



Metal concentrations, selenium-mercury balance, and potential health risk assessment for consumer of whiting (*Merlangius merlangus euxinus* L., 1758) from different regions of the southern Black Sea

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Abstract

The significant increase in the human population and the associated industrial wastes have a widespread impact on coastal areas. It is important to monitor trace elements that affect food safety and pose a potential consumer health threat. All over the Black Sea coast, people enjoy consuming whiting as both meat and roe. In February 2021, whittings were caught by bottom trawling from four different locations on the coasts of Kastamonu, Sinop (Sarıkum, Adabaşı), and Samsun in the southern Black Sea region. The meat and roe extracts obtained from whiting samples were analyzed through an optical emission spectrophotometer (ICP-MS). Trace element concentrations of whiting meat and roe in this study were Zn > Fe > Sr > As > Al > Se > B > Mn > Cu > Hg > Li > Ni > Ba > Pb > Cr > Cd and Zn > Fe > Al > As > Cu > Sr > Mn > Se > B > Ba > Li > Ni > Hg > Cr > Pb > Cd, respectively. These amounts were lower than the acceptable values accepted by the EU Commission. In case of whiting and roe consumption of a maximum of three portions (860.33 g) for Adabaşı, six portions for Kastamonu (1432.37 g), three portions for Samsun (828.55 g), and five portions (1253.04 g) for Sarıkum per month do not pose a health risk.

Keywords The Black Sea · Whiting · Trace elements · Assessment of Health Risk · Target hazard quotient · Selenium health benefit

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Introduction

Trace element concentrations in marine habitats elevate due to the growing population, thriving businesses, agriculture, expedition, urbanization, and other human-related processes (Jerome and Chukwuka 2016; Marengo et al. 2018). Trace elements are toxic and nonbiodegradable as environmental pollutants can cause serious damage to the circulatory, central nervous, excretory, and reproductive systems of organisms when they accumulate in their tissues and reach high level (Bayraklı 2021b).

Elements such as zinc (Zn), iron (Fe), manganese (Mn), and copper (Cu) are essential for the metabolic processes of organisms. Nevertheless, large quantities of such elements are likely to have toxic consequences (Mol et al. 2010; Makedonski et al. 2017). Metals prove thoroughly toxic, which are mercury (Hg), arsenic (As), lead (Pb), and cadmium (Cd), all being possible to remain in bodies of aquatic organisms (Mol et al. 2019). Now that the rapidly rising human population and its associated industrial discharges have mainly affected coastal areas, benthic regions of the

sea shores have been more affected by mineral contamination (Hwang et al. 2017). Considering that pollution caused by trace elements is of global concern, studies on people's exposure to water-carried contaminants are increasing (Zhuang et al. 2013). Recent research on exposure to water-borne contaminants has become popular today because trace and heavy metal contamination is a global concern (Sobhanardakani et al. 2018). Some universally valid parameters, such as the estimated target hazard quotient (THQ), cancer risk (CR), and daily intake (EDI), are used to predict the critical level for human health of the elements that accumulate along the food chain of organisms living in increasingly polluted water resources and thus to determine safe food criteria (US-EPA 2000; Yi et al. 2011). Natural geological and anthropogenic factors are responsible for the presence of heavy metals in the marine environment. (Gedik and Ozturk 2019). As the Black Sea is constantly exposed to pollutants, pollution has gradually increased (Bat et al. 2015).

The Black Sea, which is constantly fed by the fresh-water of various voluminous rivers in Europe (Danube, Dniester and Dnieper) and Anatolia (Sakarya, Kızılırmak ve Yeşilırmak), is considered one of the most contaminated seas in the world, and elevated concentration of nutritious elements over the last few years has accounted for a higher amount of eutrophication (Makedonski et al. 2017).

The different heavy metal concentration observed in marine biota depends on their geography. Karşı (2021) found metal concentrations in fish muscles vary significantly based on the location. Hence, the sources of pollution in the Black Sea are numerous and large-scale, and their impacts on species need to be determined periodically.

Whiting is mostly fished with gillnets in the east and throughout the southern Black Sea region and bottom trawlers in the west (Satilmis et al. 2014). An average of

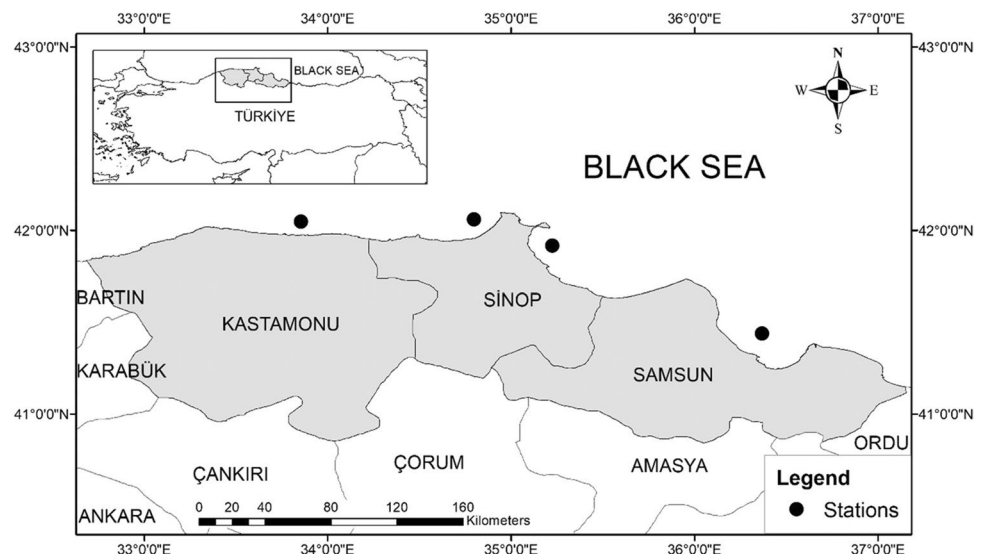
$10\,197 \pm 2\,616$ tonnes of whiting has been fished annually in Turkey since 2000, accounting for 2.24% of total fishing (TUIK 2021). Consumers relish not only white meat but also the whiting roe (Kaba et al. 2013, 2014). The objectives of this study are three-fold: first, investigating the metal content (Al, As, B, Ba, Cd, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Se, Sr, and Zn) in the meat and roe tissues of whiting from Kastamonu, Sinop (Sarıkum, Adabaşı) ve Samsun coasts of the Black Sea; second, comparing these data with national and international limit values; and third, assessing the public health risk arising from the consumption of whiting meat and roe.

Materials and methods

Sampling and study area

Whiting was captured by bottom trawl from 4 different locations along the coasts of Kastamonu, Sinop (Sarıkum, Adabaşı) and Samsun in the southern Black Sea region (Fig. 1). Samples were obtained from commercial fishermen in February 2021. Approximately 1000 g of whiting samples was taken from each location. After determining the total length and weight, the samples were labeled and frozen in the bags. The average length and weight of the samples were 12.80 ± 0.570 cm and 16.92 ± 1.913 g for Kastamonu ($n=59$), 12.74 ± 0.727 cm and 16.04 ± 2.378 g for Sarıkum ($n=62$), 13.25 ± 0.354 cm and 19.65 ± 0.664 g for Adabaşı, and 11.90 ± 0.224 cm and 13.648 ± 1.504 g for Samsun ($n=74$) stations, respectively. Frozen samples were transferred to Sinop University Scientific Research Laboratory within the cold chain. After the samples were washed with ultrapure water, the meat and roe parts of the whiting were

Fig. 1 Sampling regions in the southern Black Sea coasts



separated. Finally, the homogenized samples were analyzed to determine the whiting metal content.

