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Nutritional and Toxicological Importance of Macro, Trace, and Ultra-Trace Elements in Algae Food Products

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The content of 5 macro elements (Na, K, Ca, Mg, and P), 6 trace elements (Fe, Mn, Zn, Cu, Se, and I), and 4 ultra-trace elements (As, Pb, Cd, and Hg) in 34 edible dried seaweed products of brown algae (*Laminaria* sp., *Undaria pinnatifida*, and *Hizikia fusiforme*) and red algae (*Porphyra* sp.) originated from China, Japan, and Korea and bought by retail in Germany was determined. The content of these elements was analyzed by spectrometric methods (ICP–AES, ICP–MS, HGAAS, and CVAAS). Assuming a daily intake with 5 g FM of algae, the contribution of the essential elements to the diet is low, with the exception of I. Brown algae contained as much as 1316 ± 1669 mg of I/kg FM. More than 4000 mg of I/kg FM were found in several *Laminaria* sp. Moreover, some brown algae, such as *Hizikia fusiforme*, had high contents of total As (87.7 ± 8.2 mg/kg FM).

KEYWORDS: Edible seaweeds; macro elements; trace elements; ultra-trace elements; nutritional requirement; toxicity of arsenic and iodine

INTRODUCTION

Macro algae (seaweeds) are rich in proteins, fibers, vitamins, macro and trace elements, as well as physiologically important fatty acids. Thus, seaweeds can contribute to the nutritional requirement of humans and may be beneficial in human health (*1–15*). However, macro algae may also contain trace and ultra-trace elements with toxicological potential to humans.

Marine algae, in particular brown algae, are known as primary accumulators for As (*16–18*). Thus, algae are responsible for the transfer of As into the food chain. In contrast, reports on the Hg content of Spanish algae products (*18*) and Canadian red and brown algae (*19*) can be regarded as harmless. Also the reported contents of Pb and Cd in algae are no cause for concern (*4, 18*).

The high contents of individual macro, trace, and ultra-trace elements in algae are represented by their high ash contents, which amount to 20.6–21.1 and 30.1–39.3% in red and brown algae, respectively. In comparison, terrestrial plants contain only 5–10% ash (*20*). For example, *Undaria pinnatifida* contains 70.6 g of Na/kg, 87.0 g of K/kg, 9.3 g of Ca/kg, and 11.8 g of Mg/kg.

Seaweeds are generally rich in I. Brown algae are especially able to accumulate I from the seawater. While *Porphyra* sp. contain maximal 550 mg of I/kg dry matter (DM), *Laminaria* sp. may contain 1700–11 580 mg of I/kg DM (*21*). Such high I contents in edible seaweed products may represent a considerable health risk to humans.

During the past few decades, the consumption of seaweed products has increased in many European countries. The seaweed products marketed in Europe differ in their composition, origin, appearance, color, consistence, and labeling. Therefore, in the present investigation, the contents of 15 elements including 5 macro elements (Na, K, Ca, Mg, and P), 6 trace elements (Fe, Mn, Zn, Cu, Se, and I), and 4 ultra-trace elements (As, Pb, Cd, and Hg) in 34 commercially available seaweed products originated from China, Japan, and Korea and purchased in German food stores and specialty shops were determined. The contents of these elements in red and brown algae were compared. The nutrimental importance of the essential elements and the toxicological potential of I, As, Pb, Cd, and Hg were assessed on the basis of intake recommendations and limitations, respectively.

MATERIALS AND METHODS

Samples. The 34 macro algae products consisted of 17 red algae (*Rhodophyta*) and 17 brown algae (*Phaeophyta*). Among brown algae samples, there were 8 *Laminaria* sp. (Konbu), 7 *Undaria pinnatifida* (Wakame), and 2 *Hizikia fusiforme* (Hijiki) products. The brown algae products originated from China, Japan, and Korea. The red algae products belonged to *Porphyra* sp., commercially named Nori. A total of 12 red algae products came from Japan and Korea, and 5 products were from China.

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Table 1. Macro Element Contents of Seaweed Products (g/kg FM) Marketed in Germany ($n = 34$) and Daily Element Intake with 5 g FM of Algae Products (mg/day) Compared to the Recommended Daily Intake of the DGE for Adults (*24*)[a]

