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Heavy Metals in Marine Algae from Şile in the Black Sea, 1994–1997

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Marine organisms have been used successfully as bioindicators in heavy metal pollution studies. For many reasons marine macroalgae appear to be an attractive candidate for use as a bioindicator in an environmental monitoring programe of coastal areas (Phillips, 1977).

Heavy metals are introduced through rivers or by direct discharge of industrial wastes into the Black Sea. In addition, the heavy metal levels in the Black Sea marine environment have increased from oil pollution and airborn contaminants. Şile is the main station where our investigation on metal polluttion of algae have been carried out since 1979, because it is on the route of the water courrents coming from the Danube, as shown on the map (Fig. 1) and is located near the metropolis of Istanbul. The fishing potential of this region is important. Moreover, the anthropogenic activities and deterioration of the coastal area during the last 20 years also has affected the pollution.

Some papers have been published concerning heavy metal convcentrations measured in algal species collected from Turkish Black Sea coast (Güven et al., 1992; 1998), Bosphorus (Güven et al., 1993; Kut et al., 2000), Marmara Sea (Esen et al., 1999) and northern Aegean Sea (Sawidis & Voulgaropoulos, 1986). In this paper, heavy metal pollution is reported on the marine algae collected at Şile 1994-1997.

MATERIALS AND METHODS

The sampling station of algae is shown in Fig. 1. About 0.5 Kg fresh weight were harvested during autumn season from 1994 to 1997 at low tide. The algae species were: brown; *Cystoseira barbata* (Good. et Woodw.), red; *Pterocladia capillacea* (Gmel.) Born et Thur., *Phyllophora nervosa* (D.C) Grev., *Corallina granifera* (Ellis et Sol.), *Ceramium rubrum* (Huds.) C. Ag., green; *Enteromorpha linza* J. Agardh, *Ulva lactuca* L. The samples were not found at the station in all year. The samples were washed in sea water at the sampling site and transferred to the laboratory at the same day in refrigerated conditions. They were cleaned in sea water to remove sand, particulate matter and epiphytes at the laboratory. Finally, samples were rinsed in tap water and distilled water. They were dried at 85 ^{o}C (to

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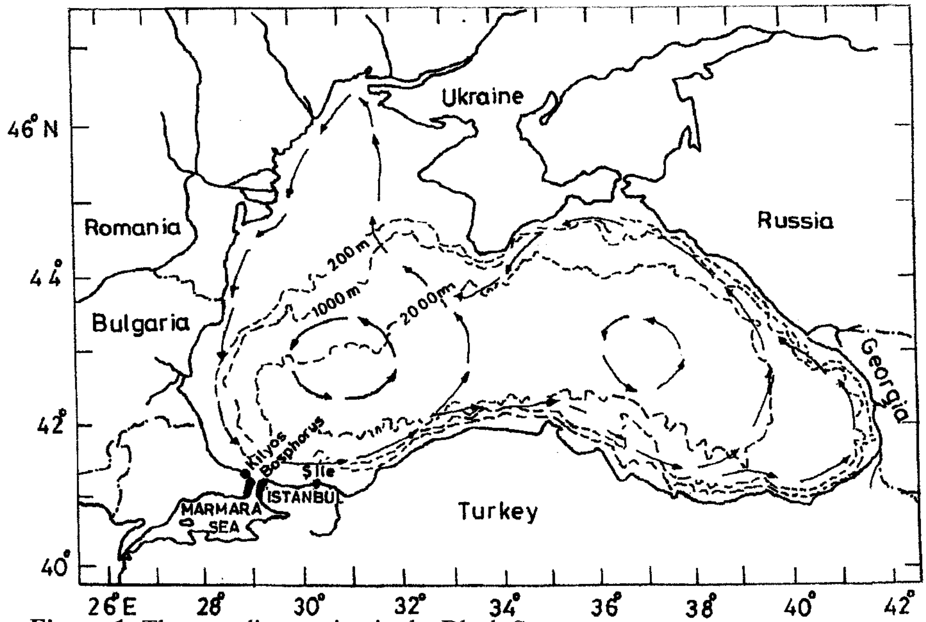

Figure 1. The sampling station in the Black Sea

constant weight), homogenized and kept away from metallic materials and dusty conditions to avoid contamination.

