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Short Communication

Seasonal and spatial accumulation of heavy metals in *Cystoseira barbata* C. Agardh 1820 from Northeastern Black Sea coast

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This study is aimed to reveal the heavy metal contamination in brown seaweed species distribute in the Northeastern Black Sea coast. This study provides important preliminary information about heavy metal accumulation in brown seaweed. Indirectly, this also provides information on the environmental pollution in the study area. Heavy metal accumulations observed were Cr: 6.8-34.9 Mn: 32.8-116, Fe: 1721-5685, Co: 0.90-3.12, Ni: 31.8-173, Cu: 6.01-20.3, Zn: 24.3-88.2, Cd: 0.16-0.69 and Pb: 0.84-3.15 mg kg^{-1}. Such studies should be conducted occasionally to update the knowledge on accumulation of heavy metals in marine organisms and to verify the results of this study.

[**Keywords**: Bio-accumulation, Brown algae, Heavy metals, Northeastern Black Sea coast, Seasonal and spatial variations]

Introduction

Brown alga, *Cystoseira barbata*, is a marine species living in the upper sub-littoral zone (open and sheltered rocky shores), up to 0.2 m depth in semi-closed areas and coastal lagoons[1]. In general, algae are sedentary, easy to collect and identify and are widely distributed in the aquatic environment. The bioaccumulation of trace metals in algae occur in high degrees satisfying all the fundamental requirements of bio-indicators[2]. Therefore algal populations are been extensively used as indicators of water pollution. In fact, algae play an important role in the functioning and ecological balance of all the aquatic ecosystems and they also contribute significantly to the economic activity in several countries across the world[3]. Owing to the bioaccumulation ability, macro algal species are used all over the world to determine the heavy metal levels in both estuaries and coastal waters. In benthic food webs, macroalgae play a key role and act also as time integrators of pollutants. The inactivity of algal species is another reason why they are widely used as biomonitor species for heavy metal contamination[4]. Several research papers on the heavy metal accumulation in other marine organisms from Black Sea coastal waters have been published in the past[5-10]. However, limited number of studies on heavy metal accumulation in marine algae (especially in recent years on *Cystoseira barbata*) from Black Sea coastal waters has been carried out[11-13]. The aim of this study is to investigate the seasonal and spatial accumulation of heavy metals in Brown algae from the coastal waters of Northeastern Black Sea.

Material and Methods

Seaweed specimens were seasonally collected from three stations of Northeastern Black Sea coast, Piraziz, PR (40°57' N, 38°7.0' E), Giresun, GR (40°53' N, 38°20' E) and from Espiye, ES (40°57' N, 38°42' E), Turkey. After collection, specimens were cleaned, washed with distilled water, and were dried at 105 °C for 24 h. After homogenization, the seaweed samples were stored at -18 °C until analysis[8]. All glass and plastic containers used in the analysis were kept in 10 percent HNO_3 for one day and were then washed with pure water. 0.5 g algae of samples were digested in 7 ml HNO_3 and 2 ml H_2O_2 in a microwave device (CEM MARSX, 240/50, USA). The residue was then made up to 50 ml using a volumetric flask with deionized water.

The samples were then filtered using a 0.45 micron filter before being analyzed. Certified fish protein Dorm-4 from the National Research Council, Ontario, Canada was used as the calibration and verification standard. Percent recoveries were 92 for Cd, 119 for Pb, 101 for Cu, 115 for Cr, 95 for Ni and 103 for Zn. The heavy metal contents in each filtered sample were analyzed three times with the ICP-MS device (BRUKER 820-MS, Germany), and the results were expressed as mg kg^{-1}. Detection limits in ppm are 0.002 for Cd, Cr, Ni, Pb and Mn, 0.001 for Co, 0.003 for Cu, 0.04 for Zn and 0.4 for Fe. One-way analysis of variance (ANOVA) and Duncan test were applied to test the differences between stations and between seasons ($p < 0.05$).

