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Distribution of toxic and trace metals in fish from the Black Sea: Implications for human health risks

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ABSTRACT

This study focused on the investigation of toxic and trace metal levels in fish caught from the Black Sea, which is facing pollution threats from various human activities. It also aimed to assess the potential health risks associated with consuming fish and contribute to the development of strategies for sustainable fisheries management. Metal presence was observed in the muscle tissues of four commercially consumed fish species (anchovy, whiting, horse mackerel and red mullet) from nine different stations in the Black Sea. Among the metals, the highest average concentration was observed for aluminium (Al) in anchovy and the lowest concentration for cadmium (Cd) in whiting. However, the levels were generally below the maximum allowable limits recommended by the FAO, WHO, EC, and Turkish Food Codex. The study results showed that metal concentrations in the analyzed fish species did not pose significant non-carcinogenic health risks to consumers. Although research findings show that some fish species studied from the Black Sea exhibit high metal levels, the concentrations of toxic and trace elements are generally within acceptable thresholds for safe fish consumption. The findings of this study are thought to help stakeholders develop strategies for environmental protection and sustainable fisheries management in the region.

1. Introduction

Contamination of aquatic ecosystems with metals has become an important environmental problem in recent years, as it has significant adverse effects on the health of fish populations and may have potential consequences for human health [[1,2]]. Various sources of metal pollution enter aquatic ecosystems, including natural sources such as rock weathering, volcanic eruptions, and soil erosion, as well as anthropogenic sources such as industrial activities, agricultural runoff, and sewage disposal [3]. Metals can be classified as essential, such as copper, selenium, iron, chromium, manganese, and zinc, which are essential for the metabolism of the human body, and non-essential, such as mercury, lead, and cadmium, which can be toxic even at low concentrations [4].

Fish have often been used for many years as excellent biomarkers to assess their ecological and health risks because of their high trophic levels, wide distribution, long lifespan and being an important source of protein in the human diet [[5–7]]. Metals accumulate in fish, both by absorption from the waters through their gills or skin and by consumption of their diet [8]. Once the metals enter the fish, they can be stored in tissues such as muscles, liver and gills, and then transferred to humans through the food chain [9]. Consumption of fish contaminated with metals can lead to a range of adverse health effects including neurological damage, teratogenic effects, impaired reproductive capacity, hypertension, kidney damage, and cancer [10]. For this reason, many researchers have evaluated the risk to human health of consuming fish contaminated with metals.

The Black Sea is a closed sea that takes the discharge of Europe's largest rivers such as the Danube, Dnieper and Don into its basin and is connected to the Mediterranean by a narrow Turkish Straits System [11]. In addition to having rich mineral diversity, the Black Sea region has important agricultural areas, and surface fresh water resources are quite abundant in this region [12,13]. Also, the Black Sea has an important position in Türkiye's fisheries. According to Ref. [14] the amount of fisheries fishing in the seas of Türkiye was determined as 295,025 tons, and 77 % of this amount was obtained from the Black Sea.

This study aimed to investigate the metal levels of fish caught

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from the Black Sea, which is threatened by pollution due to various industrial activities, maritime traffic, mining and human activities. The aim of this study is: i) to determine metal levels in four different commercial fish species caught from the Black Sea, ii) to evaluate human health and toxic risks with fish consumption, iii) to update metal pollution levels in these fish species in the literature. Besides all these objectives, this study can assist stakeholders to develop strategies for environmental protection and sustainable fisheries management.

