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Heavy metal levels in water, brown algae (*Cystoseira barbata*), and eelgrass (*Zostera marina*) from the Southern Black Sea coast of Bulgaria

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Abstract
The heavy metals concentration in algae and marine water can be used as a bioindicator of an ecosystem pollution. In the present study, we determined the levels of the elements As, Pb, Cd, Hg, Mn, Zn, and Al in brown algae of the species *Cystoseira barbata* (Agardh, 1820), eelgrass *Zostera marina* (Linnaeus, 1753) and also in cold seawater. The samples were collected during the summer period of 2020 from the region of the Southern Bulgarian Black Sea coast. Our results showed low levels of heavy metals in seawater and much higher in the studied plant species, especially of aluminum in brown algae.

Keywords: Heavy metals, brown algae, eelgrass, seaweed, seawater, black sea

Introduction
Determination of heavy metal levels in marine flora and fauna can be used in the monitoring of biome pollution (Topcuoglu *et al*., 2010) [21]. Marine algae belong to the group of primitive non-flowering photosynthetic macrophytes and their habitat are the seas and oceans. Algae and seaweed can be used as a reliable indicator of chemical pollution status due to their ability to bioaccumulate heavy metals (Jordanova *et al*. 1999; Strezov and Nonova 2003; Abdallah *et al*., 2005; Strezov and Nonova 2005; Alkhalifa, 2012; Culha *et al*., 2013, Ali *et al*., 2017) [1, 2, 3, 7, 18, 19]. Lewis and Devereux (2008) [12] pointed to the eelgrass of the species *Zostera marina* as one of the most suitable species as a bioindicator of pollution. In addition, the same authors observed a characteristic periodicity and seasonality in the heavy metal level in algae. The element absorption by aquatic plants is a part of their biological cycle (Strezov and Nonova, 2005) [19]. According to Jordanova *et al*. (1999) [10] the content of chemical elements in seawater and in the aquatic inhabitants can severely vary. Significantly lower concentrations were observed in seawater compared to flora and fauna samples.
The Black Sea is a semi-enclosed type of sea basin, well isolated from the waters of the World ocean, but in a connection with most of the major European rivers (Stoichev *et al*., 2007) [17]. Based to this Black Sea is considered one of the most polluted seas, which in turn leads to a decline in the fishing and tourism industry (Mirinchev *et al*., 1999; Stancheva *et al*., 2014) [13, 16]. Jitar *et al*. (2013) [11] concluded that heavy metals are one of the main pollutants in the Black Sea.
The aim of our study was to determine heavy metal levels (As, Pb, Cd, Hg, Mn, Zn and Al) in brown algae of the species *Cystoseira barbata*, eelgrass *Zostera marina* and seawater from the Southern Black Sea region.

Materials and Methods
Algae and seawater samples were collected from the Southern Black Sea Coast area (Burgas region) during the summer of 2020. Samples of *Cystoseira barbata* and *Zostera marina* were collected from the shallow part of the seabed and from the coastline, carefully rinsed with seawater, and packed in plastic bags. They were stored at -20 °C until analysis. Water samples were taken from the same area in 0.5-liter plastic bottles and stored in a refrigerated state at a temperature of 0 to 4 ºC until the test, which was performed within 24 hours.

Cystoseira barbata
(https://en.wikipedia.org/wiki/Cystoseira)

Zostera marina
(https://en.wikipedia.org/wiki/Zostera_marina#/media/File:Zostera_marina_-_National_Museum_of_Nature_and_Science,_Tokyo_-_DSC07663.JPG)

The analysis of algae was carried out after homogenization (Vortex Homogenizer), followed by microwave assisted acid digestion procedure (ETHOS UP high-performance Microwave digestion system, Milestone Inc). After digestion with nitric acid an appropriate spectroscopy determination with inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher TM) was performed. The summarized results of this study were presented as mean values (X) (mg/kg) weight- for algae and (mg/l) for water ± standard deviation (SD). The data were subjected to a statistical analysis with Student's-test to estimate the significance of values ($p < 0.05$).

Results and Discussion

The results of the tested metals in the seawater are presented in Table. 1 and of brown algae and seaweed are summarized in Table 3. The order of the levels of the heavy metal concentrations was Al = As = Zn > Pb = Mn >Cd > Hg for seawater, Al > As > Mn > Zn > Pb > Cd > Hg for *Cystoseira barbata*, Al > Mn > As > Zn > Pb > Cd = Hg for *Zostera marina*.

The data obtained in Tables 1 and 3 showed that heavy metal pollution of seawater is significantly lower than that of algae. This fact could be explained by the property of living organisms to bioaccumulate, which was confirmed by the results of Jordanova *et al*. (1999) [10]. In general, our results for arsenic, zinc and aluminum levels in seawater were lower than 0.05 mg/l and they were below the limit of detection. The values for manganese and lead were < 0,01 mg/l, and the lowest concentration was for the Hg (<0.001 mg/l). The seawater levels for arsenic, zinc, lead, mercury, and cadmium were below the maximum permissible concentrations for the quality of the coastal waters, specified in Ordinance № 8 of 25.01.2001 [14].

Table 1: Heavy metal concentrations (mg/l) in seawater from Southern Bulgarian Black Sea coast

Element (X±SD)	Unit	Sea water
As	mg/l	< 0.05*
Pb	mg/l	< 0.01*
Cd	mg/l	< 0.005*
Hg	mg/l	< 0.001*
Mn	mg/l	< 0.01*
Zn	mg/l	< 0.05*
Al	mg/l	< 0.05*

*Method detection limits

The results of Peycheva *et al*. (2016) [15] (Table 2) showed significantly lower values of the studied elements compared to those obtained in the present study. At the same time the cadmium and mercury concentrations of Ukrainian sea water samples were with higher levels compared to the Bulgarian region (Dyatlov, 2015) [8]. The published values of Boran and Altinok (2010) [5] from the Turkey coast were in accordance with the current data, with the exception for the higher levels of Mn (0.039281 mg/l).

