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The Determination of Some Heavy Metal and Mineral Levels in Frozen Shrimp and Frozen Squid

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Abstract

In this study, the levels of some heavy metals (copper, iron, zinc, cadmium, cobalt, nickel, lead, mercury and arsenic) and minerals (calcium and magnesium) were determined in three different brands of frozen shrimp and frozen squid samples available in local markets of Elazig (Turkey). Concentrations of elements were determined by Inductively Coupled Plasma (ICP). Only Cu, Fe, Zn, Cd, Ca and Mg were detected in frozen shrimp and frozen squid samples analyzed. Co, Ni, As, Hg and Pb were found to be undetectable levels in all samples. Heavy metal and mineral levels in frozen shrimp were found to be in range of 2.27-5.24 ppm for copper, 1.62-4.62 ppm for iron, 2.12-7.28 ppm for zinc, 0.02-0.09 ppm for cadmium, 1.03-1.98 ppm for calcium and 1.00-1.92 ppm for magnesium. Heavy metals and minerals in frozen squids were found to be in range of 1.22-3.39 ppm for copper, 2.84-6.97 ppm for iron, 2.19-6.29 ppm for zinc, 0.04-0.1 ppm for cadmium, 1.00-1.96 ppm for calcium and 1.01-1.99 ppm for magnesium. These results show that heavy metal levels in the frozen shrimp and frozen squid samples were under the dangerous limits given by WHO and FAO and there is no any risk for public health by consuming.

Keywords: Frozen shrimp, frozen squid, heavy metals, minerals, Elazig, Turkey

Dondurulmuş Karides ve Kalamarda Bazı Ağır Metal ve Mineral Düzeylerinin Belirlenmesi

Özet

Bu çalışmada, Elazığ (Türkiye)'da yerel marketlerden elde edilen üç farklı firmaya ait dondurulmuş karides ve kalamarda bazı ağır metallerin (bakır, demir, çinko, kadmiyum, kobalt, nikel, kurşun, civa ve arsenik) ve minerallerin (kalsiyum ve magnezyum) düzeyleri İndüktif Eşleşmiş Plazma (ICP) ile belirlenmiştir.
Dondurulmuş karides ve kalamarda sadece Cu, Fe, Zn, Cd, Ca ve Mg düzeyleri belirlenirken, bütün örneklerde Co, Ni, As, Hg ve Pb düzeyleri cihazın okuma duyarlılığının altında olduğundan tespit edilememiştir. Dondurulmuş karidesde bazı ağır metallerin ve minerallerin düzeyleri bakır 2.27-5.24 ppm, demir 1.62-4.62 ppm, çinko 2.12-7.28 ppm, kadmiyum 0.02-0.09 ppm, kalsiyum 1.03-1.98 ppm ve magnezyum 1.00-1.92 ppm olarak bulunmuştur. Dondurulmuş kalamarda ise bazı ağır metal ve mineral düzeyleri bakır 1.22-3.39 ppm, demir 2.84-6.97 ppm, çinko 2.19-6.29 ppm, kadmiyum 0.04-0.1 ppm, kalsiyum 1.00-1.96 ppm ve magnezyum 1.01-1.99 ppm olarak belirlenmiştir. Dondurulmuş karides ve kalamar için verilen bu ağır metal düzeylerinin WHO ve FAO tarafından verilen değerlerin altında olduğu ve insanlar tarafından tüketildiğinde sağlık açısından bir risk oluşturmadığı tespit edilmiştir.

Anahtar Kelimeler: Dondurulmuş karides, dondurulmuş kalamar, ağır metal, mineral madde, Elazığ, Türkiye

1. Introduction

Seafood products have attracted considerable attention as important sources of nutrients in the human diet. A part from their delicacy, crustacean species such as shrimp, prawn, crab and lobster consist of amino acids, protein and other useful nutrients [1,2]. Shrimp is one of the world most popular species and is a part of almost every rations traditional meal reach in protein and minerals. The meat has a sweet, delicate flavor and is considered to be a healthy diet choice. Shrimp is a rich source of antioxidants like selenium [2].

