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ENVIRONMENTAL MONITORING OF HEAVY METALS IN BULGARIAN BLACK SEA GREEN ALGAE

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Abstract. Fe, Mn, Cu, Pb and Cd concentration distribution in six green macroalgae species from the Bulgarian Black Sea coast were determined. The measurement of these metals was carried out during six seasons from 1996 to 2002 using atomic absorption spectrometry (AAS). Samples were collected from eight different sites–Shabla, Kaliakra, Tuzlata, Ravda, Ahtopol and Sinemoretz. The obtained heavy metal (HM) data (mean values μg/g) for all algae are: 650 ± 100 for Fe, 184 ± 15 for Mn, 5.6 ± 0.5 for Cu, 3.3 ± 0.3 for Pb and 1.1 ± 0.2 for Cd. The obtained HM contents indicate that different species demonstrate various degree of metal accumulation and the obtained higher values in the northern sector of the studied zone can be attributed to the discharge influence of the big rivers, entering the Black Sea–Danube, Dnyepr, Dnester and local pollutant emissions. All data show that there is no serious contamination in green macroalgae with heavy and toxic metals along the whole Bulgarian Black Sea coast.

Keywords: Black Sea, green macroalgae, heavy metals, pollution

Introduction

Black Sea is a unique ecosystem because it is an inner sea with low salinity, half-isolated from the Mediterranean with hydrology and phytobentos different from the other seas in the same biogeographic region.

The antropogenic contamination of marine ecosystems is a very important stress factor and defines the necessity for systematic monitoring and control of contaminants (heavy metals – HM, radionuclides, etc.) that affect marine biota. The main sources of Black Sea pollution are atmospheric fallout, the big rivers run-off as well as local pollutant emissions (Mee, 1992; Tuncer *et al.*, 1998).

Macrophytic algae, being one of the primary stages in the trophic chain, play a major role in marine ecosystems (Kilgore *et al.*, 1993). Algae interact with the environment through processes that include chemical bioconcentration, excretion, organic matter production and decomposition (Carpenter and Lodge, 1986). They have been used as a signal for the living status of marine ecosystems and considered as valuable indicators for HM assessment in the major components of the water ecosystems because of their accumulation capacity (Försberg *et al.*, 1988). Some algae possess ecological mutability so they can survive in contaminated habitat (Kalugina-Gutnik, 1975). Closely related species may exhibit different accumulation capabilities for trace elements, so there is a need to identify indicators that are biologically dominant and widespread in the ecosystems. This will allow intraspecific comparison of accumulated metal concentrations over large geographical areas (Rainbow, 1995; Rainbow and Phillips, 1993).

HM are among the most studied contaminants in marine ecosystems. Their effect is through direct poisoning as well as by accumulation and transfer along the trophic chain, by which they influence the functioning of biosphere (Babich *et al.*, 1985).

Metal levels in algae reflect local geology or local anthropogenic activities and the contamination is generally similar to background levels of the sites. Today's HM concentrations in marine environment are generally more than 10 times higher than it was in prehistoric times. The levels are consistently higher in surface waters than in deeper layers. The macrophytic species from phylum Chlorophyta (green) are widely distributed in the coastal Black Sea ecosystems and some of them (*Ulva rigida*, *Enteromorpha intestinalis*, *Cladophora vagabunda*) can be found in almost all areas and environmental pollution was studied by means of green algae. These species have been extensively used to monitor marine pollution for Mn, Cu, Pb and Cd in various geographical areas (Favero *et al.*, 1996; Muse *et al.*, 1999; Ho, 1981, 1990; Brix *et al.*, 1983; Haritonidis and Malea, 1995, 1999).

Many authors have investigated biogeochemical migration of anthropogenic contaminants (HM, radionuclides) in the Black Sea environment (Polikarpov *et al.*, 1991; Roeva, 1996; Güven *et al.*, 1992; Topcuoglu *et al.*, 1998, 1999, 2001) while information about heavy and toxic metals at the Bulgarian coastal zone is scarce and insufficient.

