

Seaweed Minerals as Nutraceuticals

Ladislava Mišurcová,^{*,1} Ludmila Machů,[†] and Jana Orsavová[‡]

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Abstract

Seaweed is known as an abundant source of minerals. Mineral composition of seaweed is very changeable because of many exogenous and endogenous factors and differs also within the same species.

* Department of Food Technology and Microbiology, Faculty of Technology, Tomas Bata University in Zlín, Zlín, Czech Republic

† Department of Food Analysis and Chemistry, Faculty of Technology, Tomas Bata University in Zlín, Zlín, Czech Republic

‡ Jana Orsavová is not employed in academic institution but contributed to this chapter.

¹ Corresponding author: Ladislava Mišurcová, E-mail address: misurcova@ft.utb.cz

Principally, seaweed is an excellent source of some essential elements. Mainly, iron and iodine are in high concentration. Seaweeds could be prospective as functional foods and also producers of mineral nutraceuticals.

I. INTRODUCTION

Seaweeds are well-known source of many different bioactive compounds with many health benefit activities. Thus, seaweeds are categorized into the group of functional foods. Because of abundant amounts of many minerals, seaweeds could be utilized as nutraceuticals. The most abundant elements in seaweed tissue are iron (Fe) and iodine (I). Mineral composition of seaweeds is very changeable according to many exogenous and endogenous factors, and it is obviously corresponding with the concentration of minerals in the seawater or a growth medium.

Minerals are structural components and significantly important elements that perform many necessary functions in the living body, including the cell transport and wide range of metabolic processes serving as various catalytic metalloenzymes cofactors. This chapter is focused on some trace elements that are abundantly contained in seaweed. Common feature of all trace elements is their important participation in the formation of binding site of metalloenzymes, where each element plays specific roles in living systems and many of them have a lot of beneficial functions.

II. FUNCTIONS OF IODINE, IRON, ZINC, AND MANGANESE IN THE HUMAN BODY

A. Iodine

Dietary iodine is essential for the production of thyroid hormones, thyroxine and triiodothyronine, which regulate many important physiological processes in humans (Haldimann *et al.*, 2005). More than 1.9 billion individuals are estimated to have inadequate iodine nutrition; the lowest iodine deficiency is in America and the highest in Europe (de Benoist *et al.*, 2003).

Iodine deficiency has effects on growth and development because of inadequate production of thyroid hormones. Health consequences of iodine deficiency are goiter, increased occurrence of hypothyroidism in moderate-to-severe iodine deficiency or decreased occurrence of hypothyroidism in mild iodine deficiency, and increased susceptibility of the thyroid gland to nuclear radiation. Abortion, stillbirth, congenital

anomalies, perinatal and infant mortality, or endemic cretinism may occur in neonates. Iodine deficiency during child and adolescent age could cause delay of physical development and impairment of mental function or iodine-induced hyperthyroidism in adults as well (Zimmermann and Crill, 2010). In severe iodine deficiency, hypothyroidism and developmental brain damage are the dominating disorders (Laurberg *et al.*, 2010).

Excess iodine could lead to thyrotoxicosis and may be connected with hyperthyroidism, euthyroidism, hypothyroidism, or autoimmune thyroid disease (Bürge, 2010; Laurberg *et al.*, 2010). However, thyroid possesses the adaptation mechanisms regulating thyroid hormones synthesis and secretion and protecting from thyrotoxicosis (Wolff, 1989).

B. Iron(Fe)

Iron is an essential element for humans because of its participation in fundamental cell functions. Iron is the most abundant transition metal in the body, which takes part in the utilization of oxygen, and as a component of numerous enzymes, it affects many vitally important metabolic processes, including oxygen transport, DNA synthesis, and electron transport (Lieu *et al.*, 2001; Puntarulo, 2005). The main part, 60–70% of Fe is bound to hemoglobin in circulating erythrocytes, 10% of Fe is present in the form of myoglobins, cytochromes, and iron-containing enzymes, and 20–30% of surplus Fe is stored as ferritins and hemosiderins (Lieu *et al.*, 2001). Iron is stored in the liver, spleen, and bone marrow in specific proteins (Puntarulo, 2005).

Iron deficiency is considered as the most common nutritional disorder worldwide, which results mainly from excessive bleeding (Deegan *et al.*, 2005; Puntarulo, 2005), but partly can be induced also by plant-based diets of vegans, which contains less bioavailable Fe (Martínez-Navarrete *et al.*, 2002). Iron deficiency adversely affects the cognitive performance, behavior, physical growth, the immune status, and morbidity from infections of all age groups. Iron-deficient humans have impaired gastrointestinal functions and altered patterns of hormone production and metabolism (Walker, 1998; WHO, 2001).

