Influences of Sex and Seasons on Levels of Heavy Metals in Muscle Tissues of *Callinectes sapidus* Obtained from the Göksu Delta

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Abstract

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The levels of some heavy metals in muscle tissues of female and male *Callinectes sapidus* obtained from the Göksu Delta, between Autumn (2018)—Summer (2019) were determined by Inductively Coupled Plasma-Mass Spectroscopic (ICP-MS) methods and the results varied as follows; Al: 0.45–5.22 and 0.6–4.43, Fe: 1.49–25.52 and 4.62–6.60, Cu: 3.15–5.58 and 2.99–5.48, Zn: 41.95–63.04 and 41.51–56.75, As: <0.0001–3.70 and <0.0001–2.01 mg kg⁻¹ w.w respectively. The seasonal estimated weekly intakes (EWI), target hazard quotients (THQ) of metals and cancer risk (CR) levels of As were determined. The EWI levels of analyzed samples were found well below the provisional tolerable weekly intakes (PTWI) of the metals in all seasons. It was concluded that the consumption of female and male *C. sapidus* may cause carcinogenic and non-carcinogenic effects in terms of As target hazard quotients. Moreover, Zn levels in 30% of female and 17.5% of male individuals were found higher than standards which proposed by Turkish Food Codex.

Keywords Callinectes sapidus · Göksu Delta · North-East Mediterranean · Heavy metals · Health risk assessment

Introduction

Seafood such as fish, oysters, crab and shrimp are very important protein sources for humans due to their low calorie and fat content, high essential amino acids, vitamins and beneficial minerals (Skonberg and Perkins 2002; Baki et al. 2018). Polyunsaturated fatty acids of seafood such as omega-3 is known to reduce the risk of Alzheimer's and heart disease in humans (Cederholm 2017; Fakhri et al. 2018; Mazrouh and Mourad 2019). With the continuous improvement of living standards, human communities give more importance to nutrition and health, hence they consume more aquatic organisms such as fish and crustaceans each day (Guérin et al. 2011).

Blue crabs (*Callinectes sapidus*) originate from North America and are distributed in the Göksu Delta of the Mediterranean in Turkey (Bilen and Yesilyurt 2014). *C. sapidus* is one of the most important species among the crabs and 11 tons of *C. sapidus* were collected from the coastal regions of Turkey in 2018 (RTMAF 2020). Despite the economic

Gulsemin Sen Agilkaya gulseminsen@mersin.edu.tr and nutritious benefits of *C. sapidus*, they are highly susceptible to heavy metals because of their living habitats and they deposit more metals in their tissues than other aquatic species (Erdem 2015; Dizman et al. 2017). Additionally, *C. sapidus* and other crab species are considered as bioindicator organism in studies which investigate heavy metal contamination (Turoczy et al. 2001; El-Said et al. 2021) and metal accumulation varies with ecological factors, gender, size, and seasons (Yılmaz and Yılmaz 2007).

Göksu Delta is a geographical region formed by the Göksu River, located on the Mediterranean coast and in the south of Turkey's Mersin province. Delta is classified as an internationally important wetland according to the Ramsar Convention (Demirel et al. 2011a, b), and agricultural activities in Göksu intensively continue throughout the year due to its fertile soil and favorable climate. Pesticide and fertilizer usage is well above the country average because of the agricultural activities (Demirel et al. 2011a, b; Demir 2021) and it has been determined that the most used pesticides and fertilizers in the region contain various heavy metals (Demirel et al. 2011a, b). Moreover, the delta is also under the effects of anthropogenic pollution. Therefore, monitoring of metals and assessing their potential health risks in Göksu Delta is important for the safety and health of the ecosystem and the human populations that consume seafood

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derived from there. Moreover, in recent studies, it has been reported that aquatic foods obtained from the Mediterranean region contain high levels of arsenic, pose risks for human consumption, and do not comply with the codex standards in terms of zinc levels (Korkmaz et al. 2019a, b).

Hence, the influence of sex and seasons on levels of aluminum, iron, copper, zinc, arsenic, cadmium, and lead in the muscle tissues of *C. sapidus*, hunted from Göksu Delta were determined. After statistical evaluation, the results obtained from the muscle tissues were compared with the standards of the Turkish Food Codex (TFC) and the Food and Agriculture Organization of the United Nations (FAO 2015), and the estimated weekly intakes (EWI) calculated and compared for each metal with the provisional tolerable weekly limits (PTWI) of US Environmental Protection Agency (US EPA). Additionally, target hazard quotients (THQ) and cancer risk (CR) levels of the metals were evaluated for human consumption in muscle tissues of female and male *C. sapidus* obtained from Göksu Delta.

