MINERAL COMPOSITION OF MARINE MACROALGAE FROM THE BULGARIAN BLACK SEA COAST

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ABSTRACT

The present study focuses on the trace metal and mineral composition analysis of various seaweeds such as Chlorophyceae (*Ulva rigida* and *Chaetomorpha linum*), Phaeophyceae (*Cystoseira barbata* and *Cystoseira crinita*) and Rhodophyceae (*Gelidium crinale*) collected from the Bulgarian Black Sea Coast. The concentration ranges found for each sample, were as follows: Na, 2.59–5.90; K, 0.28–10.9, Ca, 5.52–21.4; Mg, 2.31–4.22; Sr, 0.05–1.18 (in mg/g dw); Pb, 0.02–0.12; Cr, 0.02–0.33; Co, 0.02–0.15; Fe, 6.1–105; Zn, 1.30–3.80; Mn, 1.60–29.4; Cu, 0.24–0.91; As, 0.18–1.54; Ni, 0.04–0.11; Ba, 0.01–1.95; Se, 0.004–0.12 (in mg/100 g dw); Hg, 0.01–0.03 and Cd, 0.03–0.34 expressed in µg/g dw. Among species analyzed, green algae *Chaetomorpha linum* and *Ulva rigida* showed the maximum contents of mineral elements such as Mg, Na, Cr, Co, Fe, Mn, As, Pb and Hg, red alga *Gelidium crinale* – Cu, Zn and Se, while brown algae *Cystoseira barbata* and *Cystoseira crinita* – Ni, Cd, Ca, K, Sr and Ba. Mineral composition of different Black Sea macroalgae species was found relatively higher as compared to the land vegetables as well as to other edible seaweeds. They could therefore be used as food supplement or as a spice to improve the nutritive value in animal or human diet.

Key words: *macroalgae, Black Sea, minerals*

INTRODUCTION

Seaweeds belong to a group of plants known as algae. Currently biodiversity of seaweed in Bulgarian aquatory is represented by 165 species referred to the three genuses. Most numerous are red (Rhodophyta), followed by green (Chlorophyta) and brown (Phaeophyta) (2). Like other plants, seaweeds contain various inorganic and organic substances which can benefit human health. Algae have been used since ancient times as food, fodder, fertilizer and as source of medicine. Nowadays seaweeds represent an inexhaustible source of raw materials used in pharmaceutical, food industries, medicine and cosmetics. They are nutritionally valuable as fresh or dried vegetables, or as ingredients in a wide variety of prepared foods. In particular, seaweeds contain significant quantities of protein, lipids, minerals and vitamins (5). All seaweeds contain high amounts of both macro minerals (Ca, Mg, Na, P and K) and trace elements (Zn, I and Mn) (7,10). Seaweeds are one of the most important sources of calcium and phosphorus, since they showed higher contents than those of apples, oranges, carrots and potatoes (1).

Bulgarian Black Sea coast is rich in algae, regarding biomass and algal biodiversity (9). However, information available about the mineral composition of local macroalgae species is scarce. Seaweeds are still under-utilized in Bulgaria because the knowledge about their chemical composition is limited.

The main objective of this investigation was to provide knowledge on mineral composition of green algae – Ulva rigida and Chaetomorpha linum, brown algae – Cystoseira barbata and Cystoseira crinita and red alga – Gelidium crinale.

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Received: December 19, 2013
Accepted: January 16, 2013

MATERIALS AND METHODS

Algal samples

Ulva rigida, Chaetomorpha linum, Cystoseira barbata, Cystoseira crinita and Gelidium crinale were collected in July, 2012 from the region of Varna, Bulgaria. All of the samples were harvested manually from their respective sites and then transported to the laboratory in wet tissue towels in an ice box. They were thoroughly cleaned to remove epiphytes and detritus attached to the fronds. Algal samples were spread on blotting paper to remove excess amount of water and shade dried at room temperature until constant weight was obtained. The formal taxonomy of the chosen seaweeds is shown in Table 1.

