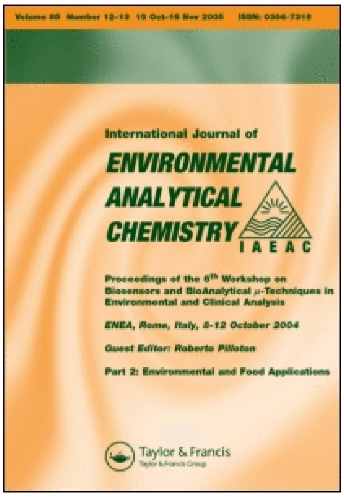

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Multielemental analysis of macroalgae from the Baltic Sea by ICP-OES to monitor environmental pollution and assess their potential uses

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Multielemental analysis of macroalgae from the Baltic Sea by ICP-OES to monitor environmental pollution and assess their potential uses

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The aim of this article was to discuss the mineral composition of marine edible macroalga *Enteromorpha* spp. sampled from the coast of the Gulf of Gdańsk and from the open Baltic Sea, with the consideration of its use both as biomonitor and also as a future feed additive for animals and food for humans. The mineral content of Baltic seaweed was determined by the multielemental analysis by ICP-OES Vista-MPX instrument from Varian (Australia). The results indicated geographical and seasonal differences between concentrations of elements. The content of microelements in all examined macroalgae was at a rather steady level. Significant fluctuations were observed in the content of macroelements – generally, *Enteromorpha* spp. from the southern Baltic contained more alkali (Na, K) and alkaline earth metals (Ba, Mg, Ca) than macroalga from the Gulf of Gdańsk. In order to determine the degree of accumulation of each element by the green alga, concentration factors (CFs) with respect to seawater were calculated. This factor for Fe, Al, Cu, Mn and Ti in algae was much higher, than for K, Ca, Mg and Na. The composition of *Enteromorpha* spp. was also compared with grains (corn, spring wheat, spring triticale, spring barley, oat, rye), which are commonly used as feed material. Macroalgae contained on average 56 times more Na(I), 11 times more Mg(II), 8 times more Ca(II), 5 times more K(I) and 3 times more Cu(II) than the grains mentioned previously. The content of Mn(II) was 20% higher.

Keywords: macroalgae; biomonitor; mineral content of macroalgae; seawater pollution

1. Introduction

The Baltic Sea is especially subjected to contaminants flowing from the surrounding area, mainly due to developed shoreline and drainage systems. Eutrophication is a major problem in the Baltic Sea. Since the 1800s, the Baltic Sea has changed from an oligotrophic clear-water sea into a eutrophic marine environment. Nitrogen and phosphorus are the main nutrients, which stimulate the growth of algae. Algal blooms lead to the production of excess organic matter, increase oxygen consumption and finally to death of benthic organisms, including fish. Additionally, due to intensive algal growth, many beaches are closed and this causes frequent public concern about the future suitability of the Baltic Sea as a site for recreation purposes [1]. Therefore, it would be advantageous to find a method of utilisation of macroalgae. In the literature, it is suggested that the biomass of

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macroalgae from the Sopot beach (the Baltic Sea) could be used as a biofertiliser [2] or can be consumed directly from the beach shore by animals [3,4]. Nevertheless, it is necessary to investigate the mineral content of the algae (especially the level of toxic elements), since the Baltic Sea is highly sensitive to the environmental impacts of human activities due to its geographical, climatological and oceanographic characteristics. Considering the application of macroalgae as feed for animals, the requirements of Polish and European Directive concerning the level of toxic metals in fodder materials must be met [5,6]. This arises from the fact, that marine macroalgae on the basic level are primary producers of the trophic web and can be responsible for the transfer of toxic metals from the environment to the biota and finally for biomagnification through the food web, which can result in severe health risks.

In this article, a special attention was paid to an edible macroalga *Enteromorpha prolifera*, due to its dominance in the macrophytobenthos on the Polish coast of the southern Baltic and its availability almost throughout the year [7]. It is important to mark, that *Enteromorpha* genera in some publications was reduced to synonym of *Ulva* (according to Hayden *et al*. [8] and Shimada *et al*. [9]). In the literature, this macroalga was studied as a biomonitor of metal contamination in many coastal waters and estuaries (e.g. coast of the southern Baltic Sea [10], northwest coast of Spain [11,12], estuaries and the British North Sea coast [13], tropical estuary in Fiji [14], Gulf of Thermaikos – the Aegean Sea [15,16]) and also as a source of nutrients for humans and animals. This edible macroalga is characterised by high nutritional value, as it is rich in proteins [17–20], minerals [17,19,21–23], essential amino acids [19], essential fatty acids [18–20], fibre [18,19] and carbohydrates [17,18,20]. Since marine macroalgae are continuously bathed in nutrient-rich seawater, they accumulate high level of minerals. The study of the mineral composition of macroalgae is important for the investigation of their applications in industrial, agricultural, nutritional and pharmaceutical fields [23]. In the literature, there are several reports, which examined the content of micro- and macroelements [17,21,24] and toxic metals such as: Cd, Cu, Ni, Pb, Zn, Hg [10,21,22,25] in *Enteromorpha* spp. from the Baltic Sea.

