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Essential elements and contaminants in edible tissues of European and American lobsters

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ABSTRACT

In several European countries clawed lobsters, such as the European (*Homarus gammarus*) and American (*H. americanus*) ones are widely consumed. Yet, information about essential elements and contaminants in both species is still scarce. Therefore, the aim of this work was to characterise the elemental content in the edible part (muscle, hepatopancreas, gonads and roe) of both homarids and to compare them with the daily intake recommendations and maximum allowed levels. Two techniques were employed: energy-dispersive X-ray fluorescence (EDXRF) to quantify Cl, S, K, Ca, Fe, Cu, Zn, As, Se, Br and Sr; and flame atomic-absorption spectrometry (FAAS) to analyse Na, Mg, Mn, Cd, Hg and Pb. Significant differences were found in the elemental composition of edible tissues of both species, likely reflecting the distinct physiological role of those tissues: muscle (higher: Na, Mg, Ca and Sr; lower: Fe, Se, Cd); hepatopancreas (higher: Fe, Cu, Br and Cd); gonads (lower: Cl, Ca, Zn and Hg); and roe (higher: Na and Br; lower: K and As). Statistical differences in the elemental composition of each tissue were found between both homarids: Muscle (Na, Se, As and Hg); Hepatopancreas (Na, Mg, Fe, Cu, Se, Br and Hg); and gonads (S and Zn). Since the geographical distribution of both species is different, the differences likely reflect distinct elemental composition in the aquatic environment and, consequently in the feed chain. Both lobster species were rich sources of Na, Cl, Cu, Zn and Se for human consumption. Regarding contaminants, only Cd was detected at high concentrations in the hepatopancreas of both homarids. Despite Cd values were well above the maximum allowed level set by the European Commission for crustaceans' muscle, so far any limit value was set for crustaceans' hepatopancreas. Nonetheless, the present study recommends avoiding or moderately consuming this tissue in homarids.

1. Introduction

In the last years, the health benefits related with seafood consumption have been extensively publicized. Seafood is rich in protein, contains low cholesterol and high percentage of ($n-3$) polyunsaturated fatty acids, liposoluble vitamins and essential minerals (Adeyeye, 2002; Chen, Zhang, & Shrestha, 2006; Tahvonen, Aro, Nurmi, & Kallio, 2000; Zalloua et al., 2007). Epidemiological studies have indicated that populations with a rich seafood diet have low risk of coronary heart disease, hypertension and cancer (Simopolpoulos, 1997).

In recent years, attention has been focused on determination of elements in seafood due to nutritional benefits of essential elements and toxicological concerns related to anthropogenic influx of contaminants. Lack of essential elements (*e.g.* Na, Mg, Cl, P, S, K, Ca, Mn, Fe, Cu, Zn, Se) leads to improper enzyme mediated metabolic functions and results in organ malfunctions, chronic diseases and ultimately death (FAO/WHO, 2002; Simopolpoulos, 1997). Other trace elements, such as Br and Sr, are still being categorised as essentials (Oehlenschläger, 1997). Therefore, regular intake of these elements via food ingestion is vital. On the other hand, environmental contaminants (*e.g.* As, Cd, Hg and Pb) are a major concern in aquatic environments, since they cause severe human health disorders (Carvalho, Santiago, & Nunes, 2005; Francesconi, 2007).

Clawed lobsters (*Homarus gammarus* and *H. americanus*) are worldwide highly prized delicacies (Holmyard & Franz, 2006). In Southern Europe, especially in coastal areas of Mediterranean countries (*e.g.* Italy, France, Spain, Greece and Portugal), these crustaceans are widely consumed. The European lobster *H. gammarus* production in 2005 was 2326 tons in all EU countries (EUROSTAT., 2007). This species typically inhabits the North Eastern Atlantic coast, Mediterranean Sea and Black Sea down to 100 m depth

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(Holmyard & Franz, 2006; Ingle, 1997). In order to satisfy the high consuming demands in Europe, American lobster *H. americanus* has been extensively imported from USA and Canada (16,000 tons, corresponding to 140 million € economic value; data from 2006; INFOFISH., 2007). *H. americanus* is mostly found along the North Western Atlantic coast down to 50 m depth (Holmyard & Franz, 2006).

Several studies have documented crustaceans' mineral value (Gokoolu & Yerlikaya, 2003; Kuçukgulmez, Çelik, Yanar, Ersoy, & Çikrikçi, 2006; Skonberg & Perkins, 2002) and contaminants content (Kádár, Costa, & Santos, 2006; Mishra et al., 2007; Mohapatra, Rautray, Vijayan, Mohanty, & Dey, 2007; Páez-Osuna & Bdjorquez-Leyva, 1999; Páez-Osuna & Ruiz-Fernández, 1995a, 1995b). Yet, as far as clawed lobsters are concerned there is still limited information on their essential elements and contaminants composition. This knowledge is fundamental, especially considering the high consumption of both homarids, but also because the edible tissues of *H. americanus* are available in a wide variety of forms for human consumption (Holmyard & Franz, 2006). These forms include processed hepatopancreas, presented as a green coloured meat (named tomalley), roe and muscle. Since each tissue has distinct functions, it is assumed that their mineral content also varies. In this context, the aim of the present work was to quantify the essential elements and contaminants contents in the muscle, hepatopancreas, gonads and roe of *H. americanus* and *H. gammarus*, and to compare such values with the daily intake recommendations and maximum limit levels.