	red algae			brown algae[b]					intake with 5 g FM of algae	
macro elements	*Porphyra* sp.[c]	*Porphyra* sp.[d]	mean	*Undaria pinnatifida*	*Laminaria* sp.	*Hizikia fusiforme*	mean	DGE recommendations	red algae	brown algae
	g/kg FM (mean ± SD)								mg/day	
DM	93.5 ± 1.5 a	92.3 ± 0.7 a,c	93.1 ± 1.3	89.3 ± 1.4 b	91.0 ± 2.2 c,d	89.4 ± 0.5 b,d	90.0 ± 1.9			
Na	5.87 ± 3.31 c	7.06 ± 3.11 c	6.22 ± 3.21	98.4 ± 15.7 a	25.9 ± 3.2 b	14.0 ± 3.4 b,c	58.6 ± 40.3	550	31.1	293
K	27.2 ± 11.4 b	29.0 ± 3.1 b	27.7 ± 9.6	4.80 ± 1.04 c	102 ± 30.6 a	35.4 ± 10.1 b	48.4 ± 50.9	2000	139	242
Na/K	0.26 ± 0.22 b	0.24 ± 0.09 b	0.25 ± 0.19	21.1 ± 4.9 a	0.28 ± 0.11 b	0.43 ± 0.22 b	10.1 ± 11.2			
Mg	3.50 ± 0.50 c	3.48 ± 0.32 c	3.49 ± 0.44	8.68 ± 3.02 a	5.70 ± 0.58 b	6.67 ± 0.87 a,b	7.22 ± 2.51	300–400	17.5	36.1
Ca	3.39 ± 0.92 d	3.11 ± 0.73 d	3.30 ± 0.85	8.99 ± 1.37 b	7.42 ± 1.04 c	13.3 ± 0.6 a	8.85 ± 2.16	1000–1200	16.5	44.3
P	5.10 ± 1.56 a	5.57 ± 0.31 a	5.23 ± 1.32	3.62 ± 0.72 b	2.66 ± 1.39 b,c	1.01 ± 0.04 c	2.92 ± 1.30	700–1250	26.2	14.6
Ca/P	0.74 ± 0.38 c	0.56 ± 0.13 c	0.69 ± 0.33	2.55 ± 0.58 b	3.61 ± 2.24 b	13.3 ± 1.1 a	4.25 ± 3.73			

[a] Within each row, values not sharing the same letter differ, $p < 0.05$. [b] Brown algae was from China, Japan, and Korea. [c] *Porphyra* sp. was from Japan and Korea. [d] *Porphyra* sp. was from China.

Digestion of Na, K, Ca, Mg, P, Fe, Mn, Zn, Cu, and Se. The dried, pulverized, and homogenized sample (0.5 g) was digested with 3 mL of nitric acid (65% p.a. plus; Sigma-Adrich Chemie GmbH, Taufkirchen, Germany) and 1 mL of hydrogen peroxide (30%, suprapure; Merck, Darmstadt, Germany) in a closed polytetrafluoroethylene vessel (PDS-6; Loftfields Analytische Lösungen LAL, Neu Eichenberg, Germany) for 8 h at 170 °C. After the extract was cooled, it was transferred into polypropylene tubes (Sarstedt, Nümbrecht, Germany) and filled with pure water to a volume of 15 mL.

Extraction of I. The dried, pulverized, and homogenized sample (0.5 g) was extracted by a mixture of 5 mL of pure water and 1 mL of tetramethylammoniumhydroxide (25%, Tama Chemicals, Kawasaki-ku, Japan) for 3 h at 90 °C. After the extract was cooled, it was filled up with 14 mL of pure water and centrifuged (4500 units/min for 15 min).

Digestion of As, Pb, Cd, and Hg. A total of 0.5 g of the dried, pulverized, and homogenized sample was digested with 5 mL of nitric acid (65%, p.a. plus; Sigma-Adrich) and 2 mL of hydrogen peroxide (30%, suprapure; Merck) in the quartz reaction vessels of a multiwave sample digestion system (PerkinElmer LAS, Rodgau-Jügesheim, Germany) for 30 min at 160 °C. After the extract was cooled, it was transferred into polypropylene tubes (Sarstedt) and filled with pure water to a volume of 15 mL.

Determination of Na, K, Ca, Mg, P, Fe, Mn, Zn, and Cu. The determination of Na, K, Ca, Mg, P, Fe, Mn, Zn, and Cu was conducted by means of inductively coupled plasma–atomic emission spectrometry (ICP–AES, Optima 3000, PerkinElmer) according to DIN EN ISO 11885:1997-11.

Determination of As and Se. As and Se were determined by hydride generation atomic absorption spectrometry (HGAAS, Aanalyst 100, PerkinElmer) according to DIN EN ISO 11969:1996-11.

Determination of I, Pb, and Cd. The contents of I, Pb, and Cd were determined by means of inductively coupled plasma mass spectrometry (ICP–MS, ELAN 6000, PerkinElmer) according to DIN 38406 E24-2:1993-03. While rhodium was used as an internal standard for the measurement of Pb and Cd, tellurium was applied for the correction of the nonspectral matrix interferences at I.

Determination of Hg. Hg was determined by use of cold vapor atomic absorption spectrometry (CVAAS, Aanalyst 100, PerkinElmer) according to DIN EN 1483:1997-05.

Statistics. Results were expressed as mean ± standard deviation (SD) (Excel; Windows Office package 1998). All statistical analyses were performed using the SPSS software package, version 11.5 (SPSS, Inc., Chicago, IL). The unpaired *t* test was employed to compare the values between red and brown algae products. Analysis of variation (ANOVA) multivariate test was used to evaluate the variance between the nutrimental characteristics of the algae products. Differences were considered significant at $p < 0.05$.

