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Original Research

Heavy Metal Concentrations (Cd, Pb, Cu, Zn, Fe) in Giant Red Shrimp (*Aristaeomorpha foliacea* Risso 1827) from the Mediterranean Sea

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Abstract

This study was carried out to detect concentrations of heavy metals (Cd, Pb, Cu, Zn, Fe) in the muscle and liver of female and male specimens of commercially important giant red shrimp (*Aristaeomorpha foliacea*) obtained from the Mediterranean Sea. Samples of species were collected in summer and winter. The results show that the concentrations of heavy metals in liver for male and female shrimps were higher than those in muscle. Also, the average Cd, Pb, Cu, Zn, and Fe concentrations in both liver and muscle for male shrimp were slightly higher than the average levels of female shrimp. Significant differences were observed only for Cu in liver and for Fe in muscle ($p<0.05$). The comparison of our results with the International Standards showed that the concentrations of Cd, Pb, Cu, Zn, and Fe in the muscle tissue is less than the authorized range of WHO and FDA standards.

Keywords: heavy metals, giant red shrimp, Mediterranean Sea, *Aristaeomorpha foliacea*

Introduction

The giant red shrimp *Aristaeomorpha foliacea* (Risso 1827) belongs to the family Aristeidae, which includes other important species such as the blue and red shrimps (*Aristeus antennatus* Risso 1816) and scarlet shrimp (*Plesiopenaeus edwarsianus* Johnson 1868) [1]. *A. foliacea* is widely distributed in the eastern and western Atlantic, Indian Ocean, and western Pacific, in the waters of Japan, Austalia, New Zealand, and in the Mediterranean Sea. In the Mediterranean the species inhabits muddy bottoms of the continental slope between approximately 100 and 1200 meters depth. This species plays an important role in the ovearall biomas of the Mediterranean and represents an important commercial resource among the other shrimp species since 1959 [2-4]. Due to its economic relevance, there are many studies on this species in the Mediterranean, but not much known about concentrations of heavy metals in the muscle and liver.

Heavy metals are of particular concern due to their toxicity and ability to be bioaccumulated in aquatic ecosystems. In general, they are not biodegradable and have long biological halflives. According to the World Health Organization (WHO), heavy metals must be controlled in food sources in order to assure public safety [5]. Heavy metals are taken up and accumulated by aquatic organisms both from the surrounding medium and via food sources. The extent of heavy metal accumulation is affected by external (dissolved metals, physicochemistry, dissolved oxygen, interactions between metals, sediment, food, seasonal effects, geographical differences) and internal (individual variability, body size and development stage, sex, breeding condition, brooding, moulting and growth, behaviour) factors [6]. Aquatic organisms, especially marine

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Table 1. The mean weights (g) of female (F) and male (M) shrimp in summer and winter.

Parameter	Sex	Summer	Winter
Weight±SD	F	20.72±2.45	29.96±6.53
	M	13.22±2.20	12.26±2.07

invertebrates such as mussels, oysters, or lobster, are used to observe sea pollution [7] and their livers are also a good indicator of the presence of contaminants in the medium. Liver plays an important role in the storage, redistribution, detoxification, and transformation of contaminants [8].

The utilization of marine shrimps as bioindicators of heavy metal pollution in environmental monitoring studies has been emphasized by many investigators. Meanwhile, shrimp are widely consumed in many parts of the world by humans, and polluted shrimps may endanger human health. During the last several decades, heavy metals pollution in the aquatic environment has become a serious problem and concentrations in these organisms can be influenced by many environmental and biological factors [5, 9, 10].

The present study aims to highlight the level of five metals, namely cadmium (Cd) , lead (Pb), copper (Cu), zinc (Zn), and iron (Fe) in liver and muscle tissue of commercially important female and male species of shrimp (*A. foliacea)*, contributing to the effective monitoring of both environmental quality and the health of the organisms collected from the Mediterranean in winter and summer.

Materials and Methods

Collection and Preparation of Samples

The samples were caught by bottom trawlers at between 450 and 500 m depth during summer and winter 2013 in the Mediterranean from Turkey (36º22'707" N-24º25' 941"/ 36º14'919" N-34º19'163" E).

Immediately after collection shrimp were stored in a container, preserved in crushed ice, and transferred to the laboratory, where the muscle, liver, and shell were separated and placed in labeled polyethylene bags respectively and stored at -20ºC until processing for metal analysis. For each season, 20 female and 20 male samples of *A. foliacea* were obtained by random sub-sampling.