The purpose of this paper is to give information about the accumulation and seasonal distribution of Fe, Mn, Cu, Pb and Cd in six green macrophytes, collected from eight locations along the Bulgarian Black Sea coast during the period spring 1996 to summer 2002.

Materials and Methods

Sampling sites in this study were selected to cover all regions of the Bulgarian coastline – Shabla, Kaliakra, Tuzlata, Ravda, Ahtopol, Sinemoretz and Rezovo. Six species of green macroalgae (*Bryopsis plumosa*, *Chaetomorpha gracilis*, *E. intestinalis*, *U. rigida*, *C. vagabunda* and *Cladophora coleothrix*) were collected at 1–4 m depth during the eight sampling periods – spring 1996, autumn 1996, summer 1997, spring 1998, spring 1999, summer 2000, autumn 2001 and autumn 2002. Samples were taken also from the site Rossenetz in summer 97, which is anthropogenically contaminated with HM from the nearby copper mine. The samples were rinsed in clean seawater and washed with distilled water to remove the attached particulate material. The plants (bulk 1–1.5 kg wet weight) were dried to constant weight (85 °C), grinded and 0.5 g of each sample was digested with HNO_3 (Merck).

The HM concentrations were determined by ETAAS (graphite furnace AAS, Perkin-Elmer Zeeman 3030) to determine Pb and Cd. Flame AAS (Pye Unicam

TABLE I
Results of the quality assurance check for *Chlorella*

Element	Certified ($\times 10^{-6}$)	Experimental	SR (%)
Fe	1850	1672 ± 24	12
Mn	69	63 ± 2	14
Cu	3.5	3.1 ± 0.2	21
Pb	0.6	0.5 ± 0.1	23
Cd	0.026	0.025 ± 0.002	35

SP 1950 atomic absorption spectrophotometer with air–acetylene flame) was used for Fe, Mn and Cu. Certified reference material NIES-CRM-3 (*Chlorella*) was run together with each series of samples.

The application of the analytical procedure can be evaluated by SR values for each element compared to the standard material (McFarren *et al.*, 1970).

$$\mathrm{SR}(\%) = \frac{|C_\mathrm{e} - C_\mathrm{c}| + 2\sigma}{C_\mathrm{c}} \times 100$$

$$(\mathrm{SR} < 25\% :\ \text{excellent}; 25\% < \mathrm{SR} < 50\% : \text{acceptable}; \mathrm{SR} > 50\% : \text{unacceptable})$$

where C_e is the experimental value, C_c the certificate value and σ the standard deviation.

The SR data (Table I) show that coincidence for C_e and C_c about Fe, Mn, Cu and Pb is excellent (SR < 25%) and acceptable (25% < SR < 50%) for Cd. This fact leads to the conclusion that the applied analytical procedure produces results with good precision and can be applied for HM estimation in algae.

Results

The results for HM concentrations in six green macroalgae from eight locations of the Bulgarian Black Sea coast (see map – Figure 1) are presented in Table II. Mean metal concentrations in all studied algae decrease in the order: Fe > Mn > Cu > Pb > Cd. *C. coleothrix* and *C. gracilis* samples from spring 1998 differ from this order because the highest Cd concentrations were measured in these algae and Pb > Cu.