2. Material methods

2.1. Sampling area and tissue sampling

The Black Sea is a semi-enclosed sea with a surface area of 4.2×105 km^2 and a volume of 5.3×105 km^3 [15,16]. Although it has a maximum depth of 2200 m, the hydrogen sulfide (H_2S) layer begins after 100−150 m of depth, limiting the habitable water column [16–18]. Anchovy (*Engraulis encrasicolus* Linnaeus, 1758), whiting (*Merlangius merlangus* Linnaeus, 1758), horse mackerel (*Trachurus mediterraneus* Steindachner, 1868) and red mullet (*Mullus barbatus* Linnaeus, 1758), which are the most consumed commercial fish, were collected from 9 different stations in the Black Sea between October and November 2022. As sampling stations, Artvin (S1), Rize (S2), Trabzon (S3), Giresun (S4), Samsun (S5), Sinop (S6), Zonguldak (S7), Sakarya (S8) and Kırklareli (S9) provinces were selected (Fig. 1). Fish samples were caught by the fishermen fishing at each station using nets. Collected fish were kept with ice in polyethylene bags, tagged, and delivered to the laboratory the same day. The samples were then washed with ultrapure water. Each fish sample was provided with approximately 200 g of dorsal muscle for analysis of metal content. Immediately following the quest, samples were refrigerated and stored at −20 °C for further chemical analysis in the laboratory.

2.2. Metal analysis

In this study, about 0.5 g (wet weight) of each fish sample's edible fraction was weighed and put in containers to test for metals. The samples were mixed with 9 mL of 65 % concentrated HNO_3 and 3 mL of 30 % concentrated HNO_3. It was then burned at 200 °C for 20 min in a BERGHOF Speedwave microwave burner. After taking the samples out of the microwave, the containers were given 20 min to cool [19]. ISOLAB was filtered through 125 mm filter paper after centrifugation, and the volume was adjusted to 100 mL. Each solution's data was documented and kept cold in a fridge. Bayburt University Central Research Centre utilized ICP-MS for metal studies. Each sample was tested for each element three times. The limit of detection (LOD) was calculated as three times the standard deviation of ten measurements of the blank solution prepared according to the recommendations of the International Union of Pure and Applied Chemistry (IUPAC) and then divided by the slope of the calibration curve [20]. Accordingly, the detection limits of metals were Cr, Fe, Ni, Cu, Zn and Pb 0.018, 0.06, 0.020, 0.10, 0.01 and 0.010 mg/kg, respectively. For accuracy and reproducibility of sample preparation, the certified reference material DORM-3 (National Research Council, Canada) was used for trace elements in fish tissue. Triplicate readings of the reference sample were used to evaluate recoveries and the percentage was observed to range from 94 % to 103 %.

2.3. Statistical analysis

Shapiro-Wilk and Levene tests were used to determine the suitability of the data for normal distribution and the homogeneity of variances. If there were significant differences, the Tukey test was used to determine these differences. One-way analysis of variance was used to detect significant differences ($p < 0.05$) of metals between tissues and species. (ANOVA). In all cases, the significance level was set at 95 % (i.e., $\alpha = 0.05$). Statistical analyzed were performed using the IBM-SPSS statistical software package.

2.4. Health risk assessment

2.4.1. Estimated daily intake (EDI)

The human health risks associated with metal intake in food are determined by Estimated Daily Intake (EDI) [21]. The specific formula is as follows;