The goal of this article was to compare the mineral composition of *Enteromorpha* spp., which was collected from two different locations of the Baltic Sea: small seaside resort (Niechorze) and highly urbanised area (Gdańsk), in different time period. To study the content of macroalgal samples, simultaneous multielemental analysis was carried out by inductively coupled plasma optical emission spectroscopy (instrument Vista-MPX, Varian, Australia) [26]. The analysis was aimed also at assessing the usefulness of macroalgae as mineral feed additives in animal diet in comparison with biological materials, which are commonly used as conventional feeds.

2. Experimental

2.1 *Sampling of macroalgae*

The species of *Enteromorpha* spp. were collected from the Baltic Sea (Niechorze–Poland) in July 2006, August 2007 and in June 2008 and from the Gulf of Gdańsk (Gdańsk–Brzeźno–Poland) in April 2007 and in June 2008 (Figure 1). They were identified in the Department of Botany and Plant Ecology of the Wrocław University of Environmental and Life Sciences. The collected samples of algae were washed with tap water several times to remove foreign matter and afterwards with deionised water three times. Then, the algae

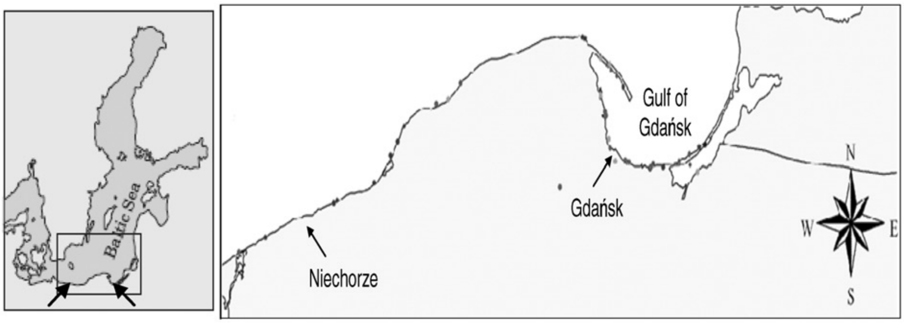

Figure 1. Map showing location of the green alga *Enteromorpha* spp. sampling sites.

were dried at 60°C until the constant mass was reached (to determine moisture content) grinded (to unify the sample), digested and the composition of mineralisate was analysed by ICP-OES.

2.2 *Multielemental analysis of marine macroalgae*

Approximately, 0.5 g of the natural macroalga was digested with 5 mL of concentrated 69% m/m nitric acid (Supra pure grade from Merck, Darmstadt, Germany) in a microwave oven (type Milestone MLS-1200 MEGA, Bergamo, Italy). The solution after mineralisation was diluted to 50 mL. The concentrations of elements in the samples and in the seawater were determined by inductively coupled plasma-optical emission spectrometer-Varian VISTA-MPX ICP-OES (Victoria, Australia) in the Laboratory of Multielemental Analyses at Wrocław University of Technology, which is accredited by ILAC-MRA and PCA (Polish Centre for Accreditation – No. AB 696). The quality assurance of the analytical measurements and the validation is included in the documentation of the quality management system of the Laboratory of Multielemental Analyses (No. AB 696); Research Procedures, 2008. The relative error (±5%) for all examined elements was checked through the measurements of the 'check standard'.

The samples of seawater were previously filtered through No. 2 paper filter. The samples were analysed in three repeats (the relative SD of the measurement did not exceed 5%). The presented data are the arithmetic average from three measurements. Uncertainty was also reported. For the preparation of standard solutions (1.0, 10, 50, 100 mg L^{-1}) the multielemental standard (100 mg L^{-1} Astasol®, Prague, Czech Republic) was used. Mercury was analysed with Mercury analyser AMA 254 atomic absorption spectrometer (Prague, Czech Republic). The operating parameters were: sample mass: 0.05 g, drying time: 40 s, decomposition time: 150 s, waiting time: 40 s. The presented data are the arithmetic average of measurements. Uncertainty was also reported.

2.3 *Concentration factors*

In order to determine a correlation between the concentration of a given element in macroalgae and in the surrounding environment, concentration factors (CF) were calculated: $CF = C_1/C_2$, where C_1 and C_2 is element content in dry weight of macroalgae and in the seawater, respectively.

3. Results and discussion

3.1 *Multielemental analysis of the marine macroalgae*

In order to facilitate the interpretation of experimental results, general characteristics of examined macroalgae is presented in Table 1. It is important to emphasise that mineral content of macroalgae varies according to species, oceanic or marine residence time, geographical place of harvest, wave exposure, seasonal, annual, environmental and physiological factors, type of processing and method of mineralisation [23,27,28]. The examined samples of *Enteromorpha* spp. were collected from two different locations. The first was the Gulf of Gdańsk – area, which is exposed to emissions of heavy metals from municipal and industrial sources with the main contribution of ship building industry and seaport. Additionally, pollutants enter the Baltic Sea via the Vistula River, which is a carrier of pollutions from industrial or municipal wastewater treatment plants, and from agriculture, scattered dwellings and atmospheric deposition [1]. The second location of sampling is a non-industrialised seaside resort – Niechorze.