RESULTS AND DISCUSSION

The mean DM content of the seaweed products analyzed was estimated at 93.1 ± 1.3 g/100 g and 90.0 ± 1.9 g/100 g in red and brown algae, respectively (**Table 1**). The estimated element contents refer to fresh matter (FM) and not DM.

The nutritional and toxicological importance of the elements tested were assessed on the basis of an intake with 5 g FM of algae products, derived from the consumption of 1.6 kg DM of seaweeds per capita and year in Japan, corresponding to an intake of about 4–5 g per capita and day (*22*), and on the basis of the intake recommendations of the German Society of Nutrition (DGE) and/or the provisional tolerable weekly intake (PTWI) values of the World Health Organization (WHO) for the relevant elements.

According to the National Nutrition Survey in Japan (*23*), the daily intake of seaweeds in Japan has been almost stable, ranging from 4.9 to 6.1 g DM over 25 years from 1975 to 2000. However, in Japan, the methods to estimate the weight of seaweeds eaten were changed in 2001. Since this year, the process of cooking has been taken into account in the weight estimation, leading to a national average intake of 14 g per day and capita. The higher intake value is mainly caused by water absorption of the seaweeds through swelling in water. Thus, this intake value is not equivalent to DM.

Content of Macro Elements (Na, K, Ca, Mg, and P). Generally, the mean contents of Na, K, Mg, and Ca were higher in brown algae than in red algae, whereas the mean content of P was higher in red algae than in brown algae. The mean Ca content in red algae was almost 3 times lower than in brown algae, among them, in *Hizikia fusiforme*, the highest Ca contents were found, but the mean P content in red algae was twice as large as in brown algae. Therefore, the physiologically important Ca/P ratio of brown algae was about 6 times higher than that of red algae (**Table 1**). However, according to the latest information, there is no need for maintaining a definite Ca/P ratio in human nutrition (*24*).

The mean Na content in brown algae was about 10-fold higher than that in red algae, mainly caused by the high Na content in *Undaria pinnatifida*. In contrast, *Undaria pinnatifida* showed a low K content. On average, the K content in brown algae was twice as high as in red algae, but differed greatly between *Undaria pinnatidida* and *Laminaria* sp., with a ratio of 1:20. Accordingly, the mean Na/K ratio in brown algae was 40 times higher than in red algae (**Table 1**). Thus, red algae, *Laminaria* sp., and *Hizikia fusiforme* had a favorably low Na/K quotient, with 0.25, 0.28, and 0.43, respectively. In contrast, in traditional European food products, such as meat and sausage, the Na/K ratio is 2.9–7.5 (*25*). The consumption of foods with a high Na/K quotient may cause high blood pressure, as shown in experimental rats (*26*).

Table 2. Trace Element Contents of Seaweed Products (Fe, Mn, Zn, Cu, and I: mg/kg FM; Se: μg/kg FM) Marketed in Germany ($n = 34$) and Daily Element Intake with 5 g FM of Algae Products Compared to the Recommended Daily Intake of the DGE for Adults (*24*)[a]

	red algae			brown algae[b]					intake with 5 g FM of algae	
trace elements	*Porphyra* sp.[c]	*Porphyra* sp.[d]	mean	*Undaria pinnatifida*	*Laminaria* sp.	*Hizikia fusiforme*	mean	DGE recommendations	red algae	brown algae
	mg/kg FM (mean ± SD)								mg/day	
Fe	131 ± 47.8 b	991 ± 362 a	384 ± 445	184 ± 107 c	264 ± 317 c	679 ± 270 a	275 ± 268	10–15	1.92	1.38
Mn	31.2 ± 19.7 b	54.6 ± 4.9 a	38.1 ± 19.8	7.46 ± 28.9 c	11.1 ± 11.8 c	24.5 ± 10.3 b,c,d	11.0 ± 9.6	2.0–5.0	0.19	0.06
Zn	37.9 ± 17.6 a	35.6 ± 8.7 a	37.2 ± 15.3	33.1 ± 9.8 a,c	9.71 ± 3.18 b	15.7 ± 7.9 b,c	21.4 ± 13.5	7–10	0.19	0.11
Cu	8.95 ± 3.00 a	10.8 ± 2.9 a	9.49 ± 3.00	1.51 ± 0.57 b	1.07 ± 0.51 b	2.61 ± 1.16 b	1.45 ± 0.75	1.0–1.5	0.05	0.01
I	26.7 ± 12.4 b	33.2 ± 21.4 b	34.8 ± 22.0	163 ± 75.3 b	2934 ± 1489 a	262 ± 70.0 b	1316 ± 1669	0.180–0.200	0.174	6.58
	μg/kg FM (mean ± SD)								μg/day	
Se	39.9 ± 20.1 a	55.8 ± 6.3 a,b	44.6 ± 18.5	61.3 ± 17.1 b	23.7 ± 14.9 c	63.0 ± 29.7 a,b	46.0 ± 25.2	30–70	0.22	0.23

[a] Within each row, values not sharing the same letter differ, $p < 0.05$. [b] Brown algae was from China, Japan, and Korea. [c] *Porphyra* sp. was from Japan and Korea. [d] *Porphyra* sp. was from China.

