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RESEARCH ARTICLE

Determination of Heavy Metal in Anchovy (*Engraulis encrasicolus* L 1758) and Whiting (*Merlangius merlangus euxinus* Nordman, 1840) Fish in The Middle Black Sea [1]

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Summary

In this research, the determination of heavy metals in fishes (anchovy and whiting) caught in Samsun which is the province of Middle Black Sea was aimed. Having been washed, dried and cut in to small pieces the fishes HNO_3 and $HClO_4$ were added and using wet ash method, heavy metal concentrations were determined. By taking three samples from each fish the concentrations of Fe, Mn, Zn, Cu, Pb, Cd were determined with Flame AAS to be the result of analysis in fishes. In the resulting analysis, in 2009, metal concentration of anchovy have been found 34.0±2.5 µg/g for Fe; 2.0±0.0 µg/g for Mn; 129.3±15.0 µg/g for Zn; 3.7±1.6 µg/g for Cu; 0.4±0.2 µg/g for Pb; 0.2±0.05 µg/g for Cd in 2009, metal concentration of whiting have been found 9.9±2.1 µg/g for Fe; 4.3±0.7 µg/g for Mn; 58.0±3.5 µg/g for Zn; 2.3±0.7 µg/g for Cu; 0.9±0.2 µg/g for Pb; 0.2±0.03 µg/g for Cd in 2010, metal concentration of anchovy have been found 51.5±5.3 µg/g for Fe; 4.2±0.9 µg/g for Mn; 221.0±10.5 µg/g for Zn; 3.8±1.9 µg/g for Cu in 2010, metal concentration of whiting have been found 7.0±4.6 µg/g for Fe; 3.0±0.0 µg/g for Mn; 28.3±1.0 µg/g for Zn; 2.7±0.7 µg/g for Cu. Anchovies and whiting in the study as a result of heavy metal concentration were high in general. In order to determine the accuracy of the method used in the wet ash method to the reference fish protein samples (DORM-3) was applied.

Keywords: *Samsun, Heavy metals, Fish, Atomic Absorption Spectrometry*

Orta Karadeniz' deki Hamsi (*Engraulis encrasicolus* L 1758) ve Mezgit (*Merlangius merlangus euxinus* Nordman, 1840) Balığında Ağır Metal Tayini

Özet

Bu çalışmada Orta Karadeniz'in Samsun ilinde avlanan balıklarda (Hamsi ve Mezgit) ağır metallerin tayin edilmesi amaçlanmıştır. İncelenen balıklar yıkanıp kurutulup küçük parçalar haline getirildikten sonra, HNO_3, $HClO_4$ eklenerek yaş yakma yöntemi uygulanmış ve ağır metal miktarları belirlenmiştir. Analizler sonucunda balıklarda bulunan Fe, Mn, Zn, Cu, Pb, Cd derişimleri her bir balıktan üçer numune alınarak alevli AAS ile saptanmıştır. Analizler sonucunda 2009 yılında hamside metal derişimleri Fe için 34.0±2.5 µg/g; Mn için 2.0±0.0 µg/g; Zn için 129.3±15.0 µg/g; Cu için 3.7±1.6 µg/g; Pb için 0.4±0.2 µg/g; Cd için 0.2±0.05 µg/g olarak bulundu. 2009 yılında mezgitte ise metal derişimleri Fe için 9.9±2.1 µg/g; Mn için 4.3±0.7 µg/g; Zn için 58.0±3.5 µg/g; Cu için 2.3±0.7 µg/g; Pb için 0.9±0.2 µg/g; Cd için 0.2±0.03 µg/g olarak bulunmuştur. 2010 yılında hamside metal derişimleri Fe için 51.5±5.3 µg/g; Mn için 4.2±0.9 µg/g; Zn için 221.0±10.5 µg/g; Cu için 3.8±1.9 µg/g bulundu. 2010 yılında mezgitte ise metal derişimleri Fe için 7.0±4.6 µg/g; Mn için 3.0±0.0 µg/g; Zn için 28.3±1.0 µg/g; Cu için 2.7±0.7 µg/g olarak bulunmuştur. Çalışmada sonuç olarak hamsi ve mezgitte bulunan ağır metal derişimleri genel olarak yüksek çıkmıştır. Yöntemin doğruluğunu belirlemek amacıyla çalışmada kullanılan yaş yakma yöntemi sertifika edilmiş referans balık protein numunesine (DORM-3) uygulanmıştır.

