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## Black Sea Whiting: Assessment of Potential Health Benefits/Risks and Differences Based on Mineral Concentrations of Meat and Roes

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ARTICLEINFO	ABSTRACT
Research Article	In this study; the human health risks of whiting meat and roes, which are frequently consumed in Turkey were evaluated in terms of minerals and heavy metals. The potential of human health risks according to consumption of whiting meats and roes were assessed by estimating of Metal Pollution
Received : 28/06/2019 Accepted : 02/10/2019	Index (MPI), Estimated Weekly Intake (EWI), Target Hazard Quotient (THQ), Total Target Hazard Quotient (TTHQ) levels of heavy metals. The Cd, Hg and Pb results found in the roes were lower than the acceptable limits identified by Turkish Codex. The results showed that the investigated fish meat's Pb levels were higher than the limit values except from in April and May. The highest Cd content was 0.22 mg.kg <sup>-1</sup> in whiting meat in December while the lowest Cd content was 0.03 mg.kg <sup>-1</sup>
<i>Keywords:</i> Fish Whiting Roe Food safety Lead	in May. The maximum value of metal pollution indices (MPI) was determined as 0.44 for whiting meat and 0.66 for roes in March. The THQ values of whiting meat and roes were lower than 1 for six months. However, the TTHQ values of whiting meat in February and March were higher than 1 indicating health risk for the consumer by consuming whiting meat.
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#### Introduction

The mineral matters play an important role to restoration of body functions, such as regulating the acidbase balance, helping to bond formation (hemoglobin formation), controlling of the water balance in the body, helping the teeth structure and catalysing many of metabolic reactions (Duran et al., 2010; Mendil et al., 2010). When compared with other meat products, the fishery products are not only a higher source of iodine, phosphorus and zinc, but also a higher nutritional value of dietary fibre content. Essential metals (Cu, Co, Zn, Fe, Ca, Mg, Se, Ni and Mn) are required in very trace quantities for the proper functioning of enzyme systems in humans (Dizman et al., 2017).

American Cancer Society (ACS) recommends a minimum of two servings of fatty fish per week for adults (ACS 2006). However, consuming the fish and its derivatives are also very important issue for safety of

human's health. When we say the safety of fishery products; the first things that comes to our mind are microbiological, chemical and physiological factors. occurred Through the 92 naturally elements. approximately 30 metals and metalloids (Be, B, Li, Al, Ti, V, Cr, Mn, Co, Ni, Cu, As, Se, Sr, Mo, Pd, Ag, Cd, Sn, Sb, Te, Cs, Ba, W, Pt, Au, Hg, Pb and Bi) are potentially toxic to humans (Bat and Arici, 2018). Due to this reason, it is a necessity to fishing from clean and safe waters for meet the conditions as human food consumption. Castritsi-Catharios et al. (2015) reported that trace elements could be in marine environment are either anthropogenic origin (e.g. agriculture, transport, mining, metalworking and pharmaceutical products) or geochemical processes.

Sinop is a city in Turkey, where is situated in the coastal area of Western Back Sea, with 175 km of coasts, approximately. In Sinop, whiting fishing has been estimated to be nearly 3760 tones/year in 2017 (TURKSTAT, 2018a). Whiting meat and its roes are widely used as food, especially in the coastal regions of Turkey, because of the whiting is one of the cheap and delicious fish. On the other hand, whiting is a quickly perishable food because of which are composed from white meat and soft roes.

The aim of this study was to compare the meat and roes of whiting (*Merlangius merlangus euxinus* Nordman, 1840) in terms of its mineral composition in Black Sea -Turkey and to evaluate the potential risks of trace elements and toxic metals to human health.

#### Material and methods

#### Sample Collection

The whiting samples (Merlangius merlangus euxinus Nordman, 1840) purchased from fisheries, they were obtained from Sinop coasts from December 2016 to April 2017 (Figure 1). A total of 36 kilograms whiting and they used in study and sampling were carried out twice a month. Whiting was transferred to the laboratory under cold chain conditions. The average weight and length (±SD) of the samples were 26.49±1.09g and 15.06±0.34cm, respectively. The fish were gutted and the roes were separated (Figure 2). Analyses were performed on the meat and roes of the fish in Sinop University Fisheries Quality Control Laboratory and SUBITAM on the obtained day.

#### Trace Element Analysis

According to the method described by Milestone (2018), which is provides the acid (7 ml of HNO<sub>3</sub> 65%, 1 ml H<sub>2</sub>O<sub>2</sub> 30%: Merck, Darmstadt, Germany) digestion of the sample in a closed vessel device using temperature control microwave (Ethos D, Milestone Inc. Sorisole, Italy) heating for the metal determination by spectroscopic methods. Analyses of 28 elements (Macro elements: Na, Mg, K, Ca; Trace elements: Li, Be, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Sb, Cs, Ba, Tl, Cd, Hg, Pb) were conducted using inductively coupled plasma mass spectrometry using dynamic reaction cell technology (Agilent Technologies / 7700X ICP-MS Systems). Analytical quality control was ensured using Agilent reference materials; std. 1: Agilent 8500-6940 2A (10 ppm in %5 HNO<sub>3</sub>): Li, Be, Na, Mg, K, Ca, Rb, Sr, Cs, Ba, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, Al, Ga, As, Se, Tl, Pb; std. 2: Agilent 8500 - 6940 Hg (10 ppm in %5 HNO<sub>3</sub>): Hg.