2 g of algae (dry weight, sample) was put into a glass beaker, 5 ml conc. H_2SO_4 added and heated on the hot plate to 70 - 80 °C. 15 min afterwards, a small amount of conc. HNO_3 was added very slowly and heating continued to 120 °C. Hydrogen peroxide was added and heating was continued at 120 °C for 30 min. Addition of hydrogen peroxide continued until the solution remained clear for two hours at 150 °C. Then the solution was diluted to 100 ml with 2% HNO_3 in a volumetric flask. The metal concentrations were determined by an atomic absorption spectrophotometer (Varian, model Spectra AA. 100/200). The values are expressed as mean in three subsamples analysis for each sample.The procedural blank samples were used inside each batch. The accuracy of the analysis was verified by analyzing the IAEA's certified reference material.

RESULTS AND DISCUSSION

The results for heavy metal concentrations in macroalgae samples are shown in Table 1. The highest accumulations of different heavy metals in the algae species were: Cd and Zn in *P. capillacea,* Co, Ni and Mn in *P. nervosa*, Pb and Cu in *U. lactuca.,* Fe in *C. barbata,* Cr in *C. granifera.* Cd in *P. capillacea* and Co, Ni and Mn in *P. nervosa* are also found high.

Correlation of the accumulation of the heavy metals with the algae divisions and variability along the years 1994 - 1997 is also given by the bar diagrams in Fig. 2. The Cd concentrations decreased from 1994 to 1997 and it was

Table 1.
Heavy metal concentrations (μg g dry^{-1} weight) in algae speces collected from Şile of the Black Sea in in 1 Nov. 1994 (a), 20 Oct. 1995 (b), 13 Sep. 1996 (c) and 22 Oct. 1997 (d)