The measured Fe content in all investigated samples varies in the interval 100–2600 μg/g dry weight (mean value – 650 μg/g), while Mn concentrations are in the range 10–350 μg/g (mean – 84 μg/g). Fe results (vs. alga type) are illustrated in Figure 2. Fe content in *U. rigida, E. intestinalis* and *B. plumosa* is

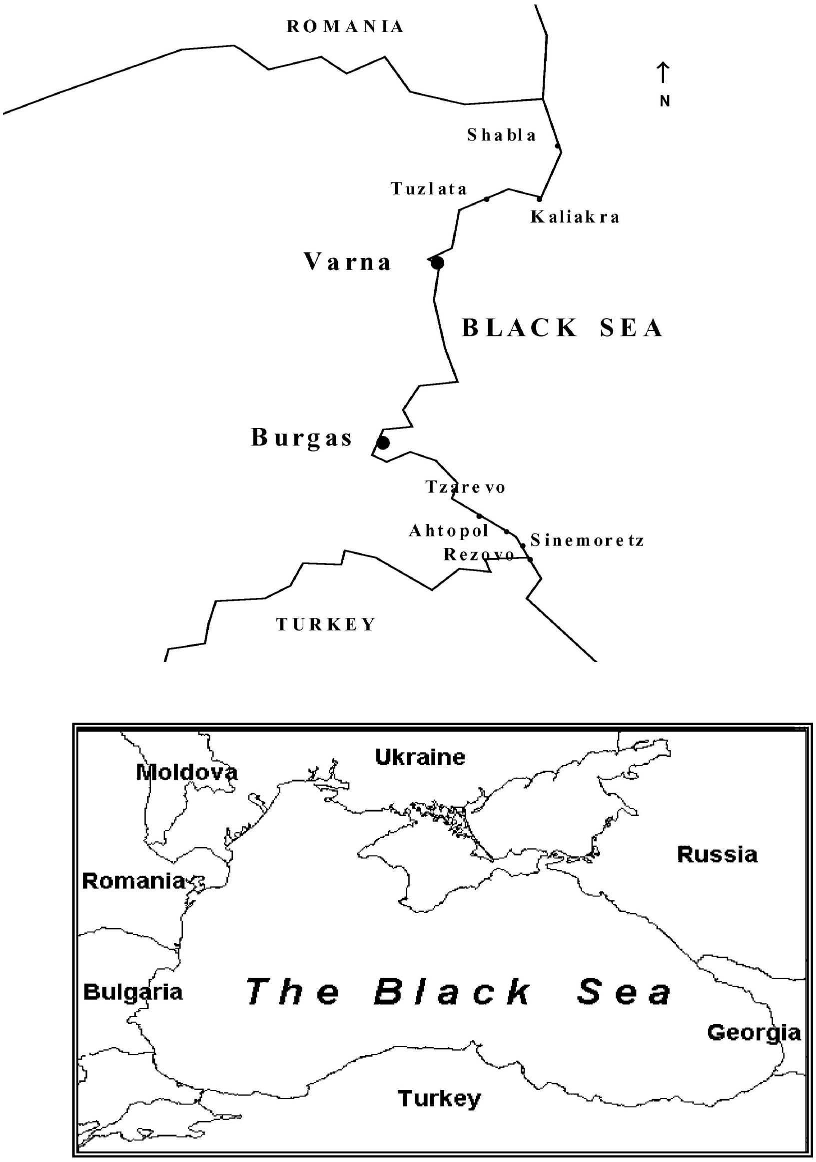

Figure 1. Diagram of sampling locations.

below 400 μg/g while in *C. gracilis* and two *Cladophora* species it is three times higher.

The data for the toxic Cu, Pb and Cd are in the range 1.4–13, 1–7.6, 0.2–3.2 μg/g, respectively and are presented in Table II as well (graphically in Figure 3). These HM (mean values) demonstrate similar accumulation patterns – Cu > Pb > Cd in five macroalgae species: *Ulva*, *Enteromorpha*, *C. vagabunda*, *Chaetomorpha* and *Bryopsis* (except *C. coleothrix* where Pb > Cu > Cd).

TABLE II
Results of heavy metal content in macroalgae (μg/g ± S.D.)

