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Essential and Toxic Elements in Seafood Available in Poland from Different Geographical Regions

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The concentrations of 15 elements (Cu, Fe, Mn, Zn, Co, Ni, Cr, Se, Cd, Pb, Hg, Ca, Na, K, and Mg) were determined in the edible parts of shellfish on sale in the local market in Gdańsk. The samples consisted of three groups—crustaceans, molluscs, and surimi—that are processed to different degrees. For the purposes of this analysis, they were dried, homogenized, and digested in an automatic microwave system. The samples were analyzed quantitatively for Cu, Zn, Fe, Mn, Co, Ni, Cr, Mg, Na, K, and Ca (F-AAS), Cd and Pb (GF-AAS), Se (HG-AAS), and Hg (CV-AAS). The elemental levels detected in shellfish were compared to those in cod, herring, pork, beef, chicken, and eggs. The recommended dietary allowance (RDA) of essential elements and the provisional tolerable weekly intake (PTWI) of toxic elements were estimated. With factor analysis of the data, taxonomically different groups of raw and processed shellfish could be distinguished.

KEYWORDS: Seafood; bioelements; toxic elements; Polish market; RDA; PTWI; FA

INTRODUCTION

Until recently, the dominant products on the Polish seafood market were fish from the Baltic Sea. However, falling catches of Baltic fish as well as changes in people's nutritional habits have led to a demand for new sources of nutrition from the sea, such as mussels, shrimps, crabs, octopus, lobsters, and squid, that is, shellfish, regarded as delicacies in Asia and elsewhere in Europe. Because consumers decide for themselves what to eat and how to ensure an adequate supply of all the essential elements, many have turned to shellfish as a supplementary source of certain macro- and microelements. Therefore, various species of shrimp (*Pandalus borealis*, *Penaeus monodon*, and *Litopenaeus vannamei*), mussel (*Mytilus edulis*, *Ostrea edulis*, *Crassostrea virginica*, and *Pecten maximus*), octopus (*Octopus* spp.), squid (*Illex* spp. and *Loligo* spp.), lobster (*Homarus* spp.), and crab (*Cancer* spp.), the so-called "frutti di mare", now make up a sizable share of the Polish shellfish market. Tasty and nutritious though these animals are, they are at the same time sensitive to pollution.

Determining the mineral elements in shellfish is important because of their effects on human health. On the one hand, they are nutritional, because the optimal intake of essential minerals such as Cu, Fe, Mn, Zn, Co, Ni, Cr, Mg, Ca, Na, and K is necessary for the maintenance of good health; on the other, they are toxicological, because certain metals such as Pb, Cd, and Hg are detrimental to health (*1*).

Seafood consumption is the main source of metals for people living in coastal regions. The metal load is higher in inshore waters and the aquatic animals inhabiting them owing to the elevated levels of elements in the coastal zone (*2*, *3*). Trace elements are continuously being released into the sea via natural and anthropogenic pathways. All aquatic invertebrates accumulate trace metals from food, from suspended matter, or directly from seawater, whether or not these metals are essential to their metabolism. Some marine invertebrates may even take up certain metals to a level above that in the surrounding waters, so the degree to which they are accumulated is very much species-specific (*4*). Thus, the accumulation of a very low quantity of a metal in one species could be considered anomalous in another; for example, the same body concentration of zinc is considered to be low in oysters but high in mussels (*2*, *5*).

On the other hand, marine invertebrates are a rich source of certain essential elements (*6*) and are used as food and food supplements all over the world (*7*). Mineral components play a vital role in the correct development and good health of the human body. The irregular intake of mineral elements is a major nutritional problem in Poland. Their bioavailability depends on a number of factors, such as the chemical form of the minerals contained in the food consumed, the daily dietary intake, the extent to which products are technologically processed, and the presence of substances that increase or reduce this bioavailability (*8*).

The consumption of fish and fishery products in Poland amounts to 9.6 kg year^{-1} person^{-1}. In comparison to data from other European Union countries, such as France (29.7 kg year^{-1} person^{-1}), Germany (12.2 kg year^{-1} person^{-1}), Greece (22.7

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Table 1. Analyzed Products

product	origin	water (%)	comments
salad shrimp	India	85.6	boiled; small size
salad shrimp	Norway	83.4	boiled; big size
deep water shrimp	India	88.7	boiled
black tiger shrimp	Thailand	85.0	boiled
black tiger shrimp	Thailand	84.1	raw
Greenland shrimp	Norway	76.5	boiled
salad shrimp in cold water	Norway	82.8	boiled
torpedo shrimp	Thailand	70.9	technologically processed (with coconut addition)
Norway lobster	Great Britain	92.0	boiled
crab	Great Britain	70.2	boiled; meat from claws
lobster	Canada	76.0	boiled; meat from claws
surimi crab	Thailand	70.0	technologically processed (fish and crab stuffing)
Kamaboko crab	Thailand	69.9	technologically processed (fish and crab stuffing; coated in bread crumbs)
baby octopus	Thailand	87.7	raw
Philippines octopus	Philippines	83.2	raw
Mediterranean octopus	Spain	83.2	raw
boiled mussels	Thailand	81.7	boiled
mussels in shell	New Zealand	77.0	raw
great scallop	Great Britain	83.9	boiled
raw squid rings	Spain	85.8	raw
coated squid rings	Spain	63.0	coated in bread crumbs and flour
squid tube	Spain	87.3	raw

kg year^{-1} person^{-1}), Italy (23.1 kg year^{-1} person^{-1}), Portugal (57.4 kg year^{-1} person^{-1}), and Norway (50.0 kg year^{-1} person^{-1}), this figure is still low (*9*). The main reasons are that seafood is more expensive than meat and that there is no strong tradition of its consumption. On the other hand, the past few years have witnessed a slow growth in the consumption of fish and fishery products and also in the seafood processing industry in Poland, which now processes more than 400 000 t of fish annually. Fishery production in 2002 in Poland amounted to 255 150 t (222 441 t from sea fishing, 32 709 t from fish farming). In 2001 the fish species most often consumed were herring, Alaska pollock (26%), mackerel (11%), and Baltic sprat and Baltic hake (7% each). However, as Polish fishermen are no longer able to satisfy the domestic fish-processing industry's requirements, many companies now import and distribute fresh and frozen shellfish products in response to consumer demand (*10*). Imports of marine invertebrates (shellfish) have grown from 266 053 t in 1999 to 334 621 t (U.S. $1000) in 2002 (*11*) and now dominate this industry.

The aim of the present investigation was to quantify the levels of essential and toxic elements in shellfish products on sale in the local market in Gdańsk (Poland) and, on the basis of the levels of these elements, to estimate the recommended dietary allowance (RDA) of essential elements and the provisional tolerable weekly intake (PTWI) of toxic elements.

MATERIALS AND METHODS

Sample Preparation. The deep-frozen shellfish products listed in **Table 1** were purchased in Gdańsk from a wholesaler, the main importer of Poland. The products, as representative of Poland and imported from worldwide regions, were as follows: all shrimps, surimi products, octopus (baby), boiled mussels and mussels in shell (13 products) as well as all squids, Mediterranean and Philippines octopuses, crabs, and lobsters (9 products). The former group of seafoods is most best known by the Polish population due to their ease of meal preparation and lower price. The products processed to different degrees (preliminary processing—boiled or raw; processed to an appreciable degree, with various additives) were carefully selected. Twenty-two purchased products (mussel, shrimp, crab, octopus, lobster, and squid) were slowly defrosted in a refrigerator. The edible parts (~150−200 g of fresh weight) were separated from the inedible parts such as crusts, shells, and viscera with stainless steel scalpels in glass laboratory equipment steeped in 32.5% HNO_3. To obtain samples of a suitably large weight (mass), pooled samples were prepared from a few to over a dozen specimens of the species in question. The samples were then put into glass vessels and dried in a furnace (Imperial V) at 65 °C to a constant weight and homogenized.

