

RESEARCH ARTICLE

Evaluation of non-essential element and micronutrient concentrations in seafood from the Marmara and Black Seas

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Abstract

Determining the presence of potentially toxic elements in the marine organisms inhabiting contaminated environments is important for human health. The present study assessed concentrations of As, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, Se, and Zn measured by ICP-MS in fish muscle and liver, as well as in the edible invertebrate parts harvested from the Marmara and Black Seas. Arsenic in 14 out of 18 fish species (i.e. *Mullus barbatus*, *Mullus surmuletus*, *Psetta maxima*, *Solea solea*, *Sciaena umbra*, *Auxis thazard*, *Engraulis encrasicolus*, *Merlangius merlangus*, *Diplodus puntazzo*, *Sardina pilchardus*, *Scomber scombrus*, *Trachurus mediterraneus*, and *Trigla lyra*) and 4 invertebrate species (i.e. *Mytilus galloprovincialis*, *Palaemon serratus*, *Penaeus* sp., and *Ommastrephes sagittatus*) and the Cu concentration in *Palaemon serratus* were determined to exceed values recommended by the Food and Agriculture Organization and by the Turkish Food Codex. Non-essential elements are accumulated consistently in the fish muscle tissue, however liver represents dietary alterations. When comparing the present results with other studies, As and Se concentrations in the muscle tissue of Marmara sea fish were found higher than previous study results. Also Fe and Hg concentrations in the muscle tissue of Black Sea fish were found higher than previous study results. Other element concentrations were determined generally comparable or lower with some exceptions.

Key words: Metal, fish, mussel, shrimp, calamari.

Introduction

It is important to monitor marine fish and invertebrates for the presence of potentially toxic elements, due to risks they can pose to animals inhabiting contaminated environments and people consuming contaminated seafood. Seafood consumption by humans is important because of its high nutritional

quality, rich in omega-3, polyunsaturated and low saturated fatty acids, biologically valuable proteins, vitamins and certain mineral content. Also consumption of fish and fish product are recommended for prevention of some illness e.g. coronary heart diseases, hypertension, certain cardiac arrhythmias, diabetes and rheumatoid arthritis (Sioen *et al.* 2007). However, marine environments can be contaminated with diverse toxins, particularly in coastal waters that receive industrial discharges and from sewage effluents.

Marine organisms are exposed to metals present in the dissolved phase and, for animals, also via diet (Fisher and Reinfelder 1995). It is known that heavy metals are assimilated, bioconcentrated, and sometimes biomagnified in food chains within aquatic ecosystems (Dutton and Fisher 2010). Metals that are accumulated in animal tissues may become toxic if present at levels high enough to cause a toxic effect. This phenomenon is important especially in populated and industrialized coastal ecosystems and the effects of metal pollution on local environments as well as organisms can be remarkable and long lasting.

The Marmara Sea, which is an inland marine body that connects the Black Sea to the Aegean Sea via the Istanbul and Canakkale Straits, can be given as a good sample of local marine environment which is endangered due to substantial industrial pollutant threatening. Beside Istanbul, the densely populated Kocaeli Province is located on the east coast of the Marmara Sea, surrounding Izmit Bay, which is known to be among the most polluted basins in Turkey. Since the 1960s, more than four hundred large industrial plants have been built around the bay, including the biggest shipyards, metallurgy and fertilizer industries and petrochemical facilities of Turkey. Although sewage treatment plants are present many waste discharges into the Marmara sea are untreated. While natural gas usage is common in the region, coal combustion is commonly used for heating. Also agricultural farmlands are situated in the catchment area. Eventually the Marmara Sea is exposed to pollution from industrial discharges, agricultural activities, heavy marine traffic and atmospheric precipitation.

In this study, most seafood samples were harvested in the coastal regions of the Marmara Sea. The other fish samples were collected in the Black Sea which is a closed ecosystem, with its only connection to the Mediterranean Sea through the Marmara Sea. Because pollution sources can vary with different geographic locations, fish samples collected also from the Black Sea which has relatively different pollution sources from the Marmara Sea. In the southern Black Sea which is the source of commercial fish for the inhabitants of Kocaeli, besides the river effects, the main metal sources are agriculture, mining (Ergül *et al.* 2008) and sewage discharges (Boran and Altinok 2010). However, fisheries are important in Turkey and among neighbors maximum fish production is realized (i.e. 342,455 metric tons) by Turkey in the Black Sea (Duzgunes and Erdogan

2008). Also seafood exporting from Turkey primarily to the European countries is increasing day by day.

