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Essential and Non-Essential Metal Concentrations in Shrimps from Iskenderun Bay, Türkiye

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Abstract: Contamination of the aquatic environment and living things with pollutants is increasing daily. Among these pollutants, heavy metals come to the forefront regarding toxicological and public health due to their widespread use, toxicity, and resistance to degradation, as well as accumulation and biomagnification in the food chain. The study aimed to determine the essential (Cr, Cu, Fe, Mn, Ni, Zn) and non-essential (As, Al, Cd, Pb) metal concentrations by ICP-OES of *Metapenaeus monoceros, Penaeus japonicus, Penaeus semisulcatus* (n=30) caught from the Northeastern Mediterranean, Iskenderun Bay. The concentration of Cd, Cr, Ni, and Pb were under LOD. The concentration (ppm) ranges were Al: 0.73-38.89, As: 2.18-9.68, Cu: 28.96-69.01, Fe: 7.85-241.36, Mn: 0.44-1.28, and Zn: 51.71-108.51 for all species. Except for the As concentrations, the differences between mean concentrations of metals in shrimp species were not statistically significant. When the results of the study are compared with the findings of other studies on shrimps caught from the Iskenderun Bay, it shows that Cd, Cr, Ni, and Pb contamination levels decreased, while Cu, Fe, and Zn contamination levels increased.
Keywords: *Essential metals, Non-essential metals, Metapenaeus monoceros, Penaeus japonicus, Penaeus semisulcatus, Iskenderun Bay.*

Türkiye İskenderun Körfezi, Karideslerinde Esansiyel ve Non-Esansiyel Metal Konsantrasyonları

Özet: Akuatik ortam ve canlıların kirleticilerle kontaminasyonu gün geçtikçe artmaktadır. Bu kirleticiler arasında ağır metaller yaygın kullanım, toksisite ve bozunmaya karşı dayanıklılığı yanında besin zincirinde birikim ve biyomagnifikasyonu nedeniyle toksikolojik ve halk sağlığı açısından ön plana çıkmaktadır. Çalışmanın amacı Kuzeydoğu Akdeniz, İskenderun Körfezi'nden avlanan *Metapenaeus monoceros, Penaeus japonicus, Penaeus semisulcatus* karideslerinde (n=30) esansiyel (Cr, Cu, Fe, Mn, Ni, Zn) ve non-esansiyel (As, Al, Cd, Pb) metal konsantrasyonlarının ICP-OES ile belirlenmesiydi. Cd, Cr, Ni ve Pb konsantrasyonu LOD'un altında tespit edilmiştir. Tüm türler için konsantrasyon (ppm) aralıkları Al: 0.73-38.89, As: 2.18-9.68, Cu: 28.96-69.01, Fe: 7.85-241.36, Mn: 0.44-1.28 ve Zn: 51.71-108.51 olarak tespit edildi. As konsantrasyonları dışında, karides türlerinde ortalama metal konsantrasyonları arasındaki farklar istatistiksel olarak önemsizdi. Çalışmanın sonuçları İskenderun Körfezi'nden avlanan karidesler üzerinde yapılan diğer çalışmaların bulguları ile karşılaştırıldığında, Cd, Cr, Ni ve Pb kontaminasyon düzeylerinin azaldığını, Cu, Fe ve Zn kontaminasyon düzeylerinin ise arttığını göstermektedir.
Anahtar Kelimeler: *Esansiyel metaller, Esansiyel olmayan metaller, Metapenaeus monoceros, Penaeus japonicus, Penaeus semisulcatus, İskenderun Körfezi.*

Introduction

Aquatic environments and living organisms in Turkey, like the rest of the world, are contaminated with toxic pollutants such as heavy metals, pesticides, and endocrine disruptors (Cucu et al., 2019; Esfahani et al., 2020; Jia et al., 2016; Nyantakyi et al., 2021; Yarsan and Yipel, 2013; Yipel and Yarsan, 2014). Because of their widespread use, toxicity, and resistance to biodegradation, as well as their accumulation and biomagnification in living beings in the food chain, heavy metals are significant among aquatic pollutants (Altınok-Yipel et al., 2022; Esfahani et al., 2020; Jia et al., 2016; Liu et al., 2019). Heavy metal contamination of aquatic environments thus poses potential risks to regional ecology, humans, and other living things at the top of the food chain (Altınok-Yipel et al., 2022; Esfahani et al., 2020; Yarsan and Yipel, 2013).