Determination of Heavy Metals

The muscle and liver samples were transported with dry ice to the Accredited Industrial Services Laboratory of Turkey/Istanbul. 2 g of shrimp muscle and liver (wet weight) were weighed and placed in a digestion vessel with 5ml of concentrated (65%) nitric acid (HNO_3) and 2 ml (30%) hydrogen peroxide (H_2O_2) and digested in a microwave oven system [11]. Graphite Furnace Atomic Absorption Spectrometry (GFAAS) was used for determination of Cd, Pb, Cu, Zn, and Fe in the samples. The concentrations were expressed as μg/g wet weight. The precision of the analytical procedure was verified by analysis of certified reference materials (SRM-2976). Mean values and standard deviations of the measured metal concentrations in the reference materials were within 10% of the certified ranges.

Data Analysis

For data analysis, independent samples t-test was employed by using SPSS 15.0 Windows Software. Statistical significance was defined at $p<0.05$. The mean values were obtained from 3 experiments and reported as X±SD.

Results and Discussion

Table 1 shows mean weights (g) of female and male species of shrimp (*Aristaeomorpha foliacea*) in summer and winter. The mean weights for female shrimp were found to be higher than mean weights for male shrimp during both seasons. Similar results were reported by Yılmaz and Yılmaz [12] for *Penaeus semisulcatus* collected from the Mediterranean of Turkey and also by Turkmen [13] and Cevik et al. [10] for *Penaeus kerathurus* and *Parapenaeus longirostris,* respectively. These results are consistent with the above-reported for some shrimp species.

There are highly significant differences among the marine organism organs for the accumulation of heavy metals. In fact, the elements Cd, Pb, Cu, Zn, and Fe are expected to vary in a wide range of concentrations cause they reflect the exposure to environmental levels and feeding behaviour [14]. Among the five metals studied in the present study, Zn, Cu, and Fe are essential elements while Pb and Cd are non-essential elements for most of the living organisms.

Tables 2 and 3 record the results of the concentrations of heavy metals (Cd, Pb, Cu, Zn, and Fe) in representative samples of muscle and liver from female and male *A. foliacea*, respectively. Permissible limits and various results of heavy metal concentrations for the selected shrimps are summarized in Table 4 for comparison.

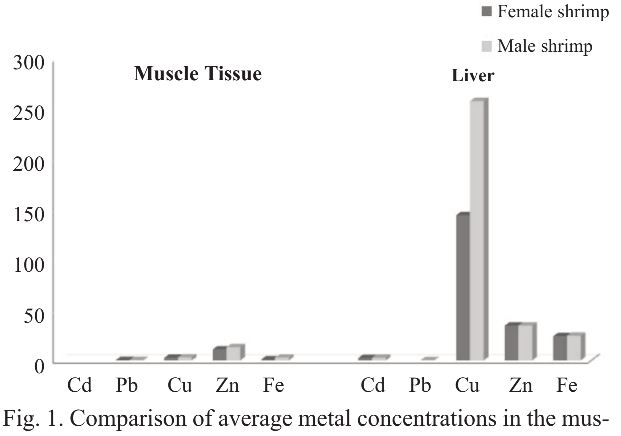

Fig. 1. Comparison of average metal concentrations in the muscle tissue and the liver of female and male shrimp (*Aristaeomorpha foliacea*) (μg/g).

Table 2. Concentrations of heavy metal in muscle tissue and liver of female shrimp (*Aristaeomorpha foliacea*) in summer and winter (μg/g).

Seasons	Muscle					Liver				
	Cd	Pb	Cu	Zn	Fe	Cd	Pb	Cu	Zn	Fe
Summer	n.d	n.d	3.43^{a}±0.02	11.33^{a}±0.02	1.08^{a}±0.08	4.76^{a}±0.35	n.d	126.0^{a}±1.11	30.45^{a}±2.75	19.69^{a}±0.99
Winter	n.d	0.43±0.01	1.99^{b}±0.01	10.99^{b}±0.04	1.10^{a}±0.10	0.24^{b}±0.04	n.d	162.24^{b}±7.51	39.13^{b}±1.16	28.74^{b}±2.52
Average	-	0.43	2.71^{a}±0.78	11.16^{a}±0.18	1.09^{a}±0.08	2.50^{a}±2.48	-	144.12^{a}±20.42	34.79^{a}±5.11	24.21^{a}±5.24

n.d.: below detection limit; limits of detection of measurements are 2.5 ppb for Cd and 1 ppb for Pb; data are expressed as mean±SD of triplicate measurements

Different superscripts in a column show significant differences between samples ($p<0.05$)

Table 3. Concentrations of heavy metal in muscle tissue and liver of male shrimp (*Aristaeomorpha foliacea*) in summer and winter (μg/g).