Anahtar sözcükler: *Samsun, Ağır metaller, Balık, Atomik Absorpsiyon Spektrometrisi*

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INTRODUCTION

Toxic effect of heavy metals on marine animals has been known since time immemorial. This effect not only holocaust of marine animals, also creates potential danger for people. Marine animals living in the water in their whole life are together with toxic substance dissolved in sea water. Water entrance and exit to their bodies for both nutrition and respiration. Dirty sea water entering to the organism makes cumulating in some organs such as kidney, lung and muscle tissue at the end of physiological activities [1]. Heavy metals having toxic and carcinogenic effects take up a lot of room in dirty sea water and cumulate in tissue and organs of fish.

Heavy metals in fish and other marine animals can be determined with some methods, namely, Inductively Coupled Plasma Atomic Emission Spectrometric Method (ICP-MS) [2], Flame Atomic Absorption Spectrometric (FAAS) [3,4], Atomic Absorption Spectrometric with Graphite Furnace (GFAAS) [5-7], Differential Puls Anodic Stripping Voltametry (DPSA) [8], Electro-Thermal Evaporation Inductively Coupled Plasma Mass Spectrometry (ETV-ID-ICP-MS) [9], Inductively Coupled Plasma Optical Spectrometry (ICP-OES)[10], Inductively Coupled Plasma Spectrometry Having Isotope (ID-ICP-Ms) [11], Inductively Coupled Plasma Flame Emission Spectrometry (ICP-AES) [12].

In fish caught Samsun coasts and consumed very much by people in Black Sea, the determination of heavy metals such as carcinogenic or toxic lead, cadmium, copper, zinc, iron or manganese having important effect on environment pollution was aimed in this study with wet ash method especially in anchovy *(Engraulis encrasicolus)* and whiting *(Merlangius merlangus)*.

MATERIAL and METHODS

In this study, determination of some heavy metals (Fe, Mn, Zn, Cu, Pb, Cd) was aimed found in fish caught in Samsun coasts in Middle Black Sea and bought from local salesmen in January 2009 and January 2010. 200 fish of each species were used for the analysis. The map showing the Samsun and its coasts where the fish was caught was given in *Fig. 1* [13]. Average wet weights of anchovy and whiting were measured 9.8±0.3 g and 15.2±0.8 g respectively. The average lengths of the fishes were measured as 11.3±0.2 cm and 12.3±0.3 cm respectively.

After cleaning the fish and boning, to purify from sea water, they washed with deionized water after washing with tap water and edible parts were separated and used for all analysis. 200 anchovies and 200 whiting were taken and homogenized. Three samples from each were taken from the homogenized mixture. Then, the samples were air-dried, homogenized, stored in polyethylene bags at -18°C until anlysis. Anchovy in washed fish was dried at 50-60°C during 24 h and whiting at 50-60°C during 48 h. Taking 5 g from fish dried and cut into small pieces with plastic knife, wet ash method was applied. For this, 50 mL mixture of acid sample HNO_3: $HClO_4$ in the ratio 4:1 was added to the fish sample and covered with watch glass and waited during one night. The mixture was evaporated until being 4 mL and HNO_3 was added into the final solution until being 20 mL. The solution filtered from glass-fiber to remove small quantities of solids. Each gained filtrate was divided into five as each one was 4 mL. The method of standart additions was used to eliminate matrix effects. One of them made up 10 mL with deionized water, others with standard solutions 0.5 mg/L, 1 mg/L, 3 mg/L, 5 mg/L