In total, 88 pooled samples were prepared for the determination of selected chemical elements concentration by four analytical techniques, that is, F-AAS (Cu, Zn, Co, Ni, Cr, Mn, Fe, Mg, Ca, K, and Na), GF-AAS (Cd and Pb), CV-AAS (Hg), and HG-AAS (Se). Three 1 g replicates of each sample were made, so in total 264 analytical subsamples were processed and analyzed for concentrations of the chemical elements examined.

Determination of Macro- and Microelements. Three replicates (1.0 ± 0.0001 g) of each sample were weighed and transferred to Teflon flasks, treated with 9 mL of 65% HNO_3 (Suprapur Merck), and then digested in an automatic microwave digestion system (MLS 1200 MEGA) according to the following steps: I, 250 W, 48 s; II, 0 W, 48 s; III, 250 W, 6 min 24 s; IV, 400 W, 4 min; V, 650 W, 4 min. The steps are described in detail in the operation manual. Each microwave digestion cycle treated four food samples and one blank sample (9 mL of 65% HNO_3). After digestion, the vessels were left to cool to room temperature. Every digested sample was made up to 10 mL with deionized water. AAS (PU-9100, Philips) with an air−acetylene flame and deuterium background correction was used for determining Mn, Fe, Cu, Zn, Cr, Ni, Co, Mg, Ca, Na, and K. In the cases of Na and K, Cs (0.2% w/v) was added to the samples as an ionization buffer, and in the cases of Ca and Mg, La (0.1% w/v) was used as a releasing agent. The F-AAS conditions are set out in the operation manual for the Philips PU-9100.

Determination of Toxic Elements and Se. To determine Cd, Pb, and Hg, ~0.3 g of dried shellfish (66 product samples for Cd and Pb and separately 66 product samples for Hg), with 5 mL of 65% HNO_3 (Baker analyzed), was digested in a microwave system (Uni Clever, Plasmatronika) for 20 min (100% power). For Se (66 product samples), the weight of shellfish was 0.02−0.04 g, and the samples were digested according to the procedure described above.

In the case of Hg analysis, 0.5 mL of 16% carbamide (Merck, analytical grade) and 0.025 mL of 20% $K_2Cr_2O_7$ (POCh, analytical grade) were added to the digested sample, and the mixture was made up to 10 mL with deionized water. Hg was reduced with 20% $SnCl_2$ (Merck, analytical grade) and then determined by CV-AAS (Avanta Σ, GBC with an HG 3000 adapter for hydride generation). The calibration curve in the range of 5−20 ng of Hg mL^{-1} was produced by adding standards to the sample.

Pb and Cd were determined by GF-AAS. The digested sample was evaporated almost to dryness and then dissolved in 5 or 25 mL of 3.25% HNO_3, respectively, for Pb or Cd. Sample volumes of 20 μL and 5 μL of modifier and 10 μL and 10 μL of modifier [1.5 mg of Pd mL^{-1} and 1 mg $Mg(NO_3)_2$ mL^{-1}] were injected into a graphite cuvette, respectively, for Pb and Cd. The calibration curve covered the ranges of 10−50 ng of Pb mL^{-1} and 0.5−2.0 ng of Cd mL^{-1}. The furnace parameters for Pb and Cd graphite furnace analysis are presented in the operation manua *Varian Instruments at Work*.

As for Se analysis, 0.8 mL of concentrated $HClO_4$ (Merck, Suprapur) was added to the sample, and the resulting mixture was evaporated at 120−130 °C in a thermostatic mineralizer (Meditherm) to a volume of 0.2−0.4 mL. The residue was made up to 10 mL with 36% HCl (Baker, instra-analyzed) and H_2O (1:1) and then heated on a water bath at 70 °C for 0.5 h. Se was determined by HG-AAS with an HG 3000 adapter and $NaBH_4$ (Merck, analytical grade) as reducing agent. The calibration curves covered the range 4−14 ng of Se mL^{-1}.

Factor Analysis (FA). The concentration data were processed by FA using Statistica for Windows (release 5.0, StatSoft, Inc., 1984−

Table 2. Measurements of Bioelement and Toxic Element Concentrations in Reference Material NRC TORT-2 (Lobster Hepatopancreas) and Other Reference Materials

element	concn determined (μg g^{-1} of dw)	concn declared (μg g^{-1} of dw)	recovery %	relative error %	RSD %	analytical method
Zn	183	180	101.7	+1.7	2.1	F-AAS
Fe	86.3	105	82.2	–17.8	4.2	F-AAS
Mn	10.8	13.6	79	–21	1.4	F-AAS
Cu	99.5	106	93.9	–6.1	1.2	F-AAS
Ni	1.87	2.5	75	–25	8.6	F-AAS
Co	<0.6[a]	0.51				F-AAS
Cr	<1.0[a]	0.77				F-AAS
Se	5.46	5.63	96.9	–3.1	7.6	HG-AAS
Hg	0.28	0.27	102.9	+2.9	16.1	CV-AAS
Pb	0.44	0.35	126	+26	8.9	GFAAS
Pb[b]	0.184	0.172	107	+7	15.2	GF-AAS
Cd	26.2	26.7	98	–2	8.6	GF-AAS
Cd[b]	0.53	0.544	97	–3	8.9	GF-AAS
Ca[c]	26914	27000	99.7	–0.3	4.8	F-AAS
Mg[c]	10435	14000	74.5	–25.5	7.1	F-AAS
K[c]	12657	13000	97.4	–2.6	2.7	F-AAS

[a] Limit of detection. [b] Bovine liver CRM 185R. [c] Sea lettuce BCR-279.

1995). This chemometric technique enables creation of "new" dimensions of the data and evaluation of a reduced number of independent factors describing the information included in a system of characteristic. Factors with eigenvalues higher than unity should be exclusively considered. The aim of FA is to decompose mixed data structure into its components. To reduce a large number of variables to a smaller number of orthogonal factors, the concentration data are treated by multivariate statistical methods, for example, FA. This chemometric approach based on mineral composition is useful in the assessment of quality of foods owing to reducing the expense for further their monitoring survey. Moreover, we expected to be able to distinguish between samples processed and unprocessed technologically on the basis of a scatter plot distribution of scores (samples) and loadings (chemical elements) in biplot F1/F2.

A total of 22 observations (22 object samples), corresponding to 264 analytical samples, and 15 variables (Hg, Cd, Pb, Cr, Co, Ni, Se, Cu, Zn, Mn, Fe, Mg, Ca, Na, and K) were taken into consideration. However, variables such as Co, Ni, Cr, and Pb had been eliminated from the data set because their levels in many samples were too low; 11 loadings constituted the ultimate data matrix.

Concentrations of Macro- and Microelements. The macro- and microelement concentration in ~1.0 g of dry weight (± 0.0001 g) of sample was calculated as $C = (C_{ps} - C_{bs}) \times V \times D/w$, where C is the metal concentration [μg g^{-1} of dry weight (dw)], C_{ps} is the metal concentration in product solution after microwave digestion (μg mL^{-1}), C_{bs} is the metal concentration in blank solution (μg mL^{-1}), V is the sample volume after microwave digestion (mL), D is the dilution coefficient, and w is the sample weight used in microwave digestion (g). Dry weight was converted to wet weight on the basis of the water content in the products (**Table 1**).