Analyses of metal contents

All metal analyses in the present study were performed in triplicate groups, following the EPA Method 200.3 (USEPA 1991). Whiting meat and roe samples (up to 1.5 g) were digested in Teflon vessels including a mixture of concentrated supra pure grade HNO_3 and H_2O_2 (7:1) according to (HPR-FO-67) temperature and pressure profile using a microwave digestion system (Milestone SK10). After adding the acid Teflon bombs closed and heated at 200 °C for 15 min and kept at the same temperature for another 15 min, the digested solution was transferred into a 50 mL polypropylene falcon tubes and filled up to 50 ml with ultra-pure water. Standard Reference Material (CRM) and blank solutions were prepared using the same procedures. The CRM materials UME CRM 1201 and SEM 2016 mix were employed to assess the precision and accuracy of the analyses. Inductively Coupled Plasma Spectrometry (ICP-MS Agilent 7700X) was utilized to measure the concentration aluminum (Al), arsenic (As), boron (B), barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), lithium (Li), manganese (Mn), mercury (Hg), nickel (Ni), selenium (Se), strontium (Sr), and zinc (Zn) by means of multielement techniques, during which all glass materials and teflon tapes were immersed in 10% HNO_3 overnight, rinsed through distilled water twice, and air-dried to refrain from any contamination before use. The certificated reference substance (NRCC-DORM-2 Dogfish Muscle) was employed as a standard for calibration verification (Table S1).

Estimations of consumer health risks

Health risks for consumers exposed to metals through oral intake have been assessed as noncarcinogenic and carcinogenic risks in the present study.

The average consumption of fish in the European population is about 23 kg per capita annually (Failler et al. 2007). Estimated daily intake (EDI, mg kg^{-1} body weight/day) of metals through ingestion of whiting meat and roe was tried to be found out by the following formula reported earlier by Copat et al. (2013), Yigit et al. (2018), and Bayrakli (2021b):

$$\text{EDI} = \frac{\text{MC} \times \text{MS}}{\text{BW}}$$

where MC stands for metal concentration (mg kg^{-1} ww) in whiting meat and roe, MS is the meal size (kg/day), the

average daily intake rate of meat the EU population, and BW represents body weight (kg) for adults (70 kg)

Noncarcinogenic risk

Noncarcinogenic risk has been evaluated via comparison of the exposure level over a specific time period (lifetime) with reference dose suggested for the same exposure duration. Target hazard quotient (THQ), representing noncarcinogenic risk, is the proportion of estimated daily intake (EDI) and reference dose (RfD), which is an assumption of an exposure level below the fact that it is improbable for even sensitive populations to experience health risks. When the exposure has been in excess of this threshold, there would be a concern for potential noncancer health effects. Risk assessment for As was conducted on the assumption that the toxic inorganic arsenic was 3% of the total (FSA 2004). The mathematical explanation of the potential risk described as THQ led by a single element within a single exposure route over a lifetime duration of 70 years was found using the following equation reported by US-EPA (1989):

$$\text{THQ} = \frac{\text{EDI}}{\text{RfD}} \times 10^{-3}$$

where EDI is estimated daily intake (mg kg^{-1} body weight/day) and RfD represents the reference doses ($\text{mg kg}^{-1} \text{day}^{-1}$) for metals according to EFSA (2010) and US-EPA (2013)

The value of acceptable guideline for THQ has been found to be “1” (US-EPA 1989). If the calculated THQ value is below “1” (< 1), it means that no harmful effect might be expected for human beings. On the other hand, human exposure to metals more than “one” (> 1) may affect people in cumulative reaction (Hallenbeck 1993). For this reason, the arithmetic sum of THQ values has been considered total target hazard quotients (TTHQ) representing the hazard index (HI), which is equivalent to the total of the hazard quotients, where EDI and the RfD implies the same exposure period. When the hazard index is more than unity, a concern for potential health-related consequences could be in question, while any single chemical with an exposure level over the toxicity value will account for the hazard index exceeding the unity. In terms of multiple chemical exposures, the hazard index can also exceed unity even when no single chemical exposure has exceeded its RfD. The mathematical equation for noncancer hazard index (HI) as the arithmetic total of THQ value was used in the this study under US EPA (1989) as earlier described by Li et al. (2013), Bonsignore et al. (2018), Yigit et al. (2020), and Bayrakli (2021b), concerning the assessment of the risks caused by multiple elements (the value n was “15” in the present study).

$$HI(TTHQ \sum_n) = (EDI_1/RfD_1) + (EDI_2/RfD_2) + (EDI_3/RfD_3) + \dots + (EDI_n/RfD_n)$$

$$HI = \sum_n THQ_m$$

where EDI_n is the estimated intake level for the n^{th} metal

Carcinogenic risks for toxic metals

The carcinogenic risk implies the incremental possibility for any of cancer type in a lifetime of a person related to his/her exposure to potential carcinogens. The cancer slope factor (CSF) directly turns estimated daily intakes averaged over a lifetime of exposure to incremental risk directly to incremental risk of a man/ woman who would develop cancer. Of the measured elements, As, Cd Cr, Ni, and Pb are known to produce risk of cancer in individuals (IARC 2012). The cancer risk all over life time (CRR) was estimated using the equation by US-EPA (1989, 2010), as earlier described by Liang et al. (2017):

$$CRR = EDI \times CSF$$

where EDI is the estimated daily intake ($\text{mg kg}^{-1}/\text{day}$)

CSF stands for the cancer slope factor for As ($1.5 \text{ mg kg}^{-1}/\text{day}$), Cd ($6.3 \text{ mg kg}^{-1}/\text{day}$), Ni ($0.84 \text{ mg kg}^{-1}/\text{day}$), Pb ($0.0085 \text{ mg kg}^{-1}/\text{day}$) (Liang et al. 2017; US-EPA 1996).

Although methylmercury (MeHg) has been categorized as a possible carcinogenicity in humans (IARC 2012), the cancer slope factor for Hg has not been issued by the US-EPA. Therefore, cancer risks for Hg was not estimated in this study. The level of cancer risk for carcinogens ranges between 10^{-4} and 10^{-6} , which presents risk of developing cancer for the entire human lifetime of 1 in 10.000 and 1 in 1.000.000, respectively. It means that a risk lower than 10^{-6} is an acceptable risk and can be ignored, but a risk exceeding 10^{-4} is considered as unacceptable. Hence, an average cancer benchmark of 10^{-5} was considered the threshold in this study (US-EPA 2010).

Safe consumption limits

The maximum allowable daily consumption rate that is the safe daily consumption limit has been defined as ADC and calculated using the following formulae (US-EPA 2000):

$$ADC = \frac{RfD \times BW}{MC}$$

where RfD is the reference doses ($\text{mg kg}^{-1} \text{ day}^{-1}$) for metals (EFSA 2010; US-EPA 2013), BW represents body weight (kg) for adults (70 kg), and MC represents metal concentration ($\text{mg kg}^{-1} \text{ ww}$) in whiting meat and roe.