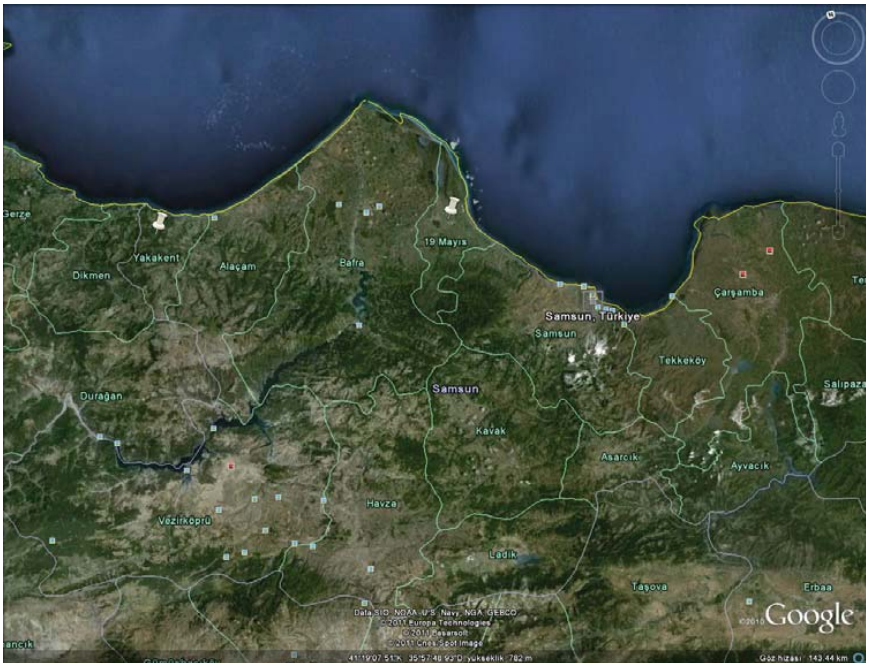

Fig 1. The map of sampling locations [13]
Şekil 1. Numune böl-gelerinin haritası [13]

that prepared before. Determination of heavy metal was done with Flame AAS and the Cu, Mn, Fe, Zn [14] concentrations of the samples were determined drawing calibration graphs. For the determination of Pb and Cd metals, the same process was done taking 50 g from dries fish. All digested samples were analyzed three times for each metal.

Detection and Quantification Limit

Detection Limit: Following the general procedure applied in wet ash method of the samples, the standard deviations of the samples were calculated measuring at AAS absorbance of five solutions (blank) not having sample. The third times of standard deviation was added into the average of evidence absorbance.

Quantification Limit: Ten times of standard deviation gained in determination of detection limit was added into the average of evidence absorbance and the quantification limit of Fe, Mn, Zn, Cu, Pb, Cd concentrations corresponding to this value was calculated as quantification limit [14]. Quantification and detection limits of these metals are given in *Table 1*.

Accuracy: In order to check the accuracy of the method used in the wet ash method to the reference fish protein samples (DORM-3) was applied for each metal. The results are given *Table 2*.

Limit values for all metals found in fish and determined by Turkish Food Codex (TFC) are given in *Table 3* [15]. According to FAO/WHO, daily permissible dose for the people is given in *Table 4* [15].

Reagents/Chemicals: Deionized water was produced by ELGA Maxima Ultra Pure.

All reagents were analytical reagent grade. Nitric acid (65%) and perchloric acid (70-72%) used was from Merck. All glassware and plasticware used were washed nitric acid and rinsed with deionized water. $CuCl_2.H_2O$, $Cd(NO_3)_2.4H_2O$, $FeCl_3.6H_2O$ used were from Merck. $ZnCl_2$ and $MnCl_2.4H_2O$ used was Carlo Erba. $Pb(NO_3)_2$ used was Scp-Surechem. Certified reference material (DORM-3) was provided by National Research Council Canada (NRCC).

Prepare of Metal Standards: 1.000 mg/L stock solutions of ions Fe (III), Mn(II), Zn(II), Cu(II) were prepared in dissolving in the deionized water taking the amounts of $FeCl_3.6H_2O$, $MnCl_2.4H_2O$, $ZnCl_2$, $CuCl_2.H_2O$, $Pb(NO_3)_2$, $Cd(NO_3)_2.4H_2O$' as determined before. 2 mg/L, 5 mg/L, 8 mg/L and 12 mg/L standard solutions from Pb, Cd salts were prepared from these solutions with the dilution at concentrations of 0.5 mg/L, 1mg/L, 3 mg/L and 5 mg/L of Fe, Mn, Zn and Cu salts.

Apparatus: In this study, UNICAM 929 Atomic Absorption Spectrometry was used to determine the metal concentrations. Weighing was done with Avery Berkery Balance which is at 0.0001 sensitivity. The hallow cathode lamp we used was UNICAM trademark, Fe, Mn, Zn, Cu and Pb lamps and CD lamp which is PHOTRON trademark were used.