Quality Assurance of the Results. The contents of Ni, Co, and Cr were below the detection limits of the method used (Ni < 0.33 μg g^{-1} of dw, Co < 0.6 μg g^{-1} of dw, Cr < 1.0 μg g^{-1} of dw).

The detection limit was $LD = x + 3d$, where x is the blank average range and d is the standard deviation of blank values (*12*).

The accuracy and precision of the method used were satisfactory, as proved by analysis of the reference materials TORT-2 (lobster hepatopancreas), BCR-279 IRMM (sea lettuce), and CRM-185R (bovine liver). From six to nine analyses for each element were performed on the certified materials. The values obtained here and certified values are listed in **Table 2**.

Calculation of Recommended Dietary Intake. The daily mineral intake (in percent) from a 100 g portion of a given product was determined as $DMI = C \times 100/RDA$ or $DMI = C \times 100/AI$, where C is the element concentration (in mg) in 100 g of wet weight of the product, RDA is the recommended dietary allowance (mg day^{-1}), and AI is the adequate intake (mg day^{-1}) according to ref *13*.

Calculation of Provisional Tolerable Weekly Intake. The respective PTWIs of Hg, Cd, and Pb were set at 5.0 (1.6 as CH_3HgX), 7.0, and 25.0 μg kg^{-1} of body weight (*14*). For a person weighing 60 kg, this is equal to 0.3, 0.42, and 1.5 mg of Hg, Cd, and Pb, respectively.

The safe weekly intake of a product containing the maximum concentration of a toxic element was calculated as $SWI = C_p/C$, where C_p is the permissible metal concentration (mg kg^{-1}) in animal products according to ref *15* and C is the maximum metal content (mg kg^{-1} of product).

The consumption of fish and fishery products in Poland amounts to 9.6 kg year^{-1} person^{-1} (*9*), which is equal to 180 g week^{-1} person^{-1}. In accordance with these data, the percentage weekly intake of an element through the consumption of such products was calculated as $PWI = 180 \times C_{mc}/10 \times PTWI_p$, where C_{mc} is the maximum metal content (mg kg^{-1} of product) and $PTWI_p$ is the provisional tolerable weekly intake for a 60 kg person (mg person^{-1}).

RESULTS AND DISCUSSION

Essential Element Concentrations and RDA. The contents of macro- and microelements are summarized in **Table 3**. Perusal of these concentrations reveals a considerable variability in the elements in the animals investigated, which depends on species, individual conditions, location, processing technologies, and environmental pollution.

The meat of crab claws was found to contain the highest concentrations of Ca, K, Mg, Zn, and Se; they also had a fairly high Na content. On the basis of the RDA/AI, consuming 100 g of this product would supply the human body with approximately 40, 20, 5, and 20% of Ca, Na, K, and Mg, respectively (**Tables 3–5**). With respect to the microelements, the same crab portion would supply approximately 80% of the RDA of Cu and 150% of Se. RDA/AIs were different for men and women, that is, 10 and 16% of Fe, 20 and 25% of Mn, 90 and 120% of Zn, respectively (*13*). Na, Ca, K, Cu, Zn, Mn, and Fe concentrations were studied in meat from the claws and bodies of two crab species from Turkey (*6*). The data reported for the macroelements (Na, K) and microelements (Zn, Mn, Fe) in *Callinectes sapidus* are very similar to those obtained in the present study (**Table 6**). The concentrations of these elements in the above-mentioned crab claws are much higher than those in reference products (*16*) such as cod, flounder, herring, pork, beef, chicken, or eggs (**Tables 3–5**).

Higher Ca levels are found in surimi crabs and lobsters. Meat from lobster claws is also a rich source of Mg, Zn, Cu, and Se. Consumption of 100 g of this crustacean provides appoximately 15% of the RDA of Ca (as AI), 10% of Mg, 40% of Zn and >100% of Cu and Se (**Tables 3–5**). Páez-Osuna et al. (*17*) reported similar results for Cu and Zn in lobsters from Mexico.

Every shrimp species analyzed here exhibited low Mn (0.01–0.09 mg 100 g^{-1}) and high Na (354–821 mg 100 g^{-1}) concentrations. Zn and Mn levels were comparable, but Fe and Cu levels were generally lower (except for Greenland shrimp and deep water shrimp) than those found in shrimps from Mexico (*18*, *19*) and Taiwan (*3*) (**Table 6**). Our data on Zn and Mn lie within the range of values reported by the above authors (**Table 6**). Greenland shrimps contain high Mg levels, as do Mediterranean octopuses and mussels in shells. The Se concentrations in shrimps measured in the present study ranged between 0.017 and 0.033 mg 100 g^{-1}. Similar levels were reported in shrimps from Spain (*20*). Boiled and raw black tiger shrimps, as well as Philippines and Mediterranean octopus tentacles, were a poor source of Fe (<0.1 mg 100 g^{-1}). Great scallops contain the highest levels of Mn and K, but the lowest

Table 3. Concentration of the Bioelements Studied in Seafood (Shrimp, Crab, Lobster, Octopus, Squid, Mussels, Surimi)