Material and Method

Sample Collection and Preparation

Female and male *C. sapidus* sampled from Göksu Delta between Autumn (2018)—Summer (2019) seasons, were brought to the Mersin University, Faculty of Fisheries and Basic Sciences Procedure Laboratory and the muscle tissues

of blue crabs were dissected and stored at -20 °C until analysis. For each season, 10 females and 10 males, a total of 80 blue crabs were sampled from Göksu Delta and the average carapace length and bodyweight of the samples were determined as; 12.1 ± 0.3 cm, and 90.3 ± 3.5 g for females and 11.8 ± 0.4 cm, and 85.2 ± 4.2 g for males respectively. The map of the sampling station is presented in Fig. 1.

Metal Analysis

The dissected tissues were wet weighted and transferred to petri dishes and burned at 115 °C for 72 h. After their dry weight calculated, they were transferred to experimental tubes and burned with 2v:1v nitric acid (HNO₃, % 65, Ö.A.: 1.40, Merck) and per chloric acid (HClO₄, % 60, Ö.A.: 1.53, Merck) mixture at 250 °C for 96 h. After burning, samples were transferred to polyethylene tubes and dilute to 10 ml with distilled water. Free blank samples were treated with same procedures. Samples then filtered with 0.45 µm membrane filter and tissue metal levels were determined by an Agilent 7500ce (Octopole Reaction System, Agilent Technologies, Japan) model ICP-MS system (Korkmaz et al. 2019a).

The metal levels were obtained as dry weight (mg kg⁻¹ dw) and then converted to wet weight (mg kg⁻¹ ww) using their water content (El-Moselhy et al. 2014). Analysis were run in triplicate. For determining the recovery values of metals, control samples of fish tissue homogenate (IAEA-407) were prepared. The recovery values founds as 98.12% for

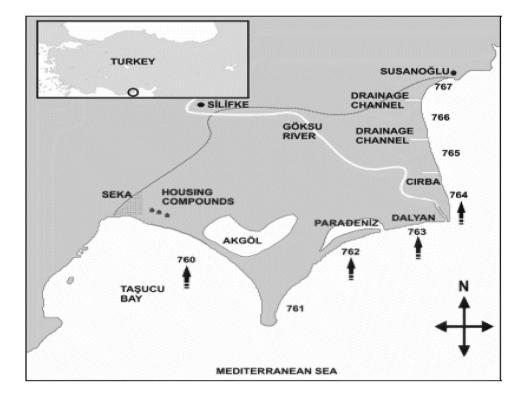


Fig. 1 Location of Göksu Delta

Al, 95.34% for Fe, 96.65% for Cu, 92.42% for Zn, 93.67% for As, 96.31% Cd and 94.87% for Pb. Standard linear regression with six standards were used for each metal. The detection limits for Al, Fe, Cu, Zn, As, Cd and Pb were as follows; 0.001, 0.001, 0.0006, 0.002, 0.005, 0.0004 and 0.0003 mg kg⁻¹ respectively.

Human Risk Assessment

The amounts of daily and weekly metal intake (EDI and EWI) by consumption of sampled fish species were calculated using Eqs. 1 and 2 (Korkmaz et al. 2019a);

$$EDI \ (\mu g/day/70kg \ body \ weight) = (C \ \times \ FIR)$$
(1)

$$EDI (\mu g/day/70kg \ body \ weight) = EDI \times 7 days$$
 (2)

C (Concentration) Mean metal level of muscle tissue (mg kg^{-1} ww).

FIR (Fish consumption ratio); Daily consumption of fish is approximately 17 g per capita according to Turkish Minister of Agriculture and Forestry (RTMAF 2020). BW (Body weight); Average body weight of Turkish people was considered as 70 kg.

The health risk of non-carcinogenic and carcinogenic effects due to the consumption of fish were evaluated based on the THQ and CR equations (Gu et al. 2018).

$$THQ = \frac{\text{EF} \times \text{ED} \times \text{EDI}}{AT \times RfD \times BW} x 10^{-3}$$
(3)

$$CR = \frac{EF \times ED \times EDI \times CSF}{AT \times BW} x 10^{-3}$$
(4)

Table 1 defines the parameters used in Eqs. (3-4), as well as data for Turkish people used in the calculations.