Our results are expressed in milligrams of element per kilogram of meat and roe (mg.kg<sup>-1</sup>). The used detection limits of metals are given in Table 1.

#### Data Analysis

All the data were expressed with the mean of six measurements. Data were presented as mean  $\pm$  std. error. Statistically analyses were performed using Minitab 18. One - way Anova was performed to test the differences between meat and roe. Significance were established at P<0.05.



Figure 1 The fishing area of Sinop Region



Figure 2 Merlangius merlangus euxinus Nordman, 1840

Table T Delection	on mint for the elements measured by using	ICF-IVIS.	
Elements	Detection Limits (mg.kg-1)	Elements	Detection Limits (mg.kg-1)
Li	0.1132	Ga	0.02863
Be	0.002037	As	0.6655
Na	0.3834	Se	0.2816
Mg	0.07421	Rb	0.002855
Κ	0.7839	Ag	0.04828
Ca	8.166	Cd	0.004838
V	0.02506	Sb	0.01398
Cr	0.02936	Cs	0.002211
Fe	0.1959	Hg	0.03357
Co	0.006183	Pb	0.003045
Ni	0.05721	U	0.002152
Cu	0.06849	Al	0.426
Mn	0.03901	Zn	2.676
Sr	0.01669	Ba	0.03248

Table 1 Detection limit for the elements measured by using ICP-MS.

#### Human Risk Assessment Analysis

*Metal pollution index (MPI):* The metal pollution index (MPI) was used to compare the overall trace element contents in the fish meat and roes. This index was obtained by calculating the geometrical mean of concentration of all the trace elements (Usero et al., 1997).

$$MPI=(C_1 \times C_2 \times \dots \times C_n)^{m}$$
(1)

Where  $C_n$  are the mean concentration of trace elements (n) in the meat or roes (mg.kg<sup>-1</sup>)

*Estimated weekly intake (EWI):* The estimated weekly intake was estimated by calculating the respective levels found in fish meat and roe, for a person weighing at 70 kg and with a consumption rate in Turkey in 2017 was 5.49 kg/person/year; 0.106 kg/person/weekly (TURKSTAT, 2018b). The EWI was determined using the following equation (Marengo et al. 2018).

$$EWI = \frac{(CM \times IRw)}{Bw}$$
(2)

- CM = Trace element concentration in fish meat or roe (mg.kg<sup>-1</sup>)
- $IR_W = The weekly ingestion rate (kg)$
- $B_W$  = The body weight (kg)

To asses' public health risks, weekly fish intakes were compared with Provisional Tolerable Weekly Intake (PTWI) recommended by the Joint FAO/WHO Expert Committee of Food Additives (FAO/WHO, 2011).

*Target hazard quotient (THQ), total target hazard quotient (TTHQ)* 

The THQ lower than 1 indicates no obvious risk (Chien et al., 2002). A THQ value below 1 indicates that the level of daily exposure is unlikely to cause any adverse effects during a persons' lifetime, although it also indicates potential no-carcinogenic effects (Jovic and Stankovic, 2014). The models for estimating THQ and TTHQ (Chien et al, 2002; Storelli, 2008; Zhang et al., 2017) calculated as below.

$$THQ = (E_F \times E_D \times F_{IR} \times C/(R_f D_o \times W_{AB} \times T_A) \times 0.003$$
(3)

- $E_F$  = Is the exposure frequency (365 days/year)
- $E_D$  = Exposure duration (70 years, average lifetime)
- $F_{IR}$  = Is the food ingestion rate (33.4 × 10<sup>-3</sup> kg per day per person for the world)

C = Is the trace metal concentration  $(mg.kg^{-1})$ 

- $R_f D_o = Is$  the oral reference doses (mg.kg<sup>-1</sup>/day)
- $W_{AB} = Is$  the average body weight (70 kg)
- $T_A$  = Is the average exposure time for non-carcinogens (365days/year × E<sub>D</sub>, assuming 70years)

$$TTHQ = THQ_1 + THQ_2 + \dots + THQ_n \tag{4}$$

The total THQ (TTHQ) was calculated as the sum of the THQ values of the individual trace elements.

#### **Results and Discussion**

#### Macro Elements

Table 2 shows the macro elements content in the meat and roes of whiting. Among the main elements, the most abundant was potassium in the meat ( $8796.34 \text{ mg.kg}^{-1}$ ) in March and in the roes ( $6150.05 \text{ mg.kg}^{-1}$ ) in February. In generally Ca contents of whiting roes were lower than meats during fishing season (P<0.05). However, in December, March and May the levels of Na, Mg and Ca were higher in the meat (P<0.05). Özden et al. (2010) were reported the Ca, Mg and Na levels of whiting meat as 586, 343 and 1227 mg/kg in December and 577, 379 and 801 mg/kg in May. The Na values reported that literature was quite higher than our results.

Na/K ratio in food should be less than 1 for the cardiovascular disease prevention (Bu et al., 2012). So that lower concentration of Na and higher of K were observed for healthy foods. The Na/K ratio of whiting meat and roes were less than 1 as shown in Table 2.

#### Trace Elements

Fe was the most dominant trace elements in both whiting meat and roes in all months (p>0.05), followed by Zn, Al, and Sr in meat; Zn, Al, Cu and Mn in roes, respectively. These results showed that the orders of the trace metal levels changed between these two parts of whiting. The maximum Fe contents were found in March (71.10 mg.kg<sup>-1</sup>) of meat and in December (142.03 mg.kg<sup>-1</sup>) of roes (Table 3).