		mg 100 g^{-1} of wet wt								
product	*N*[a]	Zn	Fe	Mn	Cu	Se	Ca	Mg	Na	K
salad shrimp (small)	3	0.72 ± 0.01 0.72–0.73	0.25 ± 0.01 0.24–0.25	0.05 ± 0.001 0.051–0.052	0.05 ± 0.001 0.051–0.052	0.033 ± 0.007 0.028–0.041	19.5 ± 0.35 19.1–19.8	19.6 ± 0.12 19.1–19.9	652 ± 31.2 633–684	3.84 ± 0.15 3.70–3.99
salad shrimp (big)	3	0.76 ± 0.01 0.75–0.77	0.11 ± 0.01 0.10–0.11	0.01 ± 0.002 0.012–0.015	0.11 ± 0.001 0.107–0.109	0.019 ± 0.002 0.017–0.021	25.6 ± 0.32 25.3–25.9	15.0 ± 0.29 14.8–15.4	821 ± 27.3 791–845	33.2 ± 1.19 31.8–34.0
deep water shrimp	3	0.52 ± 0.003 0.52–0.53	2.19 ± 0.14 2.03–2.28	0.04 ± 0.001 0.04–0.04	0.04 ± 0.001 0.04–0.04	0.026 ± 0.007 0.020–0.034	16.1 ± 0.72 15.5–16.9	16.0 ± 0.27 15.7–16.2	493 ± 10.3 483–503	3.73 ± 0.09 3.62–3.80
black tiger shrimp, boiled	3	0.73 ± 0.001 0.43–0.87	0.06 ± 0.001 0.03–0.06	0.01 ± 0.001 0.006–0.013	0.13 ± 0.003 0.07–0.16	0.023 ± 0.003 0.021–0.027	15.2 ± 0.76 9.8–15.7	10.6 ± 3.06 5.26–10.6	354 ± 36.0 241–379	8.49 ± 1.30 4.20–9.41
black tiger shrimp, raw	3	0.90 ± 0.02 0.89–0.92	0.06 ± 0.01 0.06–0.08	0.01 ± 0.002 0.01–0.02	0.15 ± 0.001 0.150–0.152	0.022 ± 0.001 0.021–0.023	12.3 ± 0.36 12.1–12.7	14.5 ± 0.15 14.4–14.7	667 ± 15.7 649–677	30.3 ± 0.26 30.0–30.5
Greenland shrimp	3	1.27 ± 0.02 1.26–1.29	0.14 ± 0.01 0.13–0.24	0.02 ± 0.003 0.019–0.023	0.50 ± 0.003 0.28–0.61	0.023 ± 0.004 0.020–0.027	50.8 ± 2.37 49.1–73.3	51.5 ± 1.74 49.6–52.9	551 ± 2.52 548–553	127 ± 1.02 126–128
salad shrimp in cold water	3	0.83 ± 0.004 0.825–0.834	0.10 ± 0.02 0.08–0.11	0.02 ± 0.002 0.016–0.019	0.12 ± 0.001 0.12–0.12	0.018 ± 0.002 0.016–0.020	35.6 ± 0.39 35.3–36.0	16.7 ± 0.22 16.4–16.8	719 ± 62.9 647–761	32.2 ± 0.31 31.9–32.5
torpedo shrimp	3	0.46 ± 0.01 0.45–0.46	0.32 ± 0.03 0.30–0.36	0.09 ± 0.004 0.085–0.092	0.06 ± 0.001 0.06–0.06	0.017 ± 0.004 0.013–0.020	11.7 ± 0.35 11.4–12.1	7.43 ± 0.17 7.24–7.57	480 ± 82.4 408–570	18.6 ± 2.05 16.4–20.4
Norway lobster	3	0.64 ± 0.02 0.62–0.65	0.66 ± 0.00 0.66–0.66	0.03 ± 0.005 0.026–0.032	0.15 ± 0.002 0.15–0.15	0.020 ± 0.002 0.019–0.022	46.2 ± 2.17 44.7–48.7	22.5 ± 0.29 22.2–22.8	158 ± 7.9 149–165	72.0 ± 0.99 70.9–72.8
crab (meat from claws)	3	9.71 ± 0.18 9.53–9.89	1.28 ± 0.12 1.21–1.42	0.44 ± 0.01 0.43–0.45	0.74 ± 0.01 0.73–0.75	0.087 ± 0.005 0.082–0.093	378 ± 49.6 323–418	72.1 ± 2.48 69.3–73.8	255 ± 2.9 252–257	221 ± 4.3 217–226
lobster (meat from claws)	3	4.27 ± 0.11 4.16–4.38	0.26 ± 0.01 0.25–0.28	0.26 ± 0.04 0.23–0.31	1.84 ± 0.06 1.79–1.91	0.067 ± 0.000 0.066–0.067	162 ± 26.3 144–192	38.25 ± 2.37 36.8–41.0	368 ± 12.4 355–380	73.7 ± 3.72 69.8–77.1
surimi crab	3	0.12 ± 0.01 0.11–0.12	0.22 ± 0.02 0.20–0.23	0.03 ± 0.002 0.03–0.04	0.01 ± 0.000 0.013–0.014	0.011 ± 0.001 0.010–0.012	313 ± 15.6 297–328	6.91 ± 0.07 6.84–6.97	685 ± 21.7 667–709	4.25 ± 0.21 4.12–4.49
Kamaboko crab	3	0.25 ± 0.01 0.24–0.26	0.25 ± 0.02 0.23–0.37	0.10 ± 0.01 0.09–0.10	0.03 ± 0.001 0.03–0.04	0.018 ± 0.004 0.014–0.022	27.3 ± 0.57 26.9–27.7	8.17 ± 0.16 8.00–8.31	486 ± 15.5 472–502	15.5 ± 0.61 14.9–16.1
baby octopus	3	1.19 ± 0.02 1.17–1.21	0.40 ± 0.06 0.36–0.47	0.06 ± 0.003 0.05–0.06	0.17 ± 0.002 0.16–0.17	0.026 ± 0.002 0.025–0.028	9.31 ± 0.05 9.27–9.37	13.3 ± 0.37 12.9–13.6	534 ± 11.6 526–548	62.8 ± 4.57 59.1–67.9
Philippines octopus	3	1.70 ± 0.05 1.64–1.74	0.09 ± 0.004 0.05–0.09	0.03 ± 0.003 0.03–0.04	0.23 ± 0.004 0.23–0.24	0.014 ± 0.003 0.011–0.018	4.11 ± 0.06 4.05–4.17	27.2 ± 0.11 27.1–27.3	125 ± 7.4 117–131	71.9 ± 20.0 56.9–94.5
Mediterranean octopus (tentacles)	3	1.18 ± 0.03 1.16–1.22	0.092 ± 0.001 0.091–0.092	0.01 ± 0.003 0.01–0.02	0.24 ± 0.004 0.235–0.242	0.015 ± 0.002 0.014–0.017	8.13 ± 0.11 8.00–8.21	45.3 ± 0.33 44.9–45.5	697 ± 8.7 688–706	238 ± 7.2 233–246
boiled mussels	3	1.63 ± 0.02 1.61–1.66	5.73 ± 0.14 5.61–5.89	0.98 ± 0.08 0.93–1.08	0.16 ± 0.004 0.16–0.17	0.046 ± 0.003 0.044–0.050	12.0 ± 1.66 10.3–13.6	17.7 ± 0.35 17.1–17.7	323 ± 11.0 316–336	4.05 ± 0.31 3.88–4.41
mussels in shell	3	1.80 ± 0.02 1.79–3.16	9.47 ± 0.16 9.31–9.62	0.23 ± 0.001 0.22–0.25	0.08 ± 0.002 0.08–0.09	0.056 ± 0.003 0.053–0.058	14.0 ± 0.17 13.8–14.2	53.2 ± 0.76 52.7–97.3	193 ± 4.0 191–198	97.51 ± 1.09 96.3–98.2
great scallop	3	4.36 ± 0.02 4.34–4.38	1.34 ± 0.28 1.02–1.57	4.00 ± 0.06 3.92–4.04	0.07 ± 0.001 0.07–0.07	0.026 ± 0.005 0.022–0.033	2.30 ± 0.08 2.24–2.39	22.1 ± 0.21 21.9–22.3	44.9 ± 1.36 43.5–46.2	229 ± 38.4 187–263
raw squid rings	3	0.88 ± 0.02 0.86–0.90	0.10 ± 0.00 0.10–0.11	0.60 ± 0.04 0.56–0.62	0.13 ± 0.0011 0.12–0.13	0.022 ± 0.001 0.021–0.023	4.01 ± 0.17 3.82–4.14	23.3 ± 0.32 23.0–23.6	673 ± 23.9 646–691	31.9 ± 3.68 29.5–36.1
coated squid rings	3	0.46 ± 0.08 0.40–0.55	0.45 ± 0.02 0.43–0.46	0.17 ± 0.00 0.16–0.17	0.06 ± 0.001 0.06–0.06	0.014 ± 0.002 0.012–0.017	27.1 ± 1.52 25.3–28.2	16.7 ± 0.15 16.6–16.9	710 ± 31.7 675–738	55.0 ± 5.61 48.8–59.8
squid tube	3	0.79 ± 0.07 0.74–0.87	0.10 ± 0.02 0.09–0.12	0.01 ± 0.002 0.008–0.011	0.09 ± 0.003 0.09–0.10	0.015 ± 0.001 0.014–0.016	2.67 ± 0.39 2.22–2.90	14.3 ± 0.42 13.8–14.6	824 ± 17.8 809–843	41.0 ± 2.02 38.8–42.8

[a] Number of pools utilized for the analysis of each product.