Using crustaceans and other aquatic organisms as bioindicators to investigate the level of heavy metal contamination in the environment is a common practice (Jia et al., 2016; Yarsan and Yipel, 2013; Yüzereroğlu et al., 2009). Moreover, human health risk assessments on aquatic organisms in the food chain are essential and current public health research topics (Baki et al., 2018; Ezemonye et al., 2019; Liu et al., 2019; Yu et al., 2020). Shrimp and other crustaceans are ideal bioindicators for aquatic contamination studies because of their hypersensitivity and rapid response to contaminants such as heavy metals (Maraschi et al., 2020; Suami et al., 2019). Since shrimps have necessary amino acids, minerals, vitamins, and long-chain unsaturated fatty acids, they have a significant position in the food chain regarding nutrition (Liu et al., 2019). About 13.3% of all seafood caught in Turkey is shrimp (Ministry of Agriculture and Forestry, 2021). Iskenderun Bay, located in the Northeast Mediterranean, is an important ecological and economic region due to its aquatic biodiversity and aquaculture potential (Aytekin et al., 2019; Yipel and Tekeli, 2016). In addition, there are studies on the levels of metals reaching the Gulf of Iskenderun in aquaculture as a result of increased agricultural, urban, and industrial activity, as well as the potential health risks associated with human consumption of these products (Aytekin et al., 2019; Duysak and Ersoy, 2014; Kaya and Turkoglu, 2017; Kaymacı and Altun, 2016). Therefore, in similar studies, monitoring the metal levels of seafood products periodically and carrying out risk assessments based on their consumption is recommended (Asare et al., 2018; Rakib et al., 2021; Sobihah et al., 2018; Yipel et al., 2016).

The study aimed to determine the essential (Cr, Cu, Fe, Mn, Ni, Zn) and non-essential (As, Al, Cd, Pb) metal concentrations in *Metapenaeus monoceros*, *Penaeus japonicus*, *Penaeus semisulcatus* shrimps caught from Iskenderun Bay in the Northeast Mediterranean.

Materials and Methods

Materials

Shrimp samples of *Metapenaeus monoceros* (n=10), *Penaeus japonicus* (n=10), and *Penaeus semisulcatus* (n=10) species were collected from the local seafood markets, which shrimping in Iskenderun Bay, Northeast Mediterranean region and kept at -20 °C until analysis. The chemicals (Nitric acid, hydrogen peroxide) used in the study were of analytical purity. This study is not subject to HADYEK permission by Article 8 (k) of the "Regulation on Working Procedures and Principles of Animal Experiments Ethics Committees".

Methods

Samples (0.5 g) were burned with microwave digestion in nitric acid (8 mL, 65%) and hydrogen peroxide (2 mL, 30%) with a 15-minute ramp and hold procedure at 1200 W, 100% power, 800 psi, and 200 °C (Cem X Press, USA). Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to determine essential (Cr, Cu, Fe, Mn, Ni, and Zn) and non-essential (Al, As, Cd, and Pb) metal concentrations (Spectro, Germany). Method validation was carried out on parameters limit of detection (LOD) (ppb; Al: 0.49, As: 11.46, Cd: 1.43, Cr: 2.66, Cu: 2.19, Fe: 2.77, Mn: 1.76, Ni: 4.49, Pb: 9.97, Zn: 2.41), recovery (74.23-98.65%), relative standard deviation (RSD) (Al: 1.243, As: 0.599, Cd: 0.753, Cr: 1.177, Cu: 0.861, Fe: 0.752, Mn: 1.022, Ni: 0.770, Pb: 0.428 and Zn: 0.625), and correlation coefficient (R^2) (<0.999) parameters.

Statistical analysis: The data were statistically analyzed using one-way analysis of variance (ANOVA) and the post hoc Duncan test. P values less than <0.05 were considered statistically significant.

Results

The arithmetic and geometric mean, median, standard error, minimum and maximum concentrations (ppm) of essential (Cr, Cu, Fe, Mn, Ni, and Zn) and non-essential (Al, As, Cd, and Pb) elements in *Metapenaeus monoceros, Penaeus japonicus,* and *Penaeus semisulcatus* tissues were presented in Table 1 and Table 2. The concentration of Cd, Cr, Ni, and Pb were under LOD. The concentration (ppm) ranges of essential elements were Cu: 28.96-69.01, Fe: 7.85-241.36, Mn: 0.44-1.28, Zn: 51.71-108.51, and the concentration (ppm) ranges of non-essential elements were Al: 0.73-38.89 and As: 2.18-9.68 for three shrimp species. The mean concentrations are sorted for essentials as Zn>Cu>Fe>Mn and for non-essential as Al>As. Except for the As concentrations ($p<0.05$), the differences between mean concentrations of selected metals in shrimp species included in the study were not statistically significant.