2. Materials and methods

2.1. Biological material

Twenty-one live American lobsters *H. americanus* (origin: USA and Canada; 580 ± 58 g average weight) and 20 European lobsters *H. gammarus* (origin: Scotland; 587 ± 81 g average weight) were purchased from a local company soon after importation and immediately transported to the laboratory. Animals were kept under refrigerated conditions during one hour to decrease their metabolism before being euthanized. The muscle tissue (from claws, legs and abdomen), hepatopancreas, gonads and roe (whenever present) were individually separated and weighed. Each tissue was subsequently homogenised with a grinder, vacuum packed and stored at −20 °C. The frozen samples were freeze–dried for 48 h at −50 °C and low pressure (approximately 10^{-1} atm). Samples were powdered and stored at −20 °C under controlled humidity conditions (vacuum packed) until further analyses.

2.2. Element analyzes

Energy dispersive X-ray fluorescence (EDXRF) spectrometer was used to quantify Cl, S, K, Ca, Fe, Cu, Zn, As, Se, Br and Sr. The EDXRF technique consists of an X-ray tube equipped with a changeable secondary target, normally of molybdenum. The characteristic radiations emitted by the elements in the sample were detected by a silicon (lithium) detector, with a 30 mm^2 active area and an 8 μm beryllium window. The energy resolution was 135 eV at 5.9 keV and the acquisition system was a Nucleus PCA card. Quantitative calculations were made by the fundamental parameters method (Mantler & Kawahara, 2004). Experimental parameters were obtained by calibration, using standard reference materials. The X-ray generator was operated at 50 kV and 20 mA and a typical acquisition time of 1000 s was used. Each sample powder (1 g) was pressed into pellets of 2 cm diameter without any chemical treatment. A minimum of three pellets (replicates) per sample were glued onto Mylar films, on sample holders, and placed directly in the X-ray beam. There are several advantages of using EDXRF to determine elemental content: no sample preparation, less time-consuming compared to conventional techniques, low amount of sample required, no need to use liquid reagents, thus eliminating reagent waste and reducing potential contamination.

The elements Na, Mg, Mn, Cd and Pb were measured by flame atomic-absorption spectrometry (FAAS), with a Variant (Australia) Spectr AA 20 spectrometer, according to official analytical methods (AOAC, 1990). The procedure is based on sample incineration (15 g) and dissolution in HNO_3. A minimum of three replicate analyses was performed per sample. Concentrations were calculated from linear calibration plots obtained by measurement of the absorbance of standard solutions (0.5 mol/ml) of $NaNO_3$, $Mg(NO_3)_2$, $Mn(NO_3)_2$, $Cd(NO_3)_2$ and $Pb(NO_3)_2$ diluted in HNO_3, all supplied by Merck.

The element Hg was also measured in triplicate by flame atomic-absorption spectrometry (FAAS), but with AMA 254 Mercury Analyser spectrometer that uses the Hg vapour generation technique spectrometer, according to official methods of analysis (AOC, 1990). The procedure is based on combustion of dry sample (40 mg), preconcentration of Hg by amalgamation with gold and atomic-absorption spectrometry. A minimum of three replicate analyses was performed per sample. Concentrations were calculated from linear calibration plots obtained by measurement of the absorbance of an Hg standard solution (Hg diluted in HNO_3; 0.5 mol/ml) supplied by Merck.

Two groups of elements were distinguished in the analyses: elements considered essential for life maintenance (macroelements: Na, Mg, Cl, S, K and Ca; trace elements: Mn, Fe, Cu, Zn, Se, Br and Sr), and elements considered harmful for animals (contaminants: As, Cd, Hg and Pb), which are related with an exogenous influence (Belitz & Grosch, 1999; Francesconi, 2007).