High variability in the composition of seaweeds (micro- and macroelement, toxic metal) was observed for the algal samples selected in Table 1. Mineral composition of

Table 1. General characteristics of examined macroalgae.

No.	Macroalga	Sampling site	Sampling time	Method of mineralisation	Method of analysis	Reference
1	*E. prolifera*	Open Baltic Sea Niechorze (Poland)	July 2006		ICP-OES	This work
2	*E. prolifera*	Open Baltic Sea Niechorze (Poland)	August 2007			This work
3	*E. prolifera*	Open Baltic Sea Niechorze (Poland)	June 2008	Microwave		This work
4	*Enteromorpha* sp.	Gulf of Gdańsk Gdańsk (Poland)	April 2007			This work
5	*Enteromorpha* sp.	Gulf of Gdańsk Gdańsk (Poland)	June 2008			This work
6	*E. crinita*	Open Baltic Sea (Poland)	July 1978/1979	NR	AAS	[21]
7	*Enteromorpha* sp.	Open Baltic Sea (Poland)	2000–2003	Microwave	FAAS	[22]
8	*E. intestinalis*	Puck Bay (Poland)	July 1978/1979	NR	AAS	[21]
9	*Enteromorpha* sp. *and Cladophora* sp.	Gulf of Gdańsk (Poland)	July 2005	Microwave	ICP-OES	[24]
10	*E. flexuosa*	Pacific Ocean (Hawai)	January 2002	NR	NR	[17]
11	*E. intestinalis*	Yellow Sea (China)	April 1997	NR	NAA	[23]

Note: NR – not reported.

examined Baltic *Enteromorpha* spp. together with literature data is presented in Figure 2 (numbers of macroalgae – Nos 1–11 in Figure 2, correspond to numbers of macroalgae listed in Table 1). In the case of Mn(II), scatter of results was observed in the species of *E. prolifera* from the open Baltic Sea (No. 1 – 16.2 mg kg^{-1}, No. 2 – 38.5 mg $kg^{-1}$and No. 3 – 51.0 mg kg^{-1}), as well as in the samples from the Gulf of Gdańsk (No. 4 – 14.2 mg $kg^{-1}$and No. 5 – 80.9 mg kg^{-1}). Generally, the content of Mn(II) ions in 2008 in alga No. 5 (Gulf of Gdańsk) was 1.5 times higher than in alga No. 3 (the open Baltic Sea). This could be explained by the Vistula River run-off of suspended matter enriched in manganese to the estuarine waters of the Gulf of Gdańsk [21]. The content of Zn(II) ions in all the examined macroalgae was at rather steady level (18.2 ± 5.5 mg kg^{-1}). In the case of copper, macroalga No. 4 had averagely five times higher concentration of copper than other collected macroalgae (Nos 1, 2, 3, 5). The content of Cu(II) in No. 4 – 15.2 mg kg^{-1} (Gulf of Gdańsk, 2007) was comparable to its content in No. 9 – 15.7 mg kg^{-1} (Gulf of Gdańsk, 2005). This high level could be suspected to be of anthropogenic origin in that time period. The examined macroalgae were characterised by high content of boron – from 166 mg kg^{-1} (No. 5) to 207 mg kg^{-1} (No. 2) (with exception of No. 1 – 10.9 mg kg^{-1}). Similar level (164 mg kg^{-1}) was observed in *E. flexuosa* No. 10. The main source of boron in seawater is from natural geological process. Boron is considered as a mineral of nutritional significance to humans and animals [29].

Significant fluctuations were observed in the content of macroelements, which varied depending on the sampling place and time period. Generally, *E. prolifera* from the southern Baltic (Nos 1, 2, 3) contained more alkali (Na, K) and alkaline earth metals (Ba, Mg, Ca) than macroalga from Gulf of Gdańsk (Nos 4 and 5). Similar trend was also reported by Żbikowski *et al.* [22].