Table 1. *Limit of detection (LOD) and limit of quantification (LOQ) for all metals studied in fish samples*

Tablo 1. *Çalışılan balık örneklerindeki bütün metaller için gözlenebilme ve tayin sınırı*

Metal	Detection Limit (µg/g)	Quantification Limit (µg/g)
Fe	1.314	2.034
Mn	0.104	0.143
Zn	0.715	0.969
Cu	0.266	0.371
Pb	0.537	0.908
Cd	0.395	0.413

Table 2. *Metal determination in standard certificated fish-protein sample (DORM-3), (n=3)*

Tablo 2. *Sertifika edilmiş standart balık protein numunesinde (DORM-3) metal tayini, (n=3)*

Metal	Certificated Values (mg/kg)	Found Values (mg/kg)	Recovery (%)
Fe	347±20	338.7±91.7	97.5
Mn	4.6	5.5±0.4	119.1
Zn	51.3±3.1	50.1±5.8	97.7
Cu	15.5±0.63	17.7±0.6	114.4
Pb	0.395± 0.050	Not determined	-
Cd	0.290±0.020	Not determined	-

Table 3. *According to TFC, the high metal contents can be found in fish*

Tablo 3. *TGK'ne göre balıklarda bulunabilecek en yüksek metal içerikleri*

Metal	Metal Contents (µg/g)
Fe	-
Mn	-
Zn	50
Cu	20
Pb	0.4
Cd	0.1

Table 4. *According to FAO/WHO, daily permissible dose for people (at weight of 60 kg)(mg/gün)*

Tablo 4. *FAO/WHO'a göre insanlarda (60 kg vücut ağırlığında) günlük izin verilebilen miktar, (mg/gün)*

Metal	Daily Permissible Dose (mg)
Iron	48
Copper	3
Zinc	60
Manganese	2-9
Lead	214 µg - Weekly 3 mg
Cadmium	Weekly 0.5 mg

RESULTS

The determination of heavy metals (Fe, Mn, Zn, Cu, Pb, Cd) in anchovy and whiting bought from local salesmen in Samsun at Middle Black Sea was aimed in this study using standard addiction method with Flame AAS. The results are given in *Table 5, 6, 7* and *8* to compare the results given in these tables, literature data of studying done in Black Sea for anchovy and whiting are given in *Table 9* and *10*.

Wet ash method used in this study to determine the accuracy of the method was applied to certified standard fish-protein sample (DORM-3) and acquired values were given in *Table 2*. According to this, of Fe, Mn, Zn, Cu, percentage values of recovery at 95% confidence limits are 97.5; 119.1; 97.7; 114.4% respectively. Pb and Cd concentrations cannot be determined since they were under the detection limits and even quantification limits. Found results described in *Table 2* were in good agreement with the certified values.

Iron concentrations in anchovy *(Engraulis encrasicolus)* and whiting *(Merlangius merlangus)* were 34.0±2.5; 9.9±2.1 µg/g in 2009 and 51.5±5.3; 7.0±4.6 µg/g in 2010 in this study. Values in literature for the iron are given in *Table 9*

Table 5. *Metal concentrations (µg/g dry weight) in anchovy, 95% confidence limit, in 2009 (n=3)*

Tablo 5. *Hamside metal derişimleri (µg/g kuru ağırlık), %95güven sınırı, 2009 yılı (n=3)*

Metals	µg/g
Fe	34.0±2.5
Mn	2.0±0.0
Zn	129.3±15.0
Cu	3.7±1.6
Pb	0.4±0.2
Cd	0.2±0.05

Table 6. *Metal concentrations (µg/g dry weight) in whiting 95% confidence limit, in 2009 (n=3)*

Tablo 6. *Mezgitte metal derişimleri (µg/g kuru ağırlık) %95 güven sınırı, 2009 yılı (n=3)*

Metals	µg/g
Fe	9.9±2.1
Mn	4.3±0.7
Zn	58.0±3.5
Cu	2.3±0.7
Pb	0.9±0.2
Cd	0.2±0.03

Table 7. *Metal concentrations (µg/g dry weight) in anchovy 95% confidence limit, in 2010 n=3)*

Tablo 7. *Hamside metal derişimleri (µg/g kuru ağırlık) %95 güven sınırı, 2010 yılı (n=3)*

Metals	µg/g
Fe	51.5±5.3
Mn	4.2±0.9
Zn	221.0±0.5
Cu	3.8±1.9
Pb	Not determined
Cd	Not determined