2.3. Accuracy levels

Accuracy was checked with certified biological material (Table 1). The elemental concentrations obtained for canned matrix meat (SMRD-2000; Swedish Meats R&D and Scan Foods/National Food Administration, Sweden; FAAS), non defatted lobster hepatopancreas (LUTS-1; National Research Council of Canada; FAAS), oyster

Table 1
Elemental concentration (μg g^{-1} DW; $n = 4$) and detection limits of certified reference material (± standard deviation) analysed by FAAS and EDXRF

	Present work	Certified value	Detection limit
Na[a]	8346 ± 280	8533 ± 281	0.37
Mg[b]	91 ± 2	90 ± 4	0.05
Cl[c]	10500 ± 1000	10000[d]	100
S[c]	8200 ± 500	7600[d]	100
K[c]	10000 ± 80	9690 ± 50	10
Ca[c]	1350 ± 50	1500 ± 200	20
Mn[b]	1.28 ± 0.03	1.20 ± 0.13	0.04
Fe[c]	210 ± 15	195 ± 34	3.1
Cu[c]	64 ± 4	63 ± 4	0.7
Zn[c]	830 ± 40	852 ± 14	1.1
As[c]	13 ± 1	13 ± 2	0.7
Se[c]	2.3 ± 0.5	2.1 ± 0.5	0.6
Br[e]	22 ± 2	22 ± 3	0.8
Sr[c]	9.9 ± 0.8	10 ± 1	0.5
Cd[f]	26.8 ± 0.1	26.7 ± 0.6	0.01
Hg[f]	0.28 ± 0.00	0.27 ±0.06	0.02
Pb[f]	0.35 ± 0.06	0.35 ± 0.13	0.02

[a] Canned matrix meat (SMRD-2000; FAAS).
[b] Non defatted lobster hepatopancreas (LUTS-1; FAAS).
[c] Oyster tissues (SRM 1566; EDXRF).
[d] Non-certified values provided by United States National Bureau of Standards.
[e] Freeze–dried animal blood (IAEA-A-13; EDXRF).
[f] Lobster hepatopancreas (TORT-2; FAAS).

tissue (SRM 1566; United States National Bureau of Standards; EDXRF), freeze–dried animal blood (IAEA-A-13; International Atomic Energy Agency; EDXRF) and lobster hepatopancreas (TORT-2; National Research Council of Canada; FAAS) were compared with certified values. The detection limits (DL) of each element (Table 1) were determined by two means: (a) EDXRF – with the signal-to-noise approach, where the equipment compares the signal of each element with blank samples and established the minimum concentration at which the element is reliably detected; (b) FAAS – with the residual standard deviation (RSD) of the response and the slope (S) of the calibration curve of each standard solution used ($DL = 3.3 \times RSD/S$). The FAAS technique requires large amount of sample, which was not possible in gonads and roe.

2.4. Nutritional quality and potential risks for consumers

To evaluate the elemental nutritional quality and potential risks of clawed lobsters' consumption, intake of elements per 100 g serving portion was estimated for the edible tissues (wet weight) (similar to the procedures used by the Food and Agriculture Organization of the United Nations, by the World Health Organization of the United Nations and by the United States Food and Drug Administration/USFDA for food risk-benefit analysis). For each homarid species, the average intake (AI) of each element per 100 g edible serving portion was calculated using the edible contributions of each tissue: *H. americanus* (muscle: 84.1%; hepatopancreas: 14.2%; gonads: 1.7%) and *H. gammarus* (muscle: 85.7%; hepatopancreas: 12.3%; gonads: 2.0%). For each homarid species the following equation was used to calculate the AI of each element per 100 g portion: $AI/portion = (AIM \times ECM) + (AIH \times ECH) + (AIG \times ECG)$, where M = muscle, H = hepatopancreas, G = gonads, EC = edible contribution. The edible contribution of roe was not considered as this tissue was only available in few animals.

The values of average intake of the essential element Na, Mg, Cl, K, Ca, Mn, Fe, Cu, Zn and Se were compared with the daily dietary reference intake (DRI) of adult females and males aged between 19 and 50 years set by the United States Department of Agriculture (USDA). The contaminants Cd, Hg and Pb were compared with the maximum allowed level (ML) set by the European Commission, whilst As was evaluated in terms of the action level (AL; similar meaning to the ML) set by the USFDA. For each element, the ratio between the average intakes per portion and the DRI, ML or AL was calculated.

2.5. Statistical analysis

Differences in the elemental concentration of edible tissues of *H. americanus* and *H. gammarus* were tested with analysis of variance (ANOVA) and Student's t-test. Whenever necessary, data were transformed to satisfy normal distribution and homoscedasticity requirements, followed by non-parametric analysis of variance (Kruskall–Wallis or Mann–Whitney tests), if transformed data could not met these assumptions. All statistical analyses were tested at 0.05 level of probability with the software STATISTICA™ 6.1.

3. Results and discussion

3.1. Element composition in the edible tissues of each species

The mean elemental concentrations (μg g^{-1} wet weight) in the edible tissues of *H. americanus* and *H. gammarus* are listed in Table 2. Quantification of Pb and Cd was not possible in the gonads due to the low amounts obtained. Sodium, Cl, S and K were the most abundant elements in all tissues.