Results and Discussion

The seasonal and spatial changes in heavy metal accumulation in the examined seaweed according to stations are presented at Table 1. The results showed that the differences between the stations and the seasons are statistically significant ($p < 0.05$). The highest concentrations of metal observed was iron, whereas cadmium showed the lowest level. In terms of seasonal changes, in PR station, Cr, Mn, Cu, Zn, Cd and Pb in winter, Fe and Co in spring, and Ni in summer showed the lowest concentration. However, Mn, Fe, Co, Cu, Zn and Pb in summer, Cr and Ni in winter, and Cd in spring showed the highest values. In GR station, Mn, Co and Cu in winter, Cr and Ni in spring, Cd in summer, and Fe, Zn and Pb in autumn showed the highest values. On the other hand, with the exception Cr and Ni in summer, surprisingly other metals showed higher levels in spring than other season. This situation may arise from heavy rains in spring season. In ES station, Cu and Cd in winter, Cr and Zn in spring, Mn, Fe, Co and Ni in summer and Pb in autumn showed the lowest values. On the contrary, Cr and Ni in winter, Mn, Fe, Pb and Co in spring, Cu in summer, and Zn and Cd in autumn showed the highest values.

In terms of spatial distributions, in winter, Cr, Fe, Co, Ni, Cu and Cd at ES station, Mn and Pb at GR station and Zn at PR station was minimum. On the other hand, Cr, Mn, Fe, Cu, Zn and Pb at PR station, and Ni, Zn and Cd at GR station showed the highest values. In spring, Mn, Fe, Cu, Zn and Pb at PR station, and Cr, Co, Ni and Cd at ES station showed lower values. However, Cr and Ni at PR station, and remaining metals at GR station showed the highest values. The reason for this can be explained as that the pollutants related to Cr and Ni can be more effective at the PR station, whereas at the GR station it can be due to intense population and industrial activities. In summer, Zn and Cd at PR station, Cu at GR station, and remaining metals at ES station showed the lowest values. On the contrary, Mn, Fe, Co and Pb at PR station, Cr, Ni, Zn and Cd at GR station, and Cu at ES station showed the highest values. Finally, in autumn, Zn and Cd at PR station, Mn and Pb at GR station, and Cr, Fe, Co, Cu and Ni at ES station showed the lowest values. On the other hand, Mn, Fe, Co and Pb at PR station, Zn at ES station, and remaining metals at GR station showed the highest levels.

Heavy metal accumulations in *Cystoseira barbata* from the Northeastern Black Sea coast reported in the present study were compared with existing literature (Table 2). It can be seen from Table 2 that, the values

Table 1 — Spatial and seasonal distribution of heavy metals (mg.kg^{-1} dry weight)