Cephalopods including cuttlefish, squid and octopus are the important marine resource since they are rich in taste and have few inedible parts [3]. Additionally, the muscle contains low saturated fat [4], high vitamin C content [5] and is a good source of minerals such as calcium, potassium, zinc, iron, phosphorus and copper [6]. However, they consist of high sodium and cholesterol contents [7]. Cephalopods are consumed not only fresh, but also manufactured into processed food in huge quantities such as dry frozen and chilled products [8-11].

Heavy metals are considered the most important form of pollution of the aquatic environment because of their toxicity and accumulation by marine organisms [12]. Marine animals are sensitive to metals when the concentrations of these substances reach a certain level in the water. This is especially so in the case of shrimp, because invertebrates tend to accumulate more metals than fish as a result of differences in the evolutionary strategies adopted by various phyla [13]. Crustaceans are reported to be important bio-indicators of heavy metal pollution [14, 15].

The consequence of heavy metal pollution can be hazardous to man and it often becomes mandatory to check chemical contaminants in foods from the aquatic environment to understand their hazard levels [16]. Therefore this study was aimed to find the levels of some heavy metals (copper, iron, zinc, cadmium, cobalt, nickel, lead, mercury and arsenic) and minerals (calcium and magnesium) in the edible portion of three different brands of frozen squid and frozen shrimp collected from markets in Elazig (Turkey).

2. Materials and Methods

2.1. Sampling

A total of three different brands (ten individuals from each brands) of frozen shrimp and frozen squid samples were assured from the food markets in Elazig (Turkey). The frozen shrimp and frozen squid were randomly purchased from this retail central. The accuracy of the analytical procedure was checked by duplication of the samples.

2.2. Reagents and Apparatus

All reagents were of analytical reagent grade unless otherwise stated. Distilled water was used for the preparation of solutions. All the plastic and glassware were cleaned by soaking, with contact, overnight 0.1 N nitric acid solution and then rinsed with distilled water prior to use. HNO_3 used for digestion supplied by Merck.

The concentrations of copper, iron, zinc, cadmium, cobalt, nickel, lead, mercury, arsenic, calcium and magnesium were determined by ICP (Perkin Elmer Optima 5300 DV).

2.3. Digestion procedure for the samples

Five gram of frozen shrimp and frozen squid samples was weighted. After they were individually transferred to 10 mL glass vials previously washed with 0.1 N nitric acid, dried and weighted. Then, they were dried in an oven for 24 h at 105ºC and kept in a desiccator for a few days until constant weight was obtained. Vials were again weighted to obtain dry weight of tissues and then samples were digested (duplicate digestion, in each case) on a hot plate by adding 2 mL of suprapure nitric acid (65%, Merck). Digested samples were kept at room temperature for 24h and then diluted to 50 mL with deionized distilled water standard solutions for calibration graphs were prepared. Blanks were also prepared using the procedure as above, but without the samples [17].

Diluted samples and blank solutions were analyzed by ICP (Perkin Elmer Optima 5300 DV) for determination of Cu, Fe, Zn, Cd, Co, Ni, Pb, Hg, As. Ca and Mg levels.

2.4. Statistical Analyses

Graphpad Prisim 5.0 package programs were used to get the statistical analysis (correlation) and graph of the data obtained during the research.

3. Results

Samples were divided into two categories namely shrimp and squid, on the basis of the ingredients and labelling name. Only Cu, Fe, Zn, Cd, Ca and Mg were detected in frozen shrimp and frozen squid samples analysed. Co, Ni, As, Hg and Pb were found to be undetectable levels in the all samples. The mean concentrations of Ca, Mg, Cu, Fe, Zn and Cd in all shrimp and squid samples are given in Figure 1 and Table 1.