Table 2 "Macro element"	composition of whiting meat and roes	(mg.kg <sup>-1</sup>	) (wet sample)

	December	January	February	March	April	May			
	Whiting meat								
Na	1687.11±103.05 <sup>Ab</sup>	1664.64±143.33 <sup>Ab</sup>	1582.78±206.20 <sup>b</sup>	2357.42±21.72 <sup>Aa</sup>	1648.50±233.69 <sup>Ab</sup>	1172.35±25.89 <sup>Ab</sup>			
Mg	$650.34{\pm}24.55^{Ab}$	664.16±36.85 <sup>Ab</sup>	689.28±92.08 <sup>Aab</sup>	$887.53 \pm 24.50^{Aa}$	628.77±53.96 <sup>Ab</sup>	$487.91{\pm}10.04^{Ab}$			
K	$6589.86{\pm}196.40^{\rm Ab}$	6193.04±212.62 <sup>Ab</sup>	6878.05±891.72 <sup>Aab</sup>	8796.34±408.26 <sup>Aa</sup>	5939.17±436.85 <sup>Ab</sup>	5279.87±263.09 <sup>Ab</sup>			
Ca	1068.49±45.24 <sup>Ac</sup>	1556.37±23.83Abc	1772.97±294.41 <sup>Ab</sup>	$2028.40{\pm}50.00^{Aab}$	2485.95±234.01Aa	2113.44±41.88 <sup>Aab</sup>			
Na/K	0.26	0.27	0.23	0.27	0.28	0.22			
			Whiting ro	e					
Na	1107.16±70.63 <sup>Bab</sup>	1053.15±248.69 <sup>Aab</sup>	1148.10±36.16 <sup>Aa</sup>	1142.25±36.06 <sup>Ba</sup>	1199.13±53.69 <sup>Aa</sup>	635.90±42.22 <sup>Bb</sup>			
Mg	336.65±10.92 <sup>Ba</sup>	329.03±53.53 <sup>Ba</sup>	$340.14{\pm}19.92^{Ba}$	365.96±9.22 <sup>Ba</sup>	323.93±4.76 <sup>Ba</sup>	$188.67 \pm 9.72^{Bb}$			
K	5584.88±66.31 <sup>Ba</sup>	5082.20±923.91 <sup>Aa</sup>	6150.05±263.49 <sup>Aa</sup>	5880.61±113.81 <sup>Ba</sup>	5882.09±516.16 <sup>Aa</sup>	3236.52±13.66 <sup>Bb</sup>			
Ca	192.58±49.69 <sup>Ba</sup>	174.29±55.91 <sup>Ba</sup>	$129.21 \pm 0.87^{Ba}$	198.66±30.51 <sup>Ba</sup>	112.36±8.64 <sup>Ba</sup>	169.40±53.13 <sup>Ba</sup>			
Na/K	0.20	0.21	0.19	0.19	0.20	0.20			

 $\rightarrow$  (a, b...) Means with different lowercase letters in the same column are significantly different (P<0.05) from month to month between the groups,  $\downarrow$  (A, B...) Means with different capital letters in the same column are significantly different (P<0.05) between groups in the different months

Table 3	"Trace element"	composition	of whiting m	neat and roes (	mg.kg <sup>-1</sup>	) (wet sample)