levels of Na and Ca. Consuming 100 g of great scallops would supply the human body with 200% of the RDA/AI of Mn, 40−55% of Zn, 5% of Mg and K, and 3% of Na (**Tables 3−5**). The great scallop contains much more Mn than mussels (*21*, *22*) (**Table 6**) and the other types of shellfish examined here (**Table 3**). However, Mn levels in boiled mussels and mussels in shells are comparable to those reported elsewhere (**Table 6**). On the other hand, these molluscs are the richest source of Fe among the shellfish examined here and the richest source of Se among the molluscs. Fe and Se levels found in mussels concur with those reported by other authors (*3*, *20*, *21*, *23*). Consuming 100 g of boiled mussels or mussels in shells provides 50 and 120% and 30 and 70% of the RDA of Fe, respectively, for men and women. The consumption of Se is estimated at 80 and 100% of the RDA for boiled mussels and mussels in shells respectively (**Tables 3−5**). The available data on Cu levels in mussels (see **Table 6**) are generally higher than the values found in our study. Zn concentrations reported in the literature are comparable to our mussel data. Like boiled mussels and those in shells, octopus tentacles from the Mediterranean and Philippines as well as “baby” octopus contain significant levels of Zn. Every product analyzed here except the great scallop contained high levels of Na. The elevated Na levels in shellfish could be due to the preprocessing of these animals on board ship: directly after being caught they are boiled in hot seawater or treated with hot steam, after which they are deep-frozen in brine. Other processes, such as the breading of squids, could make a significant contribution to the total Na content.

Table 4. Realization of Recommended Dietary Allowance or Adequate Intake (Percent) (*11*) by 100 g of Studied Seafood and Reference Products (*14*)

product	Ca[a]	Mg[b]	Mg[c]	Na[a]	K[a]	Cu	Fe[b]	Fe[c]	Mn[a,b]	Mn[a,b]	Zn[b]	Zn[c]	Se
salad shrimp (small)	2.0	4.7	6.1	43.5	0.1	5.6	3.1	1.4	2.2	2.8	6.5	9.0	56.4
salad shrimp (big)	2.6	3.6	4.7	54.7	0.7	12.2	1.4	0.6	0.4	0.6	6.9	9.5	32.7
deep water shrimp	1.6	3.8	5.0	32.9	0.1	4.4	27.4	12.2	1.7	2.2	4.7	6.5	45.5
black tiger shrimp, boiled	1.5	2.5	3.3	23.6	0.2	14.4	0.8	0.3	0.4	0.6	6.6	9.1	41.8
black tiger shrimp, raw	1.2	3.5	4.5	44.5	0.6	16.7	0.8	0.3	0.4	0.6	8.2	11.3	40.0
Greenland shrimp	5.1	12.2	16.0	36.7	2.7	55.6	1.8	0.8	0.9	1.1	11.5	15.9	40.0
salad shrimp in cold water	3.6	4.0	5.2	48.0	0.7	13.3	1.3	0.6	0.9	1.1	7.5	10.4	30.9
torpedo shrimp	1.2	1.8	2.3	32.0	0.4	6.7	4.0	1.8	3.9	5.0	4.2	5.8	29.1
Norway lobster	4.6	5.4	7.0	10.5	1.5	16.7	8.3	3.7	1.3	1.7	5.7	7.9	36.4
crab (meat from claws)	37.8	17.2	22.5	17.0	4.7	82.2	16.0	7.1	19.1	24.4	88.2	121	155
lobster (meat from claws)	16.2	9.1	11.9	24.6	1.6	204	3.3	1.4	11.3	14.4	38.8	53.4	120
Mediterranean octopus (tentacles)	0.8	10.8	14.2	46.5	5.1	26.7	1.1	0.5	0.9	1.1	10.7	14.8	27.3
Philippines octopus (tentacles)	0.4	6.5	8.5	8.4	1.5	26.7	1.1	0.5	1.3	1.7	15.5	21.3	25.5
baby octopus	0.9	3.2	4.2	35.6	1.3	18.9	5.0	2.2	2.6	3.3	10.8	14.9	47.3
raw squid rings	0.4	5.5	7.3	44.9	0.7	14.4	1.4	0.6	26.1	33.3	8.1	11.1	38.2
coated squid rings	2.7	4.0	5.2	47.3	1.2	6.7	5.6	2.5	7.4	9.4	4.2	5.8	25.5
squid tube	0.3	3.4	4.4	54.9	0.9	10.0	1.3	0.6	0.4	0.6	7.2	9.9	27.3
boiled mussels	1.2	4.1	5.4	21.5	0.1	17.8	71.5	31.8	42.6	54.4	14.8	20.4	83.6
mussels in shell	1.4	12.7	16.6	12.9	2.1	8.9	118	52.6	10.0	12.8	16.4	22.5	100
great scallop	0.2	5.3	6.9	3.0	4.9	7.8	16.9	7.5	174	222	39.6	54.5	47.3
surimi crab	31.3	1.6	2.2	45.7	0.1	1.1	2.8	1.2	1.7	2.2	1.1	1.5	20.0
Kamaboko crab	2.7	1.9	2.6	32.4	0.3	3.3	3.1	1.4	3.9	5.0	2.3	3.1	32.7
reference products													
cod (fillet without skin)	0.7	6.9	9.1	5.9	7.7	6.7	7.5	3.3	0.4	0.6	4.2	5.8	56.4
flounder	2.7	5.7	7.5	2.6	3.0	2.2	5.0	2.2	0.4	0.6	3.5	4.8	61.8
herring	3.2	6.0	7.8	3.2	2.7	13.3	11.3	5.0	0.4	0.6	5.5	7.5	109
pork loin, raw	1.5	5.7	7.5	1.9	5.0	4.4	12.5	5.6	57.0	72.8	14.0	19.3	20.0
beef loin	0.4	6.2	8.1	3.5	8.1	1.1	38.8	17.2	17.8	22.8	26.6	36.6	5.5
chicken egg, all	4.7	2.9	3.8	8.3	2.5	5.6	27.5	12.2	12.2	15.6	14.3	19.6	36.4
chicken	1.0	4.8	6.3	3.0	4.4	3.3	15.0	6.7	0.9	1.1	8.0	11.0	23.6

[a] Adequate intake. [b] Male. [c] Female.

Table 5. Recommended Dietary Allowance for Elements According to Reference *11*

	mg day^{-1}								
	Ca[a]	Mg	Na[a]	K[a]	Cu	Fe	Mn[a]	Zn	Se
males (31–50 years)	1000	420	1500	4700	0.9	8	2.3	11	0.055
females (31–50 years)	1000	320	1500	4700	0.9	18	1.8	8	0.055

[a] Adequate intake.

Toxic Element Concentration and PTWI. Every food item includes traces of heavy metals. It is important to note that crustaceans and molluscs have a natural ability to concentrate Cd, in the same way as fish concentrate Hg (*1*), so that they are one of the main sources of this toxic element in the human diet. These elements, Cd, Pb, and especially Hg, may be readily accumulated in shellfish as a result of contamination by these elements of the surrounding area. It has been reported that Hg and Se can be biomagnified along the aquatic food chain, right to the top of the trophic pyramid (*24*). Once inside human tissues, they may give rise to serious health problems. To assess the health risks of exceeding the tolerable intake of contaminants, PTWI values have been calculated. Information about the mineral component level in food as well as the quantities and types of foodstuffs consumed allows this exposure to be evaluated (*1*). The current WHO PTWIs for Pb, Cd, and Hg are estimated at 25, 7, and 5 μg kg^{-1} of body wt week^{-1}, respectively. The PTWI for MeHg was set at 1.6 μg kg^{-1} of body wt week^{-1} (*14*).

The results of Cd, Pb, and Hg determinations in the shellfish under scrutiny here are presented in **Table 7**. The concentrations of these elements ranged from 0.62 μg 100 g^{-1} (deep water shrimp) to 85.2 μg 100 g^{-1} (baby octopus) of Cd, from <0.05 to 20.1 μg 100 g^{-1} (great scallop) of Pb, and from <0.044 to 16.7 μg 100 g^{-1} of dw (crab, claw meat) of Hg.

