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MINERAL AND TRACE ELEMENT CONTENTS OF WARTY CRAB (*Eriphia verrucosa*) AND BROWN SHRIMP (*Crangon crangon*)

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ABSTRACT

This paper presents data on the mineral and trace element contents of warty crab and brown shrimp caught along Sinop coast of the Middle Black Sea. Mineral and trace element analysis of the samples were done by TUBITAK Marmara Scientific Research Center (Gebze-TURKEY). Minerals were determined according to AOAC (1998); trace elements were determined according to AOAC (1999); arsenic (Ar) was determined according to EPA (1992) and mercury (Hg) quantities were determined according to EPA (1994) methods. P, Zn, K and Na amounts in crab and P, Fe and Mg amounts in shrimp meats were higher than daily consumption limits. The amount of all mineral substances other than potassium in the shrimp and crab was significantly different from each other ($P<0.05$). P, Ca, Cu, Zn, Ni, Cr and Mn contents in the shrimp were less than crab while Fe, Ni, and Mg contents in crab were less than shrimp ($P<0,05$). The ratios of minerals in the crab and shrimp were P> K> Na> Ca> Mg> Zn> Cu> Fe> Mn> Cr> Ni and K> P> Na> Ca> Mg> Fe> Cu> Zn> Mn> Cr> N, respectively. The trace elements (Ar, Hg, Cd, Pb) detected in crab and shrimp. Except for Ar, trace element contents were higher in crab than in the shrimp. The trace element contents of the crab and shrimp were within food safety limits recommended by FAO/WHO, European Union and Turkish Food Codex. However, Pb contents of crab (1.27 $\mu g\ g^{-1}$) were over of the acceptability limit values.

Key Words: Trace elements, Minerals, Crab, Brown shrimp

INTRODUCTION

Fish and shellfish, which have rich for protein and essential fatty acid contents, are a valuable food in terms of their mineral and vitamin values (Horrocks and Yeo 1999). The meat of the crab and shrimp contains minerals like calcium (Ca), magnesium (Mg) and phosphor (P) which are essential for tooth and bone developments of especially children. Iron (Fe), copper (Cu), zinc (Zn) and manganese (Mn) are constitutive elements because they have a role in biological systems. But trace elements like cadmium (Cd), lead (Pb), mercury (Hg) and arsenic (Ar) have lethal effect in human body even existing in small quantities (Sivaperumal et al. 2007).

The Trace elements pollution in lake, river and marine environment has increased as a result of industrialization, advancing modern technology in agriculture, rising use of fertilizer and urbanization. Intensity of them in aquatic environment has considerably affected the water quality (Kalay and Karataş 1999; Bat and Öztürk 1997). Increase of heavy metal levels in water has an impact on the utilizable water requirement and damage to marine species (Canlı et al. 1988).

Atomic weights of the heavy metals are ranged from 63.5 to 200.6. Trace elements and their compounds are not degradable and cannot be removed from the body and they have carcinogenic and poisonous effects. Trace element drained into the water environment can damage both marine species diversity and ecosystems and can be accumulated in marine organisms and transferred to human body owing to the food chain (Matta et al. 1999). During the spawning period, many marine species, including the commercially valuable shrimp and fish are found near the seabed and coastal areas, so they are directly affected by the flow of chemical contaminants into the marine ecosystem (Gibson 1994). Investigation of the chemical pollutants in the marine species became necessary to determine hazardous levels. Accepted limit values of Cu, Zn, Pb, Cd are 20, 50, 2 and 1 mg kg^{-1} for the shellfish, respectively (Matta et al. 1999; FAO/WHO, 1986).

The aim of this study was to determine the mineral (phosphorus, iron, calcium, nickel, copper, zinc, potassium, sodium, chromium, manganese) and trace elements (arsenic, mercury, cadmium, lead, cobalt) contents of crab and shrimp in the Sinop-Middle Black Sea.

Figure 1. Sampling area for collecting shrimp and crab in Sinop, Turkey

MATERIALS AND METHODS

Raw Materials

Crab and shrimp samples were caught along Sinop coast, one sampling time in March (shrimp) and May (crab) 2011. The crabs were caught at depths of 10-20 m by free-diving. The shrimps were collected with beam trawl (10 mm mesh aperture and 3 m length) at depths of 0-30 m. A total of 20 crab and 75 shrimp were used to determine meat yield, mineral and trace element contents. After the operation, the catch was stored in a cold room for measuring all the crabs and shrimps by width, length and weight to the nearest millimeter for the first two categories and to the nearest gram for the last. the length and weight were measured. Then edible meat of the shrimp and crab was stored for mineral and trace element analysis at -80°C in a deep freezer.

Mineral and Trace element Contents

Mineral and trace element analysis of the samples were done by TUBITAK Marmara Scientific Research Center (Gebze-TURKEY). Phosphorus (P), calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), chromium (Cr) and manganese (Mn) were determined according to AOAC (1998); iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb) and cobalt (Co) were determined according to AOAC (1999); arsenic (Ar) was determined according to EPA (1992) and mercury (Hg) quantities were determined according to EPA (1994) methods. Analyses were performed in triplicate.