Considering the application of macroalgae as diet supplement, it was interesting from the point of view of nutrition to evaluate the ratio of sodium to potassium, since the intake of sodium chloride and diets with a high Na/K ratio have been related to the incidence of hypertension [30]. The obtained ratios for examined macroalgae and for algae from the literature are presented in Figure 3. Na/K ratios were below 1.5 in seaweeds Nos 1, 2, 3 and 5 (0.722, 0.426, 1.26 and 0.198), but higher for No. 4 – 4.25. This high difference in this ratio could result from the fact, that *Enteromorpha* sp. (No. 4) was very poor in potassium (2.367 mg kg^{-1}) and rich in sodium (10.068 mg kg^{-1}), when compared with the other examined macroalgae (for example: No. 2 – 23.580 mg $kg^{-1}$of K(I) and 10.037 mg $kg^{-1}$of Na(I), No. 3 – 15.427 mg $kg^{-1}$of K(I) and 19.405 mg $kg^{-1}$of Na(I), No. 5 – 36.742 mg $kg^{-1}$of K(I) and 7.281 mg kg^{-1} of Na(I)). Also, for all examined macroalgae the ratio of calcium to magnesium concentration was calculated. This ratio ranged from 0.411 – No. 2, 0.416 – No. 3, 0.566 – No. 4, 0.885 – No. 1 to 1.65 – No. 5. Similar results were obtained by Csikkel-Szolnoki *et al.* (2000), where this ratio for green algae ranged from 0.5 to 0.8, and what is important was much lower than for brown and red algae. This means that *Chlorophyta* are better source of magnesium than the *Phaeophyta* and *Rhodophyta* [31]. Another important ratio is Zn/Cu, since both zinc and copper, two essential trace minerals, perform important biochemical functions and are necessary for maintaining health throughout life. Cardiac abnormalities were associated with $Zn/Cu \geq 16$ [32]. For all examined macroalgae, this ratio was below 16 from 1.37 – No. 4 to 13.8 – No. 7. In the case of conventional feed, the ratios were as follows: Na/K 0.194; Ca/Mg 11.7 and Zn/Cu 4.23 (own data). These results are very similar to ratios obtained for macroalgae. The main difference is that *Enteromorpha* is much richer source of magnesium than conventional feed materials.

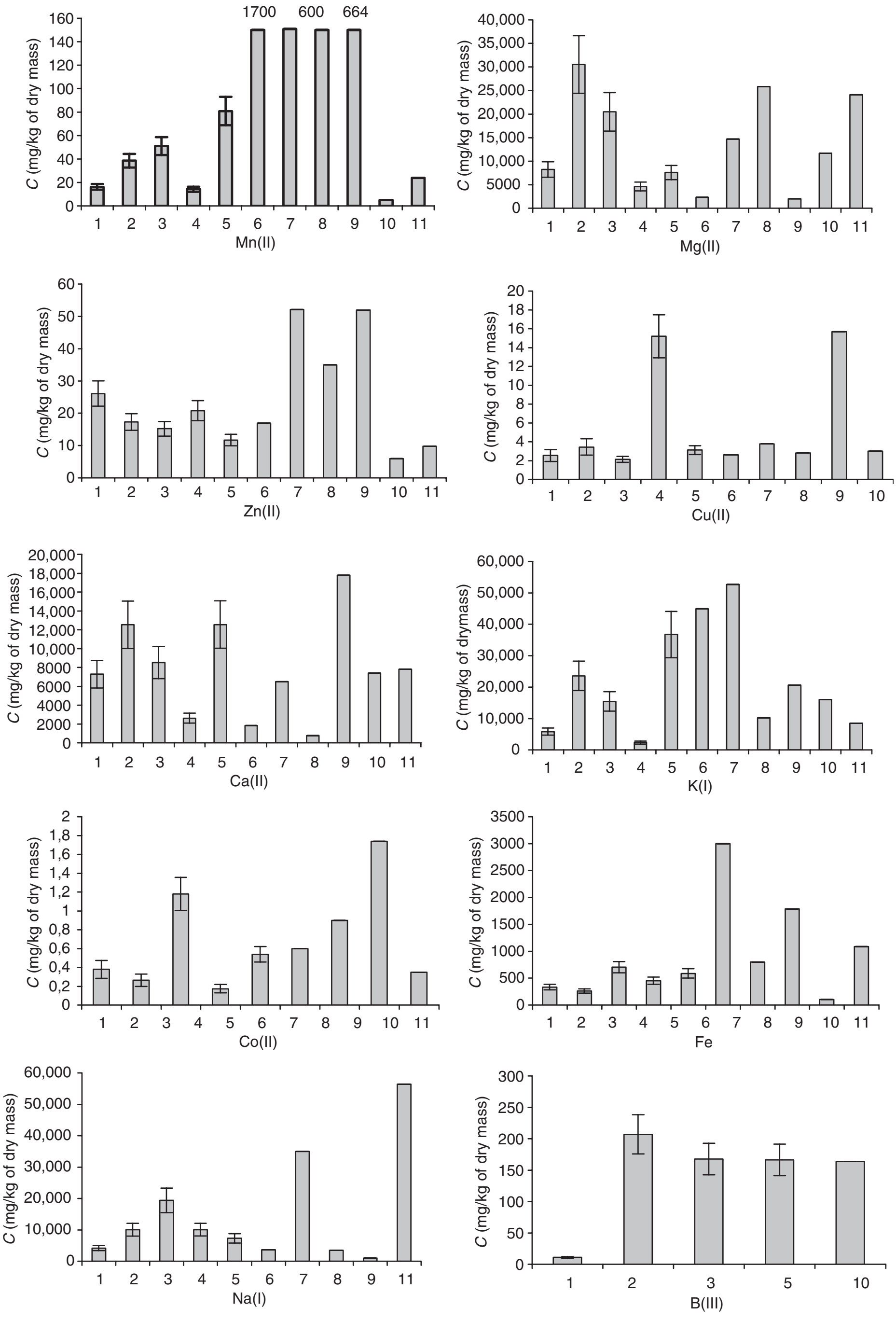

Figure 2. Mineral composition of *Enteromorpha* spp. (Numbers of macroalgae – Nos 1–11 in the Figure 2, correspond to numbers of macroalgae listed in Table 1).