Table 2
Mean elemental composition (±standard deviation) (μg g^{-1} wet weight) in the tissues of *H. americanus* and *H. gammarus*

Elements	*H. americanus*			*H. gammarus*				*H. americanus vs. H. gammarus* (p-value)	
	Muscle	Hepatopancreas	Gonads	Muscle	Hepatopancreas	Gonads	Roe	Muscle	Hepatopancreas	Gonads
Macroelements										
Sodium (Na)	3228 ± 329^{a}	2842 ± 473^{b}	1498 ± 7^{b}	1962 ± 1090^{b}	1608 ± 499^{b}	1506 ± 32 ^{b}	4006 ± 76^{a}	0.004	0.008	0.326
Magnesium (Mg)	252 ± 31^{a}	158 ± 29^{b}	112 ± 18^{b}	222 ± 183^{ab}	82 ± 48^{b}	92 ± 26 ^{b}	396 ± 209^{a}	0.821	0.005	0.420
Chlorine (Cl)	4419 ± 456^{a}	4681 ± 305^{a}	2316 ± 286^{b}	4043 ± 695^{a}	4756 ± 998^{a}	2455 ± 478^{b}	4803 ± 1496^{a}	0.050	0.804	0.436
Sulfur (S)	1716 ± 272^{a}	1955 ± 300^{a}	1320 ± 617^{a}	1695 ± 251^{a}	2029 ± 190^{a}	2168 ± 301^{a}	1696 ± 549^{a}	0.808	0.476	0.003
Potassium (K)	2629 ± 185^{a}	2694 ± 279^{a}	2135 ± 589^{a}	2613 ± 259^{a}	2534 ± 494^{a}	2314 ± 532^{a}	644 ± 253^{b}	0.821	0.339	0.474
Calcium (Ca)	473 ± 128^{a}	293 ± 50^{b}	173 ± 47^{c}	456 ± 118^{a}	335 ± 97^{b}	173 ± 53^{c}	446 ± 208^{ab}	0.663	0.199	0.944
Trace elements										
Manganese (Mn)	0.61 ± 0.24^{b}	2.7 ± 0.4^{a}	2.1 ± 0.2^{a}	0.40 ± 0.34^{b}	1.9 ± 1.2^{a}	2.2 ± 0.3^{a}	0.80 ± 0.04^{ab}	0.131	0.317	0.976
Iron (Fe)	2.3 ± 0.5^{c}	29 ± 4^{a}	12 ± 8^{b}	1.8 ± 1.1^{c}	16 ± 3^{a}	16 ± 5^{a}	7.0 ± 3.4^{b}	0.082	0.000	0.324
Copper (Cu)	10 ± 2^{b}	127 ± 87^{a}	15 ± 10^{b}	9.6 ± 5.2^{c}	270 ± 141^{a}	14 ± 7^{c}	34 ± 4^{b}	0.525	0.007	0.880
Zinc (Zn)	29 ± 4^{a}	31 ± 6^{a}	17 ± 5^{b}	26 ± 3^{b}	41 ± 11^{a}	30 ± 8^{ab}	35 ± 4^{a}	0.004	0.009	0.000
Selenium (Se)	0.85 ± 0.20^{b}	1.8 ± 0.6^{a}	3.3 ± 2.0^{a}	0.56 ± 0.12^{b}	1.1 ± 0.3^{a}	2.6 ± 1.8^{a}	1.0 ± 0.2^{a}	0.000	0.001	0.622
Bromine (Br)	23 ± 2^{b}	48 ± 14^{a}	25 ± 3^{b}	22 ± 3^{c}	74 ± 21^{b}	26 ± 7^{c}	114 ± 9^{a}	0.411	0.002	0.888
Strontium (Sr)	34 ± 11^{a}	14 ± 6^{b}	12 ± 5^{b}	35±14^{a}	20 ± 15^{ab}	12 ± 8^{b}	20 ± 4^{ab}	0.784	0.151	0.833
Contaminants										
Arsenic (As)	11 ± 3^{b}	20 ± 5^{a}	12 ± 4^{ab}	17 ± 3^{a}	24 ± 5^{a}	17 ± 3^{a}	11 ± 1^{b}	0.000	0.086	0.006
Cadmium (Cd)	0.02 ± 0.00^{b}	11 ± 5^{a}	–	0.02 ± 0.01^{b}	11 ± 9^{a}	–	–	0.086	0.922	–
Mercury (Hg)	0.10 ± 0.02^{a}	0.13 ± 0.03^{a}	0.01 ± 0.00^{b}	0.15 ± 0.04^{a}	0.09 ± 0.02^{a}	0.01 ± 0.00^{b}	0.01±0.00^{b}	0.000	0.006	0.008
Lead (Pb)	0.10 ± 0.00^{a}	0.11 ± 0.03^{a}	–	0.10 ± 0.00^{a}	0.10 ± 0.06^{a}	–	–	–	0.431	–

In each line, different letters indicate significant differences ($p < 0.05$) between the edible tissues of each homarid species. Additionally, the elements' compositions in each tissue were compared between both homarids; results are presented as p-values.