In this study the concentrations of metals in 22 different seafood items that were harvested the Marmara and Black Seas and commercially available in the Kocaeli fish markets were determined using Inductive Coupled Plasma-Mass Spectrometry (ICP-MS). The aims of this study are 1) to determine concentrations of some non-essential elements (As, Cd, Hg, and Pb) and some micronutrients (Co, Cr, Cu, Fe, Ni, Se, and Zn) in the muscle and liver tissue of fishes, and edible parts of invertebrates, 2) to calculate metal loads for human in Kocaeli city exposed via seafood 3) to compare the element concentrations in the same and different fish species from the Marmara and Black Seas which have different salinity levels and 4) to evaluate interactions between elements and seafood based on correlations in different tissues.

Materials and Methods

Twenty-two different marine (18 fish and 4 invertebrate) items were purchased as whole organism from October to December 2011. The fishing grounds from which the fishes were harvested were recorded daily according to information from fishing vessel stuff in the primary fish markets of Kocaeli (Figure 1). We obtained 9 fish species from the Black Sea and 9 fish and 4 invertebrate species, including bivalve, cephalopod and crustaceans from the Marmara Sea (Table 1). Samples were put into polyethylene beakers and kept cool for immediate transportation to the laboratory. Fish and invertebrates were filleted using porcelain knives to avoid metal contamination. At least 30 individuals were filleted except turbot, bonito, tuna and piper, for which 10 individuals were used. In this study measurements focused on the analysis of the muscle tissues and livers of fish and edible parts of invertebrates. After the wet weight was recorded, sampled tissues were kept in the oven at 55°C until constant dry weight (Table 1). Dried samples were gently powdered and homogenized by porcelain mortar and pestle that avoid any metal contamination.

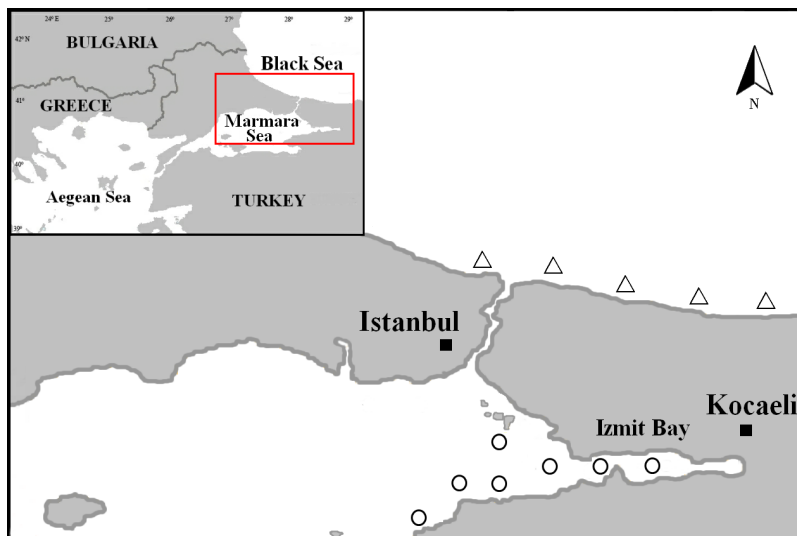


Figure 1. The map of seafood harvest locations. Circles and triangles indicate harvest locations from the Marmara and Black Seas

For ICP-MS, 0.5 g dry samples were digested for 30 minutes with mixtures of Suprapure Merck chemicals i.e. 7 mL HNO₃, 1 mL HCl and 1 mL H₂O₂ in a microwave digestion system at 200 °C (1000 W). Upon digestion, samples were diluted up to 50 mL with ultra pure water. All measurements were done using at least 3 replicates. Digested samples and analytical blanks that were prepared in the same acid matrix were analyzed with Perkin Elmer Elan DRC-e model ICP-MS which equipped with Cetax ADX-500 auto sampler and diluter. Internal standards were used for calibration. The relative standard deviations were determined as <5 %. Interferences due to Cl matrix were removed in Dynamic Reaction Cell mode using CH₄ gas. In order to validate the method for accuracy and precision, standard reference material (NIST 2977 Mussel Tissue) was analyzed for the corresponding elements (Table 2).