Homeostatic mechanisms are very important for the prevention of accumulation of excess Fe that is believed to generate oxidative stress by catalysis of variety of chemical reactions involving free radicals, which could result in cell damage (Pietrangelo, 2002; Puntarulo, 2005). Excess Fe accumulation may promote cancer and increase the cardiovascular risk (Martínez-Navarrete *et al.*, 2002). Iron overload can be observed in some cases including an excessive dietary iron intake, inherited diseases, for example, idiopathic hemochromatosis, congenital atransferrinemia, or the medical treatment of thalassemia (Fontecave and Pierre, 1993).

C. Zinc

Zinc (Zn) is one of the most important essential elements that occurs in hundreds of zinc metalloenzymes and in thousands of protein domains as zinc-fingers (Maret and Sandstead, 2006; McCall *et al.*, 2000; Tapiero and Tew, 2003). Zinc is necessary for growth and development; it is a structural ion of biological membranes; it has roles in gene expression and endocrine function, DNA synthesis, RNA synthesis, and cell division (O'Dell, 2000; Salgueiro *et al.*, 2002). Zinc is an antioxidant, regulates immune response, and has a role in vitamin A metabolism (Rink and Haase, 2007; Salgueiro *et al.*, 2000). Zinc interacts with important hormones involved in bone growth and enhances the effects of vitamin D on bone metabolism (Salgueiro *et al.*, 2002). The majority (85%) of Zn in the whole body is deposited in muscles and bones, 11% is in skin and liver, and the remaining amount is in other tissues. High level of Zn is present in the brain (Tapiero and Tew, 2003). Disturbances of Zn homeostasis have been associated with several diseases including diabetes mellitus, and the alteration of Zn homeostasis in the brain may be associated with the manifestation of epileptic seizures (Chausmer, 1998; Takeda, 2000).

Zinc deficiency occurs in populations whose diets contain high concentration of phytate, a powerful chelator, and low protein (Tapiero and Tew, 2003). Zinc deficiency negatively affects the epidermal, central nervous, immune, gastrointestinal, skeletal, and reproductive systems (Salgueiro *et al.*, 2000, 2002; Tapiero and Tew, 2003; Verstraeten *et al.*, 2004).

The exposure to elevated levels of Zn and zinc-containing compounds may cause many adverse effects in the gastrointestinal, hematological, and respiratory systems together with the alterations in the cardiovascular and neurological systems of humans (Nriagu, 2011). An excessive Zn intake leads to acute adverse effects like diarrhea, vomiting, and headache. Zinc chronic toxicity is reflecting in the effects like functional impairment in immunological response, reduced copper status, altered Fe function, or cholesterol metabolism (Scherz and Kirchhoff, 2006).

D. Manganese

Manganese (Mn) is an essential trace element required for a variety of biological processes. The highest Mn levels are concentrated in tissues with high-energy demand, such as brain, and in retina and dark skin with the high content of pigment. Further, bone, liver, pancreas, and kidney contain obviously high Mn concentration, too (Aschner and Aschner, 2005).

Mn is involved in the metabolism of protein, lipid, and carbohydrate, and performs as various enzymes cofactors. Mn is needed for normal immune function, regulation of blood sugar and cellular energy, reproduction, digestion, bone growth, aids in defense mechanisms against free

radicals, and together with vitamin K, it supports blood clotting and hemostasis and finally, it is essential for the development and function of the brain (Aschner and Aschner, 2005; Takeda, 2003).

A large portion of Mn is bound to manganese metalloproteins. Approximately 3–5% of ingested Mn is absorbed and it is cleared from the blood by the liver and excreted in bile (Mergler, 1999). Manganese absorption is influenced by the presence of other trace elements, phytate, and ascorbic acid (Aschner and Aschner, 2005).

Manganese deficiency can lead to several diseases including osteoporosis, epilepsy, impaired growth, poor bone formation and skeletal defects, abnormal glucose tolerance, and altered lipid and carbohydrate metabolism (Aschner and Aschner, 2005; Nkwenkeu *et al.*, 2002).

Manganese toxicity is associated with damaged ganglia structures and leads to neuropsychiatric symptoms and behavioral dysfunction reminiscent of Parkinson's disease, which is the most common form of parkinsonism and is caused by neurodegenerative disease, drugs, toxicants, and infections (Cersosimo and Koller, 2006; Nkwenkeu *et al.*, 2002; Ordoñez-Librado *et al.*, 2010). High liver Mn content has been reported in alcoholic liver disease and it may affect hepatic fibrogenesis (Rodríguez-Moreno *et al.*, 1997).