Table 8. *Metal concentrations (µg/g dry weight) in whiting 95% confidence limit, in 2010 (n=3)*

Tablo 8. *Mezgitte metal derişimleri (µg/g kuru ağırlık) %95 güven sınırı, 2010 yılı (n=3)*

Metals	µg/g
Fe	7.0±4.6
Mn	3.0±0.0
Zn	28.3±1.0
Cu	2.7±0.7
Pb	Not determined
Cd	Not determined

Table 9. *Metal contents in literature for anchovy caught in Black Sea (µg/g)*

Tablo 9. *Literatürde Karadeniz'de avlanan hamsi için bulunan metal içerikleri (µg/g)*

Reference	Fe	Mn	Zn	Cu	Pb	Cd
Tuzen [16]	10.45±1.63	1.96±0.12	17.38±2.01	1.94±0.10	0.38±0.02	0.20±0.03
Uluozlu et al.[15]	95.6±8.1	5.61±0.40	40.2±3.2	0.95±0.008	0.33±0.01	0.65±0.04
Turan et al.[17]	18.008±2.697	1.39±0.326	25.416±3.664	-	0.329±0.302	0.124±0.018
Nisbet et al.[19]	22.92±3.06	3.89± 0.14	26.59±1.95	2.78±0.21	0.57±0.04	0.039±0.008

Table 10. *Metal contents in literature for whiting caught in Black Sea (µg/g)*

Tablo 10. *Literatürde Karadeniz'de avlanan mezgit için bulunan metal içerikleri (µg/g)*

Reference	Fe	Mn	Zn	Cu	Pb	Cd
Uluozlu et al.[15]	104±9.8	1.96±0.10	48.6±3.9	1.25±0.10	0.93±0.07	0.55±0.04
Turan et al.[17]	4.48±0.441	0.079±0.024	6.029±0.545	-	0.502±0.104	0.192±0.020
Nisbet et al.[19]	29.93±1.91	7.33±0.83	30.60±2.68	3.70±0.26	0.54±0.04	0.001±0.001

and *10* and if these values are compared with the study we did, it is observed that the values determined for the iron concentrations in anchovy and whiting are between literature values. There is no information about maximum iron quantity found in fish in Turkish Food Codex. According to WHO *(Table 4)*, daily permissible dose for adults is 48 mg [15].

Manganese concentrations were determined as 2.0±0.0 µg/g for anchovy in 2009, 4.3±0.7 µg/g for whiting, 4.2±0.9 µg/g for anchovy in 2010 and 3.00±0.0 µg/g for whiting in 2010. When these values are compared with data in literature, it is observed that the values found for anchovy in 2009-2010 are compatible with the values in literature and values found for whiting are higher than values in literature. There is no information about manganese amount found in fish in Turkish Food Codex. According to WHO, daily permissible dose is 2-9 mg for the adults [15].

Zinc concentrations were determined as 129.3±15.0 µg/g for anchovy and 58.0±3.5 µg/g for whiting in 2009, 221.0±10.5 µg/g for anchovy and 28.3±1.0 µg/g for whiting in 2010. When these values are compared with literature, it is understood that values found for anchovy are higher than in literature. However, some values found for whiting in 2010 are higher then in literature and some are lower. According to TFC, the maximum zinc concentration in fish is 50 µg/g and the values acquired mostly are higher than detection in fish in view of TFC. However, zinc concentration in whiting in 2010 is lower than maximum limit. According to WHO, daily permissible dose is 60 mg for the adults [15]. Zinc at high are caused by organized industry in nearby, iron-steel, casting, copper plants and paint shops [14].

Copper concentration for anchovy is 3.7±1.6 µg/g and 2.3±0.72 µg/g for whiting in 2009, 3.8±1.9 µg/g for anchovy and 2.7±0.7 µg/g for whiting in 2010. When these values are compared with literature, it is observed that the values found for anchovy and whiting are higher than values in literature. According to Turkish Food Codex, maximum copper concentration in fish is 1.0 µg/g and acquired values are higher than maximum limit found in fish for TFC [15]. According to WHO, daily permissible dose is 3 mg for the adults [15].