A significant concentration of Hg was detected in crustaceans originating from Great Britain (Norway lobster and crab, claw meat), in lobsters (claw meat) from Canada, and in Greenland shrimps from Norway (**Table 7**). Cd levels were also high in this last species, values that are almost the same as those found in the soft tissues of *Mytilus galloprovincialis* (*25*) from Minamata Bay (**Table 6**). The lowest Hg contents were recorded in two shrimp species from India, in boiled mussels (preliminary processing; they are only boiled), in raw baby octopus, in torpedo shrimps with added desiccated coconut, and in breaded squid rings. The last two products are processed to an appreciable degree (**Table 7**).

In general, higher Hg concentrations in the crustaceans than in molluscs were found in our study. Jeng et al. (*3*) found also high Hg levels in crustaceans, that is, in one shrimp (sword prawn) and one crab (smooth pebble crab), 20.3 and 31.5 μg 100 g^{-1}, respectively. The Hg content in other crustaceans and molluscs (except for rock-shells) was at least 5 times lower than in the mentioned above shrimp and crab. According to Ruelas-Inzunza et al. (*26*) hepatopancreas as compared to muscle and exoskeleton of penaeid shrimp from the southeastern Gulf of California was characterized by greater bioaccumulation of Hg. Moreover, Hg levels in crab claws from Australia were found to be twice as high (*27*) as compared to those obtained in the present study (**Table 6**).

Baby octopus is characterized by the highest Cd concentrations, but Philippines and Mediterranean octopuses contain about 100 and 50 times less Cd, respectively (**Table 7**). The reason for these differences may be that the baby octopus is a small animal which is consumed as a whole body, together with the liver and its elevated Cd levels; only the ink

Table 6. Comparison of Data Obtained in the Present Study with Literature Data for Concentrations of Essential and Toxic Elements in Seafood[a]

			toxic (μg 100 g^{-1} of wet wt)			essential (mg 100 g^{-1} of wet wt)									
product	origin	comments	Pb	Cd	Hg	Se	Cu	Zn	Mn	Fe	Mg	Na	Ca	K	ref
shrimp	Taiwan		<0.75	0.45–1.35	3.60–20.3		0.24–0.30	1.02–1.25							*2*
	Spain					0.03									*18*
	Spain		5.0–7.0	0.00–0.70			0.67–1.10		0.21–0.39	0.22–0.51					*26*
			2.0–9.0	2.00–5.00			1.92–2.72		0.15–0.60	0.90–3.10					
	Mexico			2.85–19.8			0.25–0.59	0.13–1.12	0.03–0.21	0.51–6.36					*16*
	Mexico	farmed female					0.29	0.84	0.05	0.56					*17*
		farmed male					0.28	0.68	0.04	0.68					
		wild female					0.29	0.90	0.04	0.66					
		wild male					0.28	0.60	0.05	0.80					
	Greenland		3.8	1.9	10.6	0.15									*27*
	Polish market	boiled	0.87 ± 0.02	11.7 ± 25.2	2.96 ± 3.32	0.02 ± 0.01	0.16 ± 0.15	0.78 ± 0.24	0.03 ± 0.02	0.50 ± 0.77	21.7 ± 13.7	536 ± 226	29.9 ± 14.6	40.1 ± 45.3	*b*
	Polish market	raw	0.40	0.75	2.52	0.02	0.15	0.90	0.01	0.06	14.5	667	12.3	30.3	*b*
crab	Taiwan		1.80–77.4	0.30–14.4	1.50–31.5		0.32–0.90	0.41–4.02							*2*
	Spain					0.08									*18*
	Spain		0.00–64.0	2.00–28.0			2.98–5.37		1.46–8.19	3.75–42.1					*26*
	Turkey	claw meat					2.53	6.99	0.39	1.04		266	149	256	*5*
		claw meat					2.08	4.68	0.06	0.45		354	151	308	
		body meat					3.13	4.7	0.37	1.13		327	64.9	244	
		body meat					1.49	3.72	0.16	0.68		319	87.6	303	
	Australia	claws		0.6	36		1.8	9.9							*25*
	Texas		54.0–771	0.30–15.3			1.33–4.65	0.30–5.22							*19*
	Polish market	meat from claws, boiled	9.83	11.2	16.7	0.09	0.74	9.71	0.44	1.28	72.1	255	379	221	*b*
lobster	Mexico	male		3.60–9.12			0.84–1.73	2.04–3.74	0.01–0.04	0.38–2.04					*15*
		female		5.52–9.84			0.91–2.06	2.16–4.46	0.04–0.07	0.72–1.66					
	Polish market	meat from claws, boiled	<0.05	19.8	9.57	0.07	1.84	4.27	0.26	0.26	38.3	369	162	73.7	*b*
clam	Taiwan		1.00–660	1.80–57.0	1.00–4.20		0.02–0.48	0.38–1.11							*2*
	Spain								0.01						*20*
	Spain		182–312	18.0–39.0			0.29–0.44		0.82–1.76	15.9–45.8					*26*
mussel	Taiwan		1.00–1.80	7.80–24.2	1.12–4.20	0.07–0.13	0.20–0.48								*2*
	Malaysia		50.2–175	13.6–25			0.16–0.40	1.50–2.58							*6*
	Spain								0.05–0.32						*20*
	Spain					0.04									*18*
	Greenland		17.8–50.0	24.0–46.8	1.14–1.93	0.06–0.11	0.15–0.21	1.33–2.34		2.64–6.72		272–802			*21*
	Japan	Minamata Bay			0.62–12.1										*24*
		Kagoshima Bay			0.22–2.95										
	Hong Kong		40.4–87.2	9.00–28.8			0.12–0.16	1.80–2.70							*34*
	Greenland		12.7	72	1.6	0.09									*27*
	Texas		39.0–95.2	26.6–37.8			0.11–0.32	0.90–1.22	0.14–0.44	10.7–19.7					*19*
	Polish market	boiled	13.6 ± 9.33	18.6 ± 6.37	1.39 ± 0.78	0.04 ± 0.01	0.12 ± 0.07	2.99 ± 1.93	2.49 ± 2.13	3.54 ± 3.10	19.7 ± 3.36	184 ± 197	7.13 ± 6.83	117 ± 159	*b*
	Polish market	raw	4.81	7.67	2.68	0.06	0.08	1.80	0.23	9.47	53.2	194	14.0	97.5	*b*
octopus	Portugal		5.1	6.2	5										*22*
	Polish market	raw tentacles	2.28	1.27 ± 0.75	2.63 ± 0.53	0.015 ± 0.0	0.24 ± 0.00	1.44 ± 0.36	0.02 ± 0.01	0.091 ± 0.001	36.3 ± 12.8	411 ± 404	6.12 ± 2.85	155 ± 117	*b*
	Polish market	raw small	4.35	85.2	0.49	0.026	0.17	1.19	0.06	0.40	13.3	534	9.3	62.8	*b*

[a] Coefficients used for calculation (dry/wet weight) were as follows: shrimp, 6.7; crab, 3.3; lobster, 4.2; mussel, 5; and according to literature data for octopus, 5. [b] This study.