Season	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Piraziz (PR)									
WN	36.5 ± 0.45^{a}	59.0 ± 1.16^{ab}	2490 ± 158^{a}	1.63 ± 0.04^{a}	185 ± 4.55^{b}	7.01 ± 0.06^{a}	25.9 ± 0.58^{bc}	0.16 ± 0.01^{a}	1.58 ± 0.01^{ab}
SP	34.3 ± 0.65^{a}	42.2 ± 2.72^{a}	1931 ± 152^{a}	1.33 ± 0.08^{a}	172 ± 3.09^{ab}	7.00 ± 0.47^{a}	22.8 ± 1.13^{ab}	0.17 ± 0.01^{a}	1.27 ± 0.07^{a}
SM	35.1 ± 1.76^{a}	80.8 ± 17.9^{b}	6157 ± 1627^{b}	2.78 ± 0.54^{a}	161 ± 4.77^{a}	8.61 ± 0.53^{b}	28.5 ± 2.67^{c}	0.15 ± 0.01^{a}	2.16 ± 0.40^{b}
AT	34.1 ± 0.79^{a}	37.3 ± 1.61^{a}	2196 ± 130^{a}	1.36 ± 0.04^{a}	175 ± 2.32^{b}	6.10 ± 0.19^{a}	20.0 ± 0.79^{a}	0.14 ± 0.00^{a}	1.17 ± 0.11^{a}
Avg.	**34.9 ± 0.5^{y}**	**54.8 ± 6.4^{x}**	**3193 ± 627^{x}**	**1.78 ± 0.2^{xy}**	**173 ± 3.0^{y}**	**7.11 ± 0.3^{y}**	**24.3 ± 1.2^{x}**	**$0.16\pm<0.01^{x}$**	**1.51 ± 0.1^{x}**
Giresun (GR)									
WN	35.9 ± 0.42^{a}	26.2 ± 2.18^{a}	1649 ± 60.0^{a}	1.28 ± 0.05^{a}	186 ± 2.72^{a}	5.63 ± 0.50^{a}	35.9 ± 2.32^{a}	0.24 ± 0.02^{a}	0.63 ± 0.05^{a}
SP	25.7 ± 4.33^{b}	340 ± 154^{b}	12918 ± 5681^{b}	6.83 ± 2.86^{b}	86.5 ± 13.5^{b}	43.6 ± 19.3^{b}	212 ± 98.5^{b}	1.71 ± 0.78^{b}	6.89 ± 3.00^{b}
SM	39.1 ± 0.89^{a}	55.1 ± 2.13^{a}	1819 ± 41.4^{a}	1.51 ± 0.03^{a}	199 ± 14.7^{a}	8.01 ± 0.24^{a}	40.0 ± 0.48^{a}	0.20 ± 0.01^{a}	1.13 ± 0.03^{a}
AT	35.4 ± 0.41^{a}	28.4 ± 0.32^{a}	1529 ± 14.6^{a}	1.30 ± 0.01^{a}	185 ± 2.33^{a}	7.65 ± 0.12^{a}	29.9 ± 3.26^{a}	0.28 ± 0.00^{a}	0.62 ± 0.01^{a}
Avg.	**34.0 ± 1.7^{y}**	**113 ± 51.7^{x}**	**4479 ± 1904^{x}**	**2.70 ± 0.9^{y}**	**164 ± 16.5^{y}**	**16.2 ± 6.3^{y}**	**79.5 ± 31.2^{y}**	**0.60 ± 0.2^{y}**	**2.31 ± 1.0^{x}**
Espiye (ES)									
WN	22.9 ± 10.6^{a}	43.7 ± 2.17^{a}	1499 ± 65.5^{a}	1.12 ± 0.18^{bc}	118 ± 56.9^{a}	5.43 ± 0.45^{a}	29.9 ± 1.07^{a}	0.15 ± 0.01^{a}	1.20 ± 0.22^{b}
SP	0.92 ± 0.06^{b}	115 ± 9.52^{b}	2025 ± 170^{b}	1.20 ± 0.08^{c}	2.45 ± 0.59^{b}	10.1 ± 0.62^{b}	29.8 ± 0.77^{a}	0.17 ± 0.00^{ab}	1.29 ± 0.06^{b}
SM	1.38 ± 0.04^{b}	28.2 ± 1.19^{a}	1169 ± 67.1^{a}	0.76 ± 0.08^{a}	1.92 ± 0.25^{b}	12.7 ± 0.68^{c}	32.9 ± 0.91^{ab}	0.19 ± 0.01^{bc}	0.78 ± 0.05^{a}
AT	1.94 ± 0.02^{b}	32.9 ± 1.58^{a}	1440 ± 109^{a}	0.79 ± 0.04^{ab}	4.60 ± 0.27^{b}	5.62 ± 0.52^{a}	34.8 ± 1.81^{b}	0.22 ± 0.01^{c}	0.72 ± 0.03^{a}
Avg.	**6.81 ± 3.6^{x}**	**55.0 ± 10.8^{x}**	**1578 ± 125^{x}**	**0.90 ± 0.07^{x}**	**31.8 ± 19.3^{x}**	**8.40 ± 0.9^{x}**	**31.8 ± 0.8^{xy}**	**$0.18\pm<0.01$**	**1.0 ± 0.1^{x}**
Seasonal Average									
WN	31.7 ± 3.76^{x}	42.9 ± 4.84^{x}	1879 ± 163^{x}	1.35 ± 0.1^{x}	163 ± 19.9^{x}	6.01 ± 0.3^{x}	30.6 ± 1.5^{x}	0.18 ± 0.02^{x}	1.14 ± 0.15^{x}
SP	20.2 ± 5.14^{x}	166 ± 63.4^{y}	5685 ± 2442^{x}	3.12 ± 1.2^{x}	87.0 ± 27.5^{x}	20.3 ± 8.0^{y}	88.2 ± 42.0^{x}	0.69 ± 0.3^{x}	3.15 ± 1.27^{y}
SM	25.2 ± 6.0^{x}	54.7 ± 9.2^{x}	3048 ± 913^{y}	1.68 ± 0.3^{x}	121 ± 30.3^{x}	9.79 ± 0.7^{xy}	33.8 ± 1.8^{x}	0.18 ± 0.1^{x}	1.36 ± 0.24^{xy}
AT	23.8 ± 5.48^{x}	32.8 ± 1.4^{x}	1721 ± 129^{x}	1.15 ± 0.1^{x}	122 ± 29.3^{x}	6.52 ± 0.3^{x}	28.3 ± 2.4^{x}	0.22 ± 0.02^{x}	0.84 ± 0.09^{x}

