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Levels of toxic metals in edible fish species of the Tigris River (Turkey); Threat to public health

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ABSTRACT

Tigris River has international importance as it runs through the borders of three countries. The levels and probable public health risks of heavy metals (Mn, Cd, Fe, Cu, Ni, Zn, Co, Pb, Cr, As) in 72 muscle and gill samples out of six fish species in Tigris River, Turkey were determined then compared with results of prior studies. Furthermore, human health risk levels from fish consumption were assessed using multiple approaches. The mean maximum heavy metal levels in the muscles were as follow; 175.88 > 22.34 > 10.29 > 2.81 > 2.76 > 1.68> 0.33 > 0.25 > 0.05 = 0.05 mg kg⁻¹ for Fe > Zn > Mn > Cu > Ni > Cr > Pb > As > Cd = Co, respectively. The highest muscle tissue levels for 8 heavy metals out of 10 measured were found in C. macrostomus species. The mean max. levels of Cu and Pb, the remaining two heavy metals, were measured in muscle tissue of L. abu species. The mean maximum concentrations of heavy metals of Cr, Cu, and Zn in all fish samples were below the maximum permissible limits (MPLs). The carcinogenic risk (CR) values for Pb, Cr, Ni and As were calculated and evaluated respectively in all of the Tigris River's fish species. While CR values calculated for Pb in all species did not pose a risk, it was found above the threshold value of 10^{-4} for some fish species for Cr, Ni and As. Target hazard quotients (THQs) from metal intake by consuming fish species were below 1 for all heavy metals which indicated no hazard from consumption. In addition, since the hazard index (HI) is lower than "1", it has been concluded that the consumption of fish species will not pose a potential health risk. Considering by CR values exclusively, the results disclosed that the intake of the analyzed fish species might cause a toxicological hazard and impend to community health.

1. Introduction

Fish contain high protein and unsaturated omega fatty acids, which are acknowledged to contribute to human health. Therefore; they have become one of the most popular and widely consumed seafood as well as critical protein sources for the people (Ahmedet al., 2015a; Tepe et al., 2008). Fish are usually at the topmost trophic level in freshwater habitats and take heavy metals (HMs) from the environment they live in due to various factors such as species characteristics, exposure time, and concentration of the element, water parameters (Gall et al., 2015; Ginsberg and Toal, 2009). HMs are one of the worst hazardous chemical pollutants for human and natural life in terms of toxicological risk (Taş et al., 2019; Ustaoğlu et al., 2019). Harmful substances such as HMs caused by anthropogenic activities accumulate in aquatic living beings through the trophic level (Ustaoğlu and Islam, 2020). Consuming fish contaminated with these harmful chemicals can be a risk factor for public health (Türkmen et al., 2011; Varol and Sünbül, 2020). HMs with their bioaccumulation and biomagnification properties are very important toxic pollutants that can remain in aquatic systems for a long time (Chau, 2005; Chen and Chau, 2016). Even low concentrations in water can accumulate in the body and reach toxic levels (Chen and Chau, 2019; Olyaie et al., 2015; Ustaoğlu and Tepe, 2019). Accumulation of HMs above the maximum permissible levels may cause brain-related Parkinson and Alzheimer's diseases, changes in blood composition, impaired development and reproduction, health problems by affecting the function of other organs such as lung, liver and kidney (Saha et al., 2016; Türkmen et al., 2009; Varol et al., 2017). Therefore, monitoring and controlling of HMs that negatively affect public health

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Fig. 1. Map of the Tigris River basin showing the study area and sampling stations.

by leaving residue in fish seems to be very important and useful today. For this reason, monitoring and controlling the HMs that accumulate in fish, which negatively affect human health, seems vital and useful today (Alizadeh et al., 2018; Çulha et al., 2016). Fish have long been used as a good bioindicator to determine the metal levels of aquatic environments (Köse et al., 2019; Tokatli, 2018).



Fig. 2. Fish species used in the study.

The Tigris River with 57,614 km² catchment area, and the total length of 1900 km (523 km is within Turkey) is the most important water source in Mesopotamia. HM pollution of Tigris River have been studied comprehensively by taking sediment and water samples especially from up in the region (Varol et al., 2012; Varol and Sünbül, 2018). We report the metal accumulation by edible fish species in Cizre region of Tigris River where it flows thirty-two km through the border of Turkey and Syria before inflow to Iraq.

The objective of the present study is (i) to determine HMs accumulation in the both muscle and gill tissues of sampled fish commonly consumed in the nutrition of the people of the region, (ii) to evaluate HMs levels in terms of public health, and (iii) to assess toxic risk levels. In addition, the findings of this research will suggest a better identification of ecological risks, and provide positive benefits in terms of generating data on measures to be taken in environmental monitoring, control and management.

2. Material and methods

2.1. The study area and fish sampling

Cizre district of Şırnak, situated at the point where the Tigris River leave Turkey, has been determined as the study area (Fig. 1). Total of six fish species including *Chondrostoma regium, Cyprinion macrostomus, Barbus rajanorum mystaceus, Capoeta trutta, Carassius gibelio* from Cyprinidae family and *Mugil (Liza) abu* from Mugilidae family were collected seasonally in 2018 (Fig. 2). Fish samples used in the study were caught with a fishing net. Fishing was carried on until three fish in a sample were caught per species in each season.

2.2. Sample extraction and analysis

Fish caught in the Tigris River were brought to the laboratory in cold chain, their species were identified, and autopsies were performed. One gram of gill and muscle tissue samples were obtained from each fish for HMs analysis. The prepared samples were placed in labeled sampling bags and kept cold at -20 °C. For HMs extraction, tissues are taken into microwave digestion tubes and nitric acid (HNO₃) in an amount of 5 ml and hydrogen peroxide (H₂O₂) in an amount of 1 ml are added to each tube. The prepared samples were digested in the microwave oven. After digestion, we let the samples cool down to room temperature then taken into polypropylene falcon tubes and sample volumes were reconstituted to 25 ml by adding deionized water. The 0.45 µm filter paper were used for filtration (Türkmen et al., 2005). The calibration standards were set by the aid of a multi-element standard (Merck, Darmstadt, Germany). A certified reference material (DORM-4; Ontario, Canada) was run as the gauging certification standard. The measured recoveries as % were found between 92 and 115 for metals. A minimum of three measurements for all samples were performed for HMs analysis by ICP-MS. The measured levels of HMs in tissues were calculated and reported as mg kg^{-1} wet weight (ww) in fish samples.