To determine the daily exposures of metals to adults the following equation developed by the United States Environmental Protection Agency (EPA 2000) was used:

$$E_m = C_m DC / BW \quad (1)$$

where E_m is the individual exposure to chemical contaminant m from ingesting fish ($\text{mg kg}^{-1} \text{d}^{-1}$), C_m is the concentration of chemical contaminant m in the edible portion of the fish (mg kg^{-1}), DC is the mean daily consumption rate of the fish (kg day^{-1}), and BW is the body weight of a consumer (kg).

Table 1. Sampling dates, locations, dry weight ratios and total lengths of fish and calamari harvested from the Marmara and Black Seas.

	Species	Common name	Turkish name	Harvesting Date	Origin	Dry weight ratios(%)		Total length (cm)
						Muscle	Liver	
Vertebrata	<i>Liza ramada</i>	Grey mullet	Has Kefal	14.11.2011	Black Sea	25.2	-	20.7 ± 1.7
	<i>Merlangius merlangus</i>	Whiting	Mezgit	03.11.2011	Black Sea	18.5	48.9	17.9 ± 0.7
	<i>Mullus barbatus</i>	Red Mullet	Barbunya	02.12.2011	Black Sea	27.9	36.2	18.3 ± 0.7
	<i>Mullus surmuletus</i>	Surmulet	Tekir	03.11.2011	Black Sea	27.2	-	12.1 ± 0.7
	<i>Pomatomus saltatrix</i>	Bluefish	Lüfer	03.11.2011	Black Sea	30.7	41.8	17.5 ± 1.0
	<i>Psetta maxima</i>	Turbot	Kalkan	02.12.2011	Black Sea	20.3	27.4	47.9 ± 5.2
	<i>Sarda sarda</i>	Bonito	Palamut	03.11.2011	Black Sea	29.5	22.2	32.0 ± 1.4
	<i>Solea solea</i>	Sole	Dil	14.11.2011	Black Sea	23.1	-	18.4 ± 0.8
	<i>Sciaena umbra</i>	Brown meager	Eşkine	14.11.2011	Black Sea	22.9	45.0	22.0 ± 1.2
	<i>Auxis thazard</i>	Frigate tuna	Ton	02.12.2011	Marmara Sea	28.6	31.8	43.5 ± 2.8
	<i>Belone belone</i>	Garfish	Zargana	03.11.2011	Marmara Sea	29.1	40.5	51.3 ± 0.4
	<i>Engraulis encrasicolus</i>	Anchovy	Hamsi	02.12.2011	Marmara Sea	28.1	-	12.0 ± 0.9
	<i>Merlangius merlangus</i> ¹	Whiting	Mezgit	03.11.2011	Marmara Sea	19.0	66.9	16.4 ± 0.9
	<i>Merlangius merlangus</i> ²	Whiting	Mezgit	03.11.2011	Marmara Sea	19.4	67.1	23.5 ± 0.8
	<i>Diplodus puntazzo</i>	Seabream	Karagöz	02.12.2011	Marmara Sea	25.9	33.9	29.7 ± 0.6
	<i>Sardina pilchardus</i>	Pilchard	Sardalye	03.11.2011	Marmara Sea	34.1	22.2	13.5 ± 0.6
	<i>Scomber scombrus</i>	Mackerel	Uskumru	02.12.2011	Marmara Sea	26.8	-	26.9 ± 1.1
	<i>Trachurus mediterraneus</i>	Horse Mackerel	İstavrit	03.11.2011	Marmara Sea	28.0	-	12.7 ± 0.5
	<i>Trigla lyra</i>	Piper	Öksüz	02.12.2011	Marmara Sea	27.4	44.3	27.3 ± 5.8
Invertebrata	<i>Mytilus galloprovincialis</i>	Black Mussel	Midye	03.11.2011	Marmara Sea	14.3	-	-
	<i>Palaemon serratus</i>	Common prawn	Karides	01.11.2011	Marmara Sea	23.5	-	-
	<i>Penaeus sp.</i>	Shrimp	Karides	01.11.2011	Marmara Sea	20.5	-	-
	<i>Ommastrephes sagittatus</i>	Calamari	Kalamar	03.11.2011	Marmara Sea	18.2	-	37.0 ± 3.8