III. REQUIREMENTS OF MINERALS BY HUMANS

An adequate intake of minerals is essential for a high nutritional quality of the diet and contributes to the prevention of chronic nutrition-related diseases and degenerative diseases including cancer, cardiovascular disease, Alzheimer's disease, and premature aging (Fenech and Ferguson, 2001; Kersting *et al.*, 2001). However, too high intakes of trace elements could cause toxicity and too low intakes of trace elements may result in nutritional deficiencies (Goldhaber, 2003).

Dietary Reference Intakes (DRIs) are used quite a lot and refer to a set of four nutrient-based reference values that represent the approach to provide quantitative estimates of nutrient intakes. The DRIs replace and expand on the Recommended Dietary Allowances (RDAs) for the United States and the Recommended Nutrient Intakes (RNIs) for Canada. The DRIs consist of the RDAs, the Tolerable Upper Intake Level (UL), the Estimated Average Requirement (EAR), and the Adequate Intake (AI). Generally, each of these values represents average daily nutrient intake of individuals in the diet (Goldhaber, 2003; Murphy and Poos, 2002; Parr *et al.*, 2006; Trumbo *et al.*, 2001; Yates *et al.*, 1998). In addition, dietary intake data for minerals could be assessed within the context of the bioavailability and other factors affecting the utilization of elements by the human body, such as age, sex, and health aspects (Dokkum, 1995).

Table 29.1 shows the recommended daily intakes (RDIs) for the selected trace elements. Data vary according to various countries and their values are adequate of diverse dietary pattern and different levels of these elements in the population of these countries.

In light of the essentiality of trace elements in adequate dietary intakes on one side and the toxicity of trace elements in high-level intakes on the other side, there should be a set of rules for physiological benefit and safe intakes of trace elements. Table 29.2 shows the UL for selected elements suggested for the United States and Australia.

IV. CONTENT OF MINERALS IN SEAWEED

Seaweeds are a well-known source of minerals and their levels depend on different seaweed genera. Formerly, brown seaweed was used for the production of soda and potash and it has also been a source for iodine

TABLE 29.1 RDIs of selected macroelements and microelements in various countries

	EU (mg/day)	USA (mg/day)	Australia (mg/day)	Asia (mg/day)
<i>Macroelements</i>				
Calcium	800 ^a	1000 ^b	1000 ^c	700 ^d
Chloride	800 ^a	2300 ^e		
Magnesium	375 ^a	400 ^f	400 ^c	230 ^d
Phosphorus	700 ^a	700 ^f	1000 ^c	
Potassium	2000 ^a	4700 ^e		
Sodium		1500 ^e		
<i>Microelements</i>				
Chromium	0.04 ^a	0.035 ^g		
Copper	1 ^a	0.9 ^g		
Fluoride	3.5 ^a	4 ^f		
Iodine	0.15 ^a	0.15 ^g	0.15 ^c	0.15 ^d
Iron	14 ^a	8 ^g	8 ^c	15 ^d
Manganese	2 ^a	2.3 ^g		
Molybdenum	0.05 ^a	0.045 ^g	0.045 ^c	
Selenium	0.055 ^a	0.055 ^h	0.07 ^c	0.34 ^d
Zinc	10 ^a	11 ^g	14 ^c	6.5 ^d

^a European Commission (2008).

^b Institute of Medicine (2011).

^c National Health and Medical Research Council (2006).

^d International Life Sciences Institute—Southeast Asia Region (2005).

^e Institute of Medicine (2005).

^f Institute of Medicine (1997).

^g Institute of Medicine (2001).

^h Institute of Medicine (2000).

TABLE 29.2 ULs of selected macroelements and microelements in various countries

	USA (mg/day)	Australia (mg/day)
<i>Macroelements</i>		
Calcium	2500 ^a	2500 ^b
Chloride	3600 ^c	
Magnesium	350 ^d	350 ^b
Phosphorus	4000 ^d	4000 ^b
Sodium	2300 ^c	2300 ^b
<i>Microelements</i>		
Copper	10 ^e	10 ^b
Fluoride	10 ^d	10 ^b
Iodine	1.1 ^e	1.1 ^b
Iron	45 ^e	45 ^b
Manganese	11 ^e	
Molybdenum	2 ^e	2 ^b
Selenium	0.4 ^f	0.4 ^b
Zinc	40 ^e	40 ^b
Boron	20 ^e	
Nickel	1 ^e	
Vanadium	1.8 ^e	

^a Institute of Medicine (2011).^b National Health and Medical Research Council (2006).^c Institute of Medicine (2005).^d Institute of Medicine (1997).^e Institute of Medicine (2001).^f Institute of Medicine (2000).

production for many years (Chapman, 1980). Nowadays, seaweeds are considered as a potential material for the production of different nutraceuticals and food supplements (Martínez-Navarrete *et al.*, 2002; Shahidi, 2009).