	December	January	February	March	April	May
Whiting 1	meat					
Li	$0.01{\pm}0.01^{Ad}$	$0.06 \pm 0.02^{Ac}$	$0.10 \pm 0.01^{Abc}$	0.15±0.01 <sup>Aa</sup>	0.13±0.01 <sup>Aab</sup>	0.11±0.01 <sup>Aab</sup>
Be	$0.02{\pm}0.00^{Aa}$	$0.02{\pm}0.00^{Aa}$	$0.02{\pm}0.00^{Aa}$	$0.02{\pm}0.00^{Aa}$	$0.02{\pm}0.00^{Aa}$	$0.01{\pm}0.00^{Ba}$
Al	$10.09 \pm 0.20^{Ab}$	10.92±0.32 <sup>Ab</sup>	9.21±0.15 <sup>Ab</sup>	19.68±0.65 <sup>Aa</sup>	$12.34 \pm 1.77^{Ab}$	2.28±0.11 <sup>Ac</sup>
V	$0.05 \pm 0.00^{Ac}$	$0.05 \pm 0.00^{Ac}$	$0.06 \pm 0.00^{Abc}$	0.10±0.01 <sup>Aa</sup>	$0.07 \pm 0.01^{Ab}$	$0.04{\pm}0.00^{\rm Ac}$
Cr	1.25±0.42 <sup>Aa</sup>	0.46±0.11 <sup>Aab</sup>	$0.29{\pm}0.05^{\rm Ab}$	$0.60{\pm}07^{Aab}$	0.53±0.13 <sup>Aab</sup>	$0.28 {\pm} 0.03^{Ab}$
Mn	$2.82{\pm}0.72^{Aa}$	$1.31 \pm 0.04^{Ab}$	1.53±0.15 <sup>Aab</sup>	2.36±0.10 <sup>Aab</sup>	$2.02 \pm 0.08^{Aab}$	$1.41 \pm 0.04^{Ab}$
Fe	34.66±8.10 <sup>Bb</sup>	22.33±3.62 <sup>Ab</sup>	$24.29 \pm 3.94^{Ab}$	71.10±10.26 <sup>Aa</sup>	$35.00 \pm 3.42^{Ab}$	12.04±0.44 <sup>Ab</sup>
Co	$0.04{\pm}0.00^{Bb}$	$0.04 \pm 0.00^{Abc}$	$0.04 \pm 0.00^{Bbc}$	$0.06{\pm}0.00^{Aa}$	$0.04 \pm 0.00^{Bbc}$	$0.03 {\pm} 0.00^{\rm Ac}$
Ni	$0.27 {\pm} 0.01^{Bb}$	$0.26{\pm}0.05^{Ab}$	$0.19{\pm}0.01^{Ab}$	$0.61 \pm 0.14^{Aa}$	$0.26{\pm}0.01^{Ab}$	$0.41 \pm 0.11^{Aab}$
Cu	$0.75 {\pm} 0.03^{Bb}$	$0.59{\pm}0.06^{Bb}$	$0.64{\pm}0.04^{Bb}$	$1.01{\pm}0.04^{Bab}$	$0.68 {\pm} 0.05^{\text{Bb}}$	$2.10{\pm}0.67^{Aa}$
Zn	12.63±0.22 <sup>Bb</sup>	13.14±0.57 <sup>Bb</sup>	13.44±1.65 <sup>Bb</sup>	$18.52 \pm 0.60^{Ba}$	13.22±0.64 <sup>Bb</sup>	14.32±0.22 <sup>Bb</sup>
Ga	$0.01{\pm}0.00^{Aa}$	$0.01{\pm}0.00^{Aa}$	$0.01{\pm}0.00^{Aa}$	$0.01{\pm}0.00^{Aa}$	$0.01{\pm}0.00^{Aa}$	$0.01{\pm}0.00^{Aa}$
As	1.86±0.02 <sup>Aabc</sup>	$1.85 \pm 0.05^{Aabc}$	2.31±0.47 <sup>Aab</sup>	2.83±0.18 <sup>Aa</sup>	$1.74 \pm 0.28^{Abc}$	$1.14 \pm 0.03^{Ac}$
Se	$0.95{\pm}0.03^{Bab}$	$0.90{\pm}0.04^{Ab}$	0.91±0.10 <sup>Ba</sup>	1.26±0.11 <sup>Bb</sup>	$0.84{\pm}0.07^{\rm Bb}$	$0.78 \pm 0.02^{Ab}$
Rb	1.30±0.04 <sup>Ac</sup>	$1.17 \pm 0.04^{Abc}$	$1.27 \pm 0.16^{Ab}$	$1.65 \pm 0.08^{Aab}$	$1.09{\pm}0.08^{Aa}$	$0.98 {\pm} 0.05^{Aab}$
Sr	6.18±0.05 <sup>Ac</sup>	8.59±0.22 <sup>Abc</sup>	$10.02 \pm 1.47^{Ab}$	$11.34 \pm 0.44^{Aab}$	13.86±0.95 <sup>Aa</sup>	$11.84 \pm 0.43^{Aab}$
Ag	$0.03{\pm}0.00^{\rm Ab}$	$0.03{\pm}0.00^{\mathrm{Bb}}$	$0.03{\pm}0.00^{\rm Ab}$	$0.03{\pm}0.00^{Aab}$	$0.04{\pm}0.01^{Aa}$	$0.03{\pm}0.00^{Ab}$
Sb	$0.02{\pm}0.00^{Aab}$	$0.01 \pm 0.00^{Acd}$	$0.01 {\pm} 0.00^{Acd}$	$0.02{\pm}0.00^{Aa}$	$0.02 \pm 0.00^{Abc}$	$0.01{\pm}0.00^{Bd}$
Cs	$0.02{\pm}0.00^{Aab}$	$0.02 \pm 0.00^{Ab}$	$0.02{\pm}0.00^{Aab}$	$0.03{\pm}0.00^{Aa}$	$0.02{\pm}0.00^{Aab}$	$0.02{\pm}0.00^{Ab}$
Ba	$0.23{\pm}0.00^{Ab}$	0.28±0.01 <sup>Aab</sup>	$0.28 \pm 0.02^{Aab}$	0.30±0.01 <sup>Aab</sup>	0.35±0.042Aa	$0.36{\pm}0.05^{Aa}$
Tl	$0.01{\pm}0.00^{Aa}$	$0.00{\pm}0.00^{\rm Ab}$	$0.00{\pm}0.00^{\rm Abc}$	$0.00{\pm}0.00^{\rm Abc}$	$0.00{\pm}0.00^{\rm Ac}$	$0.00{\pm}0.00^{\rm Ac}$