In comparison to the recommendations of the DGE for the intake of Na, K, Ca, Mg, and P (*24*), the contents of these macro elements in algae products tested were relatively small, with the exception of a high Na content in *Undaria pinnatifida*.

Content of Trace Elements (Fe, Mn, Zn, Cu, Se, and I). The Fe content in red algae differed greatly according to the origin of algae. Red algae from China contained about 7 times more Fe than red algae from Japan and Korea. In contrast, the Fe contents in brown algae depended upon the species, with about 3–4 times higher values in *Hizikia fusiforme* than in *Laminaria* sp. and *Undaria pinnatifida* (**Table 2**).

The mean Mn content in red algae was 3–4 times higher than that in brown algae (**Table 2**). The Zn contents in red algae from China, Japan, and Korea were similar but differed among brown algae, with the highest contents in *Undaria pinnatifida*, being 2 times and 3 times higher than in *Hizikia fusiforme* and *Laminaria* sp., respectively (**Table 2**). The Cu content in red algae was found to be 4–10 times higher than in brown algae (**Table 2**). The Se content was, on average, similar in red and brown algae. However, among brown algae, *Undaria pinnatifida* and *Hizikia fusiforme* were almost 3-fold richer in Se than *Laminaria* sp. (**Table 2**).

In contrast, the tested seaweed products commercially available on the German food market contained abundant amounts of I, which proved to be highly relevant to human health. Among brown algae, *Laminaria* sp. had a mean content of almost 3000 mg/kg FM, being about 10 and 20 times higher than in *Hizikia fusiforme* and *Undaria pinnatifida*, respectively, and almost 100 times higher than in red algae (**Table 2**). Thus, the consumption of 5.4–6.7 g of red algae, 1.1 g of *Undaria pinnatifida*, 0.7 g of *Hizikia fusiforme*, and 0.06 g of *Laminaria* sp. covers the daily requirement of 0.180 mg of I (*24*), whereas the mean I intake with 5 g of brown algae amounting to 6.58 mg of I/day exceeds the nutritional recommendations for adults considerably (*24*, *27*). Three samples of *Laminaria* sp. from China, Japan, and Korea contained even more than 4000 mg of I/kg FM. Such high I contents may represent a considerable health risk. Therefore, foodstuffs and condiments from macro algae with I contents >20 mg/kg DM are not marketable in Germany (*21*). The results obtained have shown that 30 of the 34 analyzed algae products exceeded this limit value. Only three products of *Porphyra* sp. from Japan and Korea and one red algae product from China had I contents below the Federal Institute for Sanitary Consumer Protection and Veterinary Medicine (BgVV) limit value. In all, red algae had by far smaller I contents than brown algae.

Because Germany still belongs to the I-deficiency regions of the world, the recommended I intake is 180–200 μg/day for adults (*24*), whereas the WHO (*27*) recommends an I intake of 100–140 μg/day for adults in nondeficiency regions. The response of the human organism to an oversupply of I is individually different. It depends upon the previous and current I status. For example, with elderly who have an I deficiency, unrecognized functional thyroid autonomies can occur. These autonomous adenomas can be activated by an I oversupply, and then a life-threatening hyperthyroidism may develop. In contrast, Asian individuals have eaten sea products rich in I in high amounts for centuries. Thus, their thyroid gland is adapted for high I intake. In this case, the majority of I is eliminated via the urine without detrimental effects on the thyroid gland. Already, breast milk of Asian women has high I content depending upon the seaweed consumption. A study with 50 nursing women from Korea showed that babies 2–5 days after birth took in, on average, 2744 μg of I/day (*28*). These high concentrations decreased 4 weeks postpartum to 1295 μg of I/day, because the I concentration of 2170 μg/L in the colostrums is reduced to 892 μg/L in the mature milk. The WHO (*27*) has established an tolerable upper intake level (UL) or provisional maximum tolerable daily intake (PMTDI) of <1 mg of I/day [equivalent to 0.017 mg of I/kg body weight (BW)] from all sources, whereas the DGE (*24*) recommends an UL of <500 μg of I/day because of the deficiency situation in Europe and the elevated risk for hyperthyroidism in the case of an oversupply following a long-term deficiency period (*29*). The Scientific Committee on Food of the European Commission (*30*) provides an UL of 600 μg of I/day for adults, including pregnant and lactating women, and the U.S. Food and Nutrition Board (*31*) proposes an UL of 1100 μg of I/day for adults (≥19 years), including pregnant and lactating women, too.

However, in Japan, it could be observed that the biosynthesis of the thyroid gland hormones is hampered through I intakes of 2–10 mg/day (Wolff–Chaikoff block). In this case, despite a high I supply, hypothyroidism and goiter may develop (*21*).