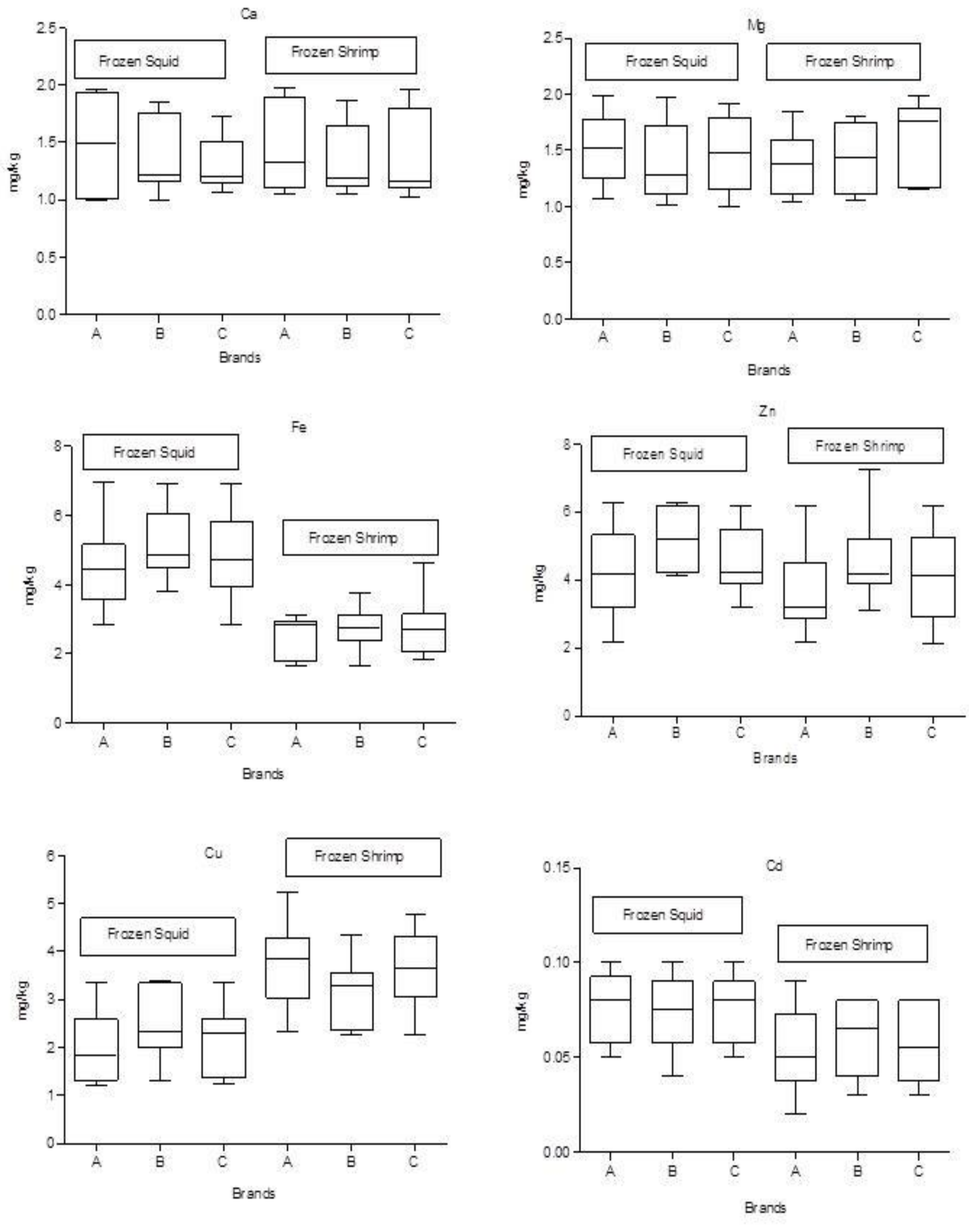

Figure 1. Box-Whisker diagram dissemination of some heavy metals concentration in frozen shrimp and frozen squid