			Whiting ro	be and the second se		
Li	0.09±0.01 <sup>Bab</sup>	0.10±0.01 <sup>Aa</sup>	$0.06 \pm 0.00^{Bbc}$	0.09±0.01 <sup>Bab</sup>	0.08±0.01 <sup>Bbc</sup>	0.05±0.01 <sup>Bc</sup>
Be	$0.01 \pm 0.00^{Bbc}$	$0.02{\pm}0.00^{\text{Bab}}$	$0.02{\pm}0.00^{Ba}$	$0.02{\pm}0.00^{\text{Bab}}$	$0.01 \pm 0.00^{Bc}$	$0.02{\pm}0.00^{Aa}$
Al	$2.47 \pm 0.07^{Bcd}$	$3.65 \pm 0.32^{Bbc}$	$4.19 \pm 0.65^{Bb}$	$6.78 \pm 0.32^{Ba}$	$3.01 \pm 0.30^{Bbc}$	$1.03 \pm 0.16^{Bd}$
V	$0.02{\pm}0.00^{Bb}$	$0.03{\pm}0.01^{Bab}$	$0.02{\pm}0.00^{\text{Bb}}$	$0.03{\pm}0.00^{Aa}$	$0.03{\pm}0.00^{\text{Bab}}$	$0.02{\pm}0.00^{\text{Bb}}$
Cr	1.24±0.31 <sup>Aa</sup>	$0.12{\pm}0.01^{Bb}$	$0.22{\pm}0.06^{Ab}$	$0.27 {\pm} 0.08^{Bb}$	$0.23{\pm}0.05^{Ab}$	$0.25 {\pm} 0.07^{Ab}$
Mn	2.29±0.30 <sup>Aa</sup>	1.62±0.29 <sup>Aabc</sup>	1.51±0.13 <sup>Aabc</sup>	$1.82{\pm}0.16^{Bab}$	$1.43 \pm 0.09^{Bbc}$	$0.79 \pm 0.09^{Bc}$
Fe	142.03±24.16 <sup>Aa</sup>	$28.00 \pm 2.49^{Ab}$	41.60±10.26 <sup>Ab</sup>	52.82±11.04Ab	$33.49 \pm 6.59^{Ab}$	33.39±10.31 <sup>Ab</sup>
Co	$0.06{\pm}0.00^{Aa}$	$0.04{\pm}0.00^{Ab}$	$0.05{\pm}0.00^{Aab}$	$0.05{\pm}0.00^{Aab}$	$0.05 {\pm} 0.00^{Aab}$	$0.03 \pm 0.00^{Ac}$
Ni	$0.41{\pm}0.05^{Aa}$	$0.23{\pm}0.02^{Ab}$	$0.21 \pm 0.03^{Ab}$	$0.39{\pm}0.06^{Aa}$	$0.21 \pm 0.02^{Bb}$	$0.18 \pm 0.02^{Ab}$
Cu	2.15±0.13 <sup>Aa</sup>	1.68±0.23 <sup>Aab</sup>	$1.78{\pm}0.14^{Aa}$	$1.88{\pm}0.08^{Aa}$	$1.70{\pm}0.02^{Aa}$	$1.15 \pm 0.01^{Ab}$
Zn	$55.94{\pm}0.58^{Aa}$	53.99±9.5.74 <sup>Aa</sup>	58.15±4.81 <sup>Aa</sup>	57.39±2.76 <sup>Aa</sup>	49.09±0.35 <sup>Aa</sup>	31.15±1.13 <sup>Ab</sup>
Ga	$0.01{\pm}0.00^{Aa}$	$0.01{\pm}0.00^{Aa}$	$0.01{\pm}0.00^{Aa}$	$0.01{\pm}0.00^{Aa}$	$0.01{\pm}0.00^{Ba}$	$0.01{\pm}0.00^{Aa}$
As	$1.29{\pm}0.02^{Ba}$	$1.17 \pm 0.16^{Bab}$	$1.21{\pm}0.06^{Ba}$	$1.36{\pm}0.02^{Ba}$	$1.28{\pm}0.01^{Aa}$	$0.90{\pm}0.02^{\text{Bb}}$
Se	$1.71 \pm 0.04^{Ab}$	$1.31 \pm 0.19^{Aab}$	$1.44{\pm}0.07^{Aab}$	$1.62{\pm}0.08^{Aa}$	1.35±0.03 <sup>Aab</sup>	$0.84{\pm}0.02^{\rm Ac}$
Rb	$1.19{\pm}0.01^{Ba}$	$1.13{\pm}0.19^{Ba}$	$1.42{\pm}0.07^{Ba}$	$1.34{\pm}0.03^{Ba}$	$1.28{\pm}0.02^{Ba}$	$0.68{\pm}0.01^{\text{Bb}}$
Sr	$1.31{\pm}0.15^{Ba}$	$1.28{\pm}0.27^{Ba}$	$1.12{\pm}0.05^{Ba}$	$1.44{\pm}0.07^{Ba}$	$0.90{\pm}0.08^{Ba}$	$1.06{\pm}0.17^{Ba}$
Ag	$0.03{\pm}0.00^{\rm Ab}$	0.16±0.06 <sup>Aa</sup>	$0.03{\pm}0.00^{\rm Ab}$	$0.03{\pm}0.00^{\rm Ab}$	$0.04{\pm}0.01^{\rm Ab}$	$0.03{\pm}0.00^{\mathrm{Ab}}$
Sb	$0.02{\pm}0.00^{Aa}$	$0.01{\pm}0.00^{b}$	$0.01{\pm}0.00^{Bb}$	$0.01{\pm}0.00^{\mathrm{Bab}}$	$0.01{\pm}0.00^{\rm Bb}$	$0.01{\pm}0.00^{Aab}$
Cs	$0.02{\pm}0.00^{\rm Bbc}$	$0.02{\pm}0.00^{Bc}$	$0.02{\pm}0.00^{\mathrm{Bbc}}$	$0.02{\pm}0.00^{\mathrm{Bab}}$	$0.02{\pm}0.00^{Ba}$	$0.02{\pm}0.00^{\rm Bc}$
Ba	$0.45{\pm}0.15^{Aa}$	$0.14{\pm}0.00^{Bb}$	$0.11{\pm}0.00^{Bb}$	$0.13{\pm}0.01^{Bb}$	$0.17{\pm}0.04^{Bb}$	$0.10{\pm}0.02^{\text{Bb}}$
Tl	$0.00{\pm}0.00^{Ba}$	$0.00{\pm}0.00^{\text{Ba}}$	$0.00{\pm}0.00^{Aa}$	$0.00{\pm}0.00^{Ba}$	$0.00{\pm}0.00^{Aa}$	$0.00{\pm}0.00^{Aa}$