Content of Ultra-Trace Elements (As, Pb, Cd, and Hg). In brown algae, the mean contents of As were about 10 times higher than that in red algae, with the highest values in *Hizikia fusiforme*, being 60 times higher than the mean values of red algae (**Table 3**). The PTWI value for inorganic As is 15 μg $(\text{kg BW})^{-1}$ week^{-1} or 2 μg $(\text{kg BW})^{-1}$ day^{-1} (*27*). Considering a mean total As content in brown algae of 16.7 mg/kg FM, the intake with 5 g FM of brown algae amounts to 65% of the PTWI but the intake with 5 g FM of *Hizikia fusiforme* exceeds the PTWI value by 340%. The authors are aware of the fact that the As estimate includes approximately total As. After pressure digestion at a temperature less than 180 °C, the organic As

Table 3. Ultra-Trace Element Contents of Seaweed Products (As, Pb, and Cd: mg/kg FM; Hg: μg/kg FM) Marketed in Germany ($n = 34$) and Daily Element Intake with 5 g FM of Algae Products Compared to the Recommended PTWI (μg/day) (*27, 36, 37*)[a]

	red algae			brown algae[b]					intake with 5 g FM of algae	
ultra-trace elements	*Porphyra* sp.[c]	*Porphyra* sp.[d]	mean	*Undaria pinnatifida*	*Laminaria* sp.	*Hizikia fusiforme*	mean	PTWI (60 kg BW)	red algae	brown algae
				mg/kg FM (mean ± SD)					μg/day	
As	0.85 ± 0.24 d	2.86 ± 2.06 d	1.46 ± 1.42	6.21 ± 1.17 c	8.42 ± 2.26 b	87.7 ± 8.2 a	16.7 ± 26.9	129[e]	7.3	83.5
Pb	0.24 ± 0.29 b	2.23 ± 2.56 a	0.83 ± 1.60	0.86 ± 0.38 b	1.23 ± 1.99 b	1.12 ± 0.64 b	1.04 ± 1.27	214	4.2	5.2
Cd	1.13 ± 1.06 b	0.92 ± 0.78 b	1.07 ± 0.97	2.15 ± 1.07 a	0.59 ± 0.21 b	1.25 ± 0.29 a,b	1.40 ± 1.04	60	5.4	7.0
				μg/kg FM (mean ± SD)					μg/day	
Hg	5.36 ± 1.91 b	6.95 ± 3.32 b	5.77 ± 2.16	18.9 ± 5.1 a	25.5 ± 20.9 a	26.6 ± 5.3 a	22.9 ± 13.6	13.7[f]	0.03	0.11

[a] Within each row, values not sharing the same letter differ, $p < 0.05$. [b] Brown algae from China, Japan, and Korea. [c] *Porphyra* sp. from Japan and Korea. [d] *Porphyra* sp. from China. [e] Inorganic As. [f] Methyl mercury.

compounds are not completely decomposed. However, the digestion includes the total amount of inorganic As. The PTWI value is based on inorganic As. The total As content is therefore only partially suitable for the assessment of the toxicological potential of As. To evaluate the health risk of As, its chemical composition in seaweeds and the biochemical properties of the individual As species are important.

Organic As compounds (e.g., arsenocholine, arsenobetaine, and arsenosugars) are considered to be nontoxic or only minimally toxic in living systems, whereas in recent years, evidence has accumulated that dimethylarsinic acid (DMA), the major As metabolite formed after exposure to inorganic As (As^{3+} and As^{5+}) via ingestion or inhalation in both humans and rodents, has cytotoxic and carcinogenic properties. DMA induces lesions, as a result of single-strand breaks in DNA, in the lungs of both mice and rats and in human lung cells *in vitro*. It acts as a promoter of urinary bladder, kidney, liver, and thyroid gland cancers in rats and lung tumors in mice (*32*).

An increase of DMA was detected in human urine after the consumption of *Porphyra* sp. containing arsenosugars only. This result indicates that nontoxic organic As can be metabolized to toxic inorganic As (*33*). In another study, it has been demonstrated that arsenosugars are biotransformed by humans to at least 12 As metabolites, with DMA consisting of 67% of the total As excreted (*34*).

Moreover, the composition of organic and inorganic As differs in macro algae. For example, *Porphyra* sp. contained only organic As species (*33*), whereas in algae products from the French market (e.g., *Hizikia fusiforme*, *Laminaria* sp., *Undaria pinnatifida*, and *Porphyra* sp.), the proportion of inorganic As constituted about half (36–74%) of the total As content (*16*).

The Agency for Toxic Substances and Disease Registry (ATSDR) (*35*) has derived a provisional minimal risk level (MRL) of 0.005 mg kg^{-1} day^{-1} for acute-duration (14 days or less) oral exposure to inorganic As based on a lowest observed adverse effect level (LOAEL) of 0.05 mg of As kg^{-1} day^{-1} for facial edema and gastrointestinal symptoms (nausea, vomiting, and diarrhea) and a MRL of 0.0003 mg kg^{-1} day^{-1} for chronic-duration (365 days or more) oral exposure to inorganic As based on a no observed adverse effect level (NOAEL) of 0.008 mg of As kg^{-1} day^{-1} for skin lesions. However, no oral MRLs were derived for organic As compounds.