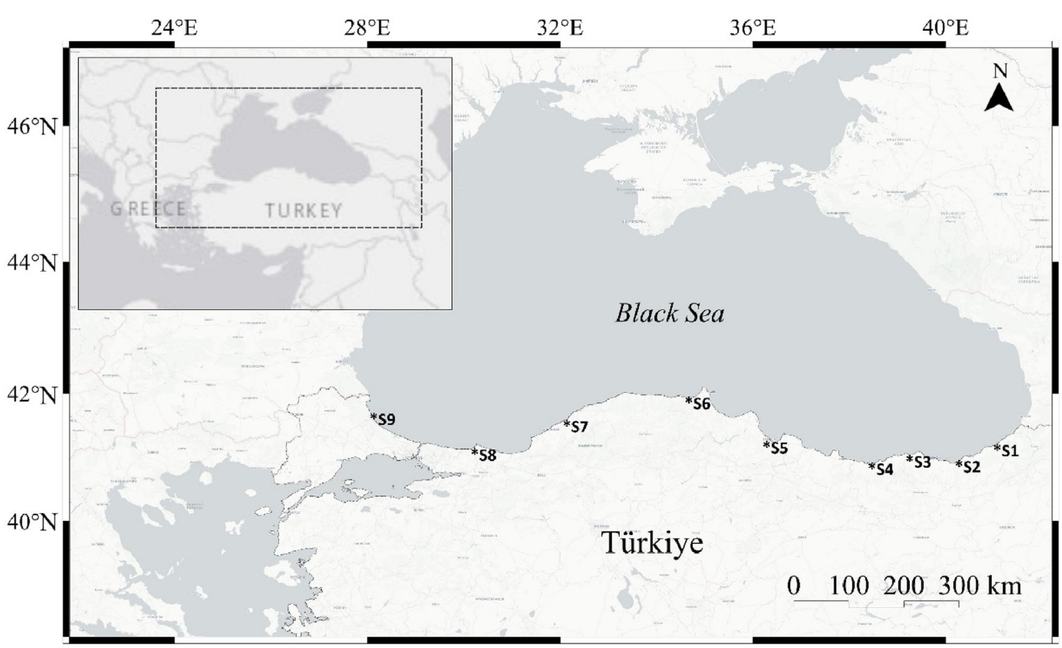

Fig. 1. Sampling area.

$$EDI = \frac{C*IR*EF*ED}{BW*AT} \quad (1)$$

where C; the content of the metals (ug/kg), IR; the ingestion rate of fish (0.020 kg/day), EF; exposure frequency (365 days/year), ED; the exposure duration in years (70 years), BW; the body weight of the exposed individual for adults (70 kg), and AT; average exposure time for non-carcinogens (365 day/year × ED) [22–24].

2.4.2. Non-carcinogenic risk

The target hazard environment (THQ) is a method recommended by the US Environmental Protection Agency (USEPA) to estimate the potential health risks of pollutants [25];

$$THQ = \frac{EDI}{RfD}$$

where THQ; the target hazard quotient, EDI; the estimated daily intake, and RfD; the reference dose (μg/kg/day). Oral reference dose (RfD) values for Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, and Zn are 1000, 0.3, 1, 3, 40, 700, 0.1, 140, 20, 3.5, 5, and 300 μg/kg/day, respectively. If THQ <1.0 indicates that there may not be any negative impact, THQ ≥ 1.0 indicates that the possibility of negative impact is evident [26].

2.4.3. Carcinogenic risk index

The potential cancer risk associated with exposure to a heavy metal dose in fish tissue is estimated as the increased likelihood of an individual developing cancer over the course of their lifetime [27]. The equation utilized for the estimation of cancer risk is presented below [28]:

$$RI = EDI \times SF$$

Where EDI is the estimated daily intake of heavy metals. SF is the slope factor from the Integrated Risk Information System database [21]. SF values were used only for As (1500 μg/kg/day), Cd (6300 μg/kg/day), Cr (41 μg/kg/day), Ni (1.7 μg/kg/day) and Pb (8.5 μg/kg/day) [29]. RI was considered insignificant ($RI < 10^{-6}$); RI assessed as permissible or tolerable ($10^{-6} < RI < 10^{-4}$); RI was considered significant ($RI > 10^{-4}$).

3. Results

3.1. Metals in fish samples

The current study presents data on the levels of seven metals (Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, and Zn) found in the muscles of four different fish species, as seen in Table 1. The highest mean concentration was observed for Al (1.501 μg/g) in anchovy, whereas the lowest concentration was observed for Cd (0.138 μg/g) in whiting.