Samples	Cd	Co	Cr	Ni	Zn	Fe	Mn	Pb	Cu
C. barbata	0.75±0.02^{a}	0.95±0.27^{a}	0.60±0.02^{a}	6.20±0.85^{a}	97.2±0.09^{a}	230.5±0.69^{a}	21.45±0.06^{a}	7.5±1.13^{a}	5.10±0.07^{a}
P. capillacea	2.00±0.01^{a}	1.15±0.19^{a}	1.15±0.01^{a}	5.25±0.48^{a}	107.9±0.10^{a}	275.4±0.55^{a}	46.65±0.27^{a}	6.0±0.83^{a}	7.25±0.06^{a}
P. nervosa	0.50±0.06^{a}	6.30±0.28^{a}	-	67.3±0.07^{a}	95.8±0.19^{a}	324.1±0.65^{a}	296.4±1.18^{a}	20.0±2.04^{a}	10.9±0.06^{a}
E. linza	0.85±0.08^{a}	<0.05^{a}	-	6.95±0.51^{a}	8.98±0.02^{a}	440.7±0.44^{a}	49.66±0.25^{a}	3.4±1.72^{a}	7.63±0.01^{a}
C. barbata	0.70±0.04^{b}	0.90±0.10^{b}	-	5.90±0.57^{b}	59.3±0.12^{b}	166.6±6.64^{b}	23.00±0.09^{b}	1.0±0.10^{b}	6.20±0.03^{b}
P. capillacea	1.50±0.04^{b}	1.60±0.36^{b}	-	3.60±0.18^{b}	82.6±0.08^{b}	351.7±0.35^{b}	71.10±0.07^{b}	3.0±0.30^{b}	8.70±0.48^{b}
P. nervosa	0.50±0.04^{b}	3.60±0.52^{b}	-	83.8±0.33^{b}	81.9±0.33^{b}	481.8±0.96^{b}	154.0±0.31^{b}	3.0±1.67^{b}	16.5±0.05^{b}
C. granifera	0.50±0.07^{b}	1.30±0.20^{b}	-	2.30±0.22^{b}	89.2±0.18^{b}	771.9±2.31^{b}	82.80±0.16^{b}	6.0±2.80^{b}	10.4±0.51^{b}
C. rubrum	0.81±0.02^{b}	1.35±0.45^{b}	-	4.32±0.75^{b}	61.6±0.31^{b}	709.5±2.19^{b}	58.64±0.29^{b}	10.8±4.44^{b}	15.9±0.19^{b}
U. lactuca	0.50±0.03^{b}	0.90±0.10^{b}	-	8.10±0.25^{b}	24.1±0.09^{b}	501.5±2.51^{b}	49.70±0.25^{b}	< 0.1^{b}	24.1±0.09^{b}
C.barbata	0.35±0.02^{c}	0.60±0.46^{c}	0.75±0.03^{c}	2.20±0.46^{c}	50.4±0.15^{c}	526.6±0.52^{c}	22.15±0.06^{c}	1.0±0.29^{c}	4.80±0.04^{c}
P. capillacea.	1.25±0.04^{c}	0.90±0.22^{c}	1.05±0.08^{c}	4.05±0.16^{c}	75.7±0.22^{c}	258.5±0.51^{c}	66.80±0.26^{c}	3.0±0.45^{c}	5.40±0.03^{c}
P. nervosa	0.50±0.03^{c}	3.35±0.05^{c}	1.20±0.03^{c}	83.2±0.24^{c}	107.6±0.21^{c}	448.7±0.48^{c}	111.1±0.11^{c}	4.0±0.73^{c}	14.5±0.10^{c}
C. granifera	0.65±0.03^{c}	1.30±0.11^{c}	1.05±0.08^{c}	1.15±0.55^{c}	49.2±0.14^{c}	382.6±1.53^{c}	85.85±0.17^{c}	0.5±0.28^{c}	2.15±0.08^{c}
C .barbata	0.40±0.01^{d}	0.65±0.27^{d}	0.95±0.05^{d}	4.50±0.01^{d}	65.1±0.06^{d}	1066±14.9^{d}	24.85±0.07^{d}	14.0±0.78^{d}	6.85±0.06^{d}
P. capillacea	0.90±0.01^{d}	0.80±0.18^{d}	1.10±0.11^{d}	3.90±0.90^{d}	97.9±0.29^{d}	403.3±0.40^{d}	72.10±0.28^{d}	9.5±1.08^{d}	7.05±0.03^{d}
P. nervosa	0.40±0.09^{d}	5.00±0.17^{d}	0.90±0.07^{d}	64.9±0.51^{d}	83.7±0.25^{d}	372.1±0.74^{d}	95.35±0.28^{d}	12.0±0.90^{d}	13.1±0.02^{d}
C. granifera	0.55±0.05^{d}	0.40±0.17^{d}	5.50±0.02^{d}	0.15±0.03^{d}	42.2±0.12^{d}	122.3±0.48^{d}	17.20±0.06^{d}	7.5±1.17^{d}	1.95±0.04^{d}
C. rubrum	0.45±0.01^{d}	0.55±0.14^{d}	1.45±0.08^{d}	1.90±0.52^{d}	41.7±0.12^{d}	664±0.66^{d}	23.75±0.04^{d}	10.0±0.11^{d}	6.05±0.02^{d}
U. lactuca	0.50±0.01^{d}	0.65±0.37^{d}	0.50±0.03^{d}	3.85±0.43^{d}	35.2±0.07^{d}	147.3±0.73^{d}	12.80±0.13^{d}	23.5±3.64^{d}	5.90±0.04^{d}