Statistical Analysis

Statistical analysis of the data obtained from muscle samples were carried out by Student-t test, One-way ANOVA and Student Newman Keuls' Procedure (SNK) on a SPSS 16 software package program.

Results and Discussion

Seasonal variations of heavy metal levels in the muscle tissues of female and male *C. sapidus* hunted from Göksu Delta are shown in Table 2.

Cd and Pb concentrations were found below the detection limits in all analyzed tissues. Mean metal levels in muscle tissues of female and male *C. sapidus* varied as follows; Al: $0.45 - 5.22 \text{ mg kg}^{-1} \text{ w.w}(\bigcirc)$ and $0.69 - 4.43 \text{ mg kg}^{-1} \text{ w.w}(\bigcirc)$, Fe: $1.49 - 25.52 \text{ mg kg}^{-1} \text{ w.w}(\bigcirc)$ and $4.62 - 16.60(\bigcirc)$ mg kg $^{-1}$ w.w, Cu: $3.15 - 5.58 \text{ mg kg}^{-1}$ w.w ($\bigcirc)$ and $2.99 - 5.48 \text{ mg kg}^{-1}$ w.w ($\bigcirc)$, Zn: $41.95 - 63.04 \text{ mg kg}^{-1}$ w.w ($\bigcirc)$ and $41.51 - 56.75 \text{ mg kg}^{-1}$ w.w ($\bigcirc)$, As: $< 0.0001 - 3.70 \text{ mg kg}^{-1}$ w.w ($\bigcirc)$ and $< 0.0001 - 2.01 \text{ mg kg}^{-1}$ w.w ($\bigcirc)$).

The highest Al, Fe and Zn levels were observed in autumn (wet season) and these changes were found statistically different (Coetzee 1996; Erkan et al. 2011). Contrary to trace elements (Al, Fe, Zn and Cu), arsenic concentrations were found to be low in the rainy season (autumn). With the first rains (autumn) after the dry season, high concentrations of

 $Total THQ (TTHQ) = THQ (metal 1) + THQ (metal 2) + \dots + THQ (metal n)$

PTWI ($\mu g/day/70kg$ body weight) = *RfD* for each metal (*Table3*) × *BW* × 7(*days*)

(6)

(5)

 Table 1
 Parameters and values used in the human health risk models

Factor	Definition	Unit	Value	Reference
RC	Daily organism consumption	g person ⁻¹ day ⁻¹	17	(USEPA 2018; Korkmaz et al. 2019a, b;
BW	Average body weight	Kg	70	RTMAF 2020)
EF	Exposure frequency	Days/year	365	
ED	Exposure duration	Years	70	
AT	Average time	Days	25,550 (BW x EF)	
RfD	Oral reference doses	mg kg ⁻¹ day ⁻¹	1E+00 (Al), 7E-01 (Fe), 4E-02(Celik et al.), 3E-01 (Zn), 3E-04 (As), 1E-03 (McDermott et al. 2015), 4E-03 (Pb)	
CSF	Cancer slop factor	$\mathrm{mg}~\mathrm{kg}^{-1}~\mathrm{day}^{-1}$	1.5E + 00 (As),	

Table 2 Seasonal variations of heavy metal levels in the muscle tissues of female and male *C. sapidus* hunted from Göksu Delta (mg kg⁻¹ w.w)