Lead concentration is 0.4±0.2 for the anchovy and 0.9±0.2 µg/g for the whiting in 2009. If these values are compared with literature, values found for anchovy and whiting are compatible with the literature. According to Turkish Food Codex, maximum lead concentration in fish is understood to be 0.4 µg/g and acquired values are higher than maximum limit in fish for TFC [15]. According to WHO, daily permissible amount is 214 µg for the adults and weekly permissible dose is 3 mg [15].

Cadmium concentration is determined as 0.2±0.05 µg/g fort he anchovy and 0.2±0.03 µg/g for the whiting in 2009. If these values are compared with the literature, both two values are observed to be compatible with the literature. According to TFC, maximum cadmium concentration in fish is 0.1 µg/g and it is higher than the maximum limit in fish for TFC [15]. According to WHO, weekly permissible dose is 0.5 mg for the adults [16].

DISCUSSION

Fish is an important protein source for living being. It is also rich in terms of vitamin and mineral. Today, determination of heavy metals such as Fe, Mn, Zn, Cu, Pb, Cd, Hg, and Ni should be done since aquatic environments have been polluted day by day. Since these metals are toxic over certain concentrations and their concentrations increase from organism to organism.

Determination of heavy metal in anchovy and whiting caught in Samsun coats in Middle Black Sea was done in this study. The maximum metal concentration in anchovy caught in 2009 belongs to (129.3 µg/g) zinc and the minimum (0.2 µg/g) belongs to cadmium. In the year of 2010, the maximum metal concentration (221.0 µg/g) belongs to zinc, the minimum (3.8 µg/g) belongs to copper since lead and cadmium concentrations are not determined. When these values are compared with values in literature given in *Table 9*, values found for zinc and copper are understood to be higher than values in literature. The maximum metal concentration for the whiting caught in 2009 belongs to zinc (58.0 µg/g) and the minimum belongs to cadmium (0.2 µg/g). As for whiting caught in 2010, the maximum metal concentration is in zinc (28.3 µg/g) and the minimum is in copper (2.7 µg/g) since the lead and cadmium concentrations are not calculated like in anchovy. When these values are compared with values in literature given in *Table 10*, it is observed that copper is higher than values in literature, but zinc is sometimes higher than values in literature and sometimes lower.

Zinc concentrations in the anchovy and whiting are respectively 25.416 µg/g; 14.062 µg/g for the anchovy and 6.029 µg/g; 5.288 µg/g for the whiting according to the data of study done by Turan et al. in Iskenderun Gulf coast of Karadeniz, Marmara and Mediterranean in 2005 [17]. These values are quietly lower than our values. Since Turan et al. did metal determination only in muscle tissue. Higher concentrations are inevitable since muscle tissue and skin is not cut loose from together in our study. For example, Uysal et al. found zinc concentration as 4.27 µg/g in muscle tissue of seabream caught in Mediterranean and Antalya in 2006 and 33.55 µg/g in skin, total zinc concentration is 37.82 µg/g in muscle and skin [18]. This study is done over wet weight and it is clear it will be higher in dry weight. Moreover, it has gained importance in regional and environmental differences. When the results are compared with the studies done in Black Sea

and Middle Black Sea, zinc concentration is high both in two fish. In the reported by Uluozlu et al. in 2007, in the European anchovy was 40.2 µg/g and 48.6 µg/g in the whiting [15]. In other study done by Nisbet et al. in Middle Black Sea, the concentrations of zinc in anchovy and whiting caught between in the years 2005-2006 were reported 26.59 µg/g and 30.60 µg/g respectively [19]. As for the reported by Tuzen in Middle Black Sea in 2003, zinc concentration was 17.38 µg/g in the anchovy [16]. If examined by years, zinc concentration has been increased day by day in Black Sea. In the reported by Guner et al. in 1998, zinc concentration in the anchovy caught between in the years 1995 and 1996 was 21.1 µg/g and 3.3 µg/g in the whiting [20]. According to Turkish Food Codex, zinc concentration in fish is 50 mg/kg and the values of zinc obtained in our study are generally higher than the maximum limits. However, it does not exceed the daily required zinc amount. According to WHO, daily permissible amount is 60 mg for the adults [15]. In Turkey, it is explained that the adults consumed average 20 g fish daily [12]. In this case, when 20 mg whiting is consumed, 1.2 mg zinc; the same amount of anchovy is consumed, 2.6 mg zinc is taken. Big part of zinc required for living beings is provided with fish. Daily 10-20 mg zinc is required for the adults [21].