2.3. Method of assessment

2.3.1. Assessment of HMs levels in sampled fish species (Metal pollution index MPI)

The Metal Pollution Index is a mathematical model that epitomize the value for all metals in a single form. MPI is a credible and accurate index to monitor HMs contamination in the food and the aquatic ecosystem. In this study, MPI values were calculated as the geometric mean of values for HMs in fish muscle and gill as below (Usero et al., 1997);

$$MPI(mg \ kg^{-1}) = (Cf_1 \times Cf_2 \times \dots \times Cf_n)^{1/n}$$
(1)

Cf: The mean concentration of HMs in the fish's muscle (mg kg^{-1})

2.3.2. The public health risk evaluation associated with fish consumption

Estimation of daily intake rate (EDI). The estimated daily intake (EDI = $mg kg^{-1}$ body-weight/day) of the HMs (Cd, Mn, Cr, Fe, Ni, Co, _iAs, Zn, Cu and Pb) was calculated by using the below equation as reported by Griboff et al. (2017):

$$EDI = \frac{C_{element} \times D_{food \ intake}}{BW}$$
(2)

where, $C_{element}$: is the concentration of HM in the muscle tissue of fish (as mg kg⁻¹ wet weight), $D_{food intake}$: is the mean food (fish) consumption daily (g/person/day), that is 5.5 kg per person per year in Turkey (GDFA, 2018) and BW: is the mean body weight (70 kg for adults).

Target hazard quotient (THQ). THQ is an estimation of the level of noncarcinogenic risk associated with HMs exposure. The method used to estimate the THQ of each HM is calculated with the following equation (Ahmedet al., 2015b):

$$THQ = \frac{E_{fr} \times ED_{tot} \times FIR \times C}{RfD_o \times BW_a \times AT_n} \times 10^{-3}$$
(3)

 E_{fr} is the exposure frequency (365 days a year), ED_{tot} is the exposure duration (the mean life expectancy of a person is 70 years), FIR is fish ingestion rate (15 g per day), C is the mean muscular HMs concentration in fish (mg kg^{-1}), *RfD_o is the reference oral dose (mg kg^{-1} day^{-1}), BW_a is the mean body weight (70 kg is taken for an adult person), AT_n is the mean exposure period for noncarcinogens (365 days per year \times exposure number per year).

The threshold value for THQ is "1", else it points out to pose probable noncarcinogenic hazards to exposed public. The assessments of public health risk set on the thoughts of most chemicals with noncancer effects, indicate a threshold response (Kawser Ahmed et al., 2016). Acceptable guide value for THQ is 1(USEPA, 2011). Recently, THQ has been accepted valid and useful method by many researchers and has been used widely (Mahmoud, 2015; Varol et al., 2019).

Hazard index (HI). The HI is the total of the THQ for all metals observed (Li et al., 2013):

$$HI = \sum_{i=1}^{n} THQ_i \tag{4}$$

where HI < 1 is safe, HI > 1 is hazardous and HI < 1 shows the health benefit for consumption of fish and that the consumers are safe, while HI > 1 shows harmful public health risks.

Target Cancer risk (CR). CR was used to point out the carcinogenic risks. CR values for Cr, Ni, Pb and As were calculated by using the below equation (USEPA, 2000):

$$TR = \frac{E_{fr} \times ED_{tot} \times FIR \times C \times CSFo}{BW_a \times AT_c} \times 10^{-3}$$
(5)

 AT_c is the mean exposure period for carcinogens (365 days per year \times sum of exposure time per year).

 CSF_o is the carcinogenic slope factor for oral route indicated by the Integrated Risk Information System (for Cr: 0.5; Ni: 1.7; Pb: 8.5 \times 10⁻³; As: 1.5 mg⁻¹ kg⁻¹ day) (USEPA, 2015).

2.4. Statistical analysis

ANOVA (One-way variance of analyses) was used to find whether there is a significant difference statistically among the HMs values in samples of fish tissue (p < 0.05). In this research, statistical analysis was performed in SPSS 22 software. The mean heavy metal levels in fish muscles and gills (mg kg^{-1} ww).