		$\frac{\text{Female } (\bigcirc)}{\overline{X} \pm S_X^- *}$	$\frac{\text{Male}}{\overline{X}} \underbrace{\overset{(\mathcal{Z})}{\pm} S_X^- *}_X$
Al	Autumn	5.22 ± 2.26^{ax}	4.43 ± 2.31^{ax}
	Winter	$1.49 \pm 0.98^{\rm ay}$	0.70 ± 0.55^{ay}
	Spring	0.45 ± 0.57^{ay}	0.75 ± 0.48^{ay}
	Summer	0.57 ± 0.26^{ay}	0.69 ± 0.27^{ay}
Fe	Autumn	25.52 ± 5.80^{ax}	16.60 ± 4.31^{ax}
	Winter	12.89 ± 1.99^{ay}	10.69 ± 0.55^{ay}
	Spring	6.94 ± 7.24^{at}	4.62 ± 0.48^{at}
	Summer	1.49 ± 2.39^{az}	5.63 ± 0.27^{at}
Cu	Autumn	3.15 ± 1.12^{ax}	2.99 ± 0.59^{ax}
	Winter	4.15 ± 1.26^{ax}	4.58 ± 1.52^{ax}
	Spring	5.58 ± 1.27^{ax}	5.48 ± 1.91^{ax}
	Summer	4.67 ± 1.32^{ax}	4.72 ± 1.18^{ax}
Zn	Autumn	63.04 ± 10.59^{ax}	56.75 ± 11.81^{ax}
	Winter	47.92 ± 4.56^{ay}	44.01 ± 2.64^{ay}
	Spring	42.95 ± 2.01^{ay}	43.42 ± 3.74^{ay}
	Summer	41.95 ± 3.72^{ay}	41.51 ± 2.16^{ay}
As	Autumn	< 0.0001 ^{ax}	< 0.0001 ^{ax}
	Winter	3.70 ± 1.75^{az}	2.01 ± 2.29^{ax}
	Spring	$3.17 \pm 3.60^{\mathrm{ayz}}$	1.92 ± 2.55^{ax}
	Summer	$1.15\pm2.09^{\rm axy}$	1.22 ± 2.33^{ax}
Cd	Autumn	< 0.0004 ^{ax}	< 0.0004 ^{ax}
	Winter	< 0.0004 ^{ax}	< 0.0004 ^{ax}
	Spring	< 0.0004 ^{ax}	< 0.0004 ^{ax}
	Summer	< 0.0004 ^{ax}	< 0.0004 ^{ax}
Pb	Autumn	< 0.0003 ^{ax}	< 0.0003 ^{ax}
	Winter	< 0.0003 ^{ax}	< 0.0003 ^{ax}
	Spring	< 0.0003 ^{ax}	< 0.0003 ^{ax}
	Summer	< 0.0003 ^{ax}	< 0.0003 ^{ax}

 $*\overline{X} \pm S_x^- = \text{Mean} \pm \text{Standard error}$

SNK Letter a show differences of a given metal between the female and male individuals and x,y,z and t show differences of given metal between seasons. Data shown with different letters are significant at 0.05 level

metals are known to transport to the delta. While crabs go to store trace elements in muscle tissues due to their metabolic function, they may have quickly activated their detoxification mechanisms against inorganic arsenic (Amiard et al. 2006; Lavradas et al. 2014). Cu levels, on the other hand, showed changes apart from the seasonal effect and these changes were not statistically significant. Strawberry cultivation is carried out in the region for four seasons and copper sulfate is extensively used during the cultivation (Ichiminami et al. 2016; Murtic et al. 2017). Agricultural activities may be the reason why there is no seasonal effect on copper levels. It is known that metal accumulation varies depending on sex in many living species. In this study however, metal concentrations did not change depending on gender (As Mohana and Subromanyam 2001; Chen et al. 2005; Olusegun et al. 2009; Beltrame et al. 2010). The reason for this may be that the crabs are not adults and show a homogeneous distribution in terms of length and weight.

Aluminum

Aluminum is one of the most abundant elements on the earth and has no metabolic activity in living organisms. (Niu 2018). It is used as a vaccine adjuvant and additive in antacid, food, skincare, cosmetics, and cooking products. (Mohamed et al. 2015). US EPA reports RfD for Al is $1000 \,\mu g \, kg^{-1} \, day^{-1}$ (USEPA 2018) and intake above these concentrations may cause neurological damage and Alzheimer's disease in humans. (Colomina and Peris-Sampedro 2017). Mean Al levels in the muscle tissues of female and male *C. sapidus* obtained from Göksu Delta varied by 0.45—5.22 mg kg⁻¹ ww and 0.69—4.43 mg kg⁻¹ ww respectively. In both gender, the highest Al concentrations were found in the autumn season.

Studies have reported that the average Al concentrations of *C. sapidus* obtained from Mediterranean vary between $1.20 - 13.70 \text{ mg kg}^{-1}$ w.w. (Mutlu et al. 2011) and $4.79 - 10.53 \text{ mg kg}^{-1}$ d.w. (Turkmen et al. 2006). Levels of Al reported in muscle tissues of other crab species differed between $1.85 - 3.35 \text{ mg kg}^{-1}$ dw (Caglak and Karsli 2017), $83.30 - 88.48 \text{ mg kg}^{-1}$ ww (Olgunoğlu and Olgunoğlu 2016), $10.06 - 20.54 \text{ mg kg}^{-1}$ dw (Bayrakli 2021) ve $25.10 - 58.70 \text{ mg kg}^{-1}$ ww (Bordon et al. 2012). Present data revealed that Al levels were lower when compared with the results of previous studies.