Season	Location	Fe	Cu	Mn	Pb	Cd
Ulva rigida						
Spring 1996	Tuzlata	974 ± 6	7.4 ± 0.4	17 ± 1	2.8 ± 0.2	0.21 ± 0.02
Autumn 1996	Tuzlata	147 ± 2	4.5 ± 0.2	9 ± 2	1.7 ± 0.1	0.15 ± 0.01
	Ravda	141 ± 4	4.7 ± 0.3	12 ± 1	1.2 ± 0.1	0.20 ± 0.02
	Ahtopol	96 ± 4	7.3 ± 0.1	12 ± 2	1.2 ± 0.1	0.16 ± 0.01
	Sinemoretz	348 ± 8	13 ± 1	12 ± 1	1.0 ± 0.1	0.17 ± 0.01
Spring 1998	Ravda	93 ± 1	6.0 ± 0.7	16 ± 2	1.7 ± 0.1	0.12 ± 0.01
	Ahtopol	100 ± 4	6.7 ± 0.8	17 ± 2	2.2 ± 0.2	0.20 ± 0.03
	Sinemoretz	363 ± 9	4.2 ± 0.6	25 ± 3	3.6 ± 0.1	0.39 ± 0.03
Spring 1999	Ravda	180 ± 1	5.6 ± 0.1	14 ± 6	1.6 ± 0.1	0.44 ± 0.01
Summer 2000	Shabla	475 ± 8	2.4 ± 0.1	15 ± 1	1.7 ± 0.1	1.53 ± 0.02
	Kaliakra	146 ± 5	2.2 ± 0.1	10 ± 1	1.8 ± 0.1	2.14 ± 0.03
	Ahtopol	138 ± 6	1.4 ± 0.1	17 ± 1	1.6 ± 0.1	1.21 ± 0.03
	Sinemoretz	405 ± 1	2.6 ± 0.1	12 ± 1	2.6 ± 0.1	0.20 ± 0.01
Autumn 2002	Ravda	500 ± 10	6.5 ± 0.5	24 ± 2	1.5 ± 0.2	0.60 ± 0.05
Enteromorpha intestinalis						
Spring 1996	Ravda	1350 ± 42	10.5 ± 0.1	41 ± 1	5.2 ± 0.3	0.26 ± 0.02
Autumn 1996	Sinemoretz	2600 ± 10	8.8 ± 0.8	82 ± 1	2.2 ± 0.1	0.20 ± 0.01
Summer 1997	Rossenetz	4890 ± 17	148 ± 3	98 ± 1	5.3 ± 0.1	0.26 ± 0.03
Spring 1998	Tuzlata	634 ± 23	4.4 ± 0.4	36 ± 3	6.6 ± 0.3	0.34 ± 0.03
Spring 1999	Shabla	390 ± 6	7.1 ± 0.1	54 ± 1	1.7 ± 0.1	1.60 ± 0.05
	Kaliakra	520 ± 5	5.0 ± 0.3	41 ± 3	2.5 ± 0.1	0.75 ± 0.01
	Tuzlata	930 ± 2	6.4 ± 0.1	89 ± 1	3.8 ± 0.2	2.80 ± 0.02
Summer 2000	Tuzlata	1230 ± 50	1.8 ± 0.1	42 ± 3	4.1 ± 0.2	2.20 ± 0.05
	Rezovo	1960 ± 50	4.7 ± 0.5	97 ± 5	3.2 ± 0.2	1.20 ± 0.08
Cladophora vagabunda						
Spring 1996	Tuzlata	2110 ± 90	10 ± 1	94 ± 2	7.3 ± 0.1	0.60 ± 0.04
Spring 1998	Tuzlata	930 ± 4	4.6 ± 0.3	168 ± 2	3.3 ± 0.3	2.50 ± 0.01
Spring 1999	Kaliakra	610 ± 10	12 ± 1	110 ± 1	2.7 ± 0.1	0.30 ± 0.01
	Tuzlata	372 ± 3	2.4 ± 0.2	230 ± 2	2.5 ± 0.2	0.20 ± 0.01
Cladophora coleothrix						
Spring 1998	Ravda	1200 ± 10	3.9 ± 0.1	347 ± 3	7.2 ± 0.1	2.30 ± 0.03
	Sinemoretz	1270 ± 20	4.8 ± 0.1	342 ± 6	6.8 ± 0.1	3.20 ± 0.07
Autumn 2001	Rezovo	780 ± 20	6.2 ± 0.2	322 ± 7	4.8 ± 0.1	2.90 ± 0.07
Chaetomorpha gracilis						
Spring 1998	Shabla	260 ± 8	4.3 ± 0.2	230 ± 4	2.5 ± 0.1	1.30 ± 0.01
	Ravda	500 ± 10	5.7 ± 0.1	225 ± 5	5.2 ± 0.1	2.90 ± 0.09
	Ahtopol	165±1	2.8 ± 0.1	100 ± 8	3.9 ± 0.1	2.20 ± 0.11
Summer 2000	Tuzlata	590 ± 42	3.4 ± 0.3	170 ± 4	4.6 ± 0.2	2.90 ± 0.14
	Sinemoretz	450 ± 10	8.5 ± 0.1	160 ± 7	3.2 ± 0.1	1.20 ± 0.01
Bryopsis plumosa						
Spring 1996	Ahtopol	400 ± 30	7.6 ± 0.4	46 ± 1	7.6 ± 0.2	0.42 ± 0.03
Spring 1998	Shabla	490 ± 8	4.9 ± 0.3	54 ± 6	3.2 ± 0.4	0.43 ± 0.03
Spring 1999	Shabla	250 ± 2	4.6 ± 0.1	56 ± 6	2.5 ± 0.1	0.30 ± 0.03