Statistical Analysis

The Minitab 13.20 (Minitab Inc., State College, PA, USA) program was used to determine significant differences among the mean values of the results. Differences between species were analysed by one-way analysis of variance (ANOVA) and Tukey (Sümbüloglu and Sümbüloglu, 2000). The P value ($P<0.05$) was used to determine significant differences.

RESULTS AND DISCUSSION

The average length, weight and meat yield values for crab and shrimp were 6.93±0.283 and 5.15±0.123 cm, 154.92±18.133 and 1.03±0.105 g and 23.53±0.924 and 41.10±0.331%, respectively (Table 1).

Table 1. The length, weight and meat yield of crab and shrimp.

Samples	Carapace Lenght (cm)	Weight (g)	Meat yield (%)
Crab	6.93 ±0.28	154.92 ±18.13	23.53 ±0.924
Brown shrimp	5.15 ±0.12	1.03 ±0.11	41.10 ±0.331

The results are expressed as mean±standard error $n_{crab}=20$, $n_{shrimp}=75$

The Minerals and Trace Elements

Significant differences were determined in the mineral and trace element amounts of crab and shrimp meats ($P<0.05$) (Table 2).

P, Zn, K and Na amounts in crab and P, Fe and Mg amounts in shrimp meats were higher than the daily accepted limits. The amount of all mineral substances other than potassium in the shrimp and crab was significantly different from each other ($P<0.05$). P, Ca, Cu, Zn, Ni, Cr and Mn contents in the shrimp were less than crab while Fe, Ni, and Mg contents in crab were less than shrimp ($P<0,05$). The ratios of minerals in the crab and shrimp were P> K> Na> Ca> Mg> Zn> Cu> Fe> Mn> Cr> Ni and K> P> Na> Ca> Mg> Fe> Cu> Zn> Mn> Cr> N, respectively. It can be said that both shrimp and crab are good sources for minerals (Table 2).

Table 2. Minerals and trace element contents in crab and shrimp meat.

Minerals	Maximum levels (mg 100 g^{-1})*	Crab mg100 g^{-1}	Shrimp mg100 g^{-1}
Phosphor (P)	1200[I]	3119 ±116[b]	2118 ±29.00[a]
Iron (Fe)	20[I]	12.92 ±0.28[a]	24.82 ±0.19[b]
Calcium (Ca)	1000[I]	896.8 ±5.60[b]	387.1 ±2.13[a]
Nickel (Ni)	0.5[I]	0.12 ±0.00[a]	0.36 ±0.00[b]
Copper (Cu)	20[I]	19.99 ±0.08[b]	13.13 ±0.88[a]
Zinc (Zn)	50[II]	53.25 ±0.10[b]	12.27 ±0.02[a]
Magnesium (Mg)	150[I,II]	101.4 ±1.77[a]	323.4 ±0.72[b]
Potassium (K)	3000[III]	3035 ±7.60[a]	2883 ±0.87[a]
Sodium (Na)	2000[III]	2300 ±5.50[b]	1662 ±0.21[a]
Chrome (Cr)	1000[III]	2.31 ±0.02[b]	1.42 ±0.03[a]
Cobalt (Co)	5[II,IV]	3.32 ±0.11[b]	1.91 ±0.14[a]
Trace elements	**Accepted limits (µg g^{-1})***		
Arsenic (Ar)	0.1[IV]-1[II]	0.02 ±0.00[a]	0.02 ±0.00[a]
Mercury (Hg)	0.5[III,IV]	0.29 ±0.00[a]	0.24 ±0.00[b]
Cadmium (Cd)	0.1[III]-0.5[II]	0.04 ±0.00[b]	0.01 ±0.00[a]
Lead (Pb)	1[IV]	1.27 ±0.07[b]	0.79 ±0.01[a]

[a,b]: Differences between groups expressed with different letters in the same row are important ($P<0,05$)

*: References (ANONYMOUS, 2002[I]; ANONYMOUS, 2003[II]; ANONYMOUS, 2010[III]; FAO/WHO 1986[IV])

In a study investigating of mineral contents of the blue crab, Ca, Mg, P, K and Na values were reported as 398.2, 117.06, 176.24, 69.15 and 663.95 mg 100 g^{-1}, respectively (Küçükgülmez et al. 2006). In another study related to *Charybdis natator* crab, it was stated that Fe, Na, K, Ca, Mn, Mg, Cu, Zn, Hg and Cd contents were 4.95, 134, 106, 47.54, 5.54, 68.82, 0.01, 1.26, 0.01 and 0.02 mg 100 g^{-1}, respectively (Soundarapandian et al. 2013).