Iron

Iron is an essential element for many living things and it is known that iron deficiency can cause anemia in humans. (Ikem and Egiebor 2005). US EPA gives RfD for Fe is 700 μ g kg⁻¹ day⁻¹ (USEPA 2018) and over which was reported to result diseases in humans such as type-2 diabetes, Alzheimer and Parkinson (Killilea et al. 2003). The mean ranges of blue crab muscle Fe concentrations in female and male individuals were between 1.49 – 25.52 mg kg⁻¹ ww and 4.62 – 16.60 mg kg⁻¹ ww respectively. The highest Fe levels were determined in autumn for both genders.

Fe levels in muscle tissues of *C. sapidus* sampled from the Mediterranean were reported as 0.49 - 0.80 mg kg⁻¹ ww (Celik et al. 2006), 21.10 - 38.20 mg kg⁻¹ ww (Mutlu et al. 2011), 7.25 - 23.27 mg kg⁻¹ dw (Turkmen et al. 2006) and 8.81 - 32.48 mg kg⁻¹ ww (Ayas and Ozogul 2011). Fe levels in muscle tissues of other crab species were found between 2.80 - 6.44 mg kg⁻¹ ww (Caglak and Karsli 2017), 146.28 -149.70 mg kg⁻¹ ww (Olgunoğlu and Olgunoğlu 2016), 16.06 -20.34 mg kg⁻¹ dw (Bayrakli 2021) and 6.00 - 21.00 mg kg⁻¹ ww (Bordon et al. 2012).

Copper

Although copper is essential for many living things, high concentrations of it may cause health problems such as liver and kidney disorders (Eisler 2000; Behbahani et al. 2013). RfD of Cu is 40 μ g kg⁻¹ day⁻¹ reported by US EPA (USEPA 2018) and excess amounts of this reported to cause organ failures such as kidney and liver (Behbahani et al. 2013). Mean Cu levels in muscle tissues of female and male *C. sapidus* were found between 3.15 – 5.58 mg kg⁻¹ ww and 2.99 – 5.48 mg kg⁻¹ ww obtained forum Göksu Delta. Cu levels were found highest in spring for both genders however, these changes were not statically significant.

The studies on *C. sapidus* which carried out in Mediterranean were reported Cu levels between $6.93 - 10.31 \text{ mg kg}^{-1}$ ww (Celik et al. 2006), $5.38 - 11.70 \text{ mg kg}^{-1}$ ww (Mutlu et al. 2011), $3.88 - 9.38 \text{ mg kg}^{-1}$ dw (Turkmen et al. 2006), $4.10 - 19.10 \text{ mg kg}^{-1}$ dw (Çoğun et al. 2017), 18.21 mg kg^{-1} ww (Genç and Yilmaz 2017) and $9.72 - 68.09 \text{ mg kg}^{-1}$ dw (Ayas and Ozogul 2011). The mean Cu levels in other crab species were stated to vary between $4.75 - 8.03 \text{ mg kg}^{-1}$ ww (Olgunoğlu and Olgunoğlu 2016), $56.49 - 88.30 \text{ mg kg}^{-1}$ dw (Bayrakli 2021) and $3.50 - 20.10 \text{ mg kg}^{-1}$ ww (Bordon et al. 2012). When compared with the previous studies our results showed lower concentrations of Cu.

Zinc

Zinc is an essential element for all living things and is involved in physiological events such as metalloenzyme, DNA, protein synthesis, and cell division. (Eisler 2000). For zinc, RfD given by US EPA is 300 μ g kg⁻¹ day⁻¹ (USEPA 2018) and high levels of this have been associated with reproductive failures and development retarders in humans (Duruibe et al. 2007). The mean muscle levels of Zn in female and male were varied *C. sapidus* were varied between 41.95 – 63.04 mg kg⁻¹ ww and 41.51 – 56.75 mg kg⁻¹ ww respectively. Zn concentrations were found highest in autumn.