Mineral content of widely used seaweeds is documented and has been very changeable in different genera across all groups of brown, red, and green seaweeds. Generally, macroelements in seaweeds have been determined in relatively low concentrations, but levels of trace elements have frequently reached the high values which exceeded RDIs. Some of the seaweeds are excellent contributors, especially of iodine and iron.

A. Contribution of seaweed minerals to daily requirements

Seaweeds could be excellent contributors of some microelements to RDIs, as it is documented in Tables 29.3 and 29.4. The contents of I and Fe, Mn, and Zn have been mentioned in mg/8 g of dry matter of particular

TABLE 29.3 Iodine content (mg/8 g) in seaweeds and its contribution to RDI (%)

Brown algae		% RDI EU, USA, Australia, Asia	Red algae		% RDI EU, USA, Australia, Asia	Green algae		% RDI EU, USA, Australia, Asia
RDI—I (mg/day)	mg/ 8 g	0.15	RDI—I (mg/day)	mg/ 8 g	0.15	RDI—I (mg/day)	mg/ 8 g	0.15
<i>Sargassum vachellianum</i> ^a	47.51	31,675	<i>Gracilaria lemaneiformis</i> ^b	34.09	22,725	<i>Enteromorpha</i> spp. ^c	60.30	40,200
<i>S. henslowianum</i> ^a	41.57	27,717	<i>Gracilaria fergusonii</i> ^d	31.92	21,280	<i>Ulva</i> spp. ^c	1.30	867
<i>Laminaria digitata</i> ^c	34.00	22,667	<i>Gracilaria fergusonii</i> ^d	16.87	11,248	<i>Codium fragile</i> ^a	1.23	821
<i>Ecklonia radiata</i> ^e	31.92	21,280	<i>Palmaria palmata</i> ^c	5.10	3400	<i>Ulva fasciata</i> ^d	1.03	688
<i>Ecklonia radiata</i> ^e	29.76	19,837	<i>Rhodomela confervoides</i> ^a	3.45	2300	<i>Enteromorpha intestinalis</i> ^a	0.92	612
<i>Laminaria japonica</i> ^a	24.32	16,213	<i>Gracilaria confervoides</i> ^a	2.82	1883	<i>Ulva rigida</i> ^f	0.52	350
<i>Laminaria japonica</i> ^b	24.32	16,213	<i>Corynomorpha prismatica</i> ^d	2.38	1584	<i>Monostroma fragile</i> ^a	0.51	339
<i>S. parvifolium</i> ^a	17.26	11,504	<i>Polysiphonia urceolata</i> ^a	2.34	1562	<i>Ulva lactuca</i> ^a	0.43	287
<i>Macrocystis pyrifera</i> ^e	16.93	11,284	<i>Chondrus crispus</i> ^c	1.90	1267	<i>Ulva pertusa</i> ^a	0.27	177
<i>Undaria pinnatifida</i> ^a	12.57	8379	<i>Laurencia okamurai</i> ^a	1.80	1199	<i>Ulva stenophylla</i> ^e	0.22	144
<i>Hormosira banksii</i> ^e	8.33	5552	<i>Gelidium amansii</i> ^a	1.63	1087			
<i>Ascophyllum nodosum</i> ^c	5.80	3867	<i>Gracilaria corticata</i> ^d	1.49	992			
<i>Sargasso NIES-09</i> ^f	4.20	2801	<i>Sarcodia ceylanica</i> ^d	1.43	955			
<i>Undaria pinnatifida</i> ^c	3.20	2133	<i>Corallina pilulifera</i> ^a	1.29	860			
<i>Himanthalia elongata</i> ^c	2.80	1867	<i>Cheilosporum spectabile</i> ^d	1.25	832			
<i>Sargassum thunbergii</i> ^a	2.69	1794	<i>Leathesia difformes</i> ^a	1.04	693			
<i>Undaria pinnatifida</i> ^f	2.44	1630	<i>Porphyra umbilicalis</i> ^c	0.94	627			

<i>Durvillaea antarctica</i> ^c	2.33	1552	<i>Spyridia aculeata</i> ^d	0.90	597
<i>Sargassum</i> <i>kjellmanianum</i> ^a	2.18	1456	<i>Myelophycus simplex</i> ^a	0.76	509
<i>Puncyaria</i> <i>plantaginea</i> ^a	1.88	1252	<i>Dictyopteris divaricate</i> ^a	0.75	498
<i>Sargassum</i> <i>kjellmanianum</i> ^a	1.63	1086	<i>Gloeosiphonia capillaris</i> ^a	0.65	433
<i>Chnoospora fastigiata</i> ^d	1.46	971	<i>Palmaria palmata</i> ^f	0.62	412
			<i>Ceramium boydenoo</i> ^a	0.57	379

^a Hou and Yan (1998).