Seasons	Muscle					Liver				
	Cd	Pb	Cu	Zn	Fe	Cd	Pb	Cu	Zn	Fe
Summer	n.d	n.d	4.26^{a}±0.02	16.06^{a}±1.30	1.44^{a}±0.31	4.64^{a}±0.40	n.d	167.1^{a}±10.34	28.4^{a}±3.80	17.16^{a}±3.63
Winter	n.d	0.43±0.01	1.88^{b}±0.02	10.69^{b}±1.15	4.26^{b}±0.05	0.79^{b}±0.01	0.36±0.00	348.67^{b}±28.43	41.37^{b}±1.32	32.36^{b}±2.08
Average	-	0.43	3.07^{a}±1.27	13.37^{a}±3.09	2.85^{b}±1.55	2.71^{a}±2.12	0.36	257.88^{b}±101.27	34.88^{a}±7.50	24.76^{a}±8.73

n.d.: below detection limit; limits of detection of measurements are 2.5 ppb for Cd and 1 ppb for Pb); data are expressed as mean±SD of triplicate measurements

Different superscripts in a column show significant differences between samples ($p<0.05$)

The average Cu, Zn, and Fe muscle tissue concentrations in males were slightly higher than the average levels for females. Significant differences were observed only for Fe ($p<0.05$) when compared with each other. The order of average heavy metal concentrations found in muscle tissue samples in both male and female species was: Zn>Cu>Fe>Pb>Cd (Fig. 1). Similarly, the average Cd, Pb, Cu, Zn, and Fe concentrations in liver for males were slightly higher than the average levels for females. Significant differences were observed only for Cu ($p<0.05$) when compared with each other. The mean concentrations of heavy metals in liver were: Cu>Zn>Fe>Cd>Pb (Fig. 1). It was reported that the relationship between metal accumulation and sex may be due to the difference in metabolic activities between the males and the females, and the faster-growing sex (usually the female) can be expected to contain lower concentrations of metals [12, 15]. Thus, the mean concentrations of these metals in males were found to be slightly higher than the females (Fig. 1).

The highest concentrations of Zn and Cu were recorded in summer, which were 16.06 μg/g and 4.26 μg/g, respectively, while the lowest concentrations were recorded in winter, which were 10.69 μg/g and 1.88 μg/g in muscle of male shrimp ($p<0.05$). The main reason for this is thought to be related to variation in seasonal feeding habits and habitats.

Zn, Cu, and Fe were detected regularly in all the samples and the Zn concentrations in the muscle samples in both males and females were found to be relatively higher when compared to other metals concentrations in the same samples. Zn, being an essential element for normal growth and metabolism of organisms, exhibited highest accumulation in the shrimp samples when compared with the other metals [16]. According to Pourang et al. [17], Zn is the most abundant element in the muscle followed by Cu. Our results are in agreement with the results reported on Zn and Cu.

In the liver the highest mean concentration was obtained as 257.88 μg/g in male and 144.12 μg/g in female shrimp for Cu. As the distribution of Cu are in the order of gills>liver>stomach>kidney>bones>muscle [18], the levels of Cu in liver were higher than the levels of Zn, Fe, Cd, and Pb. The highest concentration of Cu was detected in winter, which was 348.67 μg/g for male and 162.24 μg/g for female shrimp, while the lowest concentration was recorded in summer, which was 126.0 μg/g for female and 167.1 μg/g for male shrimp. Although livers are not consumed, it may represent good biomonitors of metals present in the surrounding environment. The results showed that the concentrations of heavy metal in liver and in muscle tissue were significantly affected by the seasons in which they were caught, except Fe in muscle tissue for female shrimp ($p<0.05$). The present study also showed that the concentrations of heavy metals in liver for males and females were higher than those in muscle, which is generally related to physiological activities of organs. Muscle is not an active tissue regarding the accumulation of metals. Liver plays an important role in accumulation and detoxification of heavy metals. For instance, Cu and Zn are involved in enzyme activities in liver, consequently higher quantities of these elements are accumulated in liver [18-20]. Thus the liver in marine organisms are more often recommended as environmental indicator organs of water pollution than other marine organism organs [19, 21]. Similar results were reported by several studies showing that muscle is not an active tissue in accumulating heavy metals. Tapia et al. [8] determined that the concentrations of the metals are higher

Table 4. Heavy metals concentrations in crustaceans collected from different parts of the world.