 $\rightarrow$  (a, b....) Means with different lowercase letters in the same column are significantly different (p<0.05) from month to month between the groups,  $\downarrow$  (A, B...) Means with different capital letters in the same column are significantly different (p<0.05) between groups in the different months

Essential trace elements (Fe and Cu) require for cofactors for a number of enzymes and other cellular activities (Thanonkaew et al., 2006). The concentration of Fe in roes decreased (P<0.05) after December.

Cu plays a crucial role in many biological enzyme systems those catalyze oxidation/reduction reactions (Bat and Arici, 2018). The Cu contents of whiting roes were higher than meat and these were statistically different in December, March and April (Table 3). The concentration of trace minerals in fish is affected some factors such as seasonal and biological differences, food source and environment (Farmer et al., 1979; Lal, 1995).

In the literature, Fe and Cu levels in whiting samples have been reported in the range of 0.33-0.13 mg/100g (dry matter) (Güner et al., 1998), 1040-486 mg.kg<sup>-1</sup> (dry meat) (Uluozlu et al., 2007), 99-23 mg.kg<sup>-1</sup> (dry weight) (Aygun et al., 2011), 299.3-37.0 mg.kg<sup>-1</sup> (Nisbet et al., 2010) in the Black Sea, Turkey. Our Fe and Cu values in Whiting meat are lower than in literatures values (Table 3). The toxic limit for Cu is 30mg.kg<sup>-1</sup> (FAO, 1983). The Cu concentrations in whiting meat and roes were found to below the toxic limit for six months (Table 3).

The concentration of Al in whiting meat was fluctuated during study but this fluctuation was not statistically significant (P>0.05) except May and March. The Al contents of roes were also low in whiting meat and statistically similar in December, January and Fe (P<0.05). And it was maximum in March (P<0.05) (Table 3).

Zinc is an essential component of many enzymes and it is very important element for supporting the immune system. Approximately 13 mg of zinc per day should be taken to the body (Demirci, 2003). Only 1-2 mg of zinc taken from the body is absorbed. The Zn contents of roes were higher than meats (P<0.05) (Table 3) and it can be said that especially roes meet (max. 12 mg/200 g whiting roe) the amount of Zn that required daily. Similarly, Güner et al. (1998) determined that Zn was present in the amount of 0.33 mg per 100 g (dry matter) in whiting caught in the Black Sea.

Barceloux, (1999) reported that selenium is an essential nutrient used in selenoproteins such as glutathione peroxidase. Selenium intake reduces methylmercury (MeHg) toxicity (Ganther et al., 1972; Ralston et al., 2008). In this study, high levels of selenium (0.84-1.71 mg.kg<sup>-1</sup>) were also found in the fish roes. In whiting meat, the selenium levels ranged between 0.78-1.26 mg.kg<sup>-1</sup>. Se contents of some fish species in the literatures have been reported as: 0.77 mg.kg<sup>-1</sup> in Japanese bluefish; 0.62 mg.kg<sup>-1</sup> in skipjack; 0.56 mg.kg<sup>-1</sup> in hoki; 0.40 mg.kg<sup>-1</sup> in pacific mackerel and pacific herring; 0.29 mg.kg<sup>-1</sup> (wet meat) in Rainbow trout (Yamashita et al., 2013); 0.066 mg.kg<sup>-1</sup> in European hake (wet meat) (Olmedo et al., 2013).

#### Heavy Metals

Bat and Arici (2016) reported that large differences in heavy metal concentration were observed between different tissues of fish. The highest Cd content was 0.22 mg.kg<sup>-1</sup> in whiting meat in December while the lowest Cd content was 0.03 mg.kg<sup>-1</sup> in May (P<0.05) (Table 4). Cadmium levels had been reported as 0.20 mg.kg<sup>-1</sup> in whiting from Middle Black Sea in 2009 (Aygün and Abanoz, 2011), 0.55 mg.kg<sup>-1</sup> (dry matter) (Uluozlu et al., 2007), 0.19 mg.kg<sup>-1</sup> (dry meat) (Turan et al., 2009). The cadmium content of whiting roes was 0.02 mg.kg<sup>-1</sup> for six months (P>0.05) (Table 4). The maximum Cd level permitted from the sea fish's meat and roes was 0.05 mg.kg<sup>-1</sup>, according to the Turkish Food Codex (Anonymous, 2018). Cadmium levels in the fish roes in this research were found to be lower than legal limits. Similarly, from September 2014 to February 2015, Cd levels of whiting roes and muscle tissues caught from Black Sea were below limits (Bat and Arici, 2016).

The minimum and maximum Pb levels observed whiting meat were 0.19 mg.kg<sup>-1</sup> in May and 0.90 in January (Table 4). Pb contents in the literature have been reported 0.50 (wet matter), 0.88 and 0.93 (dry matter) mg.kg<sup>-1</sup> (Turan et al., 2009; Güner et al., 1998; Uluzolu et al., 2007). Generally, Pb levels of whiting meats were found higher than roes in January, March and April (P<0.05). The maximum Pb level permitted for whiting meat and roes are 0.30 mg.kg<sup>-1</sup> according to the Turkish Food Codex (Anonymous, 2018). The Pb levels of whiting roes during fishing season were found to be lower than legal limits value, On the other hand for meat, it was found highest in January. Due to the high content of Pb observed in fish meat during the months of January, there may be intense air pollution experienced at that time. Bat and Arici (2018) have reported that; the most influential origin of pollution in the Black Sea is the factorial and industrial wastes that are polluted by six coastal countries (Russia, Ukraine, Romania, Bulgaria, Georgia and Turkey). The major rivers Dnieper, Dniester, Danube, Kızılırmak, Yeşilırmak, and Sakarya run through to the sea, which carry and discharge pollution from industrial, agricultural, and domestic wastes to the Black Sea basin.