The maximum safe weekly consumption rate, or allowable weekly consumption (AWC, meals per week) was calculated by converting the allowable daily consumption rate (ADC) into the food meal size (MS), that is, 0.227 kg/day for adults by US-EPA (1989, 2000). The allowable weekly consumption (AWC, meals per week) was calculated by the equation stated in a previous work by Yigit et al. (2018):

$$AWC = \frac{ADC \times 7}{MS}$$

where ADC is the maximum allowable daily consumption rate (US-EPA 2000) and MC is the analyzed metal concentration ($\text{mg kg}^{-1} \text{ ww}$) in whiting meat and roe.

Compensation of daily requirements for essential trace elements

Percent compensation of minimum daily requirements (CDRmin) for essential trace elements in human consuming meat was calculated using the following equation according to Yigit et al. (2020):

$$CDRmin = \frac{EDI \times 100}{EAR}$$

where EDI represents the estimated daily intake ($\text{mg kg}^{-1}/\text{day}$) and EAR stands for the estimated average daily requirement for a healthy human (IOM 2001, 2006).

Selenium health benefit value (Se-HBV)

The molar Se/Hg ratio was obtained by the equation below (Ralston et al. 2008; Burger and Gochfeld 2011):

$$\text{Molar ratio (Se/Hg)} = \text{molar concentration of Se } (\mu \text{ mol kg}^{-1}) / \text{molar concentration of Hg } (\mu \text{ mol kg}^{-1})$$

$$\text{Molar concentration Se} = \text{the concentration Se } (\text{mg kg}^{-1}) / 78.9 \text{ g mol}^{-1}$$

$$\text{Molar concentration Hg} = \text{the concentration Hg } (\text{mg kg}^{-1}) / 200.59 \text{ g mol}^{-1}$$

The Se-HBV exhibits that the Se /Hg equilibrium is present in tissues and diets. When the concentration of Se is lower than that of Hg in seafood, the health risk is high. In addition, higher amounts of Se provide health benefits by means of protection against Hg poisoning. Therefore, the Se-HBV is calculated to define potential risks of Hg exposure or nutritional benefits of Se. In view of the prominences of the values, the positive Se-HBV displays Se-dependent health benefits, but when the result is negative, the health risk is inevitable or emerges (Kaneko and Ralston 2007). The Se-HBVs were calculated using the equation as follows (Ulusoy et al. 2019):

$$HBV_{Se} = (Se - Hg) / (Se + Hg)$$

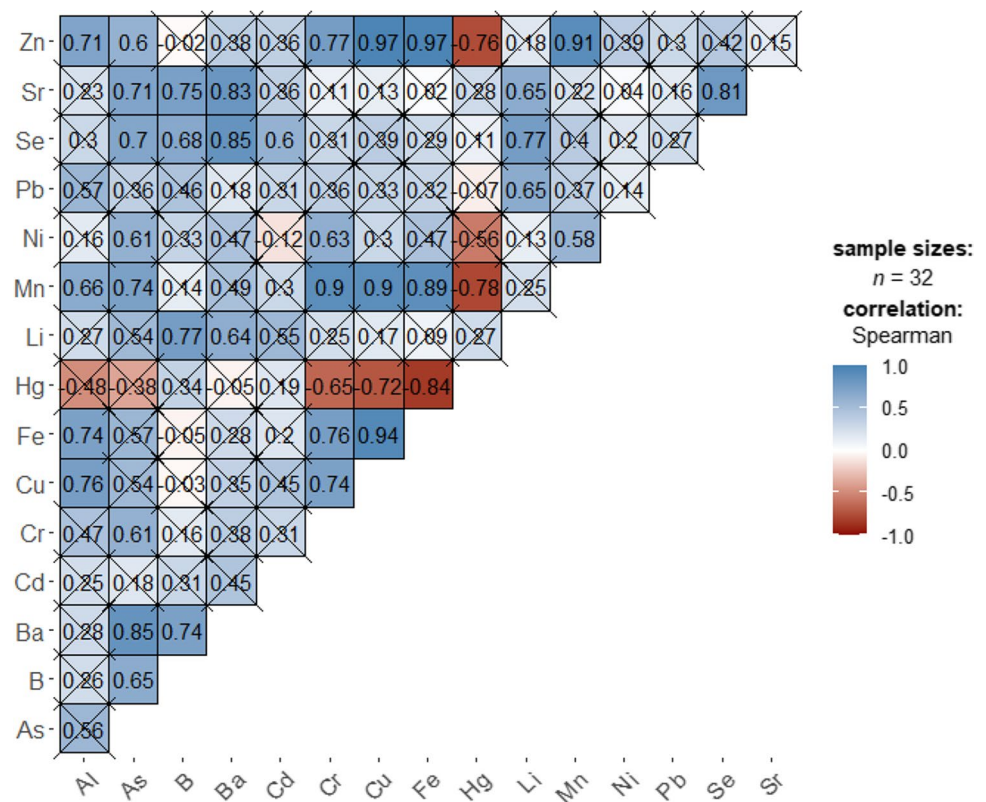
Statistical analyses

Rv4.0.5 statistical software was utilized in all statistical analyses, and the significance level was set at 0.05 level for statistical tests. Before performing statistical analyses, the Shapiro–Wilk normality test was performed to examine the structure of the data in terms of linearity.

Due to the presence of nonlinear observations in the majority of all elements, linear relationships among all investigated elements were evaluated using Spearman's rank correlation test, regardless of region and tissue factors. In addition, the relationship between meat and roe factors from the point of each element, regardless of region factor, was examined using Spearman's rank correlation test. The statistical significance of the linear relationships between the elements without considering the tissue and region factors and only considering the tissue factor was tested using Holm-Bonferroni method, also called Holm's sequential Bonferroni procedure.

To examine the statistical significance of the region and tissue factors and their interactions with each other, Friedman's two-way analysis of variance (ANOVA) by ranks was conducted for all elements. Pairwise comparisons of differences between regions in terms of each element were examined using the Tukey's range test, also called Tukey's honest significant difference (HSD) test. All detailed results, graphics, and test outputs for statistical analyses were given in the supplementary material.

Fig. 2 Correlogram of Spearman's rank correlation results between all elements regardless of the tissue factor



⊠ : non-significant at $p < 0.05$ (Adjustment: Holm)

Results

Metal levels and statistical evaluation

Fe, Zn, Cu, Se, and Mn are essential elements in the biological activities of every organism (Bayraklı 2021a, b). Based on these results, Spearman's rank correlation test results (Fig. S1) and the correlogram (Fig. 2) were examined. The correlations between all elements were obtained by considering both tissue factors (meat and roe) together. Although strong positive significant correlations between Fe-Cu, Fe-Zn, Cu-Zn, Fe-Mn, Cu-Mn, Zn-Mn, and Cr-Mn were observed, strong negative significant correlations were observed between Hg-Fe, Hg-Zn, and Hg-Mn. No relationship was observed between Cu-B, Zn-B, Fe-B, Fe-Sr, Hg-Ba, and Ni-Sr. Mercury (Hg) is a toxic element; thus, it is not considered essential for human metabolism. Mercury can cause genetic deterioration and harm to the cardiovascular and neurological systems upon exposure (Bjørklund et al. 2020).

In addition, strong positive and significant correlations were observed between Cu_{meat}-Cu_{roe}, Fe_{meat}-Fe_{roe}, and Zn_{meat}-Zn_{roe} with values of 0.76, 0.76, and 0.87, respectively (Table S4).