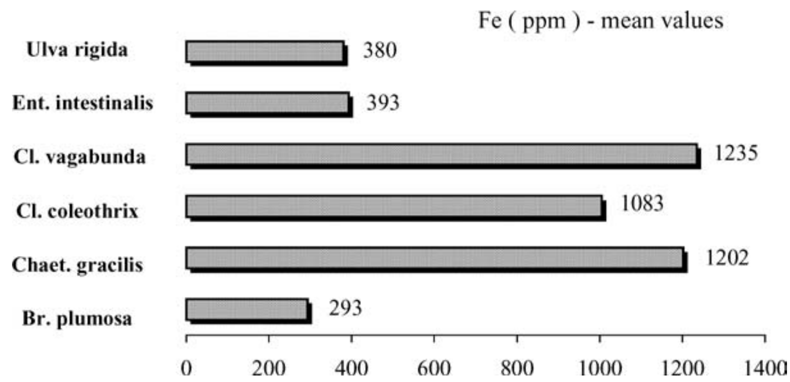

Figure 2. Fe contents (μg/g dry weight) in different green algae species – mean values.

All Black Sea green algae data were assessed by detailed descriptive statistics (STATISTICA for Windows, StatSoft Inc., 1998, www.statsoft.com), subjected to statistical calculation of HM correlation coefficients (Table IV) and statistical cluster analysis of toxic metal accumulation in green algae. The obtained tree diagram for all HM is presented in Figure 4.

The coefficient data for *Enteromorpha* and *Ulva* macroalgae show negative correlations between Cd and all measured metals in the two species. Pb also correlates with all metal ions in *Enteromorpha* and with Cu in *Ulva*. Significant correlation coefficients for the other HM were obtained only for pairs Cu–Cd in *Ulva* and Fe–Mn in *Enteromorpha*.