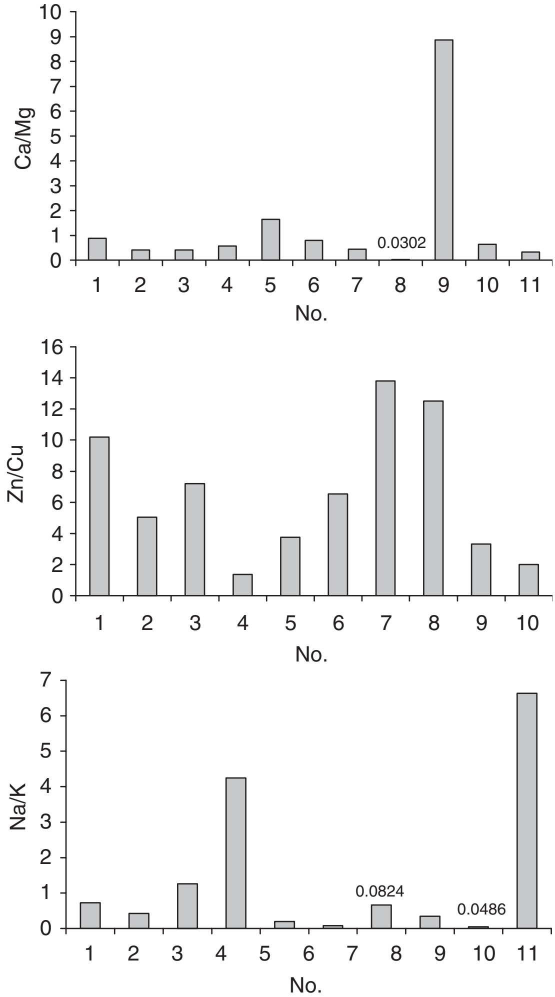

Figure 3. The ratio of elements in *Enteromorpha* spp.

When we compare the content of toxic metals in *Enteromorpha* spp. from the Gulf of Gdańsk (Nos 4 and 5), it can be seen that the content of all toxic metals (beside Hg) was reduced (Table 2). A decrease in Pb content in the samples from the open Baltic Sea was observed throughout the past few years – from 31.0 $mg\,kg^{-1}$ (No. 6) in 1978–1979, to 2.61 $mg\,kg^{-1}$ (No. 7) in 2000–2003, to 0.514 $mg\,kg^{-1}$ (No. 1) in 2006 and to the level below detection limit in 2007 (No. 2). Surprisingly, the content of Pb in the sample No. 3 (2008) increased to 11.4 $mg\,kg^{-1}$ for unknown reason. Therefore, there is a necessity to continue the research on the content of toxic metals in the macroalgae from the Baltic Sea. In this case, *Enteromorpha* sp. can act as a biomonitor of changes in the environment. According to Żbikowski *et al*. [22], the decline in atmospheric Pb deposition is caused by the reduced use of leaded petrol in the Baltic countries. The content of cadmium remained on the similar level in all examined macroalgae and small fluctuations of nickel content were observed. As it was mentioned above, macroalgae could be applied for example in animal

Table 2. Content of toxic elements in examined macroalgae (mg kg^{-1}).

Toxic element	No. 1	No. 2	No. 3	No. 4	No. 5
Cd	0.359 ± 0.072	0.198 ± 0.040	0.286 ± 0.057	0.143 ± 0.029	0.0990 ± 0.0198
As	1.69 ± 0.34	0.0568 ± 0.0114	21.9 ± 2.8	6.05 ± 1.21	16.0 ± 2.1
Pb	0.514 ± 0.103	< 0.0396*	11.4 ± 1.5	4.38 ± 0.88	< 0.0396*
Hg	0.0650 ± 0.0130	0.366 ± 0.073	0.451 ± 0.090	0.0365 ± 0.0073	0.240 ± 0.048

Note: *Values below lower detection limit.

Table 3. Standards in animal feeding.

(a) [33,34]

Microelement	Laying hens (mg kg^{-1} of fodder)	Swine (mg kg^{-1} of fodder)
Mn	60–70	30–40
Cu	5–6	20–165
Zn	50–60	70–150
Co	0	0–0.5
Fe	60–70	90–100
Se	0.15–0.2	0.1–0.2
I	0.7–1.0	0.1–1.0

(b) [5,6]

Toxic element	(mg kg^{-1} of fodder)
As	2–40
Pb	5–40
Hg	0.1–0.5
Cd	0.5–10

feeding, only if it meets the requirements of the obligatory law. One of the most important conditions is the level of toxic elements in the fodder material. The analysis of the samples of *Enteromorpha* spp. showed that the content of toxic elements such as: Pb, Cd, Hg (Table 2) was below toxic limits restricted by Polish Minister of Agriculture and Rural Development [5] and European Directive [6] (Table 3).