3.1.1. Toxic elements

Arsenic is a non-essential contaminant found in the environment through bioaccumulation and biomagnification [36]. The mean value of As in fish species was 1.94 ± 1.31 μg/g. While the highest As concentrations were in the range of 5.44 μg/g in anchovy at the S2 location, the lowest concentrations of As (0.54 μg/g) were observed in mezgin at the S6 location. The levels of arsenic found in four fish species in this study were much higher than those found in the same fish species from the Black Sea [31]. On the contrary, Alkan et al. [37] reported the As level of 2.58 μg/g in horse mackerel and 1.85 μg/g in anchovy. Arsenic is one of the most hazardous elements in the environment, originating from either anthropogenic or natural sources [38]. Mielcarek et al. [39] underlined that inorganic arsenic is more dangerous to health than organic arsenic, but reported that the risk of consuming significant amounts of inorganic arsenic from fish is generally low, as fish typically contains arsenic in organic form.

Cadmium is a toxic metal that can enter the body after magnification in the food chain, causing Cd poisoning [40]. The Cd concentration in fish muscle was highest in anchovy at S6, with values of 0.045 μg/g, and the lowest concentration of 0.004 was observed in whiting at S7. Cd levels in the present study were 0.011 μg/g in horse mackerel, 0.029 μg/g in anchovy, 0.012 μg/g in red mullet, and 0.007 μg/g in whiting which were similar to Cd values reported from the Black Sea by Nisbet et al. [32] (0.012 μg/g). On the contrary, mean concentrations of Pb in all species were lower than other studies in the Black Sea [24,36,31].

The average value of Hg observed in this study was 0.03 μg/g. The maximum concentration of Hg was observed in whiting (0.34 μg/) at S3, and the minimum concentration was detected in horse mackerel at S9 (0.05 μg/g). Bat et al. [34] and Nisbet et al. [32] reported that Hg was not detected in the muscle tissue of similar fish. In the literature, mercury levels in research conducted in the Black Sea; It was reported as 0.11 mg/kg for muscles of red mullet [41], 0.078 mg/kg for muscles of horse mackerel, 0.055 mg/kg for muscles of anchovy, 0.036 mg/kg for muscles of red mullet, and 0.084 mg/kg for muscles of whiting [31].

Compared to the literature, low levels were observed in other species, except for red mullet. Additionally, WHO recommends a maximum permissible level of 0.5 μg/g for mercury. In the present study, Mercury was found below the tolerable limits specified by WHO [42] in all fish species.

The concentrations of Ni in the fish muscles analyzed ranged from 0.05 to 0.54 μg/g, with the highest concentration in whiting at S5 station. However, the lowest concentration was measured in red mullet at S1 station. In this study, the average Cd concentrations were presented with 0.14 ± 0.08 μg/g in red mullet, 0.21 ± 0.10 μg/g in anchovy, 0.17 ± 0.09 μg/g in whiting, and 0.18 ± 0.16 μg/g in horse mackerel. It was comparatively higher than the level observed in Sinop [30] and lower than the content recorded in the Black Sea [24,29,31]. Nickel concentration found in the present study was above the permissible limit of approximately (0.15 μg/g) as recommended by FAO/WHO [43].

Pb is a ubiquitous toxic metal that can cause neurotoxicity, nephrotoxicity, and other health disorders [5,38]. Pb concentrations in fish species ranged from 0.04 to 0.25 μg/g with the lowest in red mullet at S3 and highest in whiting at S5 site. However, in another study conducted by Mutlu [33], Pb levels were reported as 1.070, 1.01, 0.72, and 1.02 μg/g in horse mackerel, anchovy, red Mullet and whiting, respectively. Besides, FAO has specified the allowable Pb value of 2 μg/g. This value is lower than the results obtained in this study [44]. The acceptable limit for Pb concentration of EC, Turkish Food Codex, and WHO is 0.2, 0.3 and 0.5 μg/g, respectively. Pb concentrations of anchovy, whiting, red mullet and horse mackerel were found to be below the acceptable limit recommended by the EC, Turkish Food Codex and WHO [42,45,46].