	Tissue ($n = 12$)	L.abu	C. regium	C. macrostomus	B. mystaceus	C. trutta	C. gibelio
Cr	М	1.53 ± 0.20^{bd}	$1.05\pm0.13^{\rm c}$	$1.68 \pm 0.25^{\text{d}}$	1.29 ± 0.23^{bc}	$1.14\pm0.13^{\rm c}$	0.78 ± 0.30^{a}
	G	2.14 ± 1.05^{a}	1.59 ± 0.29^{ab}	1.56 ± 0.41^{ab}	1.94 ± 0.37^a	$1.24\pm0.12^{\rm b}$	$1.00\pm0.12^{\rm b}$
Mn	М	5.66 ± 9.56^{ab}	$0.61\pm0.48^{\rm b}$	10.291 ± 8.06^{a}	1.42 ± 2.64^{b}	$0.43\pm0.24^{\rm b}$	0.10 ± 0.09^{b}
	G	12.24 ± 10.96^{abc}	6.82 ± 9.40^{abcd}	$14.32\pm6.77\text{ac}$	6.29 ± 3.39^{bd}	$0.35\pm0.28^{\rm d}$	$\textbf{0.14} \pm \textbf{0.09d}$
Fe	М	97.31 ± 141.50^{ab}	$16.55\pm7.95^{\mathrm{b}}$	175.88 ± 125.66^{a}	$50.66 \pm 83.36^{\rm b}$	84.18 ± 12.73^{ab}	$\textbf{57.38} \pm \textbf{19.87}^{b}$
	G	413.61 ± 319.72^{a}	$140.50 \pm 175.82^{\rm b}$	239.73 ± 77.73^{ab}	$250.15 \pm 127.17^{\rm ab}$	$87.34 \pm \mathbf{12.33^b}$	75.47 ± 11.14^{b}
Со	М	0.04 ± 0.07	0.04 ± 0.07	0.05 ± 0.05	0.04 ± 0.07	0.03 ± 0.01	$\textbf{0.04} \pm \textbf{0.01}$
	G	$0.23\pm0.20^{\rm a}$	$0.07\pm0.11^{\rm bc}$	0.13 ± 0.07^{ab}	$0.01\pm0.02^{\rm c}$	0.04 ± 0.01^{bc}	$0.04\pm0.00^{\rm bc}$
Ni	М	$1.11\pm1.41^{\rm ab}$	$0.22\pm0.19^{\rm b}$	$2.76\pm3.22^{\rm a}$	$0.38\pm0.68^{\rm b}$	$0.18\pm0.04^{\rm b}$	$0.16\pm0.18^{\rm b}$
	G	5.16 ± 4.42^{a}	$1.73\pm2.13^{\rm b}$	$2.03\pm0.93^{\rm b}$	2.20 ± 1.39^{b}	0.19 ± 0.03^{b}	$0.14\pm0.03^{\rm b}$
Cu	М	2.81 ± 2.54^{a}	$0.75\pm0.35^{\rm b}$	$0.77\pm0.46^{\rm b}$	0.29 ± 0.24^{b}	$0.05\pm0.06^{\rm b}$	$0.89 \pm 2.66^{\text{b}}$
	G	$3.51\pm1.69^{\rm ac}$	$1.18\pm0.83^{\rm ab}$	$\textbf{4.43} \pm \textbf{5.87}^{c}$	0.78 ± 0.37^{ab}	$0.05\pm0.03^{\rm b}$	$0.06\pm0.04^{\rm b}$
Zn	М	11.44 ± 4.52	10.08 ± 3.89	22.34 ± 5.86	17.91 ± 20.36	12.48 ± 12.90	$\textbf{16.69} \pm \textbf{16.27}$
	G	$17.35\pm4.99^{\rm b}$	$14.71\pm4.70^{\rm b}$	$19.37\pm5.17^{\rm b}$	$54.98 \pm 34.16^{\rm a}$	$5.66\pm8.59^{\rm b}$	$8.05 \pm 9.47^{\mathrm{b}}$
iAs	М	0.20 ± 0.07^{ab}	0.14 ± 0.01^{ac}	$0.25\pm0.08^{\rm b}$	0.19 ± 0.09^{c}	$0.02\pm0.003^{\rm d}$	$0.02\pm0.002^{\rm d}$
	G	$0.34\pm0.13^{\rm a}$	$0.19\pm0.04^{\rm b}$	0.34 ± 0.08^{a}	0.37 ± 0.16^a	0.02 ± 0.002^{c}	$0.02\pm0.002^{\rm c}$
Cd	М	0.03 ± 0.00^{a}	0.027 ± 0.004^{a}	$0.05\pm0.01^{\rm b}$	0.002 ± 0.004^{c}	$0.01\pm0.00^{ m d}$	$0.01\pm0.00^{ m d}$
	G	0.04 ± 0.01^{a}	0.04 ± 0.01^a	0.045 ± 0.01^a	$0.001\pm0.02^{\rm b}$	0.01 ± 0.00^{c}	0.013 ± 0.00^{c}
Pb	М	$0.33\pm0.18^{\rm a}$	$0.15\pm0.04^{\rm b}$	$0.19\pm0.07b$	$0.12\pm0.01^{\rm b}$	$0.11\pm0.01^{\rm b}$	$0.11\pm0.01^{\rm b}$
	G	0.45 ± 0.25^a	$0.21\pm0.14^{\rm b}$	$0.20\pm0.08^{\rm b}$	0.03 ± 0.09^{c}	$0.11\pm0.01^{\rm bc}$	$0.11\pm0.01^{\rm bc}$

Different letters in the same row show statistical differences between fish species for the same HM (P < 0.05). _iAs: Inorganic As (assumed 10% of the total As).

Table 2 The maximum concentrations of heavy metals detected in the present study and maximum permissible levels for fish muscle tissues (Adapted from Varol and Sünbül, 2018).

	_i As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	
Maximum value detected Turkish Food Codex Food Standards Australia New Zealand	0.25 2	0.05 0.05	0.05	1.68	2.81	175.88	10.29	2.76	0.33 0.3 0.5	22.3	This study (Anonymous, 2011) (FSANZ, 2013)
World Health Organisation Chinese Health Ministry European Commission Codex Alimentarius Commission	0.1	1.00 0.1 0.05		50 2.0	30	100	1	0.5–1	2.0 0.5 0.3 0.3	100	(Mokhtar et al, 2009) (MHPRC, 2013) (EC, 2006) (WHO/FAO, 2015)
Food and Agriculture Organization					30					30	(FAO, 1983)

3. Results and discussion

3.1. The levels of metal in sampled fish

Metal contamination levels were determined by using pollution index indicators in fish species from Cyprinidae and Mugilidae family caught from Cizre located along the Tigris River in Turkey-Syria border. Explanatory statistics of HMs from six analyzed fish species are presented in Table 1. Considering a total of 72 fish samples, generally the highest metal levels were measured for Fe and Zn, the lowest levels were observed in Co and Cd. Comparable consequences have been reported by many researchers in studies for different species (Tepe, 2009; Türkmen et al., 2008; Ali et al., 2020). In all six fish species analyzed, the amounts of metal levels in the gills (G) are generally higher than the levels in the muscles (M), as also seen in Table 1.

3.1.1. Chromium

Chromium (Cr) levels in fish muscle was found to be highest in *C. macrostomus* (1.68 mg kg⁻¹) and lowest in *C. gibelio* (0.78 mg kg⁻¹). The highest and lowest values of Cr levels in the gills were determined in *L. abu* (2.14 mg kg⁻¹) and *C. gibelio* (1.00 mg kg⁻¹), respectively (Table 1). The mean Cr concentrations differ significantly between fish species in both muscle and gill tissues (p < 0.05). Compared to the present study, higher mean Cr level in common carp (3.03 mg kg⁻¹) was reported by Kalyoncu et al. (2012). The average Cr levels found in all fish species are lower compared to literature values (Table 3). The mean Cr concentrations in muscles of all fish species was determined to be lower than the threshold value of 2 mg kg⁻¹ reported by the Chinese Ministry of Health (MHPRC, 2013) (Table 2).