Friedman's two-way ANOVA test results of the region and tissue factors for each element show that the region, tissue, and region tissue factors were statistically significant for Al, As, B, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Ni and Sr elements (p value < 0.05) (Table S5-S36) that the findings revealed that there was a statistically significant difference between the regions in terms of the mean concentrations of the elements. There was no statistically significant difference between the mean concentrations of Li, Pb, and Se elements in tissue factor levels (Tables S23, S29, and S31). The region and tissue factor interaction effect for only the Zn element was not statistically significant (Table S35).

The regions that make up the difference were determined by performing multiple pairwise comparisons between group mean concentrations based on Tukey's HSD test for region factor (see Supplementary material pages 6–13). It was observed that there was a statistically significant difference between all regions in terms of the mean concentrations of As, Ba, Zn, Hg, and Mn elements. It was found to be a statistically significant difference in terms of the mean concentrations of Al, As, B, Ba, Cu, Fe, Hg, Mn, Se, Sr and Zn elements between 'Kastamonu-Adabaşı', 'Samsun-Kastamonu' and 'Sarıkum-Kastamonu' regions. This difference between the mean concentrations of these elements in the Kastamonu region may depend on the geological origin (p -adj. < 0.05, Table S5-S36). The difference between the mean concentrations of Al, As, Ba, Fe, Hg, Mn, Zn and Ni elements was statistically significant between 'Sarıkum-Samsun', 'Adabaşı-Samsun' and 'Kastamonu-Samsun'

regions (p -adj. < 0.05, Table S5-S36). The results showed that there was a statistically significant difference between 'Sarıkum-Samsun', 'Adabaşı-Sarıkum' and 'Kastamonu-Sarıkum' regions from the point of the mean concentrations of As, B, Ba, Cd, Hg, Mn and Zn elements. The difference between the mean concentrations of As, Ba, Cu, Hg, Mn, Ni, Se, Sr and Zn elements was statistically significant between 'Adabaşı-Samsun', 'Adabaşı-Sarıkum' and 'Kastamonu-Adabaşı' regions (p -adj. < 0.05, Table S5-S36).

Discussion

In this study, the concentration of elements in whiting meat was determined as $Zn > Fe > Sr > As > Al > Se > B > Mn > Cu > Hg > Li > Ni > Ba > Pb > Cr > Cd$. Whiting roe was found as $Zn > Fe > Al > As > Cu > Sr > Mn > Se > B > Ba > Li > Ni > Hg > Cr > Pb > Cd$ (Table 1). Turan et al. (2019) reported that As, Pb, Hg, Al and Mn elements were high in whiting meat, and Se, Fe, and Zn elements were high in the roe, while other elements were approximately similar. Baki (2021) reported higher levels of Cd, Cr, Ni and Pb elements in whiting meat rather than whiting roe. Cu, Fe, Mn and Zn elements, which have important roles in the body functions and can be observed in this study, were found relatively high in the roes in all regions Table 2.

It would be safe to say that these elements are essential for the development of the gonad during the reproductive period. The Hg element in the meat was higher in all regions as reported by Turan et al. (2019). Meat values of other elements were higher in some regions while gonad values were higher and similar in some regions. Sönmez et al. (2012) reported that the differences between the metal amounts of the fish according to the regions might be due to the effects of the city and industrial settlements on the feeding areas, fishing areas, and the geological structure of the region. According to studies examining whiting meat in the Black Sea region, Al, Cu, Fe, Mn, Zn, Se, Cr, As, Cd, Hg, Pb, and Li levels were reported to be between 0.27–25.88, 0.26–11.83, 2.36–27.29, 0.033–8.7, 3.47–152, 0.29–2.51, 0.01–1.48, 0.03–9.67, < 0.01–1.62, 0.02–2.51, < 0.001–14.11, 0.01–3.06, and < 0.01–2.87 mg kg⁻¹, respectively. The study findings are in line with those of previous studies. All the metals except for As levels found in this study were all below the maximum acceptable values reported by the Turkish Food Codex (TFC 2011), the EU Commission (1881/2006) and Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO) (2007). Arsenic is a metalloid form commonly found in the marine environment, so it can often be encountered in seafood (Moreda-Piñeiro et al. 2012). This heavy metal exists in nature in organic or inorganic forms (Raknuzzaman et al. 2016).

Table 1 Mean element concentrations (mean $\pm$ SD) in muscle and roe tissue of whiting according to the regions (mg kg⁻¹ wet weight)

		Kastamonu	Sarıkum	Adabaşı	Samsun
Al	Meat	2.467 $\pm$ 0.082	0.355 $\pm$ 0.060	0.795 $\pm$ 0.019	0.825 $\pm$ 0.086
	Roe	8.917 $\pm$ 0.099	5.141 $\pm$ 0.270	1.433 $\pm$ 0.064	0.674 $\pm$ 0.102
As	Meat	2.913 $\pm$ 0.010	1.359 $\pm$ 0.025	0.778 $\pm$ 0.002	0.824 $\pm$ 0.009
	Roe	3.541 $\pm$ 0.042	1.234 $\pm$ 0.008	1.577 $\pm$ 0.021	0.988 $\pm$ 0.016
B	Meat	0.583 $\pm$ 0.004	0.586 $\pm$ 0.024	0.431 $\pm$ 0.008	0.539 $\pm$ 0.005
	Roe	0.701 $\pm$ 0.027	0.354 $\pm$ 0.009	0.490 $\pm$ 0.007	0.285 $\pm$ 0.002
Ba	Meat	0.102 $\pm$ 0.001	0.055 $\pm$ 0.003	0.027 $\pm$ 0.001	0.038 $\pm$ 0.001
	Roe	0.428 $\pm$ 0.010	0.016 $\pm$ 0.001	0.094 $\pm$ 0.002	0.041 $\pm$ 0.003
Cd	Meat	0.001 $\pm$ 0.000	0.000 $\pm$ 0.000	0.002 $\pm$ 0.000	0.003 $\pm$ 0.000
	Roe	0.014 $\pm$ 0.001	0.000 $\pm$ 0.000	0.006 $\pm$ 0.000	0.001 $\pm$ 0.000
Cr	Meat	0.002 $\pm$ 0.001	0.004 $\pm$ 0.000	0.000 $\pm$ 0.000	0.002 $\pm$ 0.000
	Roe	0.101 $\pm$ 0.000	0.008 $\pm$ 0.000	0.016 $\pm$ 0.004	0.005 $\pm$ 0.002
Cu	Meat	0.546 $\pm$ 0.006	0.303 $\pm$ 0.006	0.421 $\pm$ 0.002	0.318 $\pm$ 0.002
	Roe	3.432 $\pm$ 0.035	0.998 $\pm$ 0.019	1.552 $\pm$ 0.008	0.912 $\pm$ 0.013
Fe	Meat	4.541 $\pm$ 0.036	2.893 $\pm$.037	3.154 $\pm$ 0.013	2.375 $\pm$ 0.013
	Roe	26.980 $\pm$ 0.293	12.659 $\pm$ 0.101	11.592 $\pm$ 0.082	9.320 $\pm$ 0.059
Hg	Meat	0.147 $\pm$ 0.007	0.167 $\pm$ 0.002	0.244 $\pm$ 0.003	0.254 $\pm$ 0.003
	Roe	0.052 $\pm$ 0.001	0.020 $\pm$ 0.001	0.063 $\pm$ 0.001	0.032 $\pm$ 0.001
Li	Meat	0.162 $\pm$ 0.001	0.163 $\pm$ 0.002	0.157 $\pm$ 0.022	0.158 $\pm$ 0.006
	Roe	0.255 $\pm$ 0.011	0.070 $\pm$ 0.001	0.168 $\pm$ 0.016	0.020 $\pm$ 0.009
Mn	Meat	0.743 $\pm$ 0.032	0.497 $\pm$ 0.028	0.154 $\pm$ 0.006	0.209 $\pm$ 0.006
	Roe	3.297 $\pm$ 0.027	1.286 $\pm$ 0.038	1.369 $\pm$ 0.014	0.812 $\pm$ 0.036
Ni	Meat	0.056 $\pm$ 0.002	0.147 $\pm$ 0.001	0.012 $\pm$ 0.001	0.023 $\pm$ 0.000
	Roe	0.236 $\pm$ 0.004	0.065 $\pm$ 0.000	0.041 $\pm$ 0.002	0.069 $\pm$ 0.001
Pb	Meat	0.019 $\pm$ 0.002	0.020 $\pm$ 0.001	0.018 $\pm$ 0.004	0.021 $\pm$ 0.001
	Roe	0.063 $\pm$ 0.002	0.021 $\pm$ 0.000	0.020 $\pm$ 0.003	0.008 $\pm$ 0.002
Se	Meat	1.274 $\pm$ 0.022	0.888 $\pm$ 0.028	0.872 $\pm$ 0.048	0.780 $\pm$ 0.022
	Roe	2.431 $\pm$ 0.068	0.715 $\pm$ 0.013	1.486 $\pm$ 0.043	0.777 $\pm$ 0.027
Sr	Meat	3.771 $\pm$ 0.023	2.146 $\pm$ 0.009	1.367 $\pm$ 0.020	1.635 $\pm$ 0.013
	Roe	2.473 $\pm$ 0.059	0.660 $\pm$ 0.021	2.985 $\pm$ 0.061	0.675 $\pm$ 0.005
Zn	Meat	7.701 $\pm$ 0.118	7.006 $\pm$ 0.033	7.144 $\pm$ 0.029	6.985 $\pm$ 0.036
	Roe	58.930 $\pm$ 0.433	34.577 $\pm$ 0.216	44.680 $\pm$ 0.545	29.402 $\pm$ 0.189
Se/Hg	Meat	12.23	22.14	9.25	13.49
	Roe	60.20	119.09	60.93	89.41
HBVse	Meat	12.38	16.12	7.10	11.20
	Roe	18.83	30.80	9.84	9.06