The other important element for living beings is iron. If it is taken a bit, it can be end up with die since it causes to be anemia. In our study, iron concentrations in the anchovy and whiting are respectively 34.0 µg/g and 9.9 µg/g in 2009 and 51.5 µg/g and 7.0 µg/g in 2010. Although the anchovy is topminnow, if this value is high, this is caused by storing iron in its body being sablefish. As for the whiting, it does not like the anchovy but it is white fish and does store iron in its body. High amount of iron in sablefish is possibly caused by including rich lean meat in the vessel of fish [22]. If the literature is examined, in the reported by Turan et al. in 2009 (study done in 2005), in the coasts of Marmara of Mediterranean and Black Sea, respectively 21.369 µg/g and 18.008 µg/g iron for the anchovy and 6.749 µg/g and 4.488 µg/g iron fort he whiting were determined [17]. These values are quietly lower than the values we determined. This difference can be caused by working on only muscle tissue. Moreover, it can bring possibly about the iron-steel and copper plants and the drain water dropping out sea. In the reported by Uysal et al. in 2008, 13.58 µg/g iron is found in the skin of seabream and 4.05 µg/g iron in muscle tissue. This equals to 17.63 µg/g [18] in total. If the whiting and seabream that are deep-sea fish are compared, there is not a big difference in the results. In the reported by Uluozlu et al. in 2007, 95.6 µg/g iron found in the anchovy caught in Black Sea and Aegean Sea and 104 µg/g iron in the whiting [15]. Although these values are higher than the values we determined, in the article written by Tuzen in 2003, about 10 µg/g iron concentration in anchovy caught by Middle Black Sea [16]. In the reported by Guner et al. in 1998 in Balck Sea, 11.3 µg/g iron content in the anchovy and 2.5 µg/g in the whiting were determined [20]. According to the literature, there is not steady increase or decrease in the iron concentration. However, according to Turkish Food Codex, there is no information about iron amount. According to WHO, daily permissible amount is 48 mg [15]. Daily fish intake in Turkey is average 20 g [12] for the adults, iron taken from anchovy is 0.7 mg and 0.2 from the whiting, and these values are quietly lower than values given in WHO.

Fish is vital element for the health and nourishment of the people. However, high amount can be cause health problems [18]. In our study done copper concentration in the anchovy and whiting is respectively 3.7 µg/g; 2.3 µg/g in 2009, and 3.8 µg/g; 2.7 µg/g in 2010. In the reported by Uysal et al. in 2008 in Antalya Beymelek Lake, 1.21 µg/g copper in the skin of seabream, and 1.42 µg/g in the muscle tissue. This shows that there is 2.63 µg/g copper in seabream [18]. When the results are compared with the values we found, there is no big difference. In the study done by Uluozlu et al. in 2007 in Black Sea and Aegean Sea, 0.95 µg/g copper in European anchovy and 1.25 µg/g in whiting. These values are fairly lower than the values we found [15]. In the reported by Tuzen in 2003 in Middle Black Sea, 1.94 µg/g copper was found in the anchovy 1.94 µg/g [16]. In the reported by Guner in 1998 in Black Sea, 2.3 µg/g copper in anchovy and 1.3 µg/g in the whiting [20]. According to literature, there is not steady increase or decrease. According to Turkish Food Codex, permissible copper dose in fish is 20 mg/kg and these found values are fairly lower than the maximum limit. According to WHO, daily tolerable amount is 3 mg for the adults [15]. In Turkey, daily fish intake is average 20 g for the adults and so, copper taken from the anchovy is 0.1 mg and 0.05 mg from the whiting and they are fairly lower than the values given in WHO.

Manganese is a base element in many enzyme systems in the body [14]. In our study, manganese concentration was determined as respectively 2.0 µg/g and 4.3 µg/g in the anchovy and whiting in 2009 and 4.3 µg/g and 3.0 µg/g in 2010. In the reported by Turan et al. in Iskenderun Gulf coast in Black Sea, Marmara and Mediterrenan, manganese concentrations were respectively 1.390; 0.529 µg/g in anchovy and 0.079; 0.033 µg/g in the whiting [17]. These values are fairly lower than the values we found. This study is done only in muscle tissue and since the muscle and skin are not disintegrated in our study, the values are inevitable to be high. In the study done by Uysal et al in 2008, 0.19 µg/g manganese is found in muscle tissue of seaberam caught in Antalya and 0.29 µg/g manganese in its skin. This is 0.148 µg/g in total [18]. The values are different from our values. This is caused by regional and environmental differences. In the reported by Uluozlu et al. in 2007 in Black Sea and Aegean, 5.61 µg/g manganese in European anchovy and 1.91 µg/g in the whiting were