Zn levels in muscle tissues of *C. sapidus* hunted from Mediterranean were reported as $46.26 - 56.35 \text{ mg kg}^{-1}$ ww (Celik et al. 2006), $13.90 - 20.10 \text{ mg kg}^{-1}$ ww (Mutlu et al. 2011), $6.76 - 11.52 \text{ mg kg}^{-1}$ dw (Turkmen et al. 2006), $15.10 - 104.30 \text{ mg kg}^{-1}$ dw (Çoğun et al. 2017), 43.98 mg kg^{-1} ww (Genç and Yilmaz 2017) and $39.52 - 175.21 \text{ mg kg}^{-1}$ dw (Ayas and Ozogul 2011). In other crab species mean muscle Zn levels varied between $43.86 - 72.59 \text{ mg kg}^{-1}$ ww (Caglak and Karsli 2017), $334.50 - 345.94 \text{ mg kg}^{-1}$ ww (Olgunoğlu and Olgunoğlu 2016), $137.20 - 146.88 \text{ mg kg}^{-1}$ dw (Bayrakli 2021) and $20.10 - 33.80 \text{ mg kg}^{-1}$ ww (Bordon et al. 2012). Present data revealed that Zn levels in muscle tissues of *C. sapidus* were not in agreement with the result of most studies.

Arsenic

Arsenic is a naturally occurring element and broadly distributes in nature. It is known that the main sources of arsenic contamination for humans are drinking water and food. US EPA gives RfD for Asis 0.3 μ g kg⁻¹ day⁻¹ (USEPA 2018) and over levels of this were reported to cause liver cancers, low neuron transference, and dermatitis in humans. (Ikem and Egiebor 2005). Mean levels of As in muscle tissues of female and male *C. sapidus* varied between < 0.0001 – 3.70 mg kg⁻¹ ww and < 0.0001 – 2.01 mg kg⁻¹ ww respectively. For both genders, As concentrations were found lowest and below detection limits in autumn.

As levels in muscle tissues of some crustacean species such as Parapenaeus longirostris, Aristeus antennatus, Plesionika martia, and Nephrops norvegicus were reported to have 34. 00 mg kg⁻¹ ww, 15.45 mg kg⁻¹ ww, 40.76 mg kg⁻¹ ww and 45.00 mg kg⁻¹ ww respectively (Storelli and Marcotrigiano 2001). In another study carried out in the Mediterranean, average As concentrations were reported to be 46.5 mg kg⁻¹ dw, 57.3 mg kg⁻¹ dw, 79.5 mg kg⁻¹ dw and 112 mg kg⁻¹ mg kg⁻¹ dw for *Melicer*tus kerathurus, N. norvegicus, Squilla mantis and Carcinus mediterraneus respectively. Korkmaz et al. (2016) were reported that As concentrations in muscle tissues of some crustacean and mollusk species varied between $3.03 - 45.09 \text{ mg kg}^{-1}$ dw. When compared with the previous studies, present As concentrations were seemed to be lower.

Cadmium

Cadmium is an element that is generally found in nature in low amounts and is formed as a by-product of mining activities of zinc, copper, and lead (Eisler 2000). Nutrients are known to be the most major source of cadmium contamination for non-smokers (Cirillo et al. 2010). 1 mg kg⁻¹ day⁻¹ are reported for RfD of Cd by US EPA (USEPA 2018), and higher amounts of this concentration reported to cause liver, kidney, skeleton and reproductive system failures in humans (Behbahani et al. 2013). The mean muscle levels of Cd in female and male *C. sapidus* were found below detection limits in all samples. It was determined that Cd concentrations did not alter depending on seasons or gender.

The studies on *C. sapidus* carried out in Mediterranean reported Cd levels between $0.03 - 0.08 \text{ mg kg}^{-1}$ ww (Mutlu et al. 2011), 1.05 -2.50 mg kg⁻¹ dw (Turkmen et al. 2006), $0.10 - 2.50 \text{ mg kg}^{-1}$ dw (Çoğun et al. 2017), 0.16 mg kg⁻¹ ww (Genç and Yilmaz 2017) and 0.44 - 0.61 mg kg⁻¹ dw

Organization	Metals						Reference	
	Al	Fe	Cu	Zn	As	Cd	Pb	
FAO (1983)	-	-	30	30	-	0.5	0.5	(Korkmaz
European Union (EU) Limits	-	-	-	-	-	0.5	0.5	et al.
TFC	-	-	20	50	-	0.5	5	2019a)
Present Study (Mean Levels)	0.45 - 5.22	1.49 - 25.52	2.99 - 5.58	41.51 - 63.04	<0.0001 - 3.70	< 0.0004	< 0.0003	

Table 3 The maximum tolerable limits of some metals in muscle tissues of crustaceans according to national/international standards (mg kg $^{-1}$ ww)

(Ayas and Ozogul 2011). In other crab species mean muscle Cd levels varied as $0.02 - 0.05 \text{ mg kg}^{-1}$ ww (Caglak and Karsli 2017), $0.08 - 0.13 \text{ mg kg}^{-1}$ dw (Bayrakli 2021) and $0.01 - 0.02 \text{ mg kg}^{-1}$ ww (Bordon et al. 2012). When compared with the previous studies our results showed lower concentrations of Cd.