Although the inorganic form of arsenic has very harmful toxicity, the organic form has relatively low toxicity (Sarkar and Paul 2016). International organizations such as the Environmental Protection Agency (EPA), the International Agency for Research on Cancer (IARC) and the Department of Health and Human Services (DHHS) have reported that inorganic arsenic is carcinogenic for human health (Chou et al. 2007). Kalantzi et al. (2016) reported that the amount of inorganic arsenic in seafood is between 1 and 10% of the total arsenic content. Food Standards Australia and New Zealand (FSANZ 2013) reported the permissible value for inorganic arsenic to be 2 mg·kg⁻¹ ww and the Chinese Health Ministry (MHPRC 2013) a value of 0.1 mg kg⁻¹

ww. This study calculated 3% of the total arsenic amount for whiting to be inorganic As (0.02–0.10 mg kg⁻¹ ww), which is lower than the value reported by FSANZ (2013) and MHPRC (2013).

Potential health risk assessment of metals via the consumption of whiting meat and roe

Fish are an essential food source in terms of rich polyunsaturated fatty acids, nutritious amino acid structure, and mineral and vitamin content (Oztekin et al. 2018; Bayraklı and Duyar 2019; Bayraklı 2021a). However, increased domestic and industrial waste pollution affects coastal areas. Monitoring

Table 2 Literature information on trace metal contents determined for whiting meat and roe

*	As	Cd	Cr	Ni	Pb	Hg	Se	Al	Cu	Fe	Li	Mn	Zn	
ww	0.77–2.92	<0.01–0.01	<0.01–0.02	0.01–0.15	0.01–0.02	0.06–0.26	0.76–1.54	0.27–2.58	0.30–1.56	2.36–11.69	0.13–0.19	0.15–1.38	6.93–45.3	21 Meat
dw		0.002±0.00		3.78±0.38	0.58±0.03				3.72±0.59	28.84±1.69		6.92±0.71		1 Meat
dw		0.192±0.02	0.144±0.05	1.363±0.50	0.502±0.10			86.301±11.77		4.488±0.44	3.061±0.15	0.079±0.02	6.029±0.55	2 Meat
dw	0.17±0.01	0.21±0.02	0.86±0.07	1.14±0.10	0.53±0.04	0.084±0.01	0.29±0.02		1.32±0.11	98.1±7.7		7.63±0.45	65.4±4.2	3 Meat
ww	0.463	0.013			0.099	0.081								4 Meat
dw	<0.1–3.95		<0.1–0.47	<0.001–0.09	<0.001–0.04				0.41–0.68	7.45–28.20		0.63–1.34	4.69–15.34	5 Meat
ww		0.12±0.04	0.29±0.06		1.02±0.29			5.53±1.46	1.93±0.91	5.80±1.39		1.10±0.76	6.14±1.65	6 Meat
ww					0.43±0.24			3.72±0.77	0.29±0.15	25.80±17.43		2.02±1.12	8.31±2.7	7 Meat
ww		0.05–0.68	0.04–0.47	0.25–2.66	0.56–2.06				1.62–4.21	8.16–111		0.18–1.78	3.77–12.8	8 Meat
ww		0.10–0.25	0.55–1.1		0.28–0.71				1.3–2.8	9.6–58.6		1.3–8.7	16.1–28.8	9 Meat
dw	3.76–9.67	0.02–0.04	0.45–1.02	0.09–1.19	0.01–0.05				1.03–1.71			0.77–1.19	19.57–25.5	10 Meat
ww	0.82±0.02	4.05±0.14		<LOD	0.02±0.00		0.40±0.01			0.69±0.01		0.23±0.01		11 Meat
ww		0.09–0.10	0.51–0.55	1.60–2.53	0.16–0.57				0.26–0.69			0.21–0.45	4.69–9.4	12 Meat
dw	4.0	0.03	1.50	0.31	0.05	0.33	2.27		2.50	84.2			18.0	13 Meat
dw		0.2±0.03			0.9±0.2				2.3±0.7	9.9±2.1		4.3±0.7	58.0±3.5	14 Meat
dw		0.02–0.18			0.02–1.51				0.19–7.74				6.95–34.3	15 Meat
dw	1.24	<0.02			<0.05	<0.05		<0.5		0.87			3.4	16 Meat
ww		0.027±0.01	0.63±0.16		0.69±0.34				1.20±0.31	62.80±19.61			16.34±3.8	17 Meat
ww	1.14–2.83	0.03–0.22	0.28–1.25	0.19–0.61	0.19–0.90	0.13–0.23	0.78–1.26	2.28–19.68	0.59–2.10	12.04–71.10	0.01–0.15	1.31–2.82	12.63–18.5	18 Meat
dw		1.07±0.02	1.48±0.07	1.77±0.14	5.38±0.29									19 Meat
ww		0.15–0.89	0.63–1.62	1.25–2.87	2.69–17.11			11.67–25.88	6.30–11.83	59.97–150.74		1.85–2.60	37.96–152.67	20 Meat
ww	0.96–3.58	<0.01–0.01	<0.01–0.10	0.04–0.24	<0.01–0.07	0.02–0.15	0.70–2.51	0.57–9.04	0.54–3.46	4.51–27.29	0.01–0.27	0.70–3.33	7.53–59.3	21 Roe
ww	0.93±0.01	3.53±0.09		<LOD	0.09±0.01		0.74±0.01			12.6±0.1		0.90±0.01		11 Roe
ww	0.90–1.36	0.02–0.22	0.12–1.24	0.18–0.41	0.14–0.26	0.04–0.05	0.84–1.71	1.03–6.78	1.15–2.15	28.00–142.03	0.05–0.10	0.79–2.29	31.15–58.2	18 Roe
dw		0.94±0.05	0.42±0.19	0.69±0.31	1.57±0.65									19 Roe
	0.1–2	0.50	1	80	0.50	0.50	2.0	60	20–30	300		50	50–100	