Discussion and Conclusion

The consumption of shrimp and other seafood products is increasing because of their high nutritional value (protein, fat, vitamins, minerals, etc.). However, this increase also raises some concerns for public health due to the increased risk of contamination in the food chain brought on by the increased discharge of metals and other potentially toxic pollutants into the aquatic environment (Aytekin et al., 2019; Baki et al., 2018; Yarsan and Yipel, 2013; Yipel et al., 2014). According to recent studies, metal pollution in Iskenderun Bay, an important shrimp fishing area, has increased due to intense urban, agricultural, and industrial activities (Aytekin et al., 2019; Duysak and Uğurlu, 2020). Ag, Cu, Cr, Fe, Ni, Pb, and Zn concentrations in the tissues of *Penaeus semisulcatus* collected from the Iskenderun Bay were measured in the study published by Yılmaz and Yılmaz in 2007. Even though Yılmaz and Yılmaz stated that the amounts of Cr, Ni, and Pb (ppm) in the muscle tissues of *Penaeus*

Table 1. Essential metal concentrations (ppm) in tissues of *Metapenaeus monoceros, Penaeus semisulcatus,* and *Penaeus japonicus.*

Species		Cr	Cu	Fe	Mn	Ni	Zn
Metapenaeus monoceros	Mean	<LOD	45.29	24.71	0.92	<LOD	69.32
	Geometric Mean	<LOD	43.37	17.22	0.87	<LOD	67.83
	Std. Error of Mean	<LOD	5.99	7.38	0.13	<LOD	7.01
	Minimum	<LOD	29.67	2.28	0.57	<LOD	56.15
	Maximum	<LOD	65.51	50.45	1.28	<LOD	102.79
Penaeus semisulcatus	Mean	<LOD	43.43	29.13	0.87	<LOD	69.01
	Geometric Mean	<LOD	41.27	22.50	0.82	<LOD	67.02
	Std. Error of Mean	<LOD	6.47	8.88	0.12	<LOD	8.20
	Minimum	<LOD	28.96	7.85	0.53	<LOD	53.46
	Maximum	<LOD	69.01	64.78	1.26	<LOD	108.51
Penaeus japonicus	Mean	<LOD	31.72	96.17	0.74	<LOD	61.91
	Geometric Mean	<LOD	31.69	40.81	0.69	<LOD	60.54
	Std. Error of Mean	<LOD	0.58	46.16	0.13	<LOD	7.11
	Minimum	<LOD	30.14	4.97	0.44	<LOD	51.71
	Maximum	<LOD	33.27	241.36	1.16	<LOD	89.89
P value		-	0.231	0.114	0.613	-	0.303

Table 2. Non-essential metal concentrations (ppm) in tissues of *Metapenaeus monoceros, Penaeus semisulcatus,* and *Penaeus japonicus.*

Species		Al	As	Cd	Pb
Metapenaeus monoceros	Mean	15.46	7.69[a]	<LOD	<LOD
	Geometric Mean	7.77	7.59	<LOD	<LOD
	Std. Error of Mean	6.64	0.56	<LOD	<LOD
	Minimum	1.64	6.16	<LOD	<LOD
	Maximum	38.89	9.68	<LOD	<LOD
Penaeus semisulcatus	Mean	2.37	4.45[b]	<LOD	<LOD
	Geometric Mean	1.94	4.32	<LOD	<LOD
	Std. Error of Mean	0.64	0.52	<LOD	<LOD
	Minimum	0.73	3.40	<LOD	<LOD
	Maximum	4.97	6.90	<LOD	<LOD
Penaeus japonicus	Mean	2.32	3.42[b]	<LOD	<LOD
	Geometric Mean	2.02	3.31	<LOD	<LOD
	Std. Error of Mean	0.68	0.44	<LOD	<LOD
	Minimum	1.14	2.18	<LOD	<LOD
	Maximum	4.92	4.78	<LOD	<LOD
P value		0.108	0.005	-	-