^b Wen *et al.* (2006).

^c MacArtain *et al.* (2007).

^d Mageswaran *et al.* (1985).

^e Smith *et al.* (2010).

^f Romarís-Hortas *et al.* (2011).

TABLE 29.4 Content of iron, zinc, and manganese (mg/8 g) in seaweed and their contribution to RDIs (%)

Brown algae	mg/ 8 g	% RDI				Red algae	mg/ 8 g	% RDI				Green algae	mg/ 8 g	% RDI			
		EU	USA	Australia	Asia			EU	USA	Australia	Asia			EU	USA	Australia	Asia
Fe																	
RDI—Fe (mg/day)		14	8	8	15	RDI—Fe (mg/day)		14	8	8	15	RDI—Fe (mg/day)		14	8	8	15
<i>Colpomenia sinuosa</i> ^a	41.8	298	522	522	279	<i>Myelophycus simplex</i> ^a	49.7	355	621	621	331	<i>Codium fragile</i> ^a	75.4	539	943	943	503
<i>Puncyaria plantaginea</i> ^a	31.2	223	390	390	208	<i>Polysiphonia urceolate</i> ^a	43.4	310	543	543	289	<i>Ulva pertusa</i> ^a	46.3	331	579	579	309
<i>Sargassum thunbergii</i> ^a	23.8	170	297	297	158	<i>Dictyopteris divaricate</i> ^a	25.3	181	317	317	169	<i>Ulva clathrata</i> ^b	33.4	238	417	417	223
<i>Laminaria digitata</i> ^c	22.1	158	276	276	147	<i>Corallina pilulifera</i> ^a	24.7	176	309	309	165	<i>Ulva rigida</i> ^d	22.6	162	283	283	151
<i>Scytosiphon lomentarius</i> ^a	17.9	128	223	223	119	<i>Leathesia diffformes</i> ^a	22.0	157	275	275	146	<i>Monostroma fragile</i> ^a	19.0	136	238	238	127
<i>Sargassum kjellmanianum</i> ^a	14.6	104	182	182	97	<i>Gelidium amansil</i> ^a	20.3	145	254	254	135	<i>Ulva lactuca</i> ^a	16.3	116	203	203	108
						<i>Rhodomela confervoides</i> ^a	18.0	129	226	226	120						
						<i>Porphyra tenera</i> ^c	14.7	105	184	184	98						
Zn																	
RDI—Zn (mg/day)		10	11	14	6.5	RDI—Zn (mg/day)		10	11	14	6.5	RDI—Zn (mg/day)		10	11	14	6.5
<i>Undaria pinnatifida</i> ^f	5.05	51	46	36	78	<i>Chondrus ocellatus</i> ^g	2.27	23	21	16	35	<i>Ulva clathrata</i> ^b	1.51	15	14	11	23
<i>Padina gymnospora</i> ^h	2.46	25	22	18	38	<i>Spyridia clavata</i> ^h	1.20	12	11	9	18	<i>Caulerpa racemosa</i> ⁱ	0.55	6	5	4	8
<i>Hijikia fusiforme</i> ^f	2.00	20	18	14	31	<i>Acanthophora spicifera</i> ^h	0.82	8	7	6	13	<i>Ulva stenophylla</i> ^j	0.49	5	4	4	8