3.1.2. Trace elements

The mean concentrations of Fe in the muscles of red mullet, anchovy, whiting, and horse mackerel in the Black Sea were 15.08, 21.09, 11.96, and 11.25 μg/g, respectively. The highest concentration of Fe was observed in anchovy (37.45 μg/g) at S7 site. The lowest level of Fe was observed in whiting (5.11 μg/g) at S9. Iron concentrations in fish of other studies have been found to fluctuate from 4.49 to 145 μg/g [24,29,31,36]. Also, the average concentrations of all samples contain iron below 180 μg/g [44] and 109 μg/g [42].

Table 1
Mean metal concentrations (μg/kg wet weight) in fish species collected from the Black Sea.

Fish Species	Sampling Area	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Zn	References
Horse mackerel	Black Sea	14.46	1.33	0.01	0.43	0.95	15.07	0.02	0.25	0.14	0.11	0.92	12.04	Present study
Horse mackerel	Sinop	1.63	0.68	0.00	0.08	0.53	5.64	0.02	0.15	0.04	0.02	0.58	7.01	[30]
Horse mackerel	Black Sea		0.18	0.32	1.74	0.65	145.00	0.08	7.21	1.50	0.82	0.31	52.70	[31]
Horse mackerel	Middle Black Sea			0.01		1.79	21.17	ND	10.72	4.68	0.60		27.70	[32]*
Horse mackerel	Eastern Black Sea	1.21		0.12	0.31	2.09	9.93		0.78		1.07		7.85	[33]
Horse mackerel	Sinop	<0.5	0.39	<0.02		0.67	2.20	<0.05			<0.05		24.70	[34]
Anchovy	Black Sea	17.05	1.97	0.03	0.56	1.21	21.09	0.02	1.05	0.21	0.13	0.56	18.04	Present study
Anchovy	Black Sea		0.25	0.27	1.12	1.96	75.70	0.06	9.10	1.93	0.30	0.53	38.80	[31]
Anchovy	Eastern Black Sea	5.68		0.14	0.29	2.40	17.14		2.06		1.01		18.98	[33]
Anchovy	Middle Black Sea			0.04		2.73	26.06		3.93	3.12	0.70		26.25	[32] [a]
Anchovy	Black Sea	95.31		0.12	0.07		18.01		1.39	0.35	0.33		25.42	[35] [a]
Red mullet	Black Sea	15.61	3.37	0.01	0.51	0.61	11.96	0.07	0.42	0.17	0.09	0.99	11.09	Present study
Red mullet	Eastern Black Sea	0.89		0.14	0.23	1.27	7.90		0.98		0.72		7.85	[33]
Red mullet	Black Sea	9.85		0.21	1.06		21.27		0.05	0.66	0.73		7.57	[35] [a]
Red mullet	Black Sea		0.11	0.17	1.35	0.96	53.20	0.04	2.76	1.55	0.36	0.45	75.50	[31]
Red mullet	Middle Black Sea			0.02		3.14	29.17	ND	6.96	2.47	0.92		23.71	[32] [a]
Red mullet	Sinop	<0.5	1.30	<0.02		<0.5	2.30	<0.05			<0.05		3.20	[34]
Whiting	Black Sea	14.73	1.08	0.01	0.60	0.48	11.25	0.02	0.35	0.18	0.13	0.62	7.91	Present study
Whiting	Middle Black Sea			0.00		3.72	28.84	ND	6.92	3.78	0.58		31.34	[32] [a]
Whiting	Eastern Black Sea	5.53		0.12	0.29	1.93	5.80		1.10		1.02		6.14	[33]
Whiting	Black Sea	86.30		0.19	0.14		4.49		0.08	1363	0.50		6.03	[35] [a]
Whiting	Black Sea		0.18	0.21	0.86	1.32	98.10	0.08	7.63	1.14	0.53	0.29	65.40	[31]

[a] Dry weight.