semisulcatus were <LOD-13.1, 0.6-3.6, and 0.2-0.6, respectively, in their research, these metals could not be found in any of the three shrimp species in the current study (<LOD). In the same study, the range of muscle Cu concentration (ppm) was reported to be 17.2-42.4; however, in the current study, high average levels were found in the species *Penaeus semisulcatus* (43.43) and *Metapenaeus monoceros* (45.29). Muscle Fe concentration (ppm) was reported as 5.9-33.1 in the study, and the mean level determined in *Penaeus japonicus* (96.17) species was higher than in this study. Muscle Zn concentrations (ppm) have been reported to range between 4.3 and 10.3, with average levels determined in all three shrimp species being higher than in this study (Yılmaz and Yılmaz, 2007). In a study by Fırat et al. (2008) that Cu, Cd, Cr, Fe, and Zn concentrations (ppm) were found to be 34.24, 16.72, 60.38, 18.69, and 27.75, respectively, in *Penaeus semisulcatus* tissues that were caught in the Iskenderun Bay and metal levels other than Cd and Cr were lower than the current study results. Cu, Cd, Fe, Pb, and Zn concentrations were measured in the tissues of *Penaeus semisulcatus* caught in the Iskenderun Bay in the study published by Aytekin et al. (2019). While Cd and Pb concentrations (ppm) in the muscle tissues of *Penaeus semisulcatus* were reported by Aytekin et al. to range from 6.52 to 8.33 and 22.18 to 62.75, respectively, in the current findings, these two metals were not found in any shrimp species (<LOD). The same study showed the average amounts of Cu, Fe, and Zn in muscle as 19.35-34.23, 16.15-24.23, and 37.43-61.42, respectively. The current study found that all shrimp species had higher average concentrations of these three metals (Aytekin et al., 2019). Table 3 presents the research study on the shrimp species used in this study that was not conducted in Iskenderun Bay.

When the current study's findings are compared to those of other studies on shrimp caught in various parts of the world, it is clear that Cd, Cr, Ni, and Pb contamination levels are decreased, while Cu,

Table 3. Other studies that determined metal concentration in tissues of *Metapenaeus monoceros, Penaeus semisulcatus,* and *Penaeus japonicus*

Country	Area	Species	Method	Metal	Result ppm	Literature	Current study ppm
Democratic Republic of the Congo	Atlantic Coast	*Penaeus* spp.	ICP-MS	Cu	16.01 -18.71	Suami et. al., 2019	28.96 - 69.01
				Cr	0.08 -0.10		<LOD
				Ni	<LOD		<LOD
				Zn	55.90 -85.44		51.71 - 108.51
Iran	Persian Gulf	*Penaeus semisulcatus*	Neutron activation analysis	As	8.28	Heidarieh et. al., 2013	4.45
				Fe	288		29.13
				Mn	25.43		0.87
				Zn	68.73		69.01
Saudi Arabia	Red Sea Coast	*Penaeus semisulcatus*	AAS	Cu	5.33	El Gendy et. al., 2015	43.43
				Cd	1.57		<LOD
				Ni	0.8		<LOD
				Pb	2.33		<LOD
				Zn	17.33		69.01
Türkiye	Mersin	*Penaeus semisulcatus*	ICP-MS	Cu	2.98	Korkmaz et. al., 2019	43.43
				Cd	<LOD		<LOD
				Fe	6.64		29.13
				Pb	0.29		<LOD
				Zn	14.18		69.01
Egyptian	Mediterranean Coast	*Metapenaeus monoceros*	AAS	As	0.39	Abd-Elghany et. al., 2020	7.69
				Cd	0.24		<LOD
				Pb	1.13		<LOD
Mozambique	Maputo Bay (Bembe)	*Metapenaeus monoceros*	ICP-MS	As	9.9	Sturve et. al., 2021	7.69
				Cd	0.07		<LOD
				Cu	33		45.29
				Cr	<LOD		<LOD
				Mn	3.2		0.87
				Ni	0.19		<LOD
				Pb	<LOD		<LOD
				Zn	43.5		69.32
China	Beibu Gulf	*Penaeus japonicus*	AAS	As	0.65	Gu et. al., 2018	3.42
				Cu	3.78		31.72
				Cd	0.09		<LOD
				Cr	0.15		<LOD
				Pb	0.04		<LOD
				Zn	10		61.91

Fe, and Zn contamination levels are generally increased.

The Iskenderun Bay, which has significant ecological diversity and aquaculture potential, is known to be under high heavy metal contamination stress because of intensive anthropogenic activities. As a result, metal concentrations in gulf-caught shrimp and other fisheries are important environmental and public health parameters that should be monitored regularly in terms of both marine ecosystem health and human health through the food chain.

Early detection of the adverse effects of metals and other pollutants at the organism level is essential protecting the ecosystem's health in the region. On the other hand, risk assessment for consumers regarding metal and different pollutant concentrations in fisheries, which play an important role in the food chain, is vital to protecting public health.

Conflict of Interest

The authors stated that they did not have anyreal, potential or perceived conflict of interest.

Ethical Approval

This study is not subject to HADYEK permission in accordance with Article 8 (k) of the "Regulation on Working Procedures and Principles of Animal Experiments Ethics Committees".

Similarity Rate

We declare that the similarity rate of the article is 6% as stated in the report uploaded to the system.

Author Contributions

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Data Collection and / or Processing: MY, IOT
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