Lead

Lead is generally found in nature in the form of lead sulfide or a compound with iron, copper, zinc, antimony, and silver metals (Kitman 2000). It is an extremely toxic metal for terrestrial and aquatic species (Kabata-Pendias and Mukherjee 2007). The RfD of Pb is 4 μ g kg⁻¹ day⁻¹ given by US EPA (USEPA 2018), and excess amounts of this reported to cause dysfunctions in neural transmission, loss of memory, and diseases in liver, kidney, and heart (Ikem and Egiebor 2005). The mean muscle levels of Pb in female and male *C. sapidus* were found below detection limits in all samples. It was determined that Pb concentrations did not alter depending on seasons or gender.

Studies have reported that the average Pb concentrations of *C. sapidus* obtained from Mediterranean vary between 0.14 $- 0.39 \text{ mg kg}^{-1}$ ww (Celik et al. 2006), 2.66 $- 4.30 \text{ mg kg}^{-1}$

dw (Turkmen et al. 2006), $1.10 - 5.10 \text{ mg kg}^{-1}$ dw (Çoğun et al. 2017), 1.20 mg kg^{-1} ww (Bayrakli 2021) and $0.24 - 0.52 \text{ mg kg}^{-1}$ dw (Ayas and Ozogul 2011). Levels of Al reported in muscle tissues of other crab species differed between $0.25 - 0.70 \text{ mg kg}^{-1}$ ww (Caglak and Karsli 2017), 0.02 mg kg^{-1} ww (Olgunoğlu and Olgunoğlu 2016), $0.06 - 0.12 \text{ mg kg}^{-1}$ dw (Bayrakli 2021) and $0.00 - 1.72 \text{ mg kg}^{-1}$ ww (Bordon et al. 2012). Present data revealed that Pb levels were lower when compared with the results of previous studies.

Risk Assessment

Various organizations around the world have restricted the availability of some heavy metals in foodstuffs and set acceptable maximum limits for these metals. The results obtained from this study are compared with the acceptable upper limits and summarized in Table 3.

When Table 2 is examined, it is seen that the average Cu, Cd, and Pb concentrations in the muscle tissues of female and male *C. sapidus* obtained from Göksu Delta are below the acceptable upper limits determined by FAO, TFC, and EU. However, the average Zn concentration in the muscle tissues of male and female *C. sapidus* in autumn is above

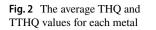
Table 4 Seasonal EWI variations of metals by consuming blue crab from Göksu Delta

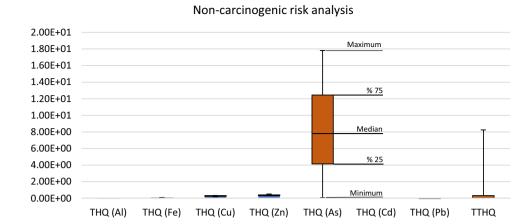
Metal	PTWI ^a	Autumn EWI ^b	Winter EWI ^b	Spring EWI ^b	Summer EWI ^b
Al	490000	621.18 (♀) – 527.17 (♂)	177.31 (♀) – 83.30 (♂)	53.55 (♀) – 89.25 (♂)	67.83 (♀) – 82.11 (♂)
Fe	343000	3036.88 (♀) – 1975.40 (♂)	1533.91 (♀) – 1272.11 (♂)	825.86 (♀) – 549. 78 (♂)	177.31 (♀) – 669.97 (♂)
Cu	19600	374.85 (♀) – 355.81 (♂)	493.85 (♀) – 545.02 (♂)	664.02 ([©] ₊) − 652.12 (^A ₀)	555.73 () – 561.88 ()
Zn	147000	7501.76 () – 6753.25 ()	5702.58 (♀) – 5237.19 (♂)	5111.05 (♀) – 5166.98 (♂)	4992.05 (♀) – 4939.69 (♂)
As ^c	147	<0.0001 (♀)(♂)	15.41 (♀) – 8.37 (♂)	13.20 (♀) – 8.00 (♂)	4.79 (♀) – 5.08 (♂)
Cd	490	<0.0004 (♀)(♂)	<0.0004 (♀)(♂)	<0.0004 (ੵ)(♂)	<0.0004 (♀)(♂)
Pb	1960	<0.0003 (♀)(♂)	<0.0003 (♀)(♂)	<0.0003 (♀)(♂)	<0.0003 (♀)(♂)