The lowest and highest Hg levels in whiting meat were  $0.13 \text{ mg.kg}^{-1}$  in January and  $0.23 \text{ mg.kg}^{-1}$  in May (P<0.05). The Hg levels of roes were found 0.04-0.05 mg.kg<sup>-1</sup> in all months (P>0.05). Hg levels of whiting meat and roes did not exceed the limit value (0.50 mg.kg<sup>-1</sup>) recommended from Turkish Food Codex (Anonymous, 2018). Bat and Arici (2016) reported that Cu, Hg and Pb levels in the edible tissue of whiting (M. merlangus) from Sinop coasts during September 2014 and February 2015 were considerably lower than the maximum levels set by the Turkish Food Codex Standards. Cd and Hg results of our studies were similar with Bat and Arıcı (2016) but the Pb concentration of whiting meat and roe were higher than literature. Mol et al. (2017) reported the Pb concentration of whiting (wet sample) muscle sample caught from Southwest Black Sea was 0.36 mg.kg<sup>-1</sup> during spring season.

# Human Risk Assessment, MPI, EWI, PTWI, THQ and TTHQ

The MPI is used to assess the degree of tissue contamination: the higher index, the greater the contamination (Usero et al., 1997). The MPI values of roes were higher than meat during six months (Table 5). However, MPI values were small than 1 value both whiting meat and roe. The maximum value of metal pollution indices (MPI) was determined as 0.44 for whiting meat and 0.66 for roes in March. Qiao-qiao et al. (2007) reported that the different organs of fish have different abilities to bind heavy metals and they found that the MPI values of gonads were higher that muscle of different fish species.

Table 4 "Heavy	v metal" compositio	n of whiting meat and	roes (mg.kg <sup>-1</sup> )	(in wet sample)

	December	January	February	March	April	May
			Whiting meat			
Cd	$0.22{\pm}0.03^{Aa}$	$0.08{\pm}0.02^{\rm Ab}$	$0.04{\pm}0.00^{\rm Ab}$	$0.08 {\pm} 0.01^{Ab}$	$0.04{\pm}0.01^{Ab}$	$0.03{\pm}0.00^{Ab}$
Hg	$0.16{\pm}0.02^{Ab}$	$0.13{\pm}0.01^{Ab}$	$0.15{\pm}0.03^{Ab}$	$0.19{\pm}0.00^{Aab}$	$0.18{\pm}0.00^{\rm Ab}$	$0.23{\pm}0.00^{Aa}$
Pb	$0.33{\pm}0.03^{Ab}$	$0.90{\pm}0.28^{Aa}$	$0.45{\pm}0.07^{Aab}$	$0.62{\pm}0.09^{Aab}$	$0.27 \pm 0.02^{Ab}$	$0.19{\pm}0.02^{Ab}$
			Whiting roe			
Cd	$0.02{\pm}0.00^{Ba}$	$0.02{\pm}0.00^{Ba}$	$0.02{\pm}0.00^{Ba}$	$0.02{\pm}0.00^{\text{Ba}}$	$0.02{\pm}0.00^{\text{Ba}}$	$0.02{\pm}0.00^{Aa}$
Hg	$0.04{\pm}0.00^{Ba}$	$0.05{\pm}0.01^{Ba}$	$0.05{\pm}0.00^{Ba}$	$0.05{\pm}0.00^{Ba}$	$0.05{\pm}0.00^{Ba}$	$0.04{\pm}0.00^{Ba}$
	±	±	±	±	±	±
Pb	$0.20{\pm}0.03^{\rm Ab}$	$0.16{\pm}0.00^{Ba}$	$0.26{\pm}0.05^{Aa}$	$0.18{\pm}0.01^{Ba}$	$0.14{\pm}0.00^{Bb}$	$0.22{\pm}0.05^{Aa}$

 $\rightarrow$  (a, b...) Means with different lowercase letters in the same column are significantly different (P<0.05) from month to month between the groups,  $\downarrow$  (A, B...) Means with different capital letters in the same column are significantly different (P<0.05) between groups in the different months

Table 5 Metal P	ollution index	(MPI) values	s of whiting mean	t and roes

	December	January	February	March	April	May
Whiting meat	0.31	0.31	0.29	0.44	0.32	0.25
Whiting roe	0.46	0.46	0.44	0.66	0.48	0.37

Table 6 The comparison between recommended values (PTWI) and estimated weekly intakes (EWI) for whiting meat and roes