Generally, significant differences were found in most elements' content amongst tissues of each homarid species, except with S and Pb, suggesting distinct physiological role of each tissue. Sulfur is present in amino acids (*e.g.* cysteine, methionine), polypeptides (*e.g.* glutathione), proteins and enzymes, which might explain its ubiquity at similar concentrations in all tissues (Walker, Hopkin, Sibly, & Peakall, 2001). Similarly, the identical content of Pb in all homarids' tissues is likely explained by the fact that Pb is a toxic contaminant related with an environmental input and without any physiological function (Al-Mohanna & Subrahmanyam, 2001).

The muscle had significantly higher concentrations of Na, Mg, Ca and Sr. Since this tissue is mostly involved in the mechanical movements of appendages and claws, it is likely these elements are vital for neuromuscular functions. In contrast, Fe, Se and Cd contents were lower in the muscle.

The hepatopancreas had statistically higher concentration of Fe, Cu, Br and Cd. The hepatopancreas is a multifunctional vital organ responsible for the regulation of essential mono and divalent ions and for detoxification of contaminants (Chavez-Crooker et al., 2003). Earlier studies reported high contents of Cu in the hepatopancreas of other crustaceans, such as blue crab, swim crab, Chinese mitten crab and shrimps (Chen et al., 2006; Gokoolu & Yerlikaya, 2003; Kádár et al., 2006). Copper levels can reflect the active accumulation of this element by homarids for incorporation into the respiratory pigment haemocyanin found in crustacean's haemolymph (Lee & Shiau, 2002). Previous studies with *H. americanus* reported elevated levels of contaminants, namely Cd, in the hepatopancreas (Chou, Paon, Moffatt, & Zwicker, 2000; Engel, Brouwer, & Mercaldo-Allen, 2001). The high concentration of Cd found in the hepatopancreas likely reflects the detoxifying role of this organ, particularly in the isolation of dietary contaminants and in complexing them with organic solutes, such as metallothionein, glutathione or inorganic anions (Chavez-Crooker et al., 2003). In this way, the hepatopancreas reduces the load of contaminants that reach the haemolymph, tissues and organs. This role is also evidenced by the lower levels of Cd obtained in the remaining tissues.

Gonads are the reproductive organs where high nutritional investments are made to produce the reproductive cells. Selenium was detected at high concentrations in this organ, likely due to the important role of this element in the modulation of growth and development, and in oxidative stress defence (FAO/WHO, 2002). In contrast, low contents of Cl, Ca, Zn and Hg were found in gonads.

The roe had significantly higher Na and Br contents and lower contents of K and Hg.

3.2. Differences in elements composition between species

No statistical differences between *H. americanus* and *H. gammarus* were found in the content of Cl, K, Ca, Mn, Sr, Cd in all edible tissues (Table 2). Such result likely reflects similar vital biochemical mechanisms in both homarids regulating these elements (Skinner, Turoczy, Jones, Barnett, & Hodges, 2004).

H. americanus had significantly higher Na and Se concentrations in the muscle and higher Na, Mg, Fe and Se content in the hepatopancreas. In contrast, *H. gammarus* had statistically higher Cu and Br values in the hepatopancreas and higher S and Zn levels in gonads. These differences might reflect distinct elemental requirements for the metabolism of each species or to different elemental availability in the aquatic environment, as the species are captured in different areas of the Atlantic Ocean. Worldwide, Se availability in sediments and live organisms show great variability due to distinct environmental conditions and agricultural practices (FAO/WHO, 2002). USA and Canada are seleniforous areas, whereas low Se concentrations are found in European countries (Popilac & Prpic-Majic, 2002). According to FAO/WHO (2002), Se content in marine fish captured in USA is usually higher than the average international values. This fact may clarify the higher contents of Se found in the muscle and hepatopancreas of *H. americanus*, though the differences found were small.

Among contaminants, variations between both homarids were only found in the concentration of As and Hg: *H. gammarus* had statistically higher As and Hg content in muscle and lower Hg level in hepatopancreas than *H. americanus*. Such differences may indicate the degree of pollution in sediments and seawater of both regions of the Atlantic Ocean (Sadiq, 1992). Arsenic and Hg enter in coastal waters by sewage and other wastewater effluents, power plant cooling water discharges, vehicle emissions, petroleum and petrochemical industrial wastes, storm drain outfalls and solid waste landfills (Al-Mohanna & Subrahmanyam, 2001). Contaminants cannot be regulated by crustaceans and, therefore, bioaccumulation of these elements occurs in specimens' edible tissues (Al-Mohanna & Subrahmanyam, 2001).