found [11]. In the reported by Tuzen in 2003 in Middle Black Sea, 1.57 µg/g manganese was found in the anchovy [16]. If the years in the literature are examined, it can be seen that there is an rise in manganese concentration. According to TFC, there is no information about maximum manganese concentration in fish samples [16]. In Turkey, in average, daily 20 g fish is consumed by the adults [12]. In this case, if 20 g anchovy is consumed daily, 0.04 mg manganese, if whiting is consumed, 0.1 mg manganese is consumed. According to WHO, daily permissible manganese dose for the adults is 2-9 mg [15]. In this case, the values we found are fairly lower than the values given in WHO.

The lead is one of the metals giving harms to the people's activities. In our study we did, 0.4 µg/g and 0.9 µg/g lead was found respectively in the anchovy and whiting. In the reported by Turan et al. in 2009 in coasts of Iskenderun Gulf of Black Sea, Marmara and Mediterrenan, lead concentrations were determined as respectively 0.329; 0.055 µg/g fort he anchovy and 0.502 ; 0.426 µg/g fort he whiting [17]. The acquired values are not different from our values too much. In the reported by Uluozlu et al. in 2007 in Black Sean and Aegean Sea, lead concentration was found as 0.33 µg/g fort he anchovy and 0.93 µg/g for the whiting [15]. The acquired values are not different from our values too much. In the reported by Tuzen et al. in Middle Black Sea in 2003, lead concentration was found as 0.38 µg/g in the anchovy [16]. As for the reported by Guner et al. in 1998, lead was respectively 0.0675 µg/g and 0.0876 µg/g for the anchovy caught in Black Sea and whiting [20]. According to TFC, maximum permissible amount is 0.4 mg/kg for the fish [15]. Although 0.4 µg/g which was found for the anchovy is at the border, lead concentration found in the whiting is higher than maximum limit. According to WHO, daily permissible lead amount fort he adults is 214 µg [15]. In Turkey, daily fish intake is 20 g [12] and lead taken from the anchovy is 0.01 mg and 0.02 mg from the whiting and these values are fairly lower than the values given in WHO. In our study in 2010, lead concentration found for two fish cannot be determined since they are lower than detection limit.

The other metal harming people is cadmium. Cadmium concentrations were respectively 0.2 µg/g and 0.2 µg/g fort he anchovy and whiting in our study. In the reported by Turan et al. in 2009 in coast of Iskenderun Gulf of Black Sea, Marmara and Mediterranean, lead concentration was found 0.124 ; 0.183 µg/g fort he anchovy and 0.192; 0.685 µg/g fort he whiting [17]. As for the reported by Uluozlu et al. in 2007 in Black Sea and Aegean Sea, 0.65 µg/g cadmium in anchovy and 0.55 µg/g in the whiting were found [15]. The acquired values are quietly lower than our values. In the study done by Tuzen et al. in 2003 in Black Sea, 0.20 µg/g cadmium was found in the anchovy [16] and there is no difference between the acquired value and the value we determined. In the study done by Guner et al. in 1998 in Black Sea, 0.0113 µg/g and 0.0131 µg/g cadmium were found respectively in the anchovy and whiting [20]. According to TFC, cadmium concentrations are higher than the acquired values. It was stated that daily average 20 g fish is consumed by the adults in Turkey [12]. In this case, if daily 20 g anchovy and whiting are consumed, 0.004 mg cadmium is taken. According to WHO, weekly permissible cadmium amount is 0.5 mg [15]. In this case, cadmium amount taken from the fish is lower than the values given in WHO. In the study done in 2010, cadmium concentration for two fish cannot be determined since they are lower than the detection limit.

In conclusion, considering daily average fish consumption is 20 g [12], although the values found in the anchovy and whiting are generally high, even 20 g fish is consumed on each day, they are again lower than the values given in WHO. For this reason, considering the benefits of metals required for the health, they should be consumed. However, if they consumed too much, since metal consumption is raised and gives harm instead of benefit, it is suggested that they should be consumed carefully.

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