* ww wet weight, dw dry weight

1—Nisbet et al. (2010), 2—Turan et al. (2009), 3—Tuzen (2009), 4—Kupulu et al. (2018), 5—Korkmaz et al. (2012), 6—Muflu (2021a), 7—Muflu (2021b), 8—Türkmen and Akaydin (2017), 9—Mendil et al. (2010), 10—Alkan et al. (2016), 11—Aydin and Tokaloğlu (2015), 12—Türkmen and Ögüçü (2020), 13—Ergül and Aksan (2013), 14—Aygun and Abanoz (2011), 15—Bat et al. (2013), 16—Bat et al. (2015), 17—Ergönül and Altındağ (2014), 18—Turan et al. (2019), 19—Baki (2021), 20—Findik and Çiçek (2011), 21—this study

Table 3 Estimated daily intake per meal size, maximum safe daily consumption rate, allowable weekly consumption, target hazard quotient, total target hazard index, and cancer risk rate for the studied metals in adults consuming fish meat based on cancer slope factor and reference dose

RfD (mg/kg/ day)	CSF (mg/kg/ day)	*	EDI (mg/kg/day, ww)		THQ		ADC (kg/day)		Cancer risk (CRR)								
			Kastamonu	Sinop	Samsun	Kastamonu	Sinop	Samsun	Kastamonu	Sinop	Samsun						
												Sarıkkum	Adabaşı	Sarıkkum	Adabaşı	Sarıkkum	Adabaşı
As	0.0003	1.5	1	8 × 10 ⁻⁵	4 × 10 ⁻⁵	2 × 10 ⁻⁵	0.262	0.122	0.070	0.074	0.24	0.52	0.90	0.85	1 × 10 ⁻⁴	6 × 10 ⁻⁵	3 × 10 ⁻⁵
			2	1 × 10 ⁻⁴	3 × 10 ⁻⁵	3 × 10 ⁻⁵	0.319	0.111	0.142	0.089	0.20	0.57	0.44	0.71	1 × 10 ⁻⁴	5 × 10 ⁻⁵	4 × 10 ⁻⁵
Cd	0.001	6.3	1	5 × 10 ⁻⁷	3 × 10 ⁻⁷	2 × 10 ⁻⁶	0.001	0.000	0.002	0.003	124.91	195.03	35.99	25.16	3 × 10 ⁻⁶	2 × 10 ⁻⁶	1 × 10 ⁻⁵
			2	1 × 10 ⁻⁵	2 × 10 ⁻⁷	5 × 10 ⁻⁶	0.013	0.000	0.005	0.001	4.99	279.33	12.46	76.11	8 × 10 ⁻⁵	1 × 10 ⁻⁶	3 × 10 ⁻⁵
Cr	0.003	0.5	1	2 × 10 ⁻⁶	4 × 10 ⁻⁶	3 × 10 ⁻⁷	0.001	0.001	0.000	0.001	124.16	49.20	551.21	84.42	8 × 10 ⁻⁷	2 × 10 ⁻⁶	1 × 10 ⁻⁶
			2	9 × 10 ⁻⁵	8 × 10 ⁻⁶	1 × 10 ⁻⁵	0.030	0.003	0.005	0.001	2.09	25.01	13.40	43.34	5 × 10 ⁻⁵	4 × 10 ⁻⁶	2 × 10 ⁻⁶
Ni	0.02	0.84	1	5 × 10 ⁻⁵	1 × 10 ⁻⁴	1 × 10 ⁻⁵	0.003	0.007	0.001	0.001	25.15	9.50	115.43	61.68	4 × 10 ⁻⁵	1 × 10 ⁻⁴	9 × 10 ⁻⁶
			2	2 × 10 ⁻⁴	6 × 10 ⁻⁵	4 × 10 ⁻⁵	0.011	0.003	0.002	0.003	5.93	21.61	34.04	20.20	2 × 10 ⁻⁴	5 × 10 ⁻⁵	5 × 10 ⁻⁵
Pb	0.002	0.0085	1	2 × 10 ⁻⁵	2 × 10 ⁻⁵	2 × 10 ⁻⁵	0.009	0.009	0.008	0.009	7.22	7.07	7.62	6.64	1 × 10 ⁻⁷	2 × 10 ⁻⁷	2 × 10 ⁻⁷
			2	6 × 10 ⁻⁵	2 × 10 ⁻⁵	2 × 10 ⁻⁵	0.028	0.010	0.009	0.004	2.23	6.63	7.10	17.32	5 × 10 ⁻⁷	2 × 10 ⁻⁷	6 × 10 ⁻⁸
Hg	0.0001	1	1 × 10 ⁻⁴	2 × 10 ⁻⁴	2 × 10 ⁻⁴	2 × 10 ⁻⁴	1.319	1.507	2.196	2.283	0.05	0.04	0.03	0.03	For carcinogenic exposure; no cancer risk if value: > 0.000001 (10 ⁻⁶) cancer risk if value: < 0.000001 (10 ⁻⁶) benchmark: < 0.00001 (10 ⁻⁵) (US-EPA 2010)		
Se	0.005	2	5 × 10 ⁻⁵	2 × 10 ⁻⁵	6 × 10 ⁻⁵	3 × 10 ⁻⁵	0.467	0.184	0.565	0.292	0.13	0.34	0.11	0.22			
			1	1 × 10 ⁻³	8 × 10 ⁻⁴	8 × 10 ⁻⁴	7 × 10 ⁻⁴	0.229	0.160	0.157	0.140	0.27	0.39	0.40	0.45		
Al	1	2	2 × 10 ⁻³	6 × 10 ⁻⁴	1 × 10 ⁻³	7 × 10 ⁻⁴	0.438	0.129	0.268	0.140	0.14	0.49	0.24	0.45			
			1	2 × 10 ⁻³	3 × 10 ⁻⁴	7 × 10 ⁻⁴	7 × 10 ⁻⁴	0.002	0.000	0.001	0.001	28.37	197.04	88.07	84.83		
Cu	0.04	2	8 × 10 ⁻³	5 × 10 ⁻³	1 × 10 ⁻³	6 × 10 ⁻⁴	0.008	0.005	0.001	0.001	7.85	13.61	48.84	103.90			
			1	5 × 10 ⁻⁴	3 × 10 ⁻⁴	4 × 10 ⁻⁴	3 × 10 ⁻⁴	0.012	0.007	0.009	0.007	5.13	9.25	6.66	8.82		
Fe	0.7	2	3 × 10 ⁻³	9 × 10 ⁻⁴	1 × 10 ⁻³	8 × 10 ⁻⁴	0.077	0.022	0.035	0.021	0.82	2.81	1.80	3.07			
			1	4 × 10 ⁻³	3 × 10 ⁻³	3 × 10 ⁻³	2 × 10 ⁻³	0.006	0.004	0.004	0.003	10.79	16.94	15.54	20.63		
Li	0.002	2	2 × 10 ⁻²	1 × 10 ⁻²	1 × 10 ⁻²	8 × 10 ⁻³	0.035	0.016	0.015	0.012	1.82	3.87	4.23	5.26			
			1	2 × 10 ⁻⁴	1 × 10 ⁻⁴	1 × 10 ⁻⁴	1 × 10 ⁻⁴	0.073	0.073	0.071	0.071	0.86	0.86	0.89	0.89		
Mn	0.14	2	2 × 10 ⁻⁴	6 × 10 ⁻⁵	2 × 10 ⁻⁴	2 × 10 ⁻⁵	0.115	0.031	0.076	0.009	0.55	2.01	0.83	7.09			
			1	7 × 10 ⁻⁴	4 × 10 ⁻⁴	1 × 10 ⁻⁴	2 × 10 ⁻⁴	0.005	0.003	0.001	0.001	13.19	19.74	63.63	46.80		
Ba	0.2	2	3 × 10 ⁻³	1 × 10 ⁻³	1 × 10 ⁻³	7 × 10 ⁻⁴	0.021	0.008	0.009	0.005	2.97	7.62	7.16	12.07			
			1	9 × 10 ⁻⁵	5 × 10 ⁻⁵	2 × 10 ⁻⁵	3 × 10 ⁻⁵	0.000	0.000	0.000	0.000	137.45	256.26	518.60	371.58		
B	0.2	2	4 × 10 ⁻⁴	1 × 10 ⁻⁵	8 × 10 ⁻⁵	4 × 10 ⁻⁵	0.002	0.000	0.000	0.000	32.72	894.94	149.15	342.38			
			1	5 × 10 ⁻⁴	5 × 10 ⁻⁴	4 × 10 ⁻⁴	5 × 10 ⁻⁴	0.003	0.003	0.002	0.002	24.03	23.89	32.51	25.98		
		2	6 × 10 ⁻⁴	3 × 10 ⁻⁴	4 × 10 ⁻⁴	3 × 10 ⁻⁴	0.003	0.002	0.002	0.001	19.97	39.51	28.59	49.12			