3.3. Nutritional quality and potential risks for consumers

Clawed lobsters are important diet sources in coastal areas of Mediterranean European countries. Therefore, intake of trace elements from *H. americanus* and *H. gammarus*, especially toxic elements, is of great concern for human health. The results obtained in Table 3 indicate that both species are good sources of Na, Cl, Cu, Zn and Se, being *H. americanus* a better source of Na than *H. gammarus*. Sodium plays an important role in many physiological processes: signal transduction in the human central nervous system, osmoregulation, arterial pressure maintenance and optimal salt and water balance in the body (Walker et al., 2001). Zinc is an essential component of several enzymes, participating in the synthesis and degradation of carbohydrates, lipids, proteins, and nucleic acids (FAO/WHO, 2002). Additionally, this element has also an essential role in the process of gene expression, particularly in polynucleotide transcription (FAO/WHO, 2002). Fish, fruit and green leaf vegetables are considered poor sources of Zn (<10 mg/kg), whilst lean meat, cereals and legumes are rich Zn sources (25–50 mg/kg, compared to 30 mg/kg in both clawed lobsters) (FAO/WHO, 2002). In both lobsters' species Cu and Se concentrations were above the DRI. Nevertheless, the tolerable upper limit (TUL) set by the USDA for Cu (10 mg/day) is well above the results found in the present study (2.7–4.0 mg/100 g portion). Copper is found in several enzymes, including the cytochrome *c* oxidase and the superoxide dismutase, and is used for biological electron transport (Walker et al., 2001). Despite Se TUL has not been set, it is important to stress that a normal adult can ingest up to 216 μg Se per day without any toxicological effect (FAO/WHO, 2002), which is higher than values found in the edible tissues of both clawed lobsters (55–70 μg/100 g portion). Several authors reported the Se protective action, especially selenite, ($Se_2O_3^{2-}$), on many toxicological effects of Cd and Hg (Early, Nonavinakere, & Weaver, 1992; Gasiewics & Smith, 1978; Skowerski, Konecki, Czechowicz, & Glowacka, 1997a; Skowerski, Konecki, Czechowicz, & Krzyszt, 1997b). Selenium is also implicated in the protection of body tissues against oxidative stress, maintenance of defenses against infection and modulation of growth and development (FAO/WHO, 2002).

Considering contaminants (As, Cd, Hg and Pb), only Cd content in both homarids was well above the ML/AL per 100 g portion (Table 3). The concentration obtained for As, Hg and Pb was in the range of the typical concentrations found in crustaceans muscle: 5–98 mg/100 g (As), 2–20 μg/100 g (Hg) and 2–10 μg/100 g (Pb) (Francesconi, 2007). In the present study, the main contribution to the high Cd concentration in both species was the hepatopancreas, whilst the Cd concentration in the muscle and gonads was below the ML (Table 2). Cadmium is toxic to many organisms since

Table 3
Average content of each element in 100 g edible serving portion (considering the contribution of all tissues) for each homarid species, and ratio between the average intake of each element per portion and the recommended daily dietary reference intakes (DRI; Na, Mg, Cl, K, Ca, Mn, Fe, Cu, Zn and Se), maximum allowed level (ML; Cd, Hg and Pb) or action level (AL; As)

Elements	DRI/ML/AL	*H. americanus*		*H. gammarus*	
		AI/portion	%	AI/portion	%
Macroelements					
Sodium (Na)	1500 mg	314	21	213	14
Magnesium (Mg)	(413–316) mg	24	(5.7–7.5)	22	(5.4–7.0)
Chlorine (Cl)	2300 mg	442	19	417	18
Sulfur (S)	NS	174	–	173	–
Potassium (K)	4700 mg	263	5.6	240	5.1
Calcium (Ca)	1000 mg	44	4.4	44	4.4
Trace elements					
Manganese (Mn)	(2.3–1.8) mg	0.09	(4.1–5.2)	0.06	(2.7–3.8)
Iron (Fe)	(8–18) mg	0.63	(7.8–3.5)	0.42	(5.2–2.3)
Copper (Cu)	900 μg	2706	301	4048	450
Zinc (Zn)	(11–8) mg	2.9	(27–37)	2.9	(26–36)
Selenium (Se)	55 μg	103	187	70	128
Bromium (Br)	NS	2.6	–	3.7	–
Strondium (Sr)	NS	3.1	–	3.2	–
Contaminants					
Arsenic (As)	7.6 mg	1.2	16	1.7	23
Cadmium (Cd)	50 μg	156	321	119	237
Mercury (Hg)	50 μg	11	22	2.8	5.5
Lead (Pb)	50 μg	10	20	8.8	18

Values in brackets for Mg, Mn, Fe and Zn refer to differences in gender: the first and second values correspond to male and female, respectively; Abbreviations: AI, average intake; NS, have not been set.

the ion form combines with sulphydryl (thiol) groups of many enzymes preventing their normal function (Walker et al., 2001). Yet, Cd absorption by humans is influenced by nutritional factors (*e.g.* Fe levels; Francesconi, 2007), and many toxicological effects of Cd are attenuated in the presence of Se (Gasiewics and Smith, 1978; Early et al., 1992; Skowerski et al., 1997a, 1997b). Since both homarids have high Fe and Se concentrations in the hepatopancreas (Table 2), the toxicological effects of Cd may be reduced. Moreover, despite *H. gammarus* and *H. americanus* are widely consumed in coastal areas of Mediterranean countries, the annual *per capita* consumption of these food items is relatively low (109 g in Spain; 64 g in France; 64 g in Italy; 23 g in Greece; 10 g in Portugal; data from 2005; EUROSTAT, 2007). Therefore, the risk of Cd contamination to homarids consumers is low.