Table 2; Some heavy metal mean values in seawater from Black Sea coast (mg/l)

Heavy metals (mg/kg)	Area	Water	Reference
As	Bulgaria	0.0011	Peycheva *et al*. (2016) [15]
Pb	Bulgaria	0.00034	Peycheva *et al*. (2016) [15]
Cd	Bulgaria	<0.00005	Peycheva *et al*. (2016) [15]
	Ukraine	0.23	Dyatlov (2015) [8]
Hg	Bulgaria	<0.00005	Peycheva *et al*. (2016) [15]
Mn	Turkey	0.039281	Borat and Altinok (2010) [5]
Zn	Bulgaria	0.0005	Peycheva *et al*. (2016) [15]
	Turkey	0.054535	Borat and Altinok (2010) [5]
	Bulgaria	0.031	Peycheva *et al*. (2016) [15]
	Ukraine	7.20	Dyatlov (2015) [8]

Heavy metal values in the table were recalculated from mcg/l.

Table 3 showed the results for the studied flora species. For both algae, the highest content was for aluminum - in *Cystoseira barbata* and *Zostera marina* - 574.36 ± 114.87 mg/kg and 85.15 ± 17.03 mg/kg respectively. We found high levels for both algae species in terms of Mn and As. We also obtained higher levels of zinc in brown algae compared to eelgrass. In both studied species the values for lead were similar, and those of mercury were below the detection limit <0.05 mg/kg. Data showed that *Cystoseira barbata* accumulated heavy metals in higher proportion compared to *Zostera marina*, with the exception of manganese, which was with 25.92% higher than in eelgrass. The present research for the Bulgarian region showed that brown algae bioaccumulated larger amounts of the studied chemical elements, with the exception of manganese, which makes them more sensitive pollution indicator than the sea water and seaweeds.

Table 3: Heavy metal concentrations (mg/kg weight) in algae from Southern Bulgarian Black Sea coast

Element (X±SD)	Unit	*Cystoseira barbata*	*Zostera marina*
As	mg/kg	28.37 ± 5.67	1.62 ± 0.32
Pb	mg/kg	0.35 ± 0.07	0.29 ± 0.06
Cd	mg/kg	0.14 ± 0.03	< 0,05*
Hg	mg/kg	< 0,05*	< 0,05*
Mn	mg/kg	26.73 ± 5.35	33.66 ± 6.73
Zn	mg/kg	8.57 ± 1.71	1.06 ± 0.21
Al	mg/kg	574.36 ± 114.87	85.15 ± 17.03

*Method detection limits
** $p< 0.05$

As could be seen from Table 4 heavy metal levels in brown algae were lower than the data presented by other authors, with the exception of Mn. Also, the level of zinc for the Bulgarian region was lower compared to the levels obtained by Topcuoglu *et al*. (2001) [20] and higher than the data of Cadar *et al*. (2018) [6].

Table 4: Some heavy metal mean values in algae from Black Sea coast (mg/kg)

Heavy metals	Area	Mean value		Reference
		Cystoseira barbata	*Zostera marina*	
As	Turkey		2	Arici and Bat. (2020) [4]
Pb	Turkey		1.9	Arici and Bat (2020) [4]
	Turkey	1.0		Topcuoglu *et al*. (2001) [20]
	Turkey		1.17	Tuncer and Yaramaz (1992) [22]
	Turkey	3.51 (2016)		Cadar, E., *et al*. (2018) [6]
	Turkey	5.51 (2017)		Cadar, E., *et al*. (2018) [6]
Cd	Turkey		0.1	Arici and Bat. (2020) [4]
	Turkey	0.70		Topcuoglu *et al*. (2001) [20]
	Turkey		1.05	Tuncer and Yaramaz (1992) [22]
	Turkey	0.281 (2016)		Cadar *et al*. (2018) [6]
	Turkey	0.330 (2017)		Cadar *et al*. (2018) [6]
Hg	Turkey		0.017	Arici and Bat. (2020) [4]
Mn	Turkey		761.8	Arici and Bat. (2020) [4]
	Turkey	23.8		Topcuoglu *et al*. (2001) [20]
	Turkey		138.8	Tuncer and Yaramaz (1992) [22]
Zn	Turkey		114.8	Arici and Bat (2020) [4]
	Turkey	59.3		Topcuoglu *et al*. (2001)
	Turkey		3.63	Tuncer and Yaramaz (1992) [22]
	Turkey	1.93 (2016)		Cadar *et al*. (2018) [6]
	Turkey	2.55 (2017)		Cadar *et al*. (2018) [6]
Al	Turkey		1847.4	Arici and Bat (2020) [4]

Heavy metal values in the table were recalculated from mcg/kg.

The established heavy metals in the current survey in *Zostera marina* were in discrepancy with Tuncer and Yaramaz (1992) [22] and with Arici and Bat (2020) [4] which reported higher values. The high levels of aluminum in algae obtained in the present study and also by Arici and Bat (2020) [4] confirmed the claim of Gillmore (2014) [9] that this element is one of the main pollutants in marine ecosystems.

Conclusions

Based on the current results we can conclude that the level of heavy metals in the sampling area was lower in the living environment - seawater, compared to the bioaccumulation in living organisms - plant species *Cystoseira barbata* and *Zostera marina.*

The heavy metal level was higher in brown algae compared to eelgrass (with the exception of manganese) which should be taken into account when assessing the bioindicative value of these species.

The current study can serve as a basis for further investigations on heavy metal pollution in various levels of the Black sea ecosystems.

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