Table 3 (continued)

RfD (mg/kg/ day)	CSF (mg/kg/ day)	*	EDI (mg/kg/day, ww)		THQ		ADC (kg/day)		Cancer risk (CRR)			
			Kastamonu	Sinop	Samsun	Kastamonu	Sinop	Samsun	Kastamonu	Sinop		
			Sarıkum		Adabaşı		Sarıkum		Adabaşı		Sarıkum	
Sr	0.6	1	3×10^{-3}	2×10^{-3}	1×10^{-3}	0.006	0.003	0.002	11.14	19.57	30.72	25.69
			2×10^{-3}	6×10^{-4}	3×10^{-3}	0.004	0.001	0.004	16.99	63.68	14.07	62.21
Zn	0.3	1	7×10^{-3}	6×10^{-3}	6×10^{-3}	0.023	0.021	0.021	2.73	3.00	2.94	3.01
			5×10^{-2}	3×10^{-2}	4×10^{-2}	0.177	0.104	0.134	0.888	0.36	0.61	0.47
		1	22.14 ^a	13.49 ^a	9.10 ^a	1.95 ^c	1.92 ^c	2.54 ^c	1.47 ^e	1.29 ^e	0.88 ^e	0.85 ^e
			119.09 ^a	89.41 ^a	60.20 ^a	1.74 ^c	0.63 ^c	1.27 ^c	4.16 ^e	10.58 ^e	3.44 ^e	6.65 ^e
		1	16.12 ^b	11.20 ^b	10.92 ^b	67.54 ^d	78.45 ^d	86.28 ^d	6.31 ^f	5.52 ^f	3.79 ^f	3.65 ^f
			30.80 ^b	9.05 ^b	18.83 ^b	26.75 ^d	29.24 ^d	44.43 ^d	17.82 ^f	45.34 ^f	14.73 ^f	28.51 ^f

1—Meat, 2—roe

RfD (mg kg⁻¹ day⁻¹) reference dose (EFSA 2010; US-EPA 2013); CSF cancer slope factors for As, Pb (US-EPA 1996), Cd, Cr, and Ni (Liang et al. 2017); EDI (mg kg⁻¹ day⁻¹) estimated daily intake per meal size, ww (wet weight) basis; ADC (kg day⁻¹) maximum allowable daily consumption rate; CRR cancer risk rate; THQ target hazard quotient

^aSe/Hg^bHBV Se^cHI hazard index representing arithmetic sum of THQs^dTHQ_{Hg}*100/HI^eAWC_{Hg} (meal/week) allowable weekly consumption for only Hg^fAMC_{Hg} (meal/month) allowable monthly consumption for only Hg

and estimating metal concentrations of live organisms, such as whiting (*Merlangius merlangus euxinus*) distributed in these dangerous areas, is important for assessing risks in terms of human health.

Table 3 provides the arithmetic sum of each THQ value for the studied metals in adults upon consuming whiting collected from the Black Sea cost stations.

Table 4 Per cent compensation of minimum daily requirements (CDR_{min}) for essential trace elements in adult men (AM) via consuming whiting, based on estimated daily average requirement levels according to IOM (2001, 2006).

Table 3 shows EDI, ADC, AWC, AMC, THQ, HI, and CRR for the studied metals in an adult human upon consuming whiting, as well as reference dose and cancer slope factor. Therefore, tolerable reference doses (RfD) of trace metals in food ingested through daily nutrition were determined by international health institutions (EFSA 2010; US-EPA 2013). In addition, an estimated daily intake (EDI) has been formulated to determine the elemental level of foods consumed at one meal (Copat et al. 2013). Cancer risk levels (ADC) were calculated to find the meal level without cancer risk via food intake (US-EPA 2000).

The EDI_{meat} values showed that all elements except for Hg in whiting meat were below the RfD level in all stations in this study. The amount of RfD for EDI_{Hg} is recommended by the US-EPA (2013) as $1 \times 10^{-4} \text{ mg kg}^{-1} \text{ day}^{-1}$. At the stations, including Adabaşı, Kastamonu, Samsun and Sarikum, EDI_{Hg} was determined in whiting meat as 2×10^{-4} , 1×10^{-4} , 2×10^{-4} , and 2×10^{-4} , respectively. In whiting roe, the estimated daily intake per meal size was found to be below the RfD level at all stations.