Table 1. Taxonomy of investigated algal species

	Gelidium crinale	Chaetomorpha linum	Ulva rigida	Cystoseira crinita	Cystoseira barbata
Phylum	Rhodophyta	Chlorophyta	Chlorophyta	Ochrophyta	Ochrophyta
Class	Florideophyceae	Ulvophyceae	Ulvophyceae	Phaeophyceae	Phaeophyceae
Order	Gelidiales	Cladophorales	Ulvales	Fucales	Fucales
Genus	Gelidium	Chaetomorpha	Ulva	Cystoseira	Cystoseira

Reagents

All solutions were prepared with analytical reagent grade chemicals and ultra-pure water (18 MΩ cm) was used for all dilutions. Nitric acid was of superb quality purchased from Fluka. All the plastic and glassware were cleaned by soaking in 2M HNO_3 for 48h.

Sample preparation

A nominal 0.5 g of dry algae tissue was directly weighed in a teflon vessel and mixture of 4 cm^3 HNO_3 and 1 cm^3 H_2O_2 was added and left to stay overnight. The vessels were digested according to the two step temperature program: 1) temperature ramp to 180 °C for 5 min and hold at 180 °C; 2) temperature ramp to 220 °C for 5 min and hold at 220 °C. Thereafter samples were allowed to cool down, transferred to 25 cm^3 plastic vials with screw caps, and diluted to the 25 cm^3 mark with MilliQ water. Determination of Cu, Fe, Mn and Zn was carried out by Flame atomic absorption spectrometer (Perkin Elmer Zeeman 1100B), As, Se, Cd, Cr, Co, Ni and Pb by Electrothermal atomic absorption spectrometer (Perkin Elmer Zeeman 3030 spectrometer with an HGA-600 atomizer), Ca, Mg, Ba, Sr, K and Na by Atomic emission spectrometry with inductively coupled plasma ICP-AES (Jobin Yvon, Ultima 2). Mercury was determined by CV-AAS (Perkin Elmer AAnalyst 400). All determinations were performed in triplicate and data represented on dry weight basis as mean values ± standard deviation.

RESULTS

The mineral compositions of the five aquatic seaweeds are presented in Table 2. A significant variation in metal contents was noticed among these plants, which may be attributed to differences in their genus and species level. As shown in Table 1, potassium and calcium were the most abundant of the elements considered, followed by sodium and magnesium. Among studied samples, Cystoseira barbata and Cystoseira crinita were shown to possess the highest amounts of Ca, K and Sr, Chaetomorpha linum and Ulva rigida – Mn, Fe and Mg, whereas Gelidium crinale contained the highest amounts of Zn, Se and Cu.

Pb, As, Cu, Cr, Ni, Zn, Cd and Hg are relevant elements and are of immediate concern due to their potential toxicity for living organisms. Pb concentration in all macroalgae species ranged from 0.02 to 0.12 mg/100g dw, As from 0.18 to 1.54 mg/100g dw, Cu – from 0.24 to 0.91 mg/100g dw, Cr – from 0.02 to 0.33 mg/100g dw, Ni – from 0.04 to 0.11 mg/100g dw, Zn – from 1.30 to 3.80 mg/100g dw, Cd – from 0.03 to 0.34 μg/g dw and Hg – from 0.01 to 0.03 μg/g dw.

DISCUSSION

The chemical composition of algae varies between species and according to culture conditions (6). It is influenced by growth phase and culture

Table 2. Macro, micro and trace elements of Ulva rigida, Chaetomorpha linum, Cystoseira barbata, Cystoseira crinita and Gelidium crinale