4. Conclusions

In general, Na, Cl, S and K were the most abundant elements in all tissues, evidencing their essential character to *H. americanus* and *H. gammarus*. Differences found in the elemental composition amongst tissues of the same species likely reflect distinct physiological roles of the tissues. Variations detected between both homarid species likely reflect distinct availability of elements in the aquatic environment, as the animals are distributed in different regions of the Atlantic Ocean. Both species can also require distinct elements to their metabolism. Considering the daily intake recommendations, both homarids are good sources of Na, Cl, Cu, Zn, and Se. As to contaminants, only Cd was above the maximum allowed level in the hepatopancreas of both homarids. Despite the low risk of Cd intake, consumers should avoid or moderately consume this tissue in both species. Future studies should evaluate the mineral composition of other crustacean species with relevance for human consumption.

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References

Adeyeye, E. I. (2002). Determination of the chemical composition of the nutritionally valuable parts of male and female common West African fresh water crab *Sudananautes africanus*. *International Journal of Food Sciences and Nutrition, 53*(3), 189–196.

Al-Mohanna, S. Y., & Subrahmanyam, M. N. V. (2001). Flux of heavy metal accumulation in various organs of the intertidal marine blue crab, *Portunus pelagicus* (L.) from the Kuwait coast after the Gulf War. *Environment International, 27*, 321–326.

AOAC (1990). *Official methods of the association of official agricultural chemists*. 15th ed. Washington DC, USA.

Belitz, H. D., & Grosch, W. (1999). *Food chemistry*. New York, USA: Springer. pp. 992–998.

Carvalho, M. L., Santiago, S., & Nunes, M. L. (2005). Assessment of the essential element and heavy metal content of edible fish muscle. *Analytical and Bioanalytical Chemistry, 382*, 426–432.

Chavez-Crooker, P., Pozo, P., Castro, H., Dice, M. S., Boutet, I., Tanguy, A., et al. (2003). Cellular localization of calcium, heavy metals, and metallothionein in lobster (*Homarus americanus*) hepatopancreas. *Comparative Biochemistry and Physiology – Part C, 136*(3), 213–224.

Chen, D., Zhang, M., & Shrestha, S. (2006). Compositional characteristics and nutritional quality of Chinese mitten crab (*Eriocheir sinensis*). *Food Chemistry, 103*(4), 1343–1349.

Chou, C. L., Paon, L. A., Moffatt, J. D., & Zwicker, B. (2000). Copper contamination and cadmium, silver, and zinc concentrations in the digestive glands of American lobster (*Homarus americanus*) from the Inner Bay of Fundy, Atlantic Canada. *Bulletin of Environmental Contamination and Toxicology, 65*, 470–477.

Early, J. L., Nonavinakere, K., & Weaver, A. (1992). Effect of cadmium and or selenium on liver mitochondria and rough endoplasmic reticulum in the rat. *Toxicology Letters, 62*, 73.

Engel, D. W., Brouwer, M., & Mercaldo-Allen, R. (2001). Effects of molting and environmental factors on trace metal body burdens and hemocyanin concentrations in the American lobster *Homarus americanus*. *Marine Environmental Research, 52*, 257–269.

EUROSTAT. (2007). http://epp.eurostat.ec.europa.eu/portal/page?_pageid=1996,45323734&_dad=portal&_schema=PORTAL&screen=welcomeref&open=/&product=EU_MASTER_fisheries&depth=2. Consulted on 14th September, 2007.

FAO/WHO. (2002). Human vitamin and mineral requirements. Report of a joint Food and Agriculture Organization of the United Nations/World Health Organization expert consultation, Bangkok, Thailand. http://www.fao.org/documents/show_cdr.asp?url_file=/DOCREP/004/Y2809E/y2809e00.htm.

Francesconi, K. A. (2007). Toxic metal species and food regulations – Making a healthy choice. *Analyst, 132*, 17–20.

Gasiewics, T. A., & Smith, J. C. (1978). Interaction between cadmium and selenium in rat plasma. *Environmental Health Perspectives, 25*, 133–136.

Gokoolu, N., & Yerlikaya, P. (2003). Determination of proximate composition and mineral contents of blue crab (*Callinectes sapidus*) and swim crab (*Portunus pelagicus*) caught off the Gulf of Antalya. *Food Chemistry, 80*, 495–498.

Holmyard, N., & Franz, N. (2006). *Lobster Markets* (Vol. 87). Rome, Italy: Food and Agriculture Organization of the United Nations/Globefish. p. 92.

INFOFISH. (2007). http://www.infofish.org/marketreports/lobster0607.html. Consulted on 29, August, 2007.

Ingle, R. (1997). *Crayfishes, lobsters and crabs of Europe, an illustrated guide to common and traded species*. New York, USA: Chapman & Hall. p. 281.