The results for Ca and Mg indicated that Ca presented higher concentrations than Mg. In this study, the average levels of Ca ranged from 1.03 to 1.98 mg/kg and Mg ranged from 1.01 to 1.99 mg/kg for frozen shrimp (Table 1). The average levels of Ca ranged from 1.00 to 1.96 mg/kg and Mg ranged from 1.01 to 1.99 mg/kg for frozen squid (Table 1). The highest concentrations Ca and Mg were found in the frozen squid. According to statistical tests, in frozen shrimps and frozen squids it was found unsignificant all metals and minerals ($P>0.5$).

Table 1. The mean concentrations of some minerals and heavy metals in three different brands frozen shrimp and frozen squid (mg/kg)

Minerals and heavy metals	Frozen Shrimp					Frozen Squid				
	Brands	Mean	Min.	Max.	Standard deviation	Brands	Mean	Min.	Max.	Standard deviation
Ca	A	1.45	1.05	1.98	0.38	A	1.49	1.00	1.96	0.43
	B	1.31	1.05	1.87	0.29	B	1.38	1.00	1.85	0.32
	C	1.39	1.03	1.96	0.36	C	1.30	1.06	1.73	0.24
Mg	A	1.38	1.04	1.85	0.27	A	1.38	1.07	1.99	0.28
	B	1.42	1.06	1.74	0.34	B	1.40	1.01	1.89	0.35
	C	1.46	1.00	1.92	0.36	C	1.62	1.15	1.99	0.39
Fe	A	2.45	1.62	2.94	0.62	A	4.50	2.84	6.97	1.29
	B	2.75	1.66	3.78	0.68	B	5.21	3.79	6.91	1.07
	C	2.80	1.84	4.62	0.84	C	4.93	2.84	6.92	1.21
Zn	A	3.69	2.20	6.19	1.27	A	4.15	2.19	6.28	1.24
	B	4.60	3.13	7.28	1.21	B	5.13	4.16	6.29	0.89
	C	4.00	2.12	6.19	1.34	C	4.61	3.19	6.19	1.07
Cu	A	3.71	2.34	5.24	0.92	A	2.02	1.22	3.37	0.83
	B	3.20	2.27	4.34	0.71	B	2.43	1.32	3.39	0.75
	C	3.60	2.28	4.76	0.83	C	2.22	1.26	3.35	0.74
Cd	A	0.05	0.02	0.09	0.02	A	0.07	0.05	0.1	0.02
	B	0.06	0.03	0.08	0.02	B	0.08	0.04	0.1	0.01
	C	0.06	0.03	008	0.02	C	0.08	0.05	0.1	0.02

In this study, the contents of investigated some heavy metals and minerals in frozen shrimp were found to be an average of 2.27-5.24 ppm for copper, 1.62-4.62 ppm for iron, 2.12-7.28 ppm for zinc and 0.02-0.09 ppm for cadmium. The contents of investigated some heavy metals and minerals in frozen squid samples were found to be an average of 1.22-3.39 ppm for copper, 2.84-6.97 ppm for iron, 2.19-6.29 ppm for zinc and 0.04-0.1 ppm for cadmium.

4. Discussion

Two types of factors affect metal bioavailability for aquatic biota: physico-chemical factors acting outside the organisms, and biological factors acting within the organisms. The former will affect all biota in almost the same way depending on the characteristics of the environment whereas the biological factors may act in different ways. Among the latter, the biological uptake from ingested food is probably the most important [18-20]. This defines the assimilation efficiencies of the contaminants, which are critical for understanding their bioaccumulation and trophic transfer in aquatic invertebrates [20,21].

Zinc is an essential trace element for both animals and humans. The recommended daily allowance is 10 mg/day in growing children and 15 mg/day for adults. A deficiency of zinc is marked by retarded growth, loss of taste and hypogonadium, leading to decreased fertility. Zinc toxicity is rare but at concentrations in water up to 40 mg/kg, may induce toxicity, characterized by symptoms of protective effect against the toxicities of both cadmium and lead [16].