Region	Metals	Species	Muscle	Liver	Author	Permissible Limits
Gulf of Antalya/Turkey	Cu	*Penaeus semisulcatus*	6.19		[6]	20 µg/g
Gulf of Antalya/Turkey-Marmara Sea Coast in Tekirdağ		*Parapenaeus longirostris*	1.33-25.48		[6, 7]	
Gulf of Antalya/Turkey		*Paleomon serratus*	5.59		[6]	
Zhanjiang Harbour Bay		*Litopenaeus vannamei*	30.37	47.27	[24]	
Persian Gulf /Iran		*Fenneropenaeus merguiensis*	1.26		[26]	
İzmir Bay/Turkey		*Penaeus kerathurus*	19.14-27.42		[13]	
Gulf of Antalya/Turkey	Cd	*Penaeus semisulcatus*	2.36		[6]	0.05 µg/g
Gulf of Antalya/Turkey		*Parapenaeus longirostris*	0.23		[6]	
		Paleomon serratus	0.88		[6]	
Zhanjiang Harbour Bay		*Litopenaeus vannamei*	n.d	1.97	[24]	
İzmir Bay/Turkey		*Penaeus kerathurus*	0.02-0.20		[13]	
Gulf of Antalya/Turkey	Zn	*Penaeus semisulcatus*	30.84		[6]	50 µg/g
Marmara Sea Coast in Tekirdağ/Turkey		*Parapenaeus longirostris*	12.16-22.42		[7]	
Gulf of Antalya/Turkey		*Paleomon serratus*	6.25		[6]	
Zhanjiang Harbour Bay		*Litopenaeus vannamei*	98.71	93.97	[24]	
Persian Gulf /Iran		*Fenneropenaeus merguiensis*	13.18		[26]	
İzmir Bay/Turkey		*Penaeus kerathurus*	44.2-62.13		[13]	
Gulf of Antalya/Turkey	Fe	*Penaeus semisulcatus*	33.89		[6]	30 µg/g
Gulf of Antalya/Turkey		*Parapenaeus longirostris*	11.81		[6]	
Zhanjiang Harbour Bay		*Litopenaeus vannamei*	149.01	51.71	[24]	
Persian Gulf /Iran		*Fenneropenaeus merguiensis*	15.13		[26]	
İzmir Bay/Turkey		*Penaeus kerathurus*	21.48-32.36		[13]	
Marmara Sea Coast in Tekirdağ/Turkey	Pb	*Parapenaeus longirostris*	0.51-2.12		[7]	0.5 µg/g
İzmir Bay/Turkey		*Penaeus kerathurus*	0.37-0.86		[13]	

in the samples of liver than in the muscle tissue samples, in both male and female marine organisms. In a study, Hoseini and Tahami [22] reported that the bioaccumulation of heavy metals in liver tissue is higher than muscle tissue in aquatic organisms. Canli and Atli [23] pointed out that Cd and Cu concentrations in liver of Mediterranean fish species are higher than the muscle tissues of the fishes. Wu and Yang [24] identified that Cu and Fe mean concentrations in liver are significantly higher than levels noted in muscle of white shrimp *Litopenaeus vannamei*. The mean heavy metal concentrations in the liver of *Aristaeomorpha foliacea* were found to be compatible with the previous studies on some aquatic species. The comparison of mean concentrations of metals in muscle tissues of shrimp (Table 4) shows that the metal levels of muscle tissues are variable in organisms. The mean metal concentrations in the muscle tissues of female and male species of *Aristaeomorpha foliacea* were found to be much lower than the maximum permitted concentrations proposed by FAO and WHO [25], and almost all metals measured in this study are relatively lower than the values recorded in aquatic organisms from other regions of the world and Turkey (mentioned in Table 4).

Conclusion

The result of the present study indicated that *Aristaeomorpha foliacea* from the Mediterranean Sea of Turkey were safe to consume since the metal (Cu, Zn, Cd, Fe, and Pb) concentrations were below international admissible limits for human consumption. But it may be suggested that continuous care must be taken, especially according to the season, to biomonitor the heavy metal levels if they exceed the maximum permitted concentrations for human consumption. On the other hand, high levels of heavy metals were found in liver of *Aristaeomorpha foliacea*. Especially, average Cu value in liver in both males and females was the highest. Although livers are not consumed, they may represent good biomonitors of metals present in the surrounding environment.

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