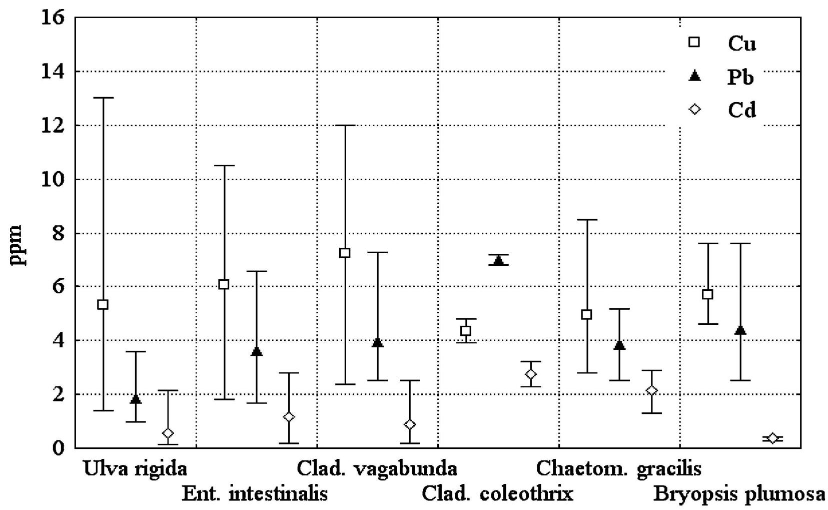

Figure 3. Mean Cu, Pb and Cd content (μg/g) in different algae species.

TABLE III

HM correlation coefficients in *Ulva rigida* and *Ent. intestinalis* species

Element	Cd	Cu	Fe	Mn	Pb
Ulva rigida ($N = 14$, $^{*}p < 0.05$)					
Cd	1.000	−0.57*	−0.05	−0.068	−0.075
Cu		1.000	0.17	0.03	−0.287
Fe			1.000	0.352	0.44
Mn				1.000	0.50
Pb					1.000
Enteromorpha intestinalis ($N = 8$, $^{*}p < 0.05$)					
Cd	1.000	−0.45	−0.29	0.30	−0.19
Cu		1.000	0.28	0.14	−0.13
Fe			1.000	0.59*	−0.17
Mn				1.000	−0.42
Pb					1.000

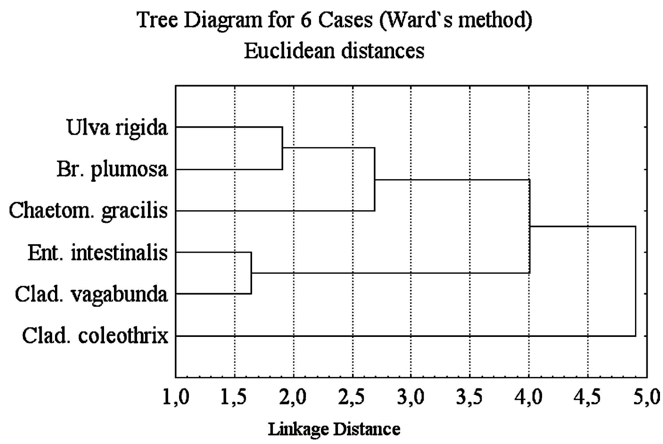

Figure 4. Tree diagram for heavy metal content in green algae species.

Discussion

There is dependence between the microelement biosorption and their function in the organism. Most intensively accumulated microelements are those that play a major role in the metabolism. A considerable number of HM form stable complexes with proteins, phosphates and lipids. Fe, Mn, Co take part in enzyme formation and as complex compounds participate in exchange reactions. The enriched in HM lipids from algae play a major biogeochemical role in the processes of fixation, transport and sedimentation in the hydrosphere.

Fe has a great binding capability for alga lipids and is accumulated to the highest degree in the Black Sea green macrophytes.

The measured Fe concentrations are with one or two orders of magnitude higher than the other HM (with mean value 650 μg/g). Maximum Fe values are obtained for *C. vagabunda*, *C. coleothrix* and *C. gracilis*, while in the other three species Fe content is three times lower (Figure 2). A higher value of Fe is observed in *E. intestinalis* from Sinemoretz and Rezovo (autumn 1996 and summer 2000, respectively). The lowest Fe concentration was measured in *U. rigida* species from Ravda (spring 1998) and at Ahtopol (autumn 1996).