When this information is taken together, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) stressed that there is a narrow margin of the PTWI and As intakes reported to have toxic effects in epidemiological studies (*27*). Thus, the consumption of brown algae can be a health risk.

The average Pb contents in red and brown algae were similar (ca. 1 mg/kg FM). However, red algae from China showed a 10-fold higher mean content than red algae from Japan and Korea (**Table 3**). This result can be put down to one red algae sample from China whose Pb content amounted to 6.79 mg/kg FM. The mean content of about 1 mg of Pb/kg FM in red and brown algae analyzed is ca. 2% of the PTWI value established at 25 μg/kg BW (*37*).

The most critical effect of Pb at low concentrations is considered to be impaired neurobehavioral development, i.e., reduced cognitive development and intellectual performance in children. Several studies have shown an association between the blood Pb concentration and reduced intelligence quotient (IQ) in children exposed pre- and postnatal. The most serious study revealed a decrease of one IQ point for every 2–4 μg of Pb/dL increase in the blood Pb concentration (*37*). The low Pb contents in algae products found in the present study should have negligible effects on the neurobehavioral development of infants and children.

The contents of Cd were high in *Undaria pinnatifida* (about 2 mg/kg FM) and low in *Laminaria* sp. (about 0.6 mg/kg FM) (**Table 3**). An intake with 5 g FM of red algae (5.4 μg Cd/day) and brown algae (7.0 μg Cd/day) contributes to ca. 10% of the PTWI value established at 7 μg/kg BW (1 μg/kg BW/day, corresponding to 60 μg/day for a 60 kg adult) (*27*).

Cd has a very long biological half-life in humans (10–30 years in liver, kidney, and muscle) (*39*) and, thus, accumulates throughout the lifetime, especially in the kidneys. Steady-state concentrations in the renal cortex are reached only after about 40 years (*36*). Cd intakes of 140–255 μg/day have been associated with low-molecular-weight proteinuria in the elderly as the first adverse functional change following chronic exposure to Cd. Mean dietary intakes in several countries range from 2.8 to 4.2 μg $(kg\ BW)^{-1}$ $week^{-1}$ constituting about 40–60% of the current PTWI (*36*). Thus, there is only a relatively small safety margin between exposure in the normal diet and exposure that causes adverse effects (*27*). The PTWI value for Cd was set by JECFA assuming an absorption rate for dietary Cd of 5% and a daily excretion rate of 0.005% of body burden to prevent the fact that total Cd intake continuously for 50 years leads to Cd levels in the renal cortex exceeding 50 mg/kg (*27*).

In brown algae, the mean Hg content was about 4 times higher than in red algae ($p < 0.05$) (**Table 3**). An intake with 5 g FM of brown algae tested contributes <1% of the PTWI for methyl mercury, which has been recently established at 1.6 μg/kg BW, i.e., lowered by half compared to the previous PTWI (*36*). The actual value is based on new data of studies performed in laboratory animals and humans and, additionally, epidemiological studies that investigated the possible effects of prenatal exposure to methyl mercury on child neurodevelopment. The present PTWI is considered sufficient to protect developing fetuses, the most sensitive subgroup of the population against toxic effects of methyl mercury to the nervous system and brain.

In light of the new PTWI for methyl mercury, the JECFA recommended that the PTWI for total mercury (300 μg/person, of which no more than 200 μg is present as methyl mercury) should also be revised (*36*, *37*). An evaluation conducted by the U.S. National Research Council (NRC) set an intake limit of 0.7 μg (kg BW)$^{-1}$ week^{-1}, being more than half lower than the PTWI (*38*). The NRC value obviously takes into account more strongly the highly toxic potential of methyl mercury to the nervous system and developing brain particularly during infancy. In all, the Hg contents presently found in seaweed products are assessed to be of no cause for health concern, with the normal consumption behavior provided.

Considering a daily intake of 5 g FM of algae, the results of the present study reveal that the mean contents of the heavy metals Pb, Cd, and Hg in algae products are far below the PTWI values (**Table 3**).

CONCLUSIONS

Red and brown algae products contribute only minor amounts to the recommended daily intake of macro elements, with the exception of the Na-rich brown alga *Undaria pinnatifida*. Also the daily intake of the trace elements Fe, Mn, Zn, Cu, and Se is far below the recommendations, with the normal consumption of 5 g FM of algae provided. Generally, the contents of the ultra-trace elements Pb, Cd, and Hg in red and brown algae can be assessed as harmless. However, new data indicate that vulnerable groups of the population (e.g., elderly) might be at an increased risk of tubular dysfunction at the present PTWI value for Cd (*36*). In contrast, particularly in brown algae, the contents of the toxicologically relevant elements I and As should be controlled to protect the consumer against potential health risks.