<i>Laminaria japonica</i> ^k	1.07	11	10	8	16	<i>Gracilaria</i> sp. ^h	0.77	8	7	6	12	<i>Caulerpa veravelensis</i> ⁱ	0.43	4	4	3	7
<i>Sargassum stenophyllum</i> ^h	0.86	9	8	6	13	<i>Palmaria palmata</i> ^e	0.30	3	3	2	5						
Mn																	
RDI—Mn (mg/day)		2	2.3			RDI—Mn (mg/day)		2	2.3			RDI—Mn (mg/day)		2	2.3		
<i>Laminaria japonica</i> ^k	2.55	128	111			<i>Porphyra tenera</i> ^e	2.88	144	125			<i>Codium fragile</i> ^a	2.22	111	97		
<i>Puncyaria plantaginea</i> ^a	1.43	72	62			<i>Ceramium boydenoo</i> ^a	2.34	117	102			<i>Ulva stenophylla</i> ^j	1.54	77	67		
<i>S. henslowianum</i> ^a	1.33	67	58			<i>Rhodomela confervoides</i> ^a	0.93	47	40			<i>Ulva pertusa</i> ^a	0.82	41	36		
<i>Sargassum vachellianum</i> ^a	0.99	50	43			<i>Gloeosiphonia capillaris</i> ^a	0.82	41	36			<i>Monostroma fragile</i> ^a	0.47	24	20		
						<i>Polysiphonia urceolate</i> ^a	0.82	41	36								

^a Hou and Yan (1998).
^b Peña-Rodríguez *et al.* (2011).
^c MacArtain *et al.* (2007).
^d Taboada *et al.* (2010).
^e Mišurcová *et al.* (2009).
^f Kikunaga *et al.* (1999).
^g McDermid and Stuercke (2003).
^h Karez *et al.* (1994).
ⁱ Kumar *et al.* (2011).
^j Smith *et al.* (2010).
^k Wen *et al.* (2006).

seaweed genera from groups of brown, red, and green together with their percentage participation on the RDIs of the minerals mentioned above. According to reported data about the seaweed consumption in Asian countries, the amount of 8 g of seaweed dry matter was considered as an average daily intake (MacArtain *et al.*, 2007; Miyake *et al.*, 2006). The seaweed participation on RDI was calculated for EU countries, the United States, Australia, and Asia. The conversion factor of 8 g was used as a daily intake for all countries though daily seaweed consumptions are lower in EU countries, the United States, and Australia. Unfortunately, data about them were not available. The participation values of particular seaweed genera on RDI were evaluated from data from several studies (Hou and Yan, 1998; Karez *et al.*, 1994; Kikunaga *et al.*, 1999; Kumar *et al.*, 2011; MacArtain *et al.*, 2007; Mageswaran *et al.*, 1985; McDermid and Stuercke, 2003; Mišurcová *et al.*, 2009; Peña-Rodríguez *et al.*, 2011; Romarís-Hortas *et al.*, 2011; Smith *et al.*, 2010; Taboada *et al.*, 2010; Wen *et al.*, 2006).

Due to high iodine concentration in seaweeds, many of them could be utilized as natural sources for the production of iodine nutraceuticals; brown seaweed of genera *Sargassum*, *Laminaria*, *Ecklonia*, *Macrocystis*, *Undaria*, *Ascophyllum*, and *Durvillaea*; red seaweed of genera *Gracilaria*, *Palmaria*, *Chondrus*, *Laurencia*, and *Gelidium*; and even green seaweed of genera *Enteromorpha*, *Ulva*, *Codium*, and *Monostroma*. Besides the well-known seaweed genera, some other seaweed genera which are used in a lesser extent—*Himalanthia* and *Chnoospora* from brown seaweed, further *Corynomorpha*, *Polysiphonia*, *Sarcodia*, *Coralina*, *Cheilosporum*, *Leathesia*, *Spiridia*, and *Myelophycus* from red seaweed genera—could be considered as an abundant source of iodine. However, the extent of utilization of these seaweeds for iodine production should be considered because of their expanse occurrence. Table 29.3 shows the participation of selected seaweeds from all seaweed groups on the RDI whose iodine value is equal for the EU, the United States, Australia, and Asia. Seaweeds with the highest content of iodine, that is, *Gracilaria lemaneiformis*—red macroalga, *Sargassum vachellianum*—brown macroalga, and *Enteromorpha* spp.—green alga, exceed the RDI up to 200, 300, and 400 times, respectively (Hou and Yan, 1998; MacArtain *et al.*, 2007; Wen *et al.*, 2006). Finally, great differences were observed not only between various seaweed genera but also within the same genus.