3.1.2. Manganese

The highest level of manganese concentration in the gills was measured in *C. macrostomus* with 14.32 mg kg⁻¹ and the closest level was in the gill of *L. abu* with 12.24 mg kg⁻¹ (Table 1). The lowest concentrations of manganese were 0.1 mg kg⁻¹ and 0.15 mg kg⁻¹ in the muscle and gill of *C. gibelio*, respectively. The mean Mn value in Rainbow trout (1.57 mg kg⁻¹) is lower than those in *L. abu* and *C. macrostomus* and higher than all other fish species of the present study (Fallah et al., 2011). In addition, Türkmen et al. (2008) reported the similar mean Mn level of 1.92 mg kg⁻¹ (ww) in Horse mackerel from Black Sea, Turkey (Table 3).

3.1.3. Iron

Iron accumulation was higher than all other metals in all sampled fish species with the exception of C. regium when the accumulation amounts of metals in the muscle tissues is evaluated (Table 1). A similar situation was observed for gill tissues, as iron accumulation was highest in all fish species. The highest iron concentration was detected in the gills of L. abu (413.62 mg kg⁻¹), and followed by gills of B. mystaceus $(250.15 \text{ mg kg}^{-1})$. Iron levels in muscle of *D. labrax* has been determined as 33.3 mg kg⁻¹ (ww) captured from the Iskenderun Bay (Türkmen et al., 2009) (Table 3). Iron levels detected in the muscle tissues of fish species caught from the Marmara Sea, the Aegean Sea and the Mediterranean have been stated as 7.46–40.1 mg kg⁻¹ (ww) (Türkmen et al., 2008). Iron concentrations were recorded between 68.6 and 163 mg kg⁻¹ in the muscles of the fish caught from the Black Sea and the Aegean Sea (Uluozlu et al., 2007). The iron levels were stated between 32.2 and $129\ mg\ kg^{-1}$ in muscle and 173–299 mg kg^{-1} in gills of fish caught from the Mediterranean (Kalay et al., 1999).

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comparison or the	mean concentrations of HIMS (1	mg kg - ww	IN USN MUSCLE	s in this stud	y with other	stuales (var	01 et al., 2019).					
	Sites	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Reference
Common carp	Karacaören Dam Lake, Turkey	ļ	0.488	0.62	3.03	0.46	0.79	2.23	0.305	0.475	3.28	(Kalyoncu et al., 2012) ^a
Rainbow trout	Iran	0.234	0.024	0.047	0.141	5.45	3.87	1.57	0.095	0.277	5.24	(Fallah et al., 2011) ^a
European seabass	Iskenderun Bay, Turkey	I	0.03	0.1	0.27	1.06	33.3	0.45	1.02	0.48	10.7	(Türkmen et al., 2009)
Ten edible fish sp.	Bangshi River, Bangladesh	0.88	0.075	I	0.28	5.7	I	5.94	0.64	1.16	42.24	(Rahman et al., 2012)
Anchovy	Black Sea, Turkey	0.25	0.27	I	1.12	1.96	75.7	9.1	1.93	0.3	38.8	(Tuzen, 2009)
Anchovy	Mediterranean Sea, Italy	5.28	0.001	I	0.009	I	I	0.257	0.046	0.005	6.58	(Copat et al., 2013)
Horse mackerel	Black Sea, Turkey	I	0.3	0.17	0.5	1.68	57.6	1.92	0.62	1.31	8.15	(Türkmen et al., 2008)
Seabream	Adana, Turkey	I	0.13	0.08	0.3	1.33	47.2	1.04	0.2	0.52	11.1	(Türkmen et al., 2016)
Bogue	Antalya Bay, Turkey	I	0.0078	I	0.12	2.83	12.47	0.16	0.135	0.138	4.58	(Tekin-Özan, 2014) ^a
Atlantic salmon	Chile	0.34	0.47	0.08	I	2.6	26.07	5.07	I	0.088	39.3	(Medeiroset al., 2014)
Red mullet	Black Sea, Turkey	13.97	0.25	0.17	I	1.14	29.4	7.51	0.85	0.37	19.81	(Durmuş et al., 2018)
Red mullet	Mediterranean Sea, Spain	19.8	0.0011	I	I	0.35	I	I	I	0.005	3.65	(Martínez-Gómez et al., 2012)
Tigris scraper	Keban Dam	0.016	0.00085	0.74	0.76	0.73	8.0	0.78	0.9	0.0386	4.3	(Varol and Sünbül, 2018)
Six edible fish sp.	Tigris River, Turkey	0.02 - 2.25	0.002 - 0.05	0.03 - 0.05	0.78 - 1.68	0.05 - 2.81	16.55 - 175.88	0.10 - 10.29	0.16 - 2.76	0.11 - 0.33	10.08 - 22.34	This research*
^a Original values ex	pressed in dry mass and here c	calculated in	wet mass (wet	mass = dry	mass divided	bv 4).						

Fable 3

 * Values present the ranges as mg kg⁻¹ wet wt

3.1.4. Cobalt

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Cobalt accumulation in the muscles and gills tissues of fish was found between 0.03 and 0.05 mg kg⁻¹ and 0.01–0.23 mg kg⁻¹, respectively. The highest Co level was detected in the gills of *L. abu* (0.23 mg kg⁻¹ and the closest level to this value was detected in the gill of C. macrostomus (0.13 mg kg⁻¹). The cobalt levels measured in our study were lower than the levels measured from the fish in the Karacaören Dam Lake (Kalvoncu et al., 2012) and the Black Sea (Türkmen et al., 2008) (Table 3). When compared with the results of the present study, Co concentrations were higher with the range of 0.528 to 2.853 mg kg $^{-1}$ in fish muscles from Iskenderun Bay (Türkmen et al., 2005), and lower with the range of <0.001 to 0.002 mg kg⁻¹ in fish muscles from the Mediterranean (Türkmen and Ciminli, 2007).