In order to determine the correlation between the concentration of a given element in the macroalga and in seawater, CFs were calculated (Table 4). *Enteromorpha* sp. appeared to be a very good bioaccumulator of dissolved metal ions, so that the metal was concentrated in macroalgae when compared with the composition of water. The values of CFs for Fe, Al, Mn and Ti in the examined macroalgae (Nos 3 and 5) were much higher than the values of CFs for K, Ca, Mg and Na for both samples. For macroalga No. 3, the values of CF for: Ti, Al and Fe; Cu, Co, Cr, B, K, Ba and Pb; Zn, Ca, Mg, Na, Cd and V were within the same order of magnitude. Similar results were obtained for macroalga No. 5. It was also found that statistically significant correlations ($p < 0.05$) were observed for the following metal pairs: positive correlation (Mn–K, Co–Ti, K–Ca, Mg–V, Na–Pb, Na–Ti, Pb–Al), negative correlation (Mn–Zn, Cr–Mg, Cr–V) (Figure 4).

Table 4. Concentration factor for examined macroalgae (calculated on a dry weight basis) related to the content of elements in the seawater.

Element	The mineral composition of the seawater ($mg\,L^{-1}$)		The mineral composition of the macroalgae ($mg\,kg^{-1}$)		Concentration Factor (CF)	
	Niechorze – the open Baltic Sea	Gulf of Gdańsk	Niechorze – the open Baltic Sea – No. 3	Gulf of Gdańsk – No. 5	Niechorze – the open Balic Sea – No. 3	Gulf of Gdańsk – No. 5
Mn	0.0170 ± 0.0043	0.0047 ± 0.0012	51.0 ± 7.7	80.9 ± 12.1	3000	17,200
Zn	0.174 ± 0.026	< 0.0651*	15.2 ± 2.3	11.7 ± 1.8	87.4	> 180
Cu	0.0043 ± 0.0011	0.0004 ± 0.0001	2.12 ± 0.53	3.12 ± 0.78	499	7520
Co	0.0118 ± 0.0030	< 0.0074*	1.18 ± 0.30	0.539 ± 0.135	100	> 72.8
Fe	0.0357 ± 0.0089	0.0084 ± 0.0021	705 ± 106	588 ± 88	19,800	70,100
Cr	0.0087 ± 0.0022	0.0127 ± 0.0032	0.999 ± 0.250	1.53 ± 0.38	115	120
B	0.570 ± 0.086	0.621 ± 0.093	167 ± 25	166 ± 25	293	267
K	79.3 ± 11.9	72.2 ± 10.8	15,400 ± 2310	36,700 ± 5510	194	509
Ca	108 ± 16	78.8 ± 11.8	8510 ± 1280	12,600 ± 1880	78.8	159
Mg	243 ± 37	119 ± 18	20,500 ± 3070	7590 ± 1140	84.2	63.7
Na	1360 ± 270	1210 ± 240	19,400 ± 2910	7280 ± 1090	14.3	6.02
Ba	0.0339 ± 0.0085	0.0187 ± 0.0047	4.06 ± 1.02	6.82 ± 1.71	120	365
Cd	0.0060 ± 0.0012	0.0056 ± 0.0011	0.286 ± 0.057	0.099 ± 0.020	48.1	17.6
Ni	< 0.0153*	< 0.0153*	< 0.0153*	< 0.0153*	–	–
Pb	0.0385 ± 0.0077	0.0283 ± 0.0057	11.4 ± 1.5	< 0.0396*	296	< 1.40
Ti	< 0.0009*	0.0035 ± 0.0009	25.9 ± 3.9	11.4 ± 1.7	> 28,800	3280
Al	0.0248 ± 0.0062	0.0081 ± 0.0020	482 ± 72	228 ± 34	19,400	28,200
V	1.63 ± 0.24	0.0007 ± 0.0002	116 ± 17	44.7 ± 6.7	71.2	64,000

Note: *Values below lower detection limit.