Further, this review is focused on the concentrations of Fe, Zn, and Mn in 8 g of dry matter of different seaweed genera and their participation on the RDIs as it is shown in the Table 29.4. Seaweeds from all groups of green, brown, and red are the excellent contributors of Fe. The highest participation on RDI was observed in green seaweed *Codium fragile*, red seaweed *Myelophycus simplex*, and brown seaweed *Colpomelia sinuosa* as their iron contents exceeded RDIs in a range from 3 to 10 times (Hou and

Yan, 1998). The other seaweed genera such as green *Ulva* and *Monostroma*, red *Polysiphonia*, *Dictyopteris*, *Corallina*, *Leathesia*, *Gelidium*, *Rhodomela*, and *Porphyra*, and finally brown seaweed genera *Puncyaria*, *Sargassum*, *Laminaria*, and *Scytosiphon* contain high amount of Fe. Considering Zn and Mn, their amounts across all seaweed groups do not reach the RDIs. Their participation on RDIs was mostly in the units and tens of percents except from *Laminaria japonica*, *Porphyra tenera*, *Ceramium boydenoo*, and *C. fragile*, whose concentrations of Mn exceeded 100% of RDI (Hou and Yan, 1998; Mišurcová *et al.*, 2009; Wen *et al.*, 2006).

B. Factors influencing mineral contents in seaweed

It was observed that seaweeds have been selective biosorbents for different metals. Concentration factors (CFs) have been determined as 10–20 times higher than those in terrestrial plants. Seaweeds have much bigger ability $>10^6$ to concentrate rare earth elements than terrestrial plants which is 10^3 . The values of CFs vary by diverse elements, for example, CFs for Al, Fe, Ce, and Th are in seaweeds much higher than CFs for Na, Mg, Cl, and Br (Hou and Yan, 1998).

Unfortunately, higher amounts of some minerals in seaweed have been the result of pollution of the seawater or natural environment. Thus, many studies were conducted with respect to the contamination of seaweed by heavy metals. Because of their high sorption capacity, they were also probed for their utilization as biosorbents to remove heavy metals from the environment and to elucidate mechanisms of metal biosorption by seaweeds (Davis *et al.*, 2003; Murphy *et al.*, 2008; Suzuki *et al.*, 2005). Further, these conclusions could be utilized for the understanding of the uptake mechanisms by seaweed. Finally, endogenous and exogenous factors have participated on the variability of seaweed mineral composition.

1. Endogenous factors

The main endogenous factor responsible for the enormous capability to absorb inorganic substances from the environment is a different structure of seaweed cell wall polysaccharides. Each of different seaweed groups possesses various structural polysaccharides such as fibrillar, nonfibrillar, and sulphated derivatives with diverse number of bound sites for metal ions resulting in dissimilar mineral sorbent capacity. Structural polysaccharides show strong ion-exchange properties.

It has been reported that brown seaweeds have higher capability to incorporate minerals into their tissue than red and green seaweeds due to larger number of compounds with anionic groups in their cell walls such as alginic acids, proteins, polygalacturonic acids, and polyphenols (Connan and Stengel, 2011; Figueira *et al.*, 2000; Michalak and

Chojnacka, 2010). On the contrary, Baumann *et al.* (2009) observed higher affinity of a red seaweed *Palmaria palmata* to accumulate heavy metals Cd and Cr than those of brown seaweeds. Different affinity of metals to various seaweed compounds also results in the variability of mineral distribution in seaweeds. Alkali metals are mainly bound to alginic acid; thus their concentrations are higher in algin than those in original algae similar to Zn, Cr, and Fe that are rather combined with proteins to form metalloproteins and their concentrations in original algae are lower too (Hou, 1999).

The level of minerals depends on particular seaweed genera because of the diverse affinity of many seaweed strains for each element, which also results in various mineral amounts in seaweed tissues (Baumann *et al.*, 2009). However, differences in mineral levels in seaweed tissues were observed also within the same seaweed species influenced by the stage of the living cycle and the age of seaweed. The highest iodine concentration was deposited in the meristematic tissue at the base of the blade in diverse seaweed genera (Teas *et al.*, 2004). The mechanism of high iodine uptake by brown seaweed from the order Laminariales was described by Küpper *et al.* (1998). The iodine uptake mechanism was explained by the oxidation of iodide to hypoiodous acid and molecular iodine by cell wall haloperoxidases. The oxidized iodine may cross the plasmatic membrane, and its accumulation in seaweed tissues could be 30,000 times more than the concentration of this element in seawater.

2. Exogenous factors

The range of seaweed capability to absorb minerals is based on many exogenous factors predestining diverse levels of various minerals in seaweed tissues, such as the environmental conditions (geographic location, season, wave exposure, seawater temperature, salinity, mineral levels in seawater, and finally pH of seawater).

The influence of different geographic locations could be documented on the mineral composition of edible red seaweed *Porphyra vietnamensis* from different localities of the central west coast India. The highest amount of Fe was observed in the wide range from 33.0 to 298.0 mg/100 g dry weight. Thanks to the high level of Fe, *P. vietnamensis* from these localities could be served as a food supplement to improve dietary intake of iron (Rao *et al.*, 2007).

