Technology, 98, 3344 – 3353.

Rybak, A., Messyasz, B., Łeska, B. (2012). Freshwater *Ulva* (Chlorophyta) as a bioaccumulator of selected heavy metals (Cd, Ni and Pb) and alkaline earth metals (Ca and Mg). Chemosphere, 89, 1066–1076. doi: 10.1016/j.chemosphere.2012.05.071.

Saeed, S.M., Moustafa, Y.T.A. (2013). The seaweed (green macroalgae), *Ulva* sp. as bioindicator of metal pollution in the Mediterranean Coast, Alexandria region, Egypt. Egypt. J. Aquat. Biol. & Fish., 17 (3), 57-68

Sahoo, D., Seckbach, J. (2015). The algae world. 17(4), 1951–65, Springer. doi: 10.1007/978-94-017-7321-8.

Sawadis, T., Brown, M.T., Zachariadis, G., Sratis, I. (2001). Trace metal concentrations in marine macroalgae from different biotopes in the Aegean Sea. Environment International, 27, 43-47.

Sun, G., Sun, L., Xie, H., Liu, J. (2016). Electrospinning of nanofibers for energy applications. Nanomaterials, 6(7), 129.

Teodorovic, I., Djukic, N., Maletín, S., Miljanovic, B. and Jugovac, N. (2000). Metal pollution index: proposal for freshwater monitoring based on trace metal accumulation in fish. Tiscia, 32, 55-60.

Tunçer, S. (1989). Heavy metals on Eel grass (*Zostere marina*) (L) and Meadow (*Posidonia oceanica*) (L) Delile in the Bay of İzmir. Plants and Pollutants in Developed and Developing Countries, (Edit. M.Öztürk). 151-159.

Türk Çulha, S., Koçbaş, F., Gündoğdu, A., Topcuoğlu, S., Çulha, M. (2010). Heavy metal levels in macroalgae from Sinop in the Black Sea, The 39th CIESM Congress (Venice 10-14 May 2010), 239.

Türkan, I., Öztürk, M., Sukatar, A. (1989). Heavy metal accumulation by algae in the Bay of Izmir, Turkey, Rew. Int. Med, 71-76.

UNEP (United Nations Environment Programme). (1984). Determination of total Cd, Zn, Pb and Cu in selected marine organisms by flameless AAS reference methods for marine pollution studies, vol. 11.

U.S.EPA (U.S. Environmental Protection Agency). (2007). Method 3051A(SW-846): Microwave Assisted Acid Digestion of Sediments, Sludges, and Oils. Revision 1. Washington, DC.

Usero, J., Gonzalez-Regalado, E., Gracia, I. (1997). Trace metals in the bivalve molluscs *Ruditapes decussatus* and *Ruditapes philippinarum* from the Atlantic Coast of Southern Spain. Environ. Int, 23, 291–298. doi: 10.1016/S0160-4120(97)00030-5.

Uysal, H. (1992). Heavy metal concentrations in selected marine species from Fisheries days of Aegean Coast, XXXes Journées Êtude Pollutions, Trieste, Italy, CIESM.

Yalçın, S., Sezer, S., Apak, R. (2012). Characterization and lead(II), cadmium(II), nickel(II) biosorption of dried marine brown macro algae *Cystoseira barbata*. Environmental Science and Pollution Research, 19, 3118–3125.

Yılmaz, H.K., Dikbaş, M.D., Bilgüven, M. (2016). Pigment substances and usage areas from cyanobacteria. Journal of Agricultural Faculty of Uludag University, 30(1).

Yozukmaz, A., Yabanli, M., Sel, F. (2018). Heavy metal bioaccumulation in *Enteromorpha intestinalis*,(L.) Nees, a macrophytic algae: the example of Kadin Creek (Western Anatolia). Brazilian Archives of Biology and Technology. V.61: e18160777. doi:10.1590/1678-4324-2018160777