*WN: Winter, SP: Spring, SM: Summer, AT: Autumn; ** Vertically, letters *a, b* and *c* or *x, y* and *z* show statistically significant differences ($p < 0.05$)

Table 2 — Comparison of the results of this study with the data in the literature

Studies	Heavy metal contaminations (mg.kg^{-1})								
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
This study	0.14-1.71	0.76-6.83	0.92-39.1	5.43-12.7	1169-12918	26.2-340	1.92-199	0.62-6.89	20-212
Khaled *et al.*[2] (Mediterranean Sea)	0.34-0.83	-	-	3.26-19.3	72.4-468	-	5.41-8.79	16.3-19.8	25.7-30.9
Topçuoğlu *et al.*[4] (Black Sea coast)	< 0.02.0.78	< 0.05-1.78	< 0.06-1.2	1.7-6	130-593	6.7-33.5	< 0.1-9.1	< 0.1-3.5	6.5-192
Tüzen *et al.*[7] (Black Sea coast)	< 0.01	0.09	0.99	2.47	242	14.9	2.05	0.0046	6.62
Güven *et al.*[11] (Black Sea coast)	1.08-1.3	0.47-1.09	< 1-3.7	< 1-12.3	< 100-604	-	-	5.3-8.3	< 7-12.1
Topçuoğlu *et al.*[12] (Black Sea coast)	< 0.02-6.41	< 0.05-2.08	< 0.06-7.76	7.33-12.7	310-869	19.4-79.9	8.2-10.7	< 0.05	44.3-111
Kut *et al.*[14] (Bosphorus)	0.55-1.38	2.0-3.59	< 0.1- ~0.3	4.60-5.15	210-615	-	-	4.2-7.5	12.4-35.6
Swadis *et al.*[15] (Aegean Sea)	0.4-2.7	-	-	0.7-8.8	-	5.6-181	4.3-28.5	0.02-2.5	8.8-58.1
Aydın-Önen & Öztürk[16] (Aegean Sea)	0.03-7.23	-	-	0.21-6.64	499-6288	22.4-391	0.90-33.0	1.5-62.1	80.3-295

reported for, cobalt (0.47-1.09), Cr (< 1-3.7), Cu (1-12.3), Fe (< 100-604) and Zn (< 7-12.1) concentrations in *C. barbata* from Black Sea coast, Turkey are lower than present study, but for Cd (1.08-1.3) and Pb (5.3-8.3) are higher[11]. Cobalt level reported from Bosphorus was similar to present study; Cd (0.55-1.38) and Pb (4.2-7.5) were higher; and others were lower than present study[14]. When compared with this study, the levels of the heavy metals reported in the Aegean Sea are similar in terms of Mn, Pb and Zn, higher in Cd (0.4-2.7), and lower in Cu (0.7-8.8) and Ni (4.3-28.5)[15]. Concentrations reported earlier from Black Sea coast, Turkey were higher for Cd and Zn; and the rest were lower than current results[12]. Cadmium level (< 0.02-0.78) reported earlier by Topçuoğlu *et al.*[4] from Black Sea coast was lower; Zn (6.5-192) was higher; the rest were lower than the current results, whereas; all metal levels reported from Black Sea by Tüzen[7] were lower than the current results. Cadmium concentration reported from Mediterranean Sea was similar; Pb level was higher; and the rests were lower than present study[2]. Similarly iron level reported from Aegean Sea was similar; Cu and Ni were lower; and the rests were greater than current results[16].

Conclusions

This study provides important information about the heavy metal content in brown seaweed from Northeastern Black Sea coast and also reveals clues about environmental contamination. These results will help us determine the chemical quality of brown seaweed. On the other hand, it will also enable us to understand the possible risks to the consumption of such herbivorous organisms and ecosystem health. Differences between seasons at same and within stations were found significant. Comparative analysis between the present study and the studies performed in Black Sea earlier revealed that it may be said that the concentrations of all studied metals with the exception of Cd and Zn have been increased since 1998. On the other hand, in the future, the accumulation of cadmium, zinc and remaining heavy metals in *C. barbata* can pose a possible risk for the consumption of herbivorous organisms, if agricultural, shipping, industrial and recreational practices in the surrounding Black Sea region are not controlled.

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Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

Author Contributions

MT: Study design, data processing and analysis, draft preparation, editing, review, funding acquisition and supervising of study, and submission to the journal and follow up to the printing stage; and TA: Study design, participation in field studies, data processing and analysis, draft preparation and editing.

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