3.1.5. Nickel

The highest Nickel level in fish muscle was detected in C. macrostomus with 2.76 mg kg $^{-1}$ and the lowest in C. gibelio with 0.16 mg kg⁻¹ according to the analysis values. Ni levels in the muscle of other fish species showed an accumulation below 1 mg kg⁻¹ except C. macrostomus and L. abu. Conversely, when the Ni levels in the gills are evaluated; the highest and lowest values were recorded in L. abu with 5.16 mg kg^{-1} and in C. gibelio with 0.14 mg kg^{-1} , respectively. The mean Ni level in the muscle tissues of D. labrax caught from the Iskenderun Bay found as 1.02 mg kg⁻¹ (Türkmen et al., 2009). Ni levels were detected in a similar range with $0.16-2.76 \text{ mg kg}^{-1}$ in the present study. The mean of nickel concentration in the present study was similar to average concentrations detected from ten fish species (0.64 mg kg⁻¹) in the Bangshi River of Bangladesh (Rahman et al., 2012). A higher amount of nickel was found in this study compared to the concentration in fish muscles (0.046 mg kg⁻¹) from Italian coasts of the Mediterranean (Copat et al., 2013) (Table 3)

3.1.6. Copper

The highest mean Cu concentrations in fish muscle were determined in L. abu (2.81 mg kg⁻¹), C. gibelio (0.89 mg kg⁻¹) and C. macrostomus $(0.77 \text{ mg kg}^{-1})$. The mean Cu concentrations in the rest of the fish species were below 0.76 mg kg $^{-1}$ (Table 1). The differences in Cu concentrations in six fish species showed that L. abu had higher Cu content than other species (p < 0.05). The highest copper concentrations in the gills of fish were 4.43 mg kg⁻¹ and 3.51 mg kg⁻¹ in *C. macrostomus* and L. abu, respectively. The copper levels in gills of commercial fish in Tuzla Lagoon have been reported as 0.26–0.82 mg kg^{-1} and 0.83–7.82 mg kg⁻¹ (dry weight) (Dural et al., 2006). A similar mean Cu concentration $(2.83 \text{ mg kg}^{-1})$ was found in Bogue fish (*Boops boops*) sampled from the Gulf of Antalya in Turkey (Tekin-Özan, 2014). The average Cu concentrations in other fish species are lower than those reported in the literatures shown in Table 3. The average Cu concentrations in this study were found to be below the maximum permissible concentrations (MPC) (30 mg kg^{-1}) determined by the Food and Agriculture Organization (FAO, 1983) (Table 2).

3.1.7. Zinc

Zinc in fish organs has been identified as the second highest concentrated metal following Iron as similar to literatures (Türkmen et al., 2016). Zn accumulations in the gills were found at the mean highest concentration (54.98 mg kg⁻¹) in *B. mystaceus* and the mean lowest concentration (5.66 mg kg⁻¹) in *C. trutta*. The mean highest and lowest zinc accumulations in the fish muscles were determined in *C. macrostomus* in the amount of 22.34 mg kg⁻¹ and in *C. regium* in the amount of 10.08 mg kg⁻¹, respectively (Table 1).

It has been observed that C. macrostomus and B. mystaceus have more Zn levels than other species when the Zn levels in the six fish species are examined (p < 0.05). Dural et al. (2006) reported mean Zn levels of 115.58 mg kg⁻¹ in the gills and 78.5 mg kg⁻¹ in the fish muscle tissues from Çamlık Lagoon in the Iskenderun Bay. The lower average level of Zn has been reported for common carp (3.28 mg kg⁻¹) from Turkey



Fig. 3. Concentration (as mg kg⁻¹) of the sum of essential metals (a) (Mn, Fe, Co, Cu, and Zn) and toxic metals (b) (Cr, Ni, iAs, Cd, and Pb) in fish species [*Carassius gibelio (CG), Capoeta trutta (CT), Barbus rajanorum mystaceus (BM), Cyprinion macrostomus (CM), Chondrostoma regium (CR), Liza abu (LA)*].

(Kalyoncu et al., 2012). The similar average Zn level (11.1 mg kg⁻¹) in the muscle of seabream from Adana, Turkey, and the lower mean Zn levels in rainbow trout's muscle (5.24 mg kg⁻¹) from Iran has been reported (Türkmen et al., 2016; Fallah et al., 2011) (Table 3). The average Zn levels in *B. mystaceus*' gill were found to be above the maximum permitted concentrations (MPC) (30 mg kg⁻¹) determined by FAO (Table 2).

3.1.8. Arsenic

Arsenic measurement in fish tissue is the total amount of organic and inorganic forms. In the present study, we have accepted that 10% of the total As was inorganic As and mentioned as _iAs: inorganic As (USEPA, 2000). Therefore, calculation of human health risk (EDI, THQ, HI and CR) values has been made with _iAs.

The highest and lowest inorganic Arsenic accumulation in the muscle of the fish was observed in C. macrostomus (0.25 mg kg⁻¹) and both C. gibelio and C. trutta (0.02 mg kg^{-1}), respectively. On the other hand, iAs accumulation in the gills as the maximum and minimum levels were determined in *B. mystaceus* with 0.37 mg kg⁻¹ and *C. gibelio* with 0.02 mg kg⁻¹, respectively (Table 1). The As levels have been reported to be an average of 0.88 mg kg^{-1} as wet weight in variety of edible fish from the Bangshi River of Bangladesh (Rahman et al., 2012). In a study carried out in the Persian Gulf, an average of 101.33 mg kg⁻¹ As was detected in the muscle of S. commerson (Rahimi and Gheysari, 2016). The MPC for As in fish by the Chinese Ministry of Health (MHPRC, 2013) and the Australian and New Zealand Food Standards (FSANZ, 2013) are $0.10~{\rm mg~kg^{-1}}$ and $2.0~{\rm mg~kg^{-1}},$ respectively. The inorganic arsenic levels measured in four fish species of this study were found to be above the maximum allowable concentrations (MAC) determined by MHPRC (2013). ¡As levels in C. trutta and C. gibelio were found to be below the maximum allowable concentrations determined by MHPRC (2013). The levels of iAs in the muscle of the six fish species is higher than that determined by Varol and Sünbül (2018) and lower than all other studies in Table 3.

3.1.9. Cadmium

The greatest and the lowest Cadmium concentration in fish muscle was detected in *C. macrostomus* (0.05 mg kg⁻¹) and in *B. mystaceus* (0.002 mg kg⁻¹), respectively. Cd levels in the muscles and gills of all other fish species were <0.05 mg kg⁻¹. Significant differences were detected statistically in Cd levels among fish species (p < 0.05). Cd levels in six fish species were found to be below the maximum levels permitted by MHPRC (2013) and the European Commission (EC, 2006) (Table 2). The average Cd levels recorded in fish species of this study are different from those stated in the literature, as presented in Table 3. In addition,

the amount of Cd detected in six fish species were below the MAC according to the Turkish Food Codex (Anonymous, 2011) (Table 2).