If we compare mean Fe values in all green algae depending on the location, we obtain a tendency of increasing Fe content from north to south. If we now plot the same Fe values for each green species vs. location, it is clear that the observed north–south tendency is mainly due to *Enteromorpha* species whose values increase southwards. Fe concentration for the other green species is more constant with geographical location (e.g., mean Fe values vs. location for *U. rigida* are in the range 300 $\pm$ 170 μg/g for the whole Black Sea coast).

The results for Mn vary in more narrow interval than Fe (mean value 84 μg/g). Low Mn content is measured for *U. rigida, E. intestinalis* and *B. plumosa*, while the highest is obtained for *C. coleothrix.*

Mn concentrations in different regions change in the following order:

Ahtopol $<$ Kaliakra $<$ Shabla $<$ Tuzlata $\approx$ Ravda $<$ Sinemoretz $<$ Rezovo.

The mean Mn values for Tuzlata, Ravda and Sinemoretz are close and it is evident that there is no geographic dependence for Mn content. Our data show that green algae from Kaliakra (north) and Ahtopol (south) sites accumulate Fe and Mn to the lowest extent while the highest content is measured at Rezovo (south).

The high Fe and Mn biosorption, compared to the other HM, is connected with their function and major role in the metabolytic processes in marine organisms.

The trace element Cu (like Fe) belongs to the group of biologically important metal ions. Trace metals should be monitored because they play an important role in metabolism and their high or low concentrations can be equally harmful to the living organisms. Cu, Pb and Cd content in green algae are presented in Figure 3.

The Cu data interval is wider compared to Pb and Cd but if mean values (μg/g) for all algae are compared, we get for Cu 5.6 $\pm$ 0.5, Pb 3.3 $\pm$ 0.3 and Cd 1.1 $\pm$ 0.2. It is clear that this accumulation patterns sequence is the same for all green algae except *C. coleothrix* where Pb prevails.

Cu mean values are relatively constant along the whole Bulgarian coast (unlike Fe and Mn), and the low Cu content in the environment means that there is no contamination in the marine ecosystems with Cu. Same is true for Pb and Cd whose mean value variations are also small. These results can be explained with the lack of industrial pollution along the coast, except close to the big cities (ports) of Burgas and Varna. The studied locations in this paper are outside the dwelling places and this is done in order to obtain the characteristic background values for the measured HM concentrations along the whole coast.

The highest Cu content is measured in *E. intestinalis* from Rossenetz – 148 μg/g, which is due to the known anthropogenic contamination of the copper mine in the vicinity. The synergism between Cu and Fe is clearly demonstrated in Rossenetz as Fe value is also high (4890 μg/g) while the Pb and Cd values are normal (Table II).

The behavior of Pb in water ecosystems is complex and its concentration in a great number of natural waters is not higher than 1 μg/g. Pb is found in seawaters mainly in the form of different organic compounds. Pb content in the studied Black Sea alga species varies in a more narrow interval than Cu.*C. gracilis*, *C. vagabunda, E. intestinalis* and *B. plumosa* species accumulate Pb in a rather similar way. Pb content variations along the coast are small (like Cu) which also means lack of contamination with Pb.

The determination of Cd content is an important task for the monitoring of HM in marine ecosystems. Cd is poisonous for living organisms even in low concentrations, so it is a hazardous anthropogenic contaminant that should be controlled. It can be concluded from the data in Figure 3 that Cd is present in green algae in comparatively low concentrations – from 0.2 to 3.2 μg/g dry weight. The lowest Cd content is in the southern region Sinemoretz, but as a whole the concentration range is narrow in all sites with no geographic dependence. Judging from the alga type, the highest degree of Cd accumulation is found in *C. coleothrix*, while the lowest in *Bryopsis* and *U. rigida.*

Data were measured for Zn and Cr content in some of the studied green algae and the obtained mean values for Zn in *Ulva, E. intestinalis* and *B. plumosa* is 15 μg/g (*C. vagabunda* – 23 μg/g) while for Cr in *Ulva, C. vagabunda* and *C. gracilis* – 1.3 μg/g is obtained (*E. intestinalis* – 3.1 μg/g). The Zn and Cr results for Black Sea macroalgae confirm the lack of HM pollution (like Cu, Pb and Cd) along the Bulgarian coast.