Seasonal variations of seaweed chemical composition are linked with the particular life stage. It was confirmed that in periods of maximum growth photosynthetic activity increased, which resulted in higher content of carbohydrates with many binding-sites for metals (Rosenberg and Ramus, 1982). Seasonal variations of mineral composition were studied in brown seaweed *Fucus vesiculosus* (Riget *et al.*, 1995). Maximum and minimum concentrations of Cd, Cu, and Pb were found in February

(middle growth stage) and August (initial and latter growth stage), respectively. For Zn, maximum and minimum concentrations occurred in March and September, respectively. Similar conclusions were deduced by Lares *et al.* (2002). The highest Cd content was in June and the lowest in October in brown seaweed *Macrocystis pyrifera*. On the contrary, no significant variations were found for the major elements Na, Ca, and Mg during a full growth seaweed period (Hou and Yan, 1998).

It is evident that the main sorption mechanism of metals based on exchange of ions by the metal binding to an anion site by either replacing an existing metal or displacing a proton depends on the pH value of the solution. Thus, pH is an important parameter on the biosorption of metal ions from aqueous solutions (Antunes *et al.*, 2003; Crist and Martin, 1999). Further, it was also established that metals differ in the ability of displacing protons. In yellow-green alga *Vaucheria*, it was determined that the capacity of proton exchange for heavy metals—Pb and Cd—increased with pH and Pb had the highest value (Crist and Martin, 1999). The pH effect on the metal sorption was established also in nonliving biomasses from green seaweed *Ulva onoi* (Suzuki *et al.*, 2005). The sorption capacity of *Ulva* biomasses for Cd was noticeably low in highly acidic (> pH 3) and highly alkaline conditions (< pH 10).

Lower salinity affects seaweed physiology and biochemical composition by decreasing phenolic contents and increasing protein content, and these changes have been shown to influence the availability of metal-binding sites (Connan and Stengel, 2011).

V. BIOAVAILABILITY OF SEAWEED MINERALS BY HUMANS

High levels of some essential trace elements in seaweed are not sufficient to cover their RDIs due to various extent of their bioavailability by humans.

Mineral bioavailability is defined as a part of the ingested nutrient that is absorbed and consecutively utilized by humans for maintaining normal physiological functions (Fairweather-Tait and Hurrell, 1996). The biological availability of minerals depends on the diet composition and is influenced by the levels and forms of present nutrient or nonnutrient components, and finally by nutrient synergistic or antagonistic interactions (Watanabe *et al.*, 1997). Dietary fiber, phytate, phenolic compounds could decrease the availability of minerals due to the formation of insoluble complexes resulting in the reduction of mineral absorption (Fairweather-Tait and Hurrell, 1996).

Dietary form of nutrient determines the extent of its utilization. The best iron source is iron from animal sources or heme iron (Whittaker, 2008). It was observed that 9–53% of heme iron and 1–25% of nonheme

iron were absorbed in a study on the health volunteers. But the absorption process is very specific and could be influenced by many factors; thus it can be used only for demonstration of different extent of iron absorption (Skikne *et al.*, 1983).

Finally, reciprocal antagonistic or synergic behavior between minerals affects the range of mineral absorption in seaweed by binding-site competition. In aqueous solutions, Fe impairs the absorption of Zn. On the other hand, Ca inhibits the absorption of Fe and Zn (Fairweather-Tait and Hurrell, 1996; Maret and Sandstead, 2006; Solomons, 1986). Finally, food preparation and cooking could determine the final mineral content of the food by the loss of water-soluble minerals (Santoso *et al.*, 2006).

VI. CONCLUSION

Usage of mineral supplements in western countries often prevents deficiency of minerals. However, effectiveness of bioavailability of some mineral supplements has been considered as insufficient. Natural sources of many trace elements are seaweed from all algal groups. Seaweed has the enormous ability to absorb minerals from a growth medium which results in high mineral concentrations in seaweed tissues often exceeding their concentration in the seawater, especially iodine and iron occurs in very high levels.

Mineral composition of seaweed is very changeable according to different factors including the environmental conditions and specific behavior of each seaweed genus. The question of minerals availability by humans may also be considered. Among the factors influencing the bioavailability of minerals derived from seaweed matter, belong mainly to the compositions of their cell walls with different polysaccharides that could bind the elements with various powers and prevent their utilization for living processes in the human body.

The aptitude of seaweed to absorb minerals from a growth medium could be utilized to pointed production of seaweed matter enrichment with specific elements and to produce natural mineral nutraceuticals.

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