3.1.10. Lead

The greatest Lead concentration in gill was detected in L. abu (0.45 mg kg⁻¹) and the lowest concentration in *B. mystaceus* (0.03 mg kg⁻¹). Lead concentrations in muscle tissue were determined in the highest level (0.33 mg kg⁻¹) in *L. abu*, and in the lowest level (0.11 mg kg⁻¹) in C. trutta and C. gibelio, equally. There were statistically important variances in Pb levels among fish species (p < 0.05). Canli et al. (1998) declared that the lead concentrations from C. carpio, B. capito and C. regium in the Seyhan River, Turkey were in the range of 2.35-11.19, 1.30–9.29 and 0.74–3.43, as mg kg^{-1} wet weight, respectively. The Pb levels of fish muscles in the present study, $(0.11-0.33 \text{ mg kg}^{-1})$ were found to be higher than the studies performed by Copat et al., 2013; Martínez-Gómez et al., 2012; Medeiros et al., 2014; Tuzen, 2009, and Varol and Sünbül (2018). The mean Pb values in the fish muscle in our study are lower than many other studies stated in the literature (Table 3). The mean levels of Pb in fish of our study were lower than MPLs set by the Codex Alimentarius Commission (WHO/FAO, 2015) (0.3 mg kg $^{-1}$), EC (0.3 mg kg $^{-1}$), FSANZ (0.5 mg kg $^{-1}$) and MHPRC (0.5 mg kg $^{-1}$).

3.2. Ranking of fish species according to metal concentration

Fish species are listed according to the sum of the average levels of toxic or possible toxic metals (Pb, Ni, Cr, Cd, $_i$ As) and essential metals (Zn, Mn, Cu, Fe, Co) in our study. The highest and lowest levels in terms of essential metals were found in *C. macrostomus* and *C. regium*, respectively (Fig. 3a). The highest toxic metal level was measured in *C. macrostomus*, whereas the lowest level was determined in *C. gibelio* (Fig. 3b). Differences among the essential and toxic metals levels accumulated in fish species may result from different environmental source levels, habitats, nutritional behaviors and physiology of fish species (Varol et al., 2019).

3.3. The assessment of potential public health risk associated to fish consumption

MPI was calculated for the gills and muscles of each fish species. The MPI values calculated from the gills were more than those from the muscles in general. MPI values in gills were 2.33 in *L. abu*, 1.17 in *C. regium* and 1.80 in *C. macrostomus*. MPI values in muscles were 1.09 in *L. abu* and 1.33 in *C. macrostomus*. In the present study, MPI values in fish were higher than MPI values reported from Belgium and France and

Table 4

Worldwide calculated Metal Pollution Index (MPI) of fish species.

Country	MPI	References
Turkey	1.38	This study
Turkey	1.67	This study
Belgium	0.77	(Schnitzler et al., 2011)
Greece	1.87	(Castritsi-Catharios et al., 2015)
Portugal	2.38	(Lourenço et al., 2012)
Spain	2.11	(Vicente-Martorell et al., 2009)
Italy	5.84	(Carpene et al., 1998)
France	0.67	(Schnitzler et al., 2011)

lower than MPI values reported from Greece, Portugal, Spain and Italy (Table 4). A greater MPI value points out the greater cumulative metal accumulations in the fish sample (Rabiul Islam et al., 2017). Consumption of fish with a high MPI value may pose a potential public health risk.

Calculated EDI values of ten metals from six fish species sampled are presented in Table 5. In general, the EDI values of each metal is higher than the TDI values depending on the fish species. For example, the EDI values of Zn and Pb are higher than the TDI values in all fish species. EDI values for Mn are higher in *L. abu, C. macrostomus* and *B. mystaceus* than TDI values. Therefore, daily intake of these metals may have a harmful effect on public health.

Potential health risk index values (THQ, HI, CR, and MPI) of fish species were calculated for adults as presented in Table 6. The THQ values of all metals were below 1 which pose no public health risks. In addition, the HI values of each fish species are lower than 1 and are thought to pose no probable public health risks (Fig. 4, Table 6).

CR values calculated for each fish species based on iAs, Cr, Ni, and Pb

 Table 5

 EDI, RfD and TDI values of metals in muscles tissues of fish in the Tigris River.

metals are given in Table 6. The calculated CR values of all fish species in Tigris River for As, Cr, Ni and Pb ranged from 7.07E-06 to 5.51E-04, 8.36E-05 to 1.80E-04, 5.83E-05 to 1.01E-03 and 2.00E-07 to 6.01E-07, respectively, (Table 6). Based on US EPA methods, CR values lower than 10^{-6} is accepted as negligible, $>10^{-4}$ is unacceptable, and in the range from 10^{-4} to 10^{-6} is assessed as acceptable (USEPA, 2015). The results of this study showed that CR values of _iAs were higher than unacceptable level of 10^{-4} in *C. macrostomus*. CR values of Cr were higher than unacceptable level in all fish with the exception of *C. gibelio*. CR values of Ni were higher than unacceptable level *L. abu, C. macrostomus* and *B. mystaceus*. On the other hand, CR values of Pb were acceptable as negligible level (Table 6). Similar results were reported in previous studies (Liu et al., 2019; Varol et al., 2019).

4. Conclusions

The present study showed that fish species, caught and consumed from the Tigris River, contain various metal concentrations and the degree of accumulation varies among different species. Fe has been the element which form the highest metal accumulation. Among the metal accumulation, Fe accumulation in the gills of *L. abu* was at the highest level. While the highest metal accumulation in the tissues was iron, the lowest accumulation was cadmium and cobalt. Except cobalt in muscle tissue, statistically meaningful differences were found between the amount of metal determined in all Tigris River fish (p < 0.05). The order of the mean maximum metal concentrations in the muscle tissues of the fish are listed as follows; Fe > Zn > Mn > Cu > Ni > Cr > Pb > iAs > Cd = Co with the values of 175.88 > 22.34 > 10.29 > 2.81 > 2.76 > 1.68 > 0.33 > 0.25 > 0.05 = 0.05 mg kg⁻¹, respectively. The highest mean level