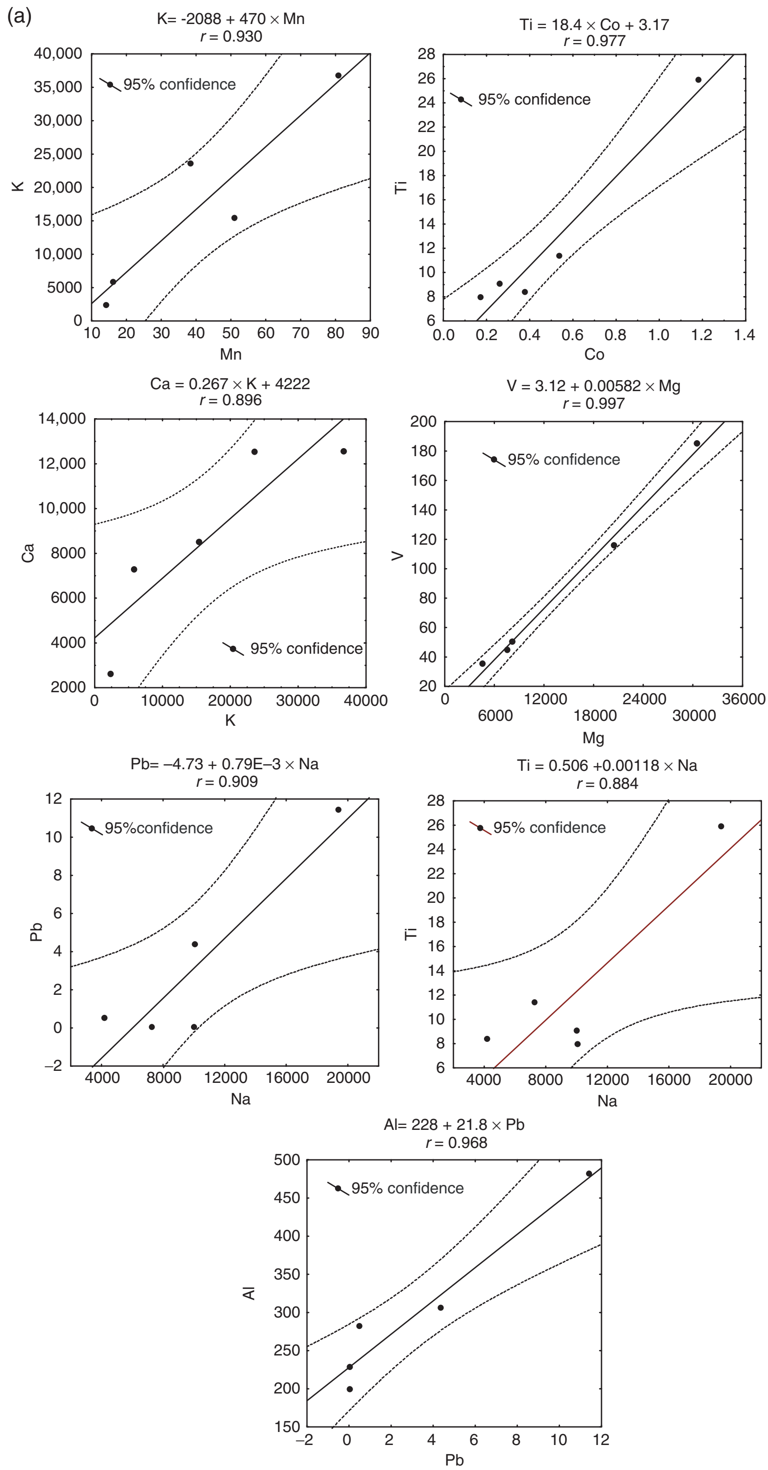

Figure 4. Statistically significant correlations for individual metal pairs in the analysed *Enteromorpha* spp. ($N = 5$): (a) positive correlation; (b) negative correlation.

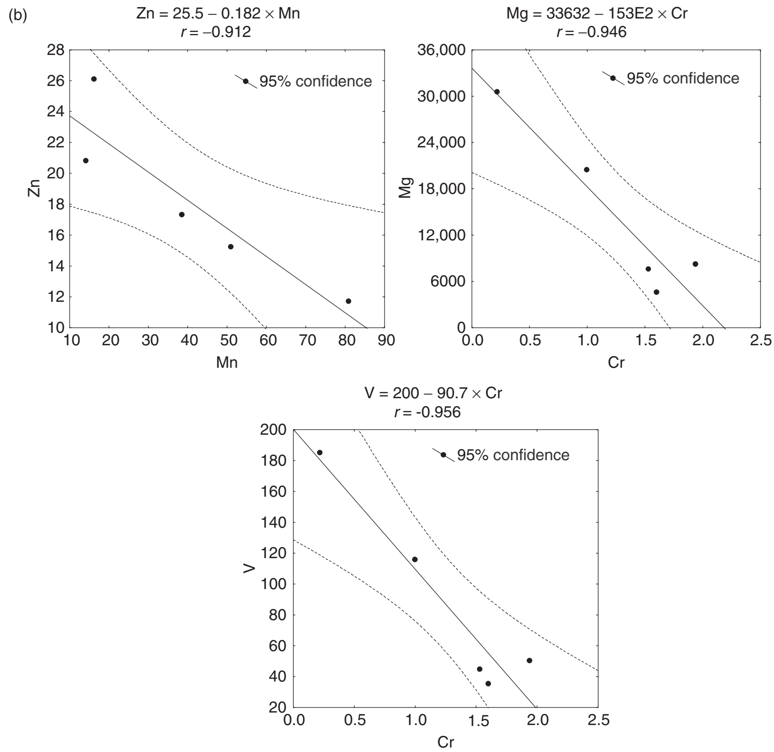

Figure 4. Continued.

Table 5. Content of minerals in grains [35] and average content of elements in grains and in examined macroalgae.