Kádár, E., Costa, V., & Santos, R. S. (2006). Distribution of micro-essential (Fe, Cu, Zn) and toxic metals in tissues of two nutritionally distinct hydrothermal shrimps. *Science of the Total Environment, 358*, 143–150.

Kuçukgulmez, A., Çelik, M., Yanar, Y., Ersoy, B., & Çikrikçi, M. (2006). Proximate composition and mineral contents of the blue crab (*Callinectes sapidus*) breast meat, claw meat and hepatopancreas. *Journal of Food Science and Technology, 41*, 1023–1026.

Lee, M. H., & Shiau, S. Y. (2002). Dietary copper requirement of juvenile grass shrimp, *Penaeus monodon*, and effects on non-specific immune responses. *Fish & Shellfish Immunology, 13*, 259–270.

Mantler, M., & Kawahara, N. (2004). How accurate are modern fundamental parameter methods? *The Rigaku Journal, 21*(2), 17–25.

Mishra, S., Bhalke, S., Saradhi, I. V., Suseela, B., Tripathi, R. M., Pandit, G. G., et al. (2007). Trace metals and organometals in selected marine species and preliminary risk assessment to human beings in Thane creek area, Mumbai. *Chemosphere, 69*(6), 972–978.

Mohapatra, A., Rautray, T. R., Vijayan, V., Mohanty, R. K., & Dey, S. K. (2007). Trace element characterization of some food crustacean tissue samples by EDXRF technique. *Aquaculture, 270*(1–4), 552–558.

Oehlenschläger, J. (1997). Marine Fish – A source for essential elements?! In J. B. Luten, T. Borresen, & J. Oehlenschläger (Eds.), *Seafood from producer to consumer, integrated approach to quality* (pp. 641–652). Amsterdam, The Netherlands: Elsevier Science B.V.

Páez-Osuna, F., & Bdjorquez-Leyva, H. (1999). Regional variations of heavy metal concentrations in tissues of barnacles from the subtropical pacific coast of Mexico. *Environment International, 25*(5), 647–654.

Páez-Osuna, F., & Ruiz-Fernández, C. (1995a). Trace metals in the Mexican shrimp (*Penaeus vannamei*) from estuarine and marine environments. *Environmental Pollution, 87*, 243–247.

Páez-Osuna, F., & Ruiz-Fernández, C. (1995b). Comparative bioaccumulation of trace metals in *Penaeus stylirostris* in estuarine and coastal environments. *Estuarine, Coastal and Shelf Science, 40*, 35–44.

Popilac, V., & Prpic-Majic, D. (2002). Soil and wheat grain selenium content in the vicinity of Koprivnica (Croatia). *Arhiv za Higijenu Rada I Toksikologiju, 53*, 125–133.

Sadiq, M. (1992). *Toxic metal chemistry in marine environments*. New York, USA: Marcel Dekker, Inc. p. 392.

Simopolpoulos, A. P. (1997). Seafood from producer to consumer, natural aspects of the fish. In J. B. Lutten, T. Borrensen, & J. Oehlenschläger (Eds.). *Seafood from producer to consumer, integrated approach to quality* (Vol. 38, pp. 587–607). Amsterdam, The Netherlands: Elsevier.

Skinner, C., Turoczy, N. J., Jones, P. J., Barnett, D., & Hodges, R. (2004). Heavy metal concentrations in wild and cultured blacklip abalone (*Haliotis rubra* Leach) from Southern Australian waters. *Journal of Agriculture Food Chemistry, 85*, 351–356.

Skowerski, M., Konecki, K., Czechowicz, K., & Glowacka, M. (1997a). Effects of interaction between cadmium and selenium on hepatic metabolism in mice. Part I: The study on DNA, RNA and protein synthesis activities in mouse hepatocytes. *Medical Science Monitor, 3*(5), 642–647.

Skowerski, M., Konecki, K., Czechowicz, K., & Krzyszt, J. (1997b). Effects of interaction between cadmium and selenium on hepatic metabolism in mice. Part II: enzymatic activity and ultrastructure. *Medical Science Monitor, 3*(5), 648–653.

Skonberg, D. I., & Perkins, B. L. (2002). Nutrient composition of green crab (*Carcinus maenas*) leg meat and claw meat. *Food Chemistry, 77*, 401–404.

Tahvonen, R., Aro, T., Nurmi, J., & Kallio, H. (2000). Mineral content in Baltic herring and Baltic herring products. *Journal of Food Composition and Analysis, 13*, 893–903.

Walker, C. H., Hopkin, S. P., Sibly, R. M., & Peakall, D. B. (2001). *Principles of Ecotoxicology* (2nd ed.). London, UK: Taylor and Francis. p. 309.

Zalloua, P. A., Hsua, Y., Terwedowa, H., Zangc, T., Genfu Tang, D. W., Li, Z., et al. (2007). Impact of seafood and fruit consumption on bone mineral density. *Maturitas, 56*, 1–11.