ABBREVIATIONS USED

AAS, atomic absorption spectrometry; ATSDR, Agency for Toxic Substances and Disease Registry; BgVV, Federal Institute for Sanitary Consumer Protection and Veterinary Medicine; BW, body weight; CVAAS, cold vapor atomic absorption spectrometry; DGE, German Society of Nutrition; DM, dry matter; DMA, dimethylarsinic acid; HGAAS, hydride generation atomic absorption spectrometry; FM, fresh matter; ICP–MS, inductively coupled plasma–mass spectrometry; ICP–AES, inductively coupled plasma–atomic emission spectrometry; JECFA, Joint FAO/WHO Expert Committee on Food Additives; LOAEL, lowest observed adverse effect level; MRL, minimal risk level; NOAEL, no observed adverse effect level; NRC, National Research Council; PMTDI, provisional maximum tolerable daily intake; PTWI, provisional tolerable weekly intake; SD, standard deviation; UL, tolerable upper intake level; WHO, World Health Organization.

LITERATURE CITED

(1) Takagi, T.; Asahi, M.; Itabashi, Y. Fatty acid composition of twelve algae from Japanese waters. *Yukagaku* **1985**, *34*, 1008–1012.
(2) Lahaye, M. Marine algae as sources of fibers: Determination of soluble and insoluble dietary fiber contents in some “sea vegetables”. *J. Sci. Food Agric.* **1991**, *54*, 587–594.
(3) Fleurence, J.; Gutbier, G.; Mabeau, S.; Leray, C. Fatty acids from 11 marine macroalgae of the French Brittany coast. *J. Appl. Phycol.* **1994**, *6*, 527–532.
(4) Jurković, N.; Kolb, N.; Colić, I. Nutritive value of marine algae *Laminaria japonica* and *Undaria pinnatifida*. *Nahrung* **1995**, *39*, 63–66.
(5) Jiménez-Escrig, A.; Cambrodon, I. G. Nutritional evaluation and physiological effects of edible seaweeds. *Arch. Latinoam. Nutr.* **1999**, *49*, 114–120.
(6) Yamada, K.; Yamada, Y.; Fukuda, M.; Yamada, S. Bioavailability of dried asakusanori (*Porphyra tenera*) as a source of cobalamin (vitamin B_{12}). *Int. J. Vitam. Nutr. Res.* **1999**, *69*, 412–418.
(7) Goñi, I.; Valdivieso, L.; Garcia-Alonso, A. Nori seaweed consumption modifies glycemic response in healthy volunteers. *Nutr. Res. (N.Y.)* **2000**, *20*, 1367–1375.
(8) Jiménez-Escrig, A.; Sánchez-Muniz, F. J. Dietary fibre from edible seaweeds: Chemical structure, physicochemical properties and effects on cholesterol metabolism. *Nutr. Res. (N.Y.)* **2000**, *20*, 585–598.
(9) Rupérez, P.; Saura-Calixto, F. Dietary fibre and physicochemical properties of edible Spanish seaweeds. *Eur. Food Res. Technol.* **2001**, *212*, 349–354.
(10) Rupérez, P.; Ahrazem, O.; Leal, J. A. Potential antioxidant capacity of sulfated polysaccharides from edible marine brown seaweed *Fucus vesiculosus*. *J. Agric. Food Chem.* **2002**, *50*, 840–845.
(11) Watanabe, F.; Takenaka, S.; Kittaka-Katsura, H.; Ebara, S.; Miyamoto, E. Characterization and bioavailability of vitamin B_{12}-compounds from edible algae. *J. Nutr. Sci. Vitaminol.* **2002**, *48*, 325–331.
(12) McDermid, K. J.; Stuercke, B. Nutritional composition of edible Hawaiian seaweeds. *J. Appl. Phycol.* **2003**, *15*, 513–524.
(13) Takenaka, S.; Takubo, K.; Watanabe, F.; Tanno, T.; Tsuyama, S.; Nanao, Y.; Tamura, Y. Occurrence of coenzyme forms of vitamin B_{12} in a cultured purple laver *Porphyla yezoensis*. *Biosci., Biotechnol., Biochem.* **2003**, *67*, 2480–2482.
(14) Yon, M.; Hyun, T. H. Folate content of foods commonly consumed in Korea measured after trienzyme extraction. *Nutr. Res.* **2003**, *23*, 735–746.
(15) Dawczynski, C.; Schubert, R.; Jahreis, G. Amino acids, fatty acids, and dietary fibre in edible seaweed products. *Food Chem.* **2007**, *103*, 891–899.
(16) McSheehy, S.; Szpunar, J. Speciation of arsenic in edible algae by bi-dimensional size-exclusion anion exchange HPLC with dual ICP–MS and electrospray MS/MS detection. *J. Anal. At. Spectrom.* **2000**, *15*, 79–87.
(17) McSheehy, S.; Pohl, P.; Lobiński, R.; Szpunar, J. Complementarity of multidimensional HPLC–ICP–MS and electrospray MS–MS for speciation analysis of arsenic in algae. *Anal. Chim. Acta* **2001**, *440*, 3–15.
(18) Almela, C.; Algora, S.; Benito, V.; Clemente, M. J.; Devesa, V.; Suner, M. A.; Velez, D.; Montoro, R. Heavy metal, total arsenic, and inorganic arsenic contents of algae food products. *J. Agric. Food Chem.* **2002**, *50*, 918–923.
(19) Phaneuf, D.; Côté, I.; Dumas, P.; Ferron, L. A.; LeBlanc, A. Evaluation of the contamination of marine algae (seaweed) from the St. Lawrence River and likely to be consumed by humans. *Environ. Res.* **1999**, *80*, S175–S182.
(20) Rupérez, P. Mineral content of edible marine seaweeds. *Food Chem.* **2002**, *79*, 23–26.
(21) Bundesinstitut für gesundheitlichen Verbraucherschutz und Veterinärmedizin (BgVV), Federal Institute for Sanitary Consumer Protection and Veterinary Medicine. Getrockneter Seetang und getrocknete Algenblätter mit überhöhten Jodgehalten (Press release, January 3, 2001), Berlin, Germany, 2001.
(22) Fujiwara-Arasaki, T.; Mino, N.; Kuroda, M. The protein value in human nutrition of edible marine algae in Japan. *Hydrobiologica* **1984**, *116/117*, 513–516.
(23) Ministry of Health, Labour and Welfare, Japan. The National Nutrition Survey in Japan, 2002.
(24) DACH, Deutsche Gesellschaft für Ernährung, German Society of Nutrition (DGE). *Referenzwerte für die Nährstoffzufuhr*, 1st ed.; Umschau/Braus: Frankfurt am Main, Germany, 2000.
(25) Elmadfa, I.; Aign, W.; Muskat, E.; Fritzsche, D. *Die große GU Nährwert-Kalorien-Tabelle*; Gräfe and Unzer Verlag: München, Germany, 2001; pp 42–49.
(26) Tsuji, K.; Nakagawa, Y.; Ichikawa, T. Effects of dietary potassium alginate on blood pressure, mineral balance and serum cholesterol