	Grains							Macroalgae (No. 1, 2, 3, 4, 5)
	Corn	Spring wheat	Spring triticale	Spring barley	Oat	Rye		
Element	($mg\,kg^{-1}$)						$\bar{x}$ and SD	$\bar{x}$ and SD
Mn	7.36	33.4	44.7	22.4	49.2	35.0	32.0 ± 15.3	40.2 ± 27.5
Zn	22.7	36.1	40.8	27.4	29.1	29.6	31.0 ± 6.47	18.2 ± 5.50
Cu	1.34	2.59	2.90	1.33	1.33	1.51	1.83 ± 0.716	5.29 ± 5.56
Mg	1200	1500	1300	1100	1300	1200	1270 ± 140	14,300 ± 10,900
K	2300	3000	3400	3500	3500	3900	3270 ± 550	16,800 ± 13,900
Na	170	160	240	160	210	150	182 ± 35.4	10,200 ± 5680
Ca	800	1000	900	1000	1900	1000	1100 ± 400	8610 ± 4140
Na/K	0.0739	0.0533	0.0705	0.0457	0.06	0.0385	0.0570 ± 0.0139	1.37 ± 1.66
Ca/Mg	0.667	0.667	0.692	0.909	1.46	0.833	0.872 ± 0.306	0.786 ± 0.520
Zn/Cu	3.08	1.08	0.913	1.22	0.591	0.846	1.29 ± 0.905	5.51 ± 3.36

One of the aims of this work was to assess the usefulness of macroalgae as mineral feed additives in animal diet. The content of the main micro- and macroelements in examined macroalgae was compared with the composition of biological material, which is commonly used as conventional feed (Table 5). *Enteromorpha* sp. from the Baltic Sea has the advantage over grains, when we consider the content of macroelements (especially Na, Mg and Ca). Macroalgae contained averagely $2480 \pm 1330\,\mathrm{meq\,kg^{-1}}$ (molar unit, which considers the valency of an ion) of Ca, Mg, Na and K, whereas grains only $250 \pm 30\,\mathrm{meq\,kg^{-1}}$. Microelements occur in algal samples on the level comparable to grains. However, algae possess unique property to significantly increase the content of microelements in the biomass. Functional groups on the surface of macroalgae are capable of exchanging light metals, which naturally occur in high concentrations in the raw algae, with microelement ions from aqueous solutions in biosorption process. As it was shown previously [36], the enrichment coefficient (EC) of the sample of *Enteromorpha* sp., which is expressed as the concentration of microelement in enriched alga related to the natural concentration in the alga, for Mn, Zn and Cu ions was as follows: 1780, 3310, 5480, respectively.

4. Conclusions

Enteromorpha sp. – the most abundant macroalga on the Polish coast could be used not only as a biomonitor but also as a future feed additive for animals and food for humans. Due to excess of biogenic substances in the Baltic Sea (mainly nitrogen and phosphorus), intensive growth of algae is observed on the Polish coast. Algal blooms lead to the production of excess of organic matter, increase oxygen consumption and finally lead to death of benthic organisms. Marine macroalgae accumulate minerals from seawater and very often reflect the composition of this environment. This kind of biomass could be used as a valuable source of micro- and macroelements. On the other hand, by collecting macroalgae, the removal of pollutants from seawater is possible.

The aim of this study was to obtain background data and relationships (inter-element interactions, CFs) for mineral content in *Enteromorpha* spp. from the coastal zone of the Baltic Sea. The content of microelements in all examined macroalgae was at rather steady level. Significant fluctuations were observed in the content of macroelements. Generally, *Enteromorpha* spp. from the southern Baltic contained more alkali (Na, K) and alkaline earth metals (Ba, Mg, Ca) than macroalga from Gulf of Gdańsk. The CFs for Fe, Al, Cu, Mn and Ti in algae were much higher, while for K, Ca, Mg and Na much lower. For macroalga No. 3, the values of CF for: Ti, Al and Fe; Cu, Co, Cr, B, K, Ba and Pb; Zn, Ca, Mg, Na, Cd and V were within the same order of magnitude. Similar results were obtained for macroalga No. 5. Statistically significant correlations ($p < 0.05$) were found for the following metal pairs: synergism (Mn–K, Co–Ti, K–Ca, Mg–V, Na–Pb, Na–Ti, Pb–Al), antagonism (Mn–Zn, Cr–Mg, Cr–V).

The obtained results showed that among all examined macroalgae from the Baltic Sea, *Enteromorpha* sp. – No. 3 (Niechorze – the open Baltic Sea) seemed to be the most appropriate material for feed additives in animal diets. It contained $86.8\,\mathrm{meq\,kg^{-1}}$. The remaining macroalge were a poorer source of elements (No. 1 – $22.6\,\mathrm{meq\,kg^{-1}}$, No. 2 – $73.6\,\mathrm{meq\,kg^{-1}}$, No. 4 – $26.1\,\mathrm{meq\,kg^{-1}}$ and No. 5 – $81.3\,\mathrm{meq\,kg^{-1}}$). Macroalgae contained on average 56 times more Na(I), 11 times more Mg(II), 8 times more Ca(II), 5 times more K(I) and 3 times more Cu(II) than the grains, which are commonly used as feed material. The content of Mn(II) was 20% higher.

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