- Not tested

higher in red algae species than in brown and green algae samples. The Co and Pb concentrations in red algae were also higher and decreased from 1994 to 1996. Cu levels in red and green algae samples increased from 1994 to 1995 and decreased afterwards . The Cu levels were higher in red algae in 1994, 1996 and 1997; in contrary, it accumulated more in green algae in 1995. The Ni levels were higher in red algae, *P. nervosa,* than in other tested algae. The concentration of Ni in the algae species increased from 1994 to 1995, was unchanged in 1996 and decreased in 1997. However, Ni concentration in other algal samples showed no definite trend with regard to algae and collection period. The Mn levels decreased from 1994 to 1997 in red algae and but did not change in brown algae during this collection period. The Zn concentrations in red and brown algae decreased from 1994 to 1996 and increased in 1997. The Fe concentrations in algae showed no correlation with algal divisions along the years.

The relations between heavy metals accumulated and algal divisions have been discussed by many authors. It has been shown that Pb accumulated at high levels in red, brown and green algae (Hagerhall, 1973; Agadi et al., 1978; Sivalingam, 1978); Fe, Co, Cu in green (Sawidis & Voulgaropoulos, 1986); Fe, Cu, Zn in brown and Mn in red (Sivalingam, 1978). Our results partly agreed with the above findings.

Concentrations of some heavy metals in algae are comparable with those reported in earlier studies at Şile station in the periods of 1979-1988 and 1991-1993 (Güven et al., 1992; 1998) for *C .barbata* and *P .nervosa*. In present study, Cd, Co and Cr levels in *C. barbata* and *P.nervosa* are lower than the same species collected in the period of 1986 - 1993. The maximum Co concentrations in *P. nervosa* were found to be 3.91 and 4.68 $\mu g\ g^{-1}$ in 1985 and 1993, respectively. In general, Zn, Mn and Cu concentrations did not change in *C. barbata* and *P. nervosa* samples from 1986 to 1997. The Mn levels in 1986 and 1987 and Cu concentration in 1993 samples of *C. barbata* are the highest values reported. The maximum Zn level was detected in *P. nervosa* in 1996. Moreover, the maximum Pb concentrations were also found in *P. nervosa* and *C. barbata* samples during 1994 and 1997 in the period of 1979-1997. The minimum Pb levels were detected in 1992 and 1995 in the algae examined.

In previous studies, the heavy metal levels were investigated in *C. barbata, P.capillacea,* and *U. lactuca* collected from the Bosphorus during the period of 1990-1991 and 1993 (Güven et al., 1993; Kut et al., 2000). Our results show that Cd, Co and Ni concentrations are higher, but Zn, Mn, Pb, and Cu levels are lower in the Bosphorus. However, Cd concentration in *P. capillacea* and Cu levels in *C. barbata* and *P. capillacea* species were alike during the period of 1993-1997. Co, Cr and Fe levels in *C. barbata, C. rubrum* and *E. linza* are lower in the present study than in same algae collected from the Kilyos station of the Black Sea in 1993 (Topcuoğlu et al., 1998). On the other hand, Zn concentrations in *C. barbata* and *C. rubrum* are higher at Şile than at Kilyos, but Zn level in *E. linza* at Kilyos is higher than Şile.