Table 7. Concentration of Toxic Elements in Seafood

		μg 100 g^{-1} of wet wt		
product	N^a	Hg	Pb	Cd
salad shrimp (small)	3	0.79 ± 0.20 0.59–0.99	0.88 ± 0.49 0.30–1.51	1.03 ± 0.11 0.90–1.09
salad shrimp (big)	3	2.93 ± 0.28 2.60–3.11	<0.05^b	2.72 ± 0.33 2.34–2.97
deep water shrimp	3	0.62 ± 0.13 0.46–0.71	<0.05^b	0.62 ± 0.02 0.61–0.64
black tiger shrimp, boiled	3	1.82 ± 0.17 1.63–1.91	<0.05^b	0.70 ± 0.11 0.59–0.81
black tiger shrimp, raw	3	2.52 ± 0.25 2.26–2.75	<0.05^b	0.75 ± 0.15 0.59–0.88
Greenland shrimp	3	10.2 ± 0.59 9.63–10.80	<0.05^b	68.7 ± 7.04 64.3–76.8
salad shrimp in cold water	3	1.26 ± 0.35 0.94–1.64	<0.05^b	2.51 ± 0.35 2.18–2.88
torpedo shrimp	3	<0.044^b	<0.05^b	0.90 ± 0.30 0.58–1.16
Norway lobster	3	3.11 ± 0.25 2.90–3.40	0.86 ± 0.43 0.37–1.28	5.48 ± 0.19 5.29–5.67
crab (meat from claws)	3	16.7 ± 1.07 15.7–17.8	9.83 ± 2.87 6.46–12.58	11.2 ± 0.84 10.4–12.1
lobster (meat from claws)	3	9.57 ± 0.88 8.88–10.6	<0.05^b	19.8 ± 2.58 16.9–22.0
surimi crab	3	3.03 ± 0.21 2.80–3.22	2.57 ± 2.08 0.51–5.39	0.90 ± 0.08 0.84–0.99
Kamaboko crab	3	1.86 ± 0.35 1.46–2.06	<0.05^b	0.84 ± 0.13 0.70–0.94
baby octopus	3	<0.044^b	4.35 ± 0.19 4.17–4.55	85.2 ± 12.0 74.2–98.1
Philippines octopus	3	2.26 ± 0.33 1.89–2.54	2.28 ± 0.99 1.23–3.50	0.74 ± 0.10 0.65–0.85
Mediterranean octopus (tentacles)	3	3.00 ± 0.19 2.82–3.19	<0.05^b	1.80 ± 0.26 1.54–2.05
boiled mussels	3	0.84 ± 0.25 0.65–1.13	7.00 ± 0.98 6.17–8.69	14.0 ± 1.63 12.2–15.3
mussels in shell	3	2.68 ± 0.47 2.20–3.14	4.81 ± 1.26 4.09–6.68	7.67 ± 0.86 6.68–8.27
great scallop	3	1.95 ± 0.18 1.79–2.14	20.1 ± 0.80 19.4–20.9	23.1 ± 2.67 20.0–25.0
raw squid rings	3	1.14 ± 0.19 0.98–1.34	<0.05^b	3.90 ± 0.27 3.60–4.12
coated squid rings	3	0.044^b	<0.05^b	2.54 ± 0.69 1.95–3.29
squid tube	3	1.18 ± 0.42 0.78–1.61	<0.05^b	3.36 ± 0.39 3.01–3.77

[a] Number of pools utilized for the analysis of each product. [b] Limit of detection: 0.044 μg of Hg g^{-1} of dw; 0.05 μg of Pb g^{-1} of dw; 0.007 μg of Cd g^{-1} of dw.

has been removed. In contrast, Philippines and Mediterranean octopuses weigh from 3 to 4 kg and only their tentacles are consumed. There are few worldwide data available on toxic elements in octopuses. According to Vaz-Pires and Barbosa (*28*), *Octopus vulgaris* (weight from 550 to 1540 g) bought on markets in northern Portugal (northeastern Atlantic coast of Europe) contained 6.20 μg of Cd 100 g^{-1} , a value that is comparable with our data obtained for Philippines and Mediterranean octopuses. Elevated Cd levels, similar to those found in mussels, were also found in great scallops (**Table 7**). Cd levels in shrimps were low (except for the Greenland shrimp mentioned earlier) but generally very similar to those published by Jeng et al. (*3*), Blasco et al. (*29*), and Johansen et al. (*30*).

The Pb content in shrimps was generally below the detection limit, that is, <0.05 μg of Pb g^{-1} of dw, except in small salad shrimps and Norway lobsters, which contained 0.90 μg of Pb 100 g^{-1} (**Table 7**). Pb levels in great scallops were relatively high (20.2 μg 100 g^{-1}). Several authors (*3, 21, 31*) have reported higher levels, for example, up to 87.2−660 μg of Pb 100 g^{-1} (**Table 6**). Concentrations of Pb in other mussels (boiled mussels and mussels in shells) and in baby octopuses were 3−4.5 times lower than those in great scallops. The concentration in baby octopuses is comparable with that reported by Vaz-Pires and Barbosa (*28*). The Pb data listed in **Table 6** are generally higher than those obtained in the present study. Also, Pb levels in crabs appear to be rather higher than those in shrimps.

Generally speaking, there are no significant differences in the levels of toxic elements and Se between squid tubes and raw squid rings from Spain or between shrimps from India and shrimps from Thailand, although one kind of shrimp is boiled and the other is raw. In contrast, shrimps from Norway contain different levels of these elements. Surimi products (Kamaboko crabs and surimi crabs) and other processed products (torpedo shrimp and breaded squid rings) contain low levels of toxic elements and Se. One of the reasons for this could be the significant proportions of different additives such as flour, bread crumbs, or desiccated coconut, which reduce the total mass of the shellfish product.

The PTWI was estimated for the highest Hg, Cd, and Pb concentrations in products such as crab (claw meat), baby octopus, and great scallops containing 16.7, 85.2, and 20.2 μg of Hg, Cd, and Pb 100 g^{-1}, respectively. **Table 8** shows the maximum levels of individual elements in shellfish. The safe weekly intake of particular products and the percentage weekly intake of elements through shellfish consumption were assessed. Taking into account the much lower shellfish consumption in comparison to that given in **Table 8**, and having compared our results with the animal product metal concentrations (mg kg^{-1}) permitted by the Regulations of the Polish Ministry of Health (*15*), as well as FDA and EPA Safety Levels in Regulations and Guidance (*32*), no risk to health is posed by the consumption of shellfish and the analyzed products do not exceed this permissible content.

It is well-known that shellfish, alongside meat, milk products, and grain, are rich in Se and could be one of the main sources of this element in the diet. In particular, the protective role of Se against heavy metal poisoning (Hg, Cd, Pb, and As) is important from the toxicological point of view (*33*). A large excess of Se relative to Hg (molar ratio of Hg/Se amounted to 0.09) was found for shellfish purchased from a wholesaler in Modena (Italy), but no significant correlation was found between concentrations of these elements (*34*). We obtained also significantly lower Hg/Se ratios for the examined seafoods as well as no significant correlation coefficients for these two elements. As our results show, products containing the highest concentrations of toxic elements, that is, Greenland shrimp, Norway lobster, crab, lobster, baby octopus, and great scallops, are also characterized by higher Se levels. Hence, the potential toxicity of these products could be lower than that resulting from assessed values of PTWI for a 60 kg person.