Elemente	PTWI*	December	January	February	March	April	May
Elements	PIWI*	EWI	EWI	EWI	EWI	EWI	EWI
			Whitin	ig meat			
As	1050	2.82	2.80	3.50	4.29	2.63	1.73
Cd	490	0.33	0.12	0.06	0.12	0.06	0.05
Cr	44,590	1.89	0.70	0.44	0.91	0.80	0.42
Cu	245,000	1.14	0.89	0.97	1.53	1.03	3.18
Fe	392,000	52.49	33.81	36.78	107.67	53.00	18.23
Pb	1750	0.50	1.36	0.68	0.94	0.41	0.27
Zn	490.000	19.13	19.90	20.35	28.04	20.02	21.68
			Whiti	ng roe			
As	1050	1.95	1.77	1.83	2.06	1.94	1.36
Cd	490	0.03	0.03	0.03	0.03	0.03	0.03
Cr	44,590	1.88	0.18	0.33	0.41	0.35	0.38
Cu	245,000	3.26	2.54	2.70	2.85	2.57	1.74
Fe	392,000	215.07	42.40	62.99	79.98	50.71	50.56
Pb	1750	0.30	0.24	0.39	0.27	0.21	0.33
Zn	490.000	84.71	81.76	88.06	86.90	74.34	47.17

\*PTWI for adult person in µg/week/70 kg body weight. EWI for adult person in µg/week/70 kg body weight (FAO/WHO

Table 7 Target Hazard Quotient (THQ) and Target Hazard Quotient (TTHQ)

RFD <sub>o</sub> value			Whiting	meat					Whiting	roe		
(mg.kg <sup>-1</sup> day)	December	January	February	March	April	May	December	January	February	March	April	May
					Т	ΉQ						
Li 0.002**	0.001	0.003	0.005	0.008	0.007	0.006	0.005	0.005	0.003	0.005	0.004	0,003
Al 1.0*	0.001	0.001	0.001	0.002	0.001	0.000	0.000	0.000	0.000	0.001	0.000	0,000
Cr 0.003*	0.042	0.015	0.010	0.020	0.018	0.009	0.041	0.004	0.007	0.009	0.008	0,008
Mn 0.14*	0.002	0.001	0.001	0.002	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0,001
Fe 0.7*	0.005	0.003	0.003	0.010	0.005	0.002	0.020	0.004	0.006	0.008	0.005	0,005
Co 0.0003*	0.013	0.013	0.013	0.020	0.013	0.010	0.020	0.013	0.017	0.017	0.017	0,010
Ni 0.02*	0.001	0.001	0.001	0.003	0.001	0.002	0.002	0.001	0.001	0.002	0.001	0,001
Cu 0.04*	0.002	0.001	0.002	0.003	0.002	0.005	0.005	0.004	0.004	0.005	0.004	0,003
Zn 0.3*	0.004	0.004	0.004	0.006	0.004	0.005	0.019	0.018	0.019	0.019	0.016	0,010
As 0.0003**	0.621	0.618	0.772	0.945	0.581	0.381	0.431	0.391	0.404	0.454	0.428	0,301
Se 0.005**	0.019	0.018	0.018	0.025	0.017	0.016	0.034	0.026	0.029	0.032	0.027	0,017
Ag 0.005**	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.003	0.001	0.001	0.001	0,001
Ba 0.2*	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0,000
Cd 0.001*	0.022	0.008	0.004	0.008	0.004	0.003	0.002	0.002	0.002	0.002	0.002	0,002
Hg 0.0001**	0.160	0.130	0.150	0.190	0.180	0.230	0.040	0.050	0.050	0.050	0.050	0,040
Pb 0.002*	0.017	0.045	0.023	0.031	0.014	0.009	0.010	0.008	0.013	0.009	0.007	0,011
					Т	ГНQ						
	0.911	0.864	1.008	1.274	0.850	0.680	0.632	0.532	0.558	0.614	0.571	0.412
*USEPA (2017),	**USEPA (2	018)										

JECFA (The Joint FAO/WHO Expert Committee on Food Additives) uses the term PTWI, or provisional tolerable daily intake, for contaminants that may accumulate in the body. Many contaminants are not cleared rapidly from the body, and for them provisional tolerable weekly intakes (PTWIs) are allocated (Herrman and Younes, 1999). To asses' public health risks, weekly fish intakes were compared with Provisional Tolerable Weekly Intake (PTWI) recommended by the joint FAO/WHO Expert Committee of Food Additives (FAO/WHO, 2011). The annual amount of fish consumed 5.49 kg/person/year; 0.106 kg/person/weekly in 2017 (TURKSTAT, 2018b). The calculated EWI (Table 6) values of whiting meat and roes were lower than the recommended PTWIs by FAO/WHO (2011) and it can be said that whiting had no bad-tempered effects to human health.

The THQ, TTHQ values of trace elements in the whiting meat and roes are shown in Table 7. THQ is a very conservative/restrictive standard and relative index for assessing risks to human health (Wang et al., 2005). The THQ lower that 1 indicates no obvious risk (Chien et al., 2002). The results show that the THQ values of whiting meat and roes were lower than 1 during six months (Table 7). However, the TTHQ values of whiting meat in February and March were higher than 1 indicating health risk for the consumer by consuming whiting meat. Total THQ value of whiting (caught by trawl from the Southwest Black Sea) were determined below 1 and indicating no significant health risk to consumer by Mol et al. (2017).

#### Conclusion

This study shows that the levels of macro, trace and heavy metal concentration of whiting meat and roes from the Middle Black Sea are difference from each other. Especially Na, K and Ca contents of whiting meat are higher than roes. The Pb and Cd results found in the roes were lower than the acceptable limits identified by Turkish Codex. On the other hands, especially in January Pb value was highest in whiting meat. The THQ values of whiting meat and roes were lower than 1 during six months and this indicates no obvious risk. Considering these data; in particular, breastfeeding mothers, pregnant women and children required to limit their whiting consumption in terms of health.

#### **Conflict of interests**

The authors declare that for this article they have no actual, potential or perceived the conflict of interests.

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