Copper is essential for health, but excessive intake can cause toxic effects on fish, invertebrates and amphibians [47]. Cu was found in all the fish samples, and the concentrations varied from 0.33 to 1.49 μg/g. The highest concentration of Cu was observed in anchovy at S3 site, and the lowest value was found in whiting at S2 site. The average Cu concentration in the fish samples of the present study was 0.81 μg/g. But the concentrations in the fish samples were much below the toxic limit of 30 μg/g [42,44]. Alkan et al. [41] reported Cu concentration in fish species from the Black Sea as follows: 1.02 μg/g for whiting; 1.12 μg/g for horse mackerel.

Manganese is an essential element for both animals and plants, and its toxicity in water can enhance the uptake and toxicity of other metals [48,49]. The lowest concentration of Mn (0.12 μg/g) was measured in whiting at S2 site, while the highest concentration of Mn (2.01 μg/g) was observed in anchovy at S8 site. These results of Mn content in the samples were lower than the results reported by Mutlu [50], Nisbet et al. [32], Turan et al. [35], and Tuzen [31] for same fish species in the Black Sea.

The Cr concentration was highest in whiting (S5), with values of 1.55 μg/g, and the lowest concentration was observed in red mullet (S1), with values of 0.12 μg/g. According to the previous literature, Cr concentrations in the same fish species range from 0.86 to 1.74 μg/g [31], which was higher than in the present study. On the contrary, Topcuoğlu et al. [51] reported similar results. In another study conducted in the Eastern Black Sea region, the Cr level (between 0.23 and 0.31 μg/g) detected in the muscles of fish was reported lower than this study [33]. Turkish standards currently do not provide any information regarding the maximum acceptable levels of chromium in fish tissues [46]. Mendil et al. [52] investigated metal levels in fish samples from the same sampling area and reported higher chromium accumulation (0.63–1.74 μg/g) than the standards.

Zinc is essential for normal growth and metabolism in humans, and its deficiency can lead to appetite, growth retardation, skin changes, and immunological abnormalities [31]. The zinc concentration in fish muscles was highest in anchovy at S8 site, in a range of 26.47 μg/g, and lowest in whiting at S4 (4.97 μg/g). In the previous studies, the range of Zn was 23.71–31.34 μg/g in the Middle Black Sea [32] and the range, 38.8–75.5 μg/g was recorded for the Black Sea [31], which were above than the findings of this study. Similarly, Mutlu [33] reported that the concentrations of Zn in red mullet, horse mackerel, anchovy and whiting in the Eastern Black Sea ranged from 4.53 to 11.60, 5.72–32.37, 12.89–25.75 and 4.76–8.65 μg/g, respectively. The maximum zinc level permitted for fishes is 30 μg/g according to FAO [44] and 50 μg/g according to Turkish food codex [46]. These study results were below the allowable limit values.

The aluminium concentration was highest in anchovy at S2 station (38.66 μg/g) and lowest in horse mackerel at S9 (3.54 μg/g). Bat et al. [34] reported the concentrations of Al in anchovy, horse mackerel, whiting and red mullet obtained from Sinop Coasts of the Black Sea as <0.5 μg/g, which were lower than the concentrations of Al reported in this study. Also, Gündoğdu et al. [53] and Mutlu [33] reported the lowest Al concentrations ranged from 0.91 to 4.15 μg/g and from <0.01 to 12.39 μg/g in the same fish samples from the Sinop Coasts and the Middle Black Sea, respectively. Higher values were observed by Turan et al. [35] as range of 9.85–95.31 μg/g in fish species caught from the Black Sea.