levels in spontaneously hypertensive rats. *Nippon Kaisei Gakkaishi* **1993**, *44*, 3–9.

(27) World Health Organization (WHO). Evaluation of Certain Food Additives and Contaminants, 33rd Report of the Joint FAO/WHO Expert Committee on Food Additives. WHO Technical Report Series 776, Geneva, Switzerland, 1989.

(28) Moon, S.; Kim, J. Iodine content of human milk and dietary iodine intake of Korean lactating mothers. *Int. J. Food Sci. Nutr.* **1999**, *50*, 165–171.

(29) Flachowsky, G.; Schöne, F.; Jahreis, G. Zur Jodanreicherung in Lebensmitteln tierischer Herkunft. *Ernährungs-Umschau* **2006**, *53*, 17–21.

(30) European Commission, Scientific Committee on Food (EC SCF) (September 26, 2002). Opinion of the Scientific Committee on Food on the Tolerable Upper Intake Level of Iodine. Brussels, Belgium, 2002.

(31) U.S. Food and Nutrition Board, Institute of Medicine. *Dietary Reference Intakes for Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium, and Zinc*; National Academy Press: Washington, D.C., 2001; pp 8-1 to 8-27.

(32) Kenyon, E. M.; Hughes, M. F. A concise review of the toxicity and carcinogenicity of dimethylarsinic acid. *Toxicology* **2001**, *160*, 227–236.

(33) Wei, C.; Li, W.; Zhang, C.; Van Hulle, M.; Cornelis, R.; Zhang, X. Safety evaluation of organoarsenical species in edible *Porphyra* from the China Sea. *J. Agric. Food Chem.* **2003**, *51*, 5176–5182.

(34) Francesconi, K. A.; Tanggaard, R.; McKenzie, C. J.; Goessler, W. Arsenic metabolites in human urine after ingestion of an arsenosugar. *Clin. Chem.* **2002**, *48*, 92–101.

(35) Agency for Toxic Substances and Disease Registry (ATSDR). Draft Toxicological Profile for Arsenic. U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA, 2005.

(36) World Health Organization (WHO). Evaluation of Certain Food Additives and Contaminants, 61st Report of the Joint FAO/WHO Expert Committee on Food Additives. WHO Technical Report Series 922, Geneva, Switzerland, 2004.

(37) World Health Organization (WHO). Evaluation of Certain Food Additives and Contaminants, 53rd Report of the Joint FAO/WHO Expert Committee on Food Additives. WHO Technical Report Series 896, Geneva, Switzerland, 2000.

(38) European Food Safety Authority (EFSA). EFSA Provides Risk Assessment on Mercury in Fish Precautionary Advice Given to Vulnerable Groups (Press release, March 18, 2004).

(39) Eisenbrand, G.; Schreier, P. *RÖMPP Lexikon Lebensmittelchemie*, 2nd ed.; Georg Thieme Verlag: Stuttgart, Germany, 2006; p 165.

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