	EDI (Estimated I	Daily Intakes = mg/k		RfD*	TDI**			
	L.abu	C. regium	C. macrostomus	B. mystaceus	C. trutta	C. gibelio	(mg/kg/day)	(mg/kg/day)
Cr	3.29E-01	2.26E-01	3.61E-01	2.78E-01	2.45E-01	1.68E-01	3.00E-03	3.00E-01
Mn	1.22E + 00	1.31E - 01	2.21E + 00	3.06E-01	9.25E-02	2.15E-02	1.40E-01	1.40E-01
Fe	2.09E + 01	3.56E + 00	3.78E + 01	1.09E + 01	1,81E + 01	1.23E + 01	7,00E-01	8,00E-01
Со	8.61E-03	8.61E-03	1.08E-02	8.61E-03	6.45E-03	8.61E-03	3.00E-04	3.00E-02
Ni	2.39E-01	4.73E-02	5.94E-01	8.18E-02	3.87E-02	3.44E-02	2.00E - 02	1.20E - 02
Cu	6.05E-01	1.61E - 01	1.66E-01	6.24E-02	1.08E - 02	1.91E-01	4.00E-02	5.00E-01
Zn	2.46E + 00	2.17E + 00	4.81E + 00	3.85E + 00	2.68E + 00	3.59E + 00	3.00E-01	3.00E-01
iAs	4.35E-02	2.95E-02	5.27E-02	2.54E - 02	4.73E-03	4.52E-03	3.00E-04	2.14E-03
Cd	6.45E-03	5.81E-03	1.08E-02	4.30E-04	2.15E-03	2.15E-03	1.00E - 03	8.00E-04
Pb	7.10E-02	3.23E-02	4.09E-02	2.58E-02	2.37E-02	2.37E-02	3.00E-03	1.50E-03

*(USEPA, 2015)

**(Varol et al., 2018)

Table 6

Target hazard quotient (THQ), Hazard index (HI), Target Cancer Risk (CR) Metal pollution index (MPI) values of metals via consumption of fish.