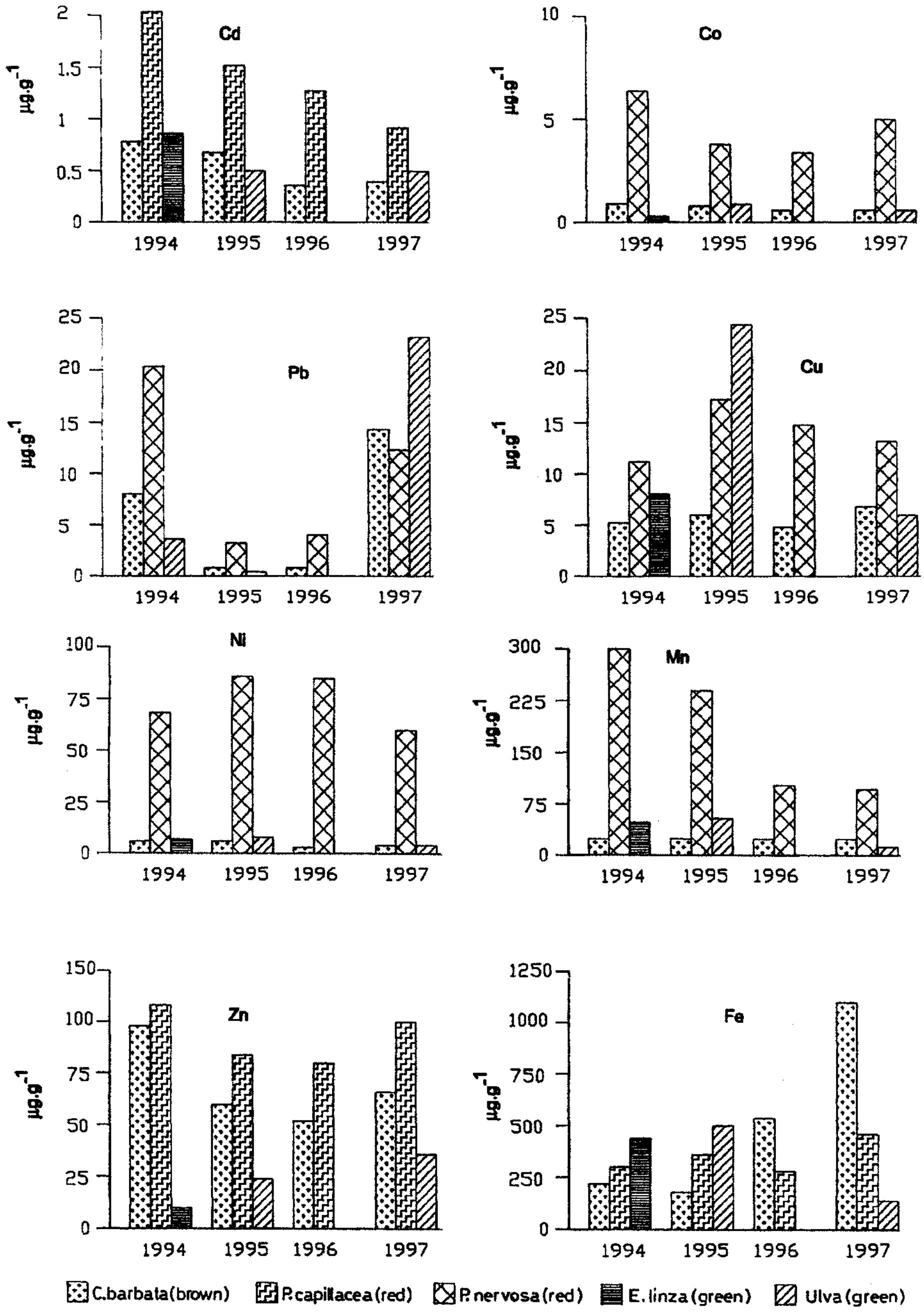

Figure 2. Mean concentrations of heavy metals in algae samples at Şile station

In the British North Sea, Zn, Cd and Pb concentrations were determined in *Enteromorpha sp.* in 1984 (Say et al., 1990). When their results are compared with the same species in the present study, much higher concentrations of the metals were found at the British North Sea sites. The Cd, Pb and Cu levels in the *U. lactuca* in the present work are higher than in *U. rigida* collected from lagoon of Venice (Favero et al., 1996). The Co, Cr, Ni, Zn, Fe and Mn concentrations are lower in the present study than the algae found in the lagoon. The wide variations of heavy metal concentrations observed were attributed to seasonal changes and to the chemical and physical characteristics of the sampling sites.

As a result, Cd, Co, and Cr concentrations decreased while Pb increased and Zn, Mn and Cu did not change in *C. barbata* and *P. nervosa* collected from Şile during last four years. It has been reached to these conclusions by comparing the data reported for same algae species at the same station during the periods of 1979 - 1988 and 1991- 1993.

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