^a*PTWI* value for an adult human of 70 kg weight (μg^{-1} week⁻¹ 70 kg body weight)

^bEWI mean amount of metal uptake by blue crab consumption (µg⁻¹ week⁻¹70 kg body weight)

^cAs concentrations were calculated as total As and 3.5 conversion factor was used to convert them into inorganic arsenic





the limits, moreover, Zn levels in 30% of female and 17.5% of male individuals were found higher than standards which proposed by TFC. The seasonal EWI of metals in muscle tissues of female and male *C. sapidus* were calculated and compared with the PTWI of each metal and the results are summarized in Table 4.

The tolerable daily intake is the amount of a substance, expressed on the basis of body weight that can be consumed every day for a lifetime without any risk. The tolerable daily intake of a metal varies depending on the metal concentration in the food consumed and the amount of food consumed. According to the data of RTMAF (2020), the average daily consumption of seafood in Turkey is 17 g per person. This corresponds to a weekly consumption of 119 g seafood per person. In Table 3, the seasonal metal concentrations that can be taken into the body were calculated by assuming that a person weighing 70 kg consumes 119 g of blue crab meat weekly and the data were compared with the PTWI values. At the end of the study, the EWI levels of analyzed samples were found well below the PTWI values of the metals in all seasons, and it was concluded that C. sapidus samples may not cause health problems in terms of human consumption. However, it is not possible to determine the safety of foods by only performing PTWI analysis. So, the THQ values of each metal and CR values of As were calculated for further risk analysis, and the non-carcinogenic effects of metals and carcinogenic effects of As were determined.

A THQ value above 1 means that the metal intake level is above the RfD. This shows that the metal consumption poses health risks to the consumer from the aspects of non-carcinogenic effects. THQ values of metals were found as $4.32E-03 \pm 4.64E-03$ (Al), $3.66E-02 \pm 2.69E-02$ (Fe), $2.68E-01 \pm 5.79E-02$ (Celik et al. 2006), $3.86E-01 \pm 6.44E-02$ (Zn), $8.24E + 00 \pm 6.55E + 00$ (inorganic As), $5.71E-05 \pm 1.45E-20$ (McDermott et al. 2015) and $1.07E-05 \pm 0.00E + 00$ (Pb). The average TTHQ value were determined as $1.28E + 00 \pm 3.07E + 00$. THQ values of As and TTHQ were found higher than 1 (Fig. 2). These results showed that, *C. sapidus* caught from Göksu Delta may show non-carcinogenic effects for consumers such as vomiting, diarrhea, heart rhythm disturbances, altered consciousness, from the point of As concentrations.

US EPA defines arsenic as a carcinogen, hence CR values determined for it. The average CR level for As was found 2.10E-04. US EPA reported that CR levels higher than 1×10^{-4} are not acceptable for public health. The found CR levels of As were higher than the acceptable limits therefore we concluded that As levels of female and male *C. sapidus* may show carcinogenic effects on humans over consumption.

Conclusion

Seafood such as fish, oysters, crab, and shrimp are very important protein sources for humans and as a result of continuous improvement in living standards, human communities consume more of them each day. Dieticians constantly remind the importance of seafood and the omega-3, vitamin, and mineral contents of aquatic foods play important roles to prevent diseases such as diabetes, Alzheimer's, and heart attacks. However, they also mediate heavy metal transport in the food chain due to the characteristics of the living environment. Furthermore, As concentrations in tissues of fish species from the Mediterranean were reported to be risky for human health by recent studies. Therefore, it is beneficial to follow up the concentration of toxic agents in edible tissues of aquatic foods with routine studies in the region.

In conclusion, we found that the consumption of female and male *C. sapidus* obtained from Göksu Delta carries carcinogenic and non-carcinogenic risks in terms of As concentrations. Zn levels in 30% of females and 17.5% of male individuals were found higher than standards proposed by TFC. Moreover, it was determined that metal levels in muscle tissues of *C. sapidus* were not affected by gender differences, but Al, Fe and Zn levels differed between seasons. Acknowledgements Mersin University, Scientific Projects Unit, supported this research project. (Project Number: 2019-2-TP2-3562).

Data Availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of Interest The authors declare that they have no conflict of interest.

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