Mineral	Gelidium crinale	Chaetomorpha linum	Ulva rigida	Cystoseira crinita	Cystoseira barbata
mg/g dw					
Ca	8.68 ± 0.70	7.30 ± 0.28	5.52 ± 0.79	19.93 ± 1.60	21.40 ± 2.40
Mg	2.31 ± 0.28	2.50 ± 0.25	7.85 ± 0.70	4.22 ± 0.19	4.14 ± 0.71
Na	5.32 ± 0.27	3.09 ± 0.31	5.90 ± 0.09	5.16 ± 0.54	1.92 ±0.04
K	5.57 ± 0.11	15.44 ± 0.97	4.60 ± 0.28	17.95 ± 0.69	11.93 ± 2.51
Sr	0.06 ± 0.01	0.05 ± 0.00	0.05 ± 0.01	1.02 ± 0.13	1.18 ± 0.13
Na/K ratio	0.95	0.20	1.28	0.29	0.02
mg/100g dw					
Mn	19.03 ± 0.40	29.40 ± 3.56	3.20 ± 0.10	1.60 ± 0.26	4.77 ± 0.35
Fe	89.27 ± 2.10	105.97 ± 3.95	24.53 ± 3.01	6.10 ± 0.92	33.43 ± 3.43
Zn	3.80 ± 0.30	1.87 ± 0.21	1.30 ± 0.26	1.63 ± 0.06	1.43 ± 0.29
Se	0.16 ± 0.04	0.11 ± 0.03	0.004 ± 0.00	0.07 ± 0.03	0.05 ± 0.00
Co	0.09 ± 0.02	0.15 ± 0.03	0.05 ± 0.01	0.02 ± 0.00	0.06 ± 0.01
Cr	0.19 ± 0.02	0.33 ± 0.02	0.13 ± 0.02	0.01 ± 0.00	0.14 ± 0.03
Cu	0.91 ± 0.07	0.76 ± 0.18	0.82 ± 0.10	0.24 ± 0.06	0.77 ± 0.10
Ni	0.10 ± 0.04	0.07 ± 0.01	0.07 ± 0.00	0.04 ± 0.00	0.11 ± 0.02
Ba	0.45 ± 0.16	0.76 ± 0.20	0.20 ± 0.05	1.95 ± 0.13	0.01 ± 0.00
As	0.18 ± 0.01	1.54 ± 0.29	1.34 ± 0.14	0.85 ± 0.16	0.72 ± 0.12
Pb	0.07 ± 0.02	0.12 ± 0.04	0.04 ± 0.01	0.02 ± 0.00	0.06 ± 0.01
µg/g dw					
Cd	0.04 ± 0.01	0.09 ± 0.01	0.03 ± 0.00	0.34 ± 0.05	0.12 ± 0.06
Hg	0.03 ± 0.02	0.02 ± 0.01	0.01 ± 0.00	0.01 ± 0.00	0.02 ± 0.00

Values are expressed as mean ± standard deviation, n=3

medium composition as well as environment factors (13). Mineral elements play an important role in regulating many vital physiological processes in the body, such as regulation of enzyme activity (cofactor or metalloenzyme), skeletal structures (e.g., calcium and phosphorus), neuromuscular irritability and clotting of blood (calcium).

The selected macro (K, Ca, Mg) and micro nutrients (Fe, Zn, Mn, Cu) were found to be higher than any of the land vegetables as well as edible seaweeds like Caulerpa lentillifera, Enteromorpha flexuosa, Monostroma oxysperum, Eucheuma denticulatum and Gracilaria parvispora reported from Hawaii (7) and Undaria pinnatifida, Laminaria digitata, Fucus vesiculosus, and Chondrus crispus reported from Spain (4,11)

The ratios of Na/K were relatively low for Cystoseira barbata, Cystoseira crinita and Chaetomorpha linum (0.02, 0.029 and 0.20, respectively). The other two seaweeds also presented Na/K ratio below 1.5. Generally, seaweeds have low Na/K ratios of 0.14-0.16 (7); >1 (12) and <1.5 (11). Intakes of low Na/K ratios help reduce the incidence of hypertension. Seaweeds can thus help balance high Na/K ratio diets common today (7).

Furthermore, the contents of some heavy metal elements (Pb, As, Cu, Cr, Ni, Zn, Cd and Hg) in the present study were below the toxic limits allowed in some countries (3).

Scripta Scientifica Medica, vol. 45, suppl. 6, 2013, pp. 42-45

CONCLUSION

Five seaweeds were analyzed for their mineral composition and were found to be potential sources of mineral supplements. Cultivated macroalgae may be used as a food supplement to provide the daily intake of some trace elements. The present study has demonstrated that, among the tested aquatic weeds, Cystoseira barbata and Cystoseira crinita from Bulgarian Black Sea coast could be important sources of minerals, suitable for incorporation in fish, animal and human diet.

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