Correlations. The correlations between the concentrations of the various metals in shellfish were statistically significant ($p < 0.001$, $p < 0.001$, and $p < 0.05$). As can be seen in **Table 9**, all of the chemical elements except Na and Cd exhibited significant positive correlations between their concentrations in

Table 8. Provisional Tolerable Weekly Intake (PTWI) and Other Indices Concerning Toxic Metal Intakes by Consumption of Seafood Products

	Hg	Cd	Pb
PTWI (μg kg^{-1} of body, according to FAO/WHO)	5.0 (total Hg) 1.6[a] (as CH_3HgX)	7.0	25.0
PTWI [mg person^{-1} (60 kg wt)]	0.3	0.42	1.5
max content of metal (mg kg^{-1}) in product	crab, meat from claws 0.17	octopus "baby" 0.85	great scallop 0.20
permissible concn of metal (mg kg^{-1}) in animal products	edible parts of fish 0.5[b] all fish (methyl mercury) 1.0[c]	edible kidney of mammals 1.5[b] clams, oysters, and mussels 4.0[c]	edible parts of fish 0.5[b] clams, oysters, and mussels 4.0[c]
safe weekly intake of the product (kg)	<3	<0.5	<7.5
percentage of weekly element intake through product consumption[d]	10	37	2.4

[a] Except pregnant and nursing women. [b] Polish Regulations of the Ministry of Health. [c] FDA and EPA Safety Levels in Regulations and Guidance (www.cfsan.fda.gov/~comm/haccp4 × 5.html). [d] According to average seafood consumption in Poland, 180 g week^{-1} (www.fao.org. – Fish and fishery products – apparent consumption).

Table 9. Significant Correlations between Trace Elements in Seafood

element	seafood[a]
Mg	(+)K,[b] (+)Hg,[c] (+)Zn,[d] (+)Se[d]
Ca	(+)Hg,[b] (+)Zn[d]
K	(+)Mg,[b] (+)Zn,[c] (+)Mn[d]
Zn	(+)Mn,[c] (+)K,[c] (+)Hg,[c] (+)Se,[c] (+)Cu,[d] (+)Ca,[d] (+)Mg[d]
Cu	(+)Hg,[b] (+)Zn,[d] (+)Se[d]
Fe	(+)Se[d]
Mn	(+)Zn,[c] (+)K[d]
Se	(+)Zn,[c] (+)Fe,[d] (+)Cu,[d] (+)Mg[d]
Hg	(+)Cu,[b] (+)Ca,[b] (+)Zn,[c] (+)Mg[c]

[a] (+) positive correlation; (–) negative correlation. [b] $p < 0.001$ [c] $p < 0.01$ [d] $p < 0.05$

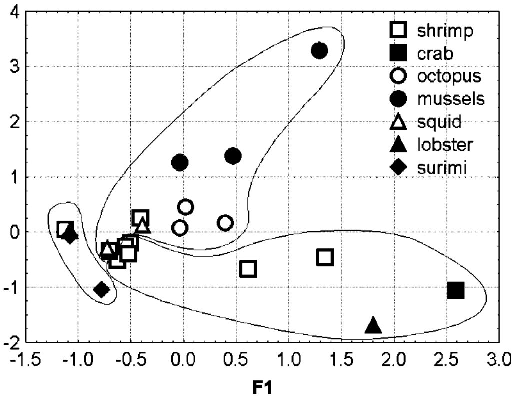

Figure 1. Biplot of the distribution of object scores for seafood.

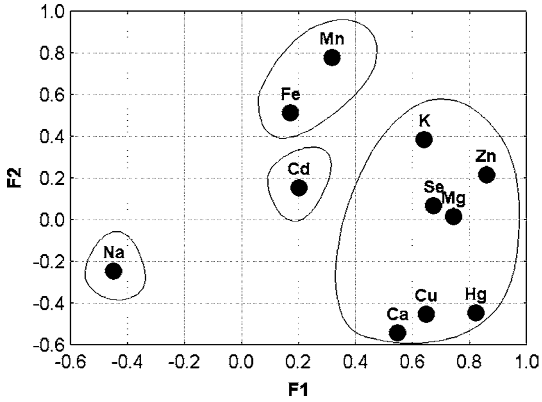

Figure 2. Biplot of the distribution of loadings in seafood.

the edible parts of shellfish. Se was significantly correlated with essential elements such as Zn ($p < 0.01$) and Fe, Cu, and Mg ($p < 0.05$), and significant positive relationships were observed between concentrations of Hg and Cu and Ca ($p < 0.001$) Zn and Mg ($p < 0.01$). Moreover, a statistically significant correlation between the concentrations of the macroelements Mg and K was noted ($p < 0.001$).

Factor Analysis. The first two factors describe 53% of the total variability contained in the raw data set. The eigenvalues of these factors are 3.93 (F1) and 1.85 (F2), respectively. To explain the causes of the diverse contents of elements in shellfish products, object scores F1−F2 (**Figure 1**) were drawn for samples to which particular groups of invertebrates correspond. As can be seen in **Figure 1**, highly processed products are generally characterized by lower values of factor F1, in contrast to initially processed ones (just boiled), which are described by higher values of F1. Thus, F1 can be interpreted as a factor associated with the influence of the processing of raw shellfish on their elemental composition.

Although the data relating to unprocessed and processed shellfish overlap somewhat, there is sufficient differentiation between mussels and octopus, with higher values of F2, and squids, which form a separate set of points with intermediate F2 values. Factor F2 can therefore be associated with the taxonomic groups of the raw shellfish, distinguishing, for example, mussels, octopuses, squids, and crustaceans (shrimps, lobsters, and crabs).

To identify the elements responsible for the grouping of the objects (shellfish), a biplot of loadings was drawn for F1−F2 (**Figure 2**). The distribution of the points corresponding to the individual elements shows that factor F1 achieves the lowest values for Na. These points are adjacent to highly processed shellfish products such as Kamaboko crab, torpedo shrimp, surimi crab, and breaded squid rings, which are clearly distinct from the group linked to other elements such as Cd, Fe, Mn, Ca, K, Se, Cu, Mg, Hg, and Zn. This latter group of elements is ascribed to the points mostly associated with boiled shellfish (**Figure 1**), that is, with higher values of F1. Presumably, a considerable pool of these essential elements reflects the natural elemental composition of the invertebrates studied. Hence, F1 is connected with the diverse ways in which some of the samples examined were or were not processed.

Factor F2 enables us to distinguish the metals responsible for grouping object samples (**Figure 1**) and which can be attributed to different features of particular taxonomic groups of the raw shellfish analyzed here. The specific elemental composition for each of these groups is the reason for the formation of two subclusters associated with Fe, Mn (mussels), and Cd (squids and octopus) described by higher values of F2 and with Hg, Cu, and Ca (crustaceans—shrimps, lobsters, and crabs) characterized by lower values of F2.

Conclusions. Shellfish can be regarded as nutritious. The edible parts of cephalopods contain essential elements and are a fairly good source of some of them. Distinct differences in the contents of macro- and microelements were found in the shellfish products analyzed. Levels of essential elements such as Ca, Cu, Mn, Zn, and Se are much higher in many shellfish species than in the reference products (cod, flounder, herring, pork, beef, chicken, or eggs). Processing technologies affect the Na content in shellfish quite considerably. Factor analysis was useful for identifying the essential and toxic elements responsible for distinguishing preliminarily and highly processed shellfish. The RDA of essential elements places the nutritional profile of crab and lobster meat in a favorable light. In view of the PTWI estimated for products containing the highest concentrations of toxic elements, no health hazard is posed by exposure to Hg, Cd, and Pb through shellfish consumption.

ABBREVIATIONS USED

F-AAS, flame atomic absorption spectrometry; GF-AAS, graphite furnace atomic absorption spectrometry; HG-AAS, hydride generation atomic absorption spectrometry; CV-AAS, cold vapor atomic absorption spectrometry; RDA, recommended dietary allowance; AI, adequate intake; PTWI, provisional tolerable weekly intake.

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