Copper are known to be essential and may enter the food materials during food processing or environmental contamination. Copper is an essential constituent of metalloenzymes and is required in hemoglobin synthesis and in catalysis of metabolic reactions [22]. It should be highlighted is a principal source of copper as an essential element available to humans [23]. However, Cu is very toxic when consumed excessively, and the presence of Cu in seafood's was limited by the Turkish Food Codex [15] 20.0 mg/kg, and by the FAO [24] for fish and fishery products to 30.0 mg/kg. In this study, the average levels of copper ranged from 2.27 to 5.24 mg/kg for frozen shrimp, ranged from 1.22 to 3.39 mg/kg for frozen squid. Although copper is an essential element, it is very toxic and a maximum limit intake was set at 30 mg/day [23].

The recommended daily intakes of zinc and copper are 15 mg Zn for adult males and 12 mg Zn for adult females and 1.5–3.0 mg Cu [25].

Iron is a mineral essential for life and for our diets [26]. Although considered a trace mineral, diets lacking in iron can contribute to the deficiency condition known as anemia. There is no information about maximum iron levels in seafood samples in Turkish standards [14].

The maximum heavy metal levels permitted in Turkey are 0.1 mg/kg (100 μg/kg) for cadmium, 20.0 mg/kg for copper, 50.0 mg/kg for zinc according to Turkish Food Codex [14].

The comparison of the present values for frozen shrimp and frozen squid with international data was given in Table 2. In this study, Fe and Zn concentration lower than reported Anna and Kamila [27] but Cu, Ca and Mg concentration below the reported Anna and Kamila [27]. According to Turkish Food Codex [14] two of the products investigated in this study had mineral matters and heavy metals concentrations were below the permitted levels. These results show that heavy metal levels in the frozen shrimp and frozen squid samples were under the dangerous limits given by Turkish Food Codex [14] and there is no any risk for public health by consuming.

Table 2. Comparison of the present study values with some others obtained in frozen shrimp and frozen squid

	Present work values (mg kg^{-1})		Literature values with relevant location/ references (mg kg^{-1})	
Metals	Frozen shrimp	Frozen squid	Frozen shrimp	Frozen squid
Fe	1.62-4.62	2.84-6.97	9.33 [27]	9.99 [27]
Zn	2.12-7.28	2.19-6.29	50.0 [14] 4.94 [27]	50.0 [14] 7.12 [27]
Cu	2.27-5.24	1.22-3.39	20.0 [14] 1.00 [27]	20.0 [14] 0.80 [27]
Cd	0.02-0.09	0.04-0.1	1.0 [14] 0.05 [27]	0.1 [14] 0.08 [27]
Ca	1.03-1.98	1.00-1.96	0.17 [27]	0.12 [27]
Mg	1.00-1.92	1.01-1.99	0.19 [27]	0.31 [27]

Botaro et al. [28] are reported lead concentrations, since frozen shrimp presented markedly lower lead concentrations (0.30-0.85 mg kg^{-1}) than fresh shrimp (0.92-2.89 mg kg^{-1}). The shrimp freezing process consists of a preliminary washing thoroughly in chlorinated water (5 ppm) to remove any remaining mud or sand, and to reduce bacterial contamination. The shrimp are drained as much as possible and then ready for freezing through quick-freezing tunnel (individually quick frozen). The is an evidence indicating that this process contributed to reduce trace metals levels in frozen shrimp, but is clear that lead, arsenic and mercury levels are markedly lower in frozen than fresh shrimp [28].

Globally, further reduction in the levels of environmental contaminants emanating from power plants and other industrial emissions and effluent discharges are highly needed to reduce contaminant inputs into the aquatic environments. More research and assessments of seafood quality is needed in many countries to provide more data and help safeguard the health of humans [29].

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