	L.abu	C. regium	C. macrostomus	B. mystaceus	C. trutta	C. gibelio
Cr	1.09E-01	7.50E-02	1.20E-01	9.21E-02	8.14E-02	5.57E-02
Mn	8.66E-03	9.34E-04	1.58E-02	2.17E-03	6.58E-04	1.53E - 04
Fe	2.98E-02	5.07E-03	5.38E-02	1.55E-02	2.58E-02	1.76E - 02
Со	2.86E-02	2.86E-02	3.57E-02	2.86E-02	2.14E-02	2.86E - 02
Ni	1.19E-02	2.36E-03	2.96E-02	4.07E-03	1.93E-03	1.71E - 03
Cu	1.51E-02	4.02E-03	4.13E-03	1.55E-03	2.68E-04	4.77E-03
Zn	8.17E-03	7.20E-03	1.60E-02	1.28E-02	8.91E-03	1.19E - 02
iAs	1.44E-01	9.79E-02	1.75E-01	8.43E-02	1.57E-02	1.50E - 02
Cd	6.43E-03	5.79E-03	1.07E-02	4.29E-04	2.14E-03	2.14E - 03
Pb	2.36E-02	1.07E-02	1.36E-02	8.57E-03	7.86E-03	7.86E-03
	3.86E-01	2.38E-01	4.74E-01	2.50E-01	1.66E-01	1.45E - 01
iAs	6.49E-05	4.40E-05	5.51E-04	3.79E-05	7.07E-06	6.75E-06
Cr	1.64E-04	1.13E-04	1.80E-04	1.38E-04	1.22E-04	8.36E-05
Ni	4.04E-04	8.01E-05	1.01E-03	1.38E-04	6.56E-05	5.83E-05
Pb	6.01E-07	2.73E-07	3.46E-07	2.86E-07	2.00E-07	2.00E - 07
Muscle	1.09E + 00	4.60E-01	1.33E + 00	4.30E-01	2.90E-01	3.20E - 01
Gill	2.33E + 00	1.17E + 00	1.80E + 00	7.10E-01	2.70E-01	2.50E - 01
	Cr Mn Fe Co Ni Cu Zn iAs Cd Pb iAs Cd Pb iAs Cr Ni Pb Muscle Gill	$\begin{tabuy}{ c c c c } \hline Labu \\ \hline Cr & 1.09E-01 \\ \hline Mn & 8.66E-03 \\ \hline Fe & 2.98E-02 \\ \hline Co & 2.86E-02 \\ \hline Ni & 1.19E-02 \\ \hline Cu & 1.51E-02 \\ \hline Cu & 1.51E-02 \\ \hline Zn & 8.17E-03 \\ \hline iAs & 1.44E-01 \\ \hline Cd & 6.43E-03 \\ \hline Pb & 2.36E-02 \\ \hline 3.86E-01 \\ \hline iAs & 6.49E-05 \\ \hline Cr & 1.64E-04 \\ \hline Ni & 4.04E-04 \\ \hline Ni & 4.04E-04 \\ \hline Pb & 6.01E-07 \\ \hline Muscle & 1.09E+00 \\ \hline Gill & 2.33E+00 \\ \hline \end{tabular}$	$\begin{tabusered} L abu C regium$ \\ \hline L abu C regium$ \\ \hline $1.09E-01$ $7.50E-02$ \\ \hline Mn $8.66E-03$ $9.34E-04$ \\ \hline Fe $2.98E-02$ $5.07E-03$ \\ \hline Co $2.86E-02$ $2.86E-02$ \\ \hline Ni $1.19E-02$ $2.36E-03$ \\ \hline Cu $1.51E-02$ $4.02E-03$ \\ \hline Cu $1.44E-01$ $9.79E-02$ \\ \hline Cd $6.43E-03$ $5.79E-03$ \\ \hline Pb $2.36E-02$ $1.07E-02$ \\ \hline $3.86E-01$ $2.38E-01$ \\ \hline $a.86E-01$ $2.38E-01$ \\ \hline $a.96E-05$ $4.40E-05$ \\ \hline Cr $1.64E-04$ $1.13E-04$ \\ \hline Ni $4.04E-04$ $8.01E-05$ \\ \hline Pb $6.01E-07$ $2.73E-07$ \\ \hline $Muscle$ $1.09E+00$ $4.60E-01$ \\ \hline $Gill$ $2.33E+00$ $1.17E+00$ \\ \hline \end{tabular}$	$\begin{tabusered} L abu$ C regium$ C macrostomus$ \\ \hline Cr 1.09E-01$ 7.50E-02$ 1.20E-01$ \\ \hline Mn 8.66E-03$ 9.34E-04$ 1.58E-02$ \\ \hline Fe 2.98E-02$ 5.07E-03$ 5.38E-02$ \\ \hline Co 2.86E-02$ 2.86E-02$ 3.57E-02$ \\ \hline Ni 1.19E-02$ 2.36E-03$ 2.96E-02$ \\ \hline Cu 1.51E-02$ 4.02E-03$ 4.13E-03$ \\ \hline Cu 1.51E-02$ 4.02E-03$ 4.13E-03$ \\ \hline Cu 1.51E-02$ 4.02E-03$ 1.60E-02$ \\ \hline as 1.74E-01$ 9.79E-02$ 1.75E-01$ \\ \hline Cd 6.43E-03$ 5.79E-03$ 1.07E-02$ \\ \hline Pb 2.36E-02$ 1.07E-02$ 1.36E-02$ \\ \hline as 6.49E-05$ 4.40E-05$ 5.51E-04$ \\ \hline Cr 1.64E-04$ 1.13E-04$ 1.80E-04$ \\ \hline Ni 4.04E-04$ 8.01E-05$ 1.01E-03$ \\ \hline Pb 6.01E-07$ 2.73E-07$ 3.46E-07$ \\ \hline $Muscle$ 1.09E+00$ 4.60E-01$ 1.33E+00$ \\ \hline $Gill$ 2.33E+00$ 1.17E+00$ 1.80E+00$ \\ \hline \end{tabuser}$	Labu C. regium C. macrostomus B. mystaceus Cr 1.09E-01 7.50E-02 1.20E-01 9.21E-02 Mn 8.66E-03 9.34E-04 1.58E-02 2.17E-03 Fe 2.98E-02 5.07E-03 5.38E-02 1.55E-02 Co 2.86E-02 2.86E-02 3.57E-02 2.86E-02 Ni 1.19E-02 2.36E-03 2.96E-02 4.07E-03 Cu 1.51E-02 4.02E-03 4.13E-03 1.55E-03 Zn 8.17E-03 7.20E-03 1.60E-02 1.28E-02 iAs 1.44E-01 9.79E-02 1.75E-01 8.43E-02 Cd 6.43E-03 5.79E-03 1.07E-02 4.29E-04 Pb 2.36E-01 2.38E-01 4.74E-01 2.50E-01 jAs 6.49E-05 4.40E-05 5.51E-04 3.79E-05 Cr 1.64E-04 1.13E-04 1.80E-04 1.38E-04 jAs 6.49E-05 4.40E-05 5.51E-04 1.38E-04 Ni 4.04E-04 <td>LabuC. regiumC. macrostomusB. mystaceusC. truttaCr1.09E-017.50E-021.20E-019.21E-028.14E-02Mn8.66E-039.34E-041.58E-022.17E-036.58E-04Fe2.98E-025.07E-035.38E-021.55E-022.58E-02Co2.86E-022.86E-023.57E-022.86E-022.14E-02Ni1.19E-022.36E-032.96E-024.07E-031.93E-03Cu1.51E-024.02E-034.13E-031.55E-032.66E-04Zn8.17E-037.20E-031.60E-021.28E-028.91E-03iAs1.44E-019.79E-021.75E-018.43E-021.57E-02Cd6.43E-035.79E-031.07E-028.57E-037.86E-03pb2.36E-012.38E-014.74E-012.50E-011.66E-01iAs6.49E-054.40E-055.51E-043.79E-057.07E-06Cr1.64E-041.13E-041.80E-041.38E-041.22E-04Ni4.04E-048.01E-055.51E-043.38E-046.56E-05Pb6.01E-072.73E-073.46E-072.00E-072.00E-07Muscle1.09E+004.60E-011.33E+004.30E-012.90E-01Gill2.33E+001.17E+001.80E+007.10E-012.70E-01</td>	LabuC. regiumC. macrostomusB. mystaceusC. truttaCr1.09E-017.50E-021.20E-019.21E-028.14E-02Mn8.66E-039.34E-041.58E-022.17E-036.58E-04Fe2.98E-025.07E-035.38E-021.55E-022.58E-02Co2.86E-022.86E-023.57E-022.86E-022.14E-02Ni1.19E-022.36E-032.96E-024.07E-031.93E-03Cu1.51E-024.02E-034.13E-031.55E-032.66E-04Zn8.17E-037.20E-031.60E-021.28E-028.91E-03iAs1.44E-019.79E-021.75E-018.43E-021.57E-02Cd6.43E-035.79E-031.07E-028.57E-037.86E-03pb2.36E-012.38E-014.74E-012.50E-011.66E-01iAs6.49E-054.40E-055.51E-043.79E-057.07E-06Cr1.64E-041.13E-041.80E-041.38E-041.22E-04Ni4.04E-048.01E-055.51E-043.38E-046.56E-05Pb6.01E-072.73E-073.46E-072.00E-072.00E-07Muscle1.09E+004.60E-011.33E+004.30E-012.90E-01Gill2.33E+001.17E+001.80E+007.10E-012.70E-01



Fig. 4. Hazard Index (HI) of metals in different fish species.

of toxic and essential metals was found in *C. macrostomus*, while the lowest mean level of toxic metal was determined in *C. Gibelio*, and the lowest mean level of essential metals was determined in *C. regium*. The mean levels of Cu, Cd, Pb, and Cr in all fish species were below the maximum permissible limits (MPLs). Although it varies according to the fish species, it has been determined that EDI values of each metal are higher than the TDI values and may have a harmful effect on human health in daily intake. THQ and HI values were below 1 indicating that it would pose no public health problems. As a result, the present study showed that the consumption of six fish species in the Tigris River is safe for public health considering THQ and HI values. However, at least one of the CR values of _iAs, Cr and Ni in all fish species is above unacceptable levels (10^{-4}) and may cause public health problems.

CRediT authorship contribution statement

Yalçın Töre: Investigation, Conceptualization, Methodology, Formal analysis, Funding acquisition, Project administration, Resources, Supervision. Fikret Ustaoğlu: Data curation, Writing - original draft, Visualization. Yalçın Tepe: Data curation, Writing - review & editing. Erkan Kalipci: Investigation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Y. Töre et al.

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