The THQ is one of the acceptable parameters for risk assessment of metals in contaminated seafood consumption (Bogdanović et al. 2014). A THQ value below 1 implies that the exposed population would not experience obvious adverse effects. If the THQ value is above 1, there is a potential for carcinogenic effects (Yigit et al. 2018). According to the results in this study, THQ_{Hg} in whiting meat was above 1 at Adabaşı, Kastamonu, Samsun, and Sarikum stations with the values of 2.196, 1.319, 2.283, and 1.507, respectively. Also, THQ values for all elements in the whiting roe were found to be below 1 at all stations. It was found that the HI index was above 1 in whiting at all stations and above 1 at Adabaşı and Kastamonu stations in whiting roe. The THQ_{Hg} amounts in whiting meat and roe were relatively high in the HI index. It constitutes 86.28%, 67.54%, 87.12%, and 78.45% of whiting meat at all stations; however, it constitutes 44.43%, 26.75%, 43.73%, and 29.24% of the whiting roe, respectively.

Cancer risk (CRR) is the maximum limit of the probability of individuals being at cancer risk after exposure to a toxic substance (Ahmed et al. 2015). When the value of CRR is less than 10^{-6} , it can be said that there is no cancer

risk. When the value is higher than 10^{-4} , cancer risk is unacceptable. However, if it ranges between 10^{-4} and 10^{-6} , the cancer risk is at an acceptable (US EPA 2010). The study results showed that CRR values for As, Cr, Cd, and Pb were within an acceptable range ($< 10^{-4}$). The ADC specifies the amount of fish meat eaten daily to prevent cancer. According to ADC results, the lowest daily whiting consumption rate at the stations was determined as ADC_{Hg}, and it was found as 0.03, 0.05, 0.03, and 0.04 kg/meal, respectively. Monthly consumption amounts were determined according to ADC_{Hg}, which has the lowest daily consumption value.

According to AMC_{meat} values, the Adabaşı station has the lowest value (four portions) while the Sarikum Station had highest value (10 portions). In addition, it was observed that there was no health risk in consuming at most four portions at Kastamonu station and six portions at Samsun station. As whiting roe contains lower Hg than meat, AMC_{roe} values at all stations do not pose a health risk when 14, 18, 28, or 45 portions are consumed, respectively. If children and adults are exposed to the same chemical exposure, children are more affected than adults (Rauh and Margolis 2016). Although exposure from other food sources is not included in the measurement data, Hg, in particular, poses a great threat to human health regarding the data estimation in this study. Hg is mainly in the form of MeHg, which is a very toxic composition. However, exposure to trace metals varies depending on the bioavailability of heavy metals, nutritional status, and differences in diet and metabolism of individuals.

Moreover consumed product is raw or cooked can significantly affect the risk level (Bradley et al. 2017). Fish cooking methods were observed to shorten the lifespan of methylmercury bioavailability. Similarly, MeHg bioavailability in boiled and fried fish was found to be 40% and 60% lower, respectively, than in the raw samples (Ouédraogo and Amyot 2011). Selenoprotein, an essential compound of Se, is responsible for reducing the toxic effect of Hg (Osman et al. 1998).

The International Roundtable on Bioindicators reported that food safety Se/Hg molar ratios should be evaluated to examine the effects of Hg toxicity on organisms in risk assessment of fish consumption (Ralston 2008). To avoid Hg toxicity and reduce the adverse effects of Hg, the molar ratio of Se/Hg should be greater than 1 (Ralston 2009).

The US Environmental Protection Agency has developed the Se-HBV formula, which is considered more reliable for fish consumption safety in MeHg exposure risk assessment (Ralston 2009). Using these formulas developed for the health risk posed by Hg exposure, research results have been published stating that the presence of Se in the diets reduces or neutralizes Hg toxicity in fish consumers (Bjerregaard et al. 2011; Gochfeld et al. 2012).

As the amount of Se in this study was higher than the amount of Hg, Se-HBVs were positive, and the Se/Hg ratios

Table 4 Percent compensation of minimum daily requirements (CDRmin) for essential trace elements in adult men (AM), via consuming whiting, based on estimated daily average requirement levels according to IOM (2001, 2006)

	EAR (mg/day, person ww)	*	CDRmin (%)			
			Kastamonu	Sinop		Samsun
				Sarıkm	Adabaşı	
Cr	0.035	Meat	0.004	0.011	0.001	0.006
		Roe	0.259	0.022	0.040	0.012
Cu	0.700	Meat	0.070	0.039	0.054	0.041
		Roe	0.441	0.128	0.200	0.117
Fe	6.000	Meat	0.068	0.043	0.047	0.036
		Roe	0.405	0.190	0.174	0.140
Mn	2.300	Meat	0.029	0.019	0.006	0.008
		Roe	0.129	0.050	0.054	0.032
Se	0.045	Meat	2.549	1.777	1.745	1.559
		Roe	4.862	1.429	2.973	1.553
Zn	9.400	Meat	0.074	0.067	0.068	0.067
		Roe	0.564	0.331	0.428	0.282

EAR estimated average daily requirement (mg/day) for a healthy human, ww (wet weight) basis; EDI ($\text{mg kg}^{-1} \text{ day}^{-1}$) estimated daily intake per meal size, ww basis; CDRmin (%) compensation of minimum daily requirement calculated according to Yigit et al. (2020)

were above 1 (Table 1). Therefore, it can be said that the Se detected in haddock and roe does not pose a health risk for the consumers, as it has a protective effect on Hg toxicity. The daily requirement amounts of elements such as Cu, Cr, Fe, Se, Zn, and Mn were determined by IOM (2006) to contribute to a healthy life. According to IOM, the highest CDRmin values (0.259, 0.441, 0.405, 0.129, 4.862 and 0.564) for Cu, Cr, Fe, Se, Mn and Zn were detected in whiting roe caught in Kastamonu (Table 4). Similar to this study results, Yigit et al. (2018) reported that an individual could only compensate 0.013% to 0.94% of the minimum daily requirement level for Cu, Zn, Fe, or Mn when consuming Mediterranean mussels (*M. galloprovincialis*) exposed to a cage farm with copper alloy mesh pens.

Conclusions

In this study, there were strong positive correlations between Cu_meat-Cu_roe, Fe_meat-Fe_roe and Zn_meat-Zn_roe. It was seen that there was a statistically significant difference between the regions in terms of the mean concentrations of each element. Cu, Fe, Mn and Zn elements, which have important roles in the body functions and can be seen in this study, were found to be quite high in the roes in all regions. It can be said that these elements are essential for the development of the gonad during the reproductive period. It was determined that whiting muscle and roe tissues contain more Se than Hg, Se/Hg ratios were over 1 with positive Se-HBVs. Thus, it may be concluded that, thanks to the protective effect of Se's on mercury's toxicity, they do not pose any health threat to people who ingest them.

Considering the risk/benefit assessment, it has been found that the whiting is healthy and beneficial for human consumption. However, a low health risk appeared in the daily ingestion of whiting in the health risk analyses of EDI, THQ, CRR and ADC calculations, especially for the Hg elements. Even though there were differences in metal amounts among regions, there was a low health risk for daily consumption at all stations due to the high Hg concentration in particular. Therefore, it revealed that AMC_{meat} does not pose a health risk as long as a maximum of three portions for Adabaşı, six portions for Kastamonu, three portions for Samsun, and five portions for Sarıkum is consumed per month.

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

Declarations

Ethics approval Not applicable for this study.

Consent to participate Informed consent was obtained from all individual participants included in the study.

Consent for publication Not applicable.

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