The correlation between accumulation levels of HM concentrations is an important factor for evaluation HM behavior in biota and the determining of these correlations is a major task in all environmental studies. The correlation matrices for Fe, Mn, Cu, Pb and Cd in Black Sea green macroalgae are presented in Table III.

The coefficient data for *Enteromorpha* and *Ulva* macroalgae show negative correlations between Cd and all measured metals in the two algae species. Pb also correlates negatively with all metal ions in *Enteromorpha* and only with Cu in *Ulva.* From all these correlations the most important coefficients are those whose values $p < 0.05$ – marked as significant.

Significant positive correlation coefficient (synergistic interaction between HM) was obtained only for the pair Fe–Mn in *Enteromorpha* while negative correlation (antagonistic) was obtained for Cu–Cd in *Ulva*.

These correlation coefficients differ from unit and therefore the correlation dependence is not clearly expressed, meaning that the variables are connected but with weak functional dependence.

All Black Sea green algae data are subjected to cluster analysis for all toxic metal accumulation. The obtained tree diagram for all HM (Figure 4) shows that the algae are combined in two main groups plus *C. coleothrix*. The first main group consist of *Ulva* and *Bryopsis* linked by *Chaetomorpha*. The second group is *Enteromorpha* and *C. vagabunda.*

If the cluster analysis is performed for the toxic elements Cu, Pb and Cd, again two main groups are obtained – first group containing *C. coleothrix* and *Chaetomorpha*. The second group is divided in two – *Enteromorpha*, *Bryopsis*, *C. vagabunda* linked with *Ulva*. The main influence on these clusters is due to the presence of Cu because if we exclude Cu from the cluster process the obtained tree diagrams are less affected.

If we assess the obtained algae data depending on the chemical nature of the HM, the obtained tree diagram clearly separates Fe and Cu while Pb and Cd are strongly linked which is understandable as these two elements belong to one and the same group of the Periodic table.

Conclusions

Data have been obtained for Fe, Mn, Cu, Pb and Cd content in the most widespread Black Sea green macroalgae for the period 1996–2002. HM environmental behavior in the marine environment of eight locations (Shabla, Tuzlata, Kaliakra, Ravda, Rossenetz, Ahtopol, Sinemoretz, Rezovo), distributed along the whole Bulgarian coast, has been studied. All obtained results prove the dependence of toxic metal accumulation on green algae species as well as on the location.

It can be concluded that Fe, Mn, Cu, Pb and Cd concentration in Black Sea green macroalgae decrease during the studied period. *U. rigida* species accumulate the lowest concentrations of the studied metals. The highest Fe, Mn, Pb and Cd content has been measured in macrophytes from Tuzlata and Rezovo. High Cu concentration is observed in the southern coastal area – Ahtopol and Sinemoretz (the highest at Rossenetz). The results of the present research are close to our previous data as well as the published by other authors.

This work establishes a database for HM content in green macroalgae and their ecological affect on marine ecosystems along the Bulgarian Black Sea coast. The data obtained for the chosen locations in the period of 8 years indicate no serious artificial pollution along the Bulgarian shore. The obtained higher HM content can be attributed to the influence of the big rivers, entering the northern part of the Black Sea – Danube, Dnyepr, Dnester and local pollutant emissions.

It is clear that more information about all the rest components of the ecosystem, water, sediment and biota, is needed to give the complete characterization for the marine environmental conditions in the observed regions.

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