Excessive intake of selenium can be toxic, causing tissue pathology and reproductive dysfunction in fish [54]. The lowest and highest Se levels in muscle tissues of the fish species were 0.48 μg/g in anchovy at S1 and 1.19 μg/g in red mullet at S8. Selenium concentration in previous studies has been reported in the range 0.96–1.86 μg/g in fish species from the Turkish Waters [55] and 0.39–0.52 μg/g in anchovy from Türkiye, Georgia and Abkhazia coasts of the Black Sea [56]. The mean concentration of Se in fish species was 0.77 μg/g. Alkan et al. [41] measured Se level in different fish species from the Black Sea as follows: 4.32 μg/g for whiting; 2.83 μg/g for red mullet. There is no information about maximum permissible selenium limits in fish tissues in FAO [44], WHO [42], and Turkish food codex [46].

Marine organisms accumulate metals through respiration, adsorption and ingestion, and the levels of these metals are increasing due to the release of anthropogenic activities into the marine environment [57]. The metal levels measured in fish may vary depending on the type and age of the fish, the season in which it is caught, the environment in which it lives and its feeding habits [58–60]. In addition, metal levels in this study were given as wet weight (ww), but some compared studies were calculated as dry weight (dw). Therefore, differences may have been observed.

Table 2
Estimated daily intakes (EDI) from fish consumption by the adults (μg/kg/day).

Metals	Horse mackerel	Anchovy	Whiting	Red mullet	TDI
Al	4.46078	4.87194	4.20785	4.13054	NA
As	0.02887	0.01684	0.00925	0.01144	2.14
Cd	0.00356	0.00826	0.00193	0.00306	0.8
Cr	0.14561	0.15989	0.17061	0.12248	300
Cu	0.17415	0.34681	0.13826	0.27023	500
Fe	3.41645	6.02565	3.21355	4.30686	800
Hg	0.02079	0.00627	0.00555	0.00520	NA
Mn	0.11903	0.30034	0.10126	0.07189	140
Ni	0.04951	0.06120	0.05268	0.03983	12
Pb	0.02650	0.03700	0.03769	0.03059	1.5
Se	0.28179	0.15881	0.17669	0.26413	NA
Zn	3.16901	5.15451	2.26004	3.43896	300

TDI: The Tolerated Daily Intake.

3.1.2.1. Risk assessment. Although fish consumption is recommended for human health due to its high nutritional values, it can directly affect the health of consumers due to the accumulation of harmful chemicals in its meat [61]. It is therefore important to compare metal concentrations in fish muscle with known safe levels to ensure safe consumption [62]. Permissible metal limit values in fish muscle tissue based on FAO [44], WHO [42], EC [45] and Turkish Food Codex [46] guidelines for human food consumption were compared with the results of this study (Table 4). Upon comparing the concentrations of Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, and Zn in the muscles of various species with the guidelines of national and international organizations, it was observed that the limit values prescribed by on FAO [44], WHO [42], EC [45] and Turkish Food Codex [46] were not exceeded.

The values of estimated daily intake (EDI) and target hazard quotient (THQ) were calculated from the mean values of the metals concentrations (Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, and Zn) in anchovy, horse mackerel, red mullet and whiting which are presented in Table 2 and Table 3.

The highest mean EDI value was observed in Al in demersal species (red mullet and whiting), while was observed in Fe in pelagic species (anchovy and horse mackerel). In addition, the lowest value was observed in Cd in other species except anchovy. EDI values of all fish species for both toxic and trace elements were below the limit values recommended by various agencies [63,64]. EDI values were compared with the values of the tolerated daily intake (TDI). TDI values determined by EFSA [65] were reported as 2.14, 0.8, 300, 500, 800, 140, 12, 1.5 and 300 μg/g for inorganic As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn, respectively. Thus, the EDI values of the specified metals were observed below the recommended TDI values. The results obtained were consistent with those reported from the Sinop coast of the Black Sea [66], the Eastern Black Sea [67], from the Black Sea [68], and the Eastern Black Sea [50].