Table 2 shows the trace elements (Ar, Hg, Cd, Pb, Co) detected in crab and shrimp. Except for Ar, heavy metal contents were higher in crab than in the shrimp. On the other hand, except for the high lead content in crab, all heavy metals in both crab and shrimp were in acceptable limits. The ratio of heavy metals in the crab and shrimp was Co> Pb> Hg> Cd> Ar and Co> Pb> Hg> Ar> Cd, respectively.

Debaka et al. (2004) reported that, average mercury concentrations ranged from 0.011 µg g^{-1} for oysters to 1.82 µg g^{-1} for swordfish in Canada where the samples were bought from a retailer. The highest mercury content in swordfish was explained by the predatory habit of the species.

Total mercury concentrations were measured in fish and shellfish and their products imported into the UK and in UK-produced farmed salmon and trout by Knowles et al. (2003). The highest levels of total mercury were in billfish (swordfish and marlin) and shark.

Cu, Zn, Pb and Cd contents were determined in 3 molluscs (*Octopus vulgaris*, *Sepia officinalis*, *Loligo vulgaris*) and in one crustacean sample (*Parapenaeus longirostris*) caught in the Gulf of Antalya. In molluscs, Cu content was between 1,82 and 6,22 mg kg^{-1} and in crustacean it was between 4.24 and 7.40 mg kg^{-1}. In the mollusc and crustacean Zn content was 10,95-21,52 mg kg^{-}1 and 11.73-14.27 mg kg^{-1}, respectively. While Pb was not found, Cd content changed from 0.26 to 0.28 mg kg^{-1} in crustacea. The researchers declared that there was no serious hazard in samples in terms of the heavy metals contents. In addition, the authors reported that the mollusc and crustacean species and fishing period effective on the amount of Cu and Zn (Yazkan et al., 2004). In an another study related with trace element contents of North Sea shrimp (*Crangon crangon*), Pb, Cd, Hg were 0.013-0.024, 0.019-0.067 and 0.025-0.040 mg kg^{-1} in May and November, respectively (Marx and Brunner, 1998).

The researchers declared that all of the samples contained lower amounts of the investigated elements than the levels of the concern of the Federal Institute for Health Protection of Consumers and Veterinary Medicine (i.e. 0.5 mg Pb kg^{-1}, 0.1 mg Cd^{-1} and 0.5 mg Hg^{-1} wet weight). Most of the samples showed significantly lower levels of contamination. The main reasons for the overall low levels of contamination might be the short period of feeding of the shrimp and with respect to Pb, an active mechanism of secretion (Marx and Brunner, 1998). In the present study it was showed that Pb, Cd and Hg in shrimp *(Crangon crangon)* were lower amounts than the acceptable levels (Table 1).

Gökoglu et al. (2008) investigated the contents of trace elements in some species of shrimp. Cu amounts were 6.19, 1.33, 5.59 µg g^{-1}; Cd amounts were 2.36, 0.23, 0.88 µg g^{-1}; Zn amounts were 30.84, 14.57, 6.25 µg g^{-1} for *Penaeus semisulcatus, Parapenaeus longirostris* and *Paleomon serratus*, respectively. Fe amounts were 33.89, 11.81, 1.84 µg g^{-1} and Mn amounts were 0.60, 1.52, 0.25 µg g^{-1} for the same species, respectively. Significant differences were detected among the species ($P<0.05$). As seen in the present study, factors such as species and hunting region may affect the accumulation of trace elements.

Yılmaz and Yılmaz (2007) investigated the seasonal changes in trace elements (Ag, Cr, Ni, Pb, Cu, Fe, Zn) concentrations in different tissue of both male and female green tiger shrimp (*Penaeus semisulcatus*) from İskenderun Bay (Northern East Mediterranean Sea, Turkey). trace element contents varied with type of metals, season and sex. Accumulations also were differed significantly in certain organs. Metal concentrations were higher in male gonads whereas the lowest in the muscle of all shrimp species.

Hashmi et al. (2002) examined the concentrations of a number of heavy metals, including Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn in muscle tissue of tiger prawn (*Penaeus monodon*). This species seemed to resist the build-up of certain metals, whereas it allowed the entry of others to the extent of exceeding the proportion that occurred in the environment. Some of the controlling factors include the nature of the metals, environmental factors, the body's reaction, physiological tolerance, tissue threshold and regulatory mechanism.

Sivaperumal et al., (2007) indicated that the marginally higher concentrations of Cd, Pb and Hg in fish sampled in a market could be related to industrialization and related activities in these areas. Metal contents in fish and shellfish from internal markets around Cochin and indirectly indicate the environmental contamination along the Cochin coastal area (Sivaperumal et al. 2007).

CONCLUSION

This study was carried out to provide information on mineral and heavy metal concentrations in crab and shrimp caught from Sinop region of Turkey. According to the results of the study, shrimp and crab in the Sinop region are a good source of minerals. Except for the high lead content in crab, all heavy metals in both crab and shrimp were in acceptable limits. Shrimp can be consumed safely in terms of heavy metal content.

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