Table 3
Target hazard quotient (THQ) of fish species (μg/kg/bw/day) for the adult.

	Rfd	THQ			
Metals		Red mullet	Anchovy	Whiting	Horse mackerel
Al	1000	0.004460776	0.004871937	0.004207849	0.0041305
As	0.3	0.09623	0.05615	0.03085	0.03814
Cd	1	0.00014	0.00031	0.00007	0.00012
Cr	3	0.04854	0.05330	0.05687	0.04083
Cu	40	0.00435	0.00867	0.00346	0.00676
Fe	700	0.00488	0.00861	0.00459	0.00615
Hg	0.1	0.20795	0.06269	0.05550	0.05198
Mn	140	0.00085	0.00215	0.00072	0.00051
Ni	20	0.00248	0.00306	0.00263	0.00199
Pb	3.5	0.00757	0.01057	0.01077	0.00874
Se	5	0.05636	0.03176	0.03534	0.05283
Zn	300	0.01056	0.01718	0.00753	0.01146

Table 4
Maximum permissible limits of metals in fish muscle (μg/g) according to international organizations.

Cd	Cu	Fe	Hg	Ni	Pb	Zn	References
0.5	30	180	0.5	55	2	30	[44]
0.5	30	109		30	0.5		[42]
0.05					0.2		[45]
0.05–0.3	20		0.50–1.0		0.3	50	[46]
0.01	0.81	14.84	0.03	0.18	0.12	12.27	This study

The THQ values were determined to assess the potential risk associated with long-term exposure to metals through fish consumption. The THQ, which is a ratio of a metal's EDI to the oral RfD, was used to quantify the human health hazards from fish consumption. The THQ values of all metals <1 indicate that a single metal ingested through fish consumption will not cause serious harm to the health of an adult human. The highest THQ values were observed in Cd, while As and Hg were the lowest in all species. Furthermore, the TTHQ of the 12 metals was computed as the total of each THQ based on fish consumption exposure. The TTHQ of metals extracted from the muscular tissues of horse mackerel, anchovy, whiting, and red mullet was less than one. Therefore, adults exposed to the consumption of 4 fish species caught from the Black Sea are unlikely to experience harmful health effects. Similar THQ values were also reported for Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Hg, and Pb in fish species from the Black Sea [68]; for As, Cd, Cu, Pb, and Zn in sea bream from Southern Mediterranean Sea [69]; for Cd, Ni, Cu, Pb, Cr, Mn, Hg, Fe, As, Zn in bottom fish from the Marmara Sea [70]. Moreover, carcinogenic risk values of different metals identified in the muscle tissues of the fish obtained in the study were calculated. Accordingly, since RI values are below 10^{-6} in all fish species, they are insignificant and the risk of cancer can be ignored.

4. Conclusion

The study analyzed the levels of various metals (Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se and Zn) in the muscles of four different fish species caught in the Black Sea. Among the metals, the highest average concentration was observed for aluminum (Al) in anchovy and the lowest concentration for cadmium (Cd) in whiting. Regarding toxic elements, arsenic (As) concentrations were higher in all four fish species compared to previous studies in the same region. However, the levels were generally below the maximum allowable limits recommended by the FAO, WHO, EC, and Turkish Food Codex. Moreover, Risk assessment based on estimated daily intake (EDI) and target hazard coefficient (THQ) revealed that metal levels in fish species were below recommended limits. Thus, THQ values indicated that prolonged exposure to metals through consumption of the fish species examined in the study is unlikely to cause serious harm to adult human health. In summary, although research findings show that some fish species studied from the Black Sea exhibit high metal levels, the concentrations of toxic and trace elements are generally within acceptable thresholds for safe fish consumption. However, continuous monitoring of toxic metal concentrations in fish is essential to maintain food safety and reduce potential health hazards associated with prolonged exposure.

CRediT authorship contribution statement

Tanju Mutlu: Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization.

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