Table 2. Expected and observed (mean \pm standard deviation) values of elemental concentrations in NIST 2977 Mussel Tissue Standard Reference Material (in mg kg⁻¹ dry weight); n: Number of observations

Element	n	Expected	Observed	Recovery %
As	5	8.83	8.16 \pm 0.82	92.4
Cd	5	0.18	0.16 \pm 0.02	90.8
Co	5	0.48	0.44 \pm 0.05	92.6
Cr	5	3.91	3.34 \pm 0.27	85.5
Cu	5	9.42	8.64 \pm 0.99	91.7
Fe	5	274	285 \pm 11.9	104
Hg	5	0.10	0.11 \pm 0.01	107
Ni	5	6.06	5.68 \pm 0.41	93.7
Pb	5	2.27	2.21 \pm 0.18	97.4
Se	5	1.78	1.58 \pm 0.11	88.9
Zn	5	135	121.8 \pm 14.6	90.2

Results and Discussion

Concentrations of As, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, Se, and Zn in fish muscle and liver, as well as in the edible invertebrate parts, are given in Table 3. For both fish and invertebrates, several elements (labelled in Table 3 with an asterisk) exceeded concentrations deemed domestically and internationally as safe for consumption (TFC 2011; TFC 2002; FAO 1983). To place the results from this study into a larger context, concentrations in fish muscle are shown together with values from other studies (Table 4).

Arsenic

Arsenic in some fish and invertebrates reached levels above the values recommended by the Food and Agriculture Organization (FAO) and by the Turkish Food Codex (Table 3). In fish from the Marmara Sea, the highest As level was present in *Scomber scombrus*. Tüzen (2009) also determined the highest As level in this species among ten species in the Black Sea, but reported concentrations that were approximately 17 times lower than our results. In a previous study higher As levels were reported from the Marmara and Black Seas (Topcuoglu *et al.* 1990). In recent studies, with one exception, average As levels in fish harvested both from Turkey and near Turkey were lower than in this study (Table 4). Higher As levels in *Merlangius merlangus* from the Marmara Sea could be due to higher salinity in this sea (~35 ppt) vs. the Black Sea (~20 ppt). Because experimental (Dutton and Fisher 2011) and field studies (Larsen and Francesconi 2003) have already suggested that As concentration in fish increases with salinity. Among all fish, As concentrations did not vary significantly between muscle and liver ($p = 0.54$) (Table 3).

Muscle As concentrations have been used for calculating the daily As intake per person according to equation 1. Based on this equation which employs the mean As concentration for fish from this study (2.27 mg kg^{-1} wet weight; Table 4), the daily intake of total As would be equal to $0.09 \text{ mg kg}^{-1} \text{ day}^{-1}$ assuming a mean body weight of 70 kg, portion size 0.224 kg (EPA 2000). Because demographic structure of the city is more or less similar, daily fish consumption was assumed 0.039 kg per individual according to study from the Kocaeli (Karademir 2004). However, because >80% of muscle As in marine fish can be in the form of arsenobetaine (Larsen and Francesconi 2003), fish in this study could likely contain $<0.02 \text{ mg kg}^{-1} \text{ day}^{-1}$ of inorganic As in wet weight. According to the EPA's guidance (2000) for assessing chemical contaminant data used in the fish advisory, a 70 kg person who consumes As contaminated fish at levels equal to 2.27 mg kg^{-1} wet weight in average, should not consume more than 4 fish portions per month to avoid systemic health effects related to chronic exposure to inorganic As. Taking into consideration the As advisories in fish (i.e. 1 mg kg^{-1} wet weight), it is evident that 14 out of 18 of fish purchased from the markets nearby Kocaeli exceed the limits provided by the Turkish Food Codex (2002) (Table 3). On the other hand it should be noted FAO/World Health Organization (WHO) Expert Committee have recently determined that lower limit on the benchmark dose for a 0.5% (BMDL_{0.5}) increased in lung cancer from epidemiological data to be $3.0 \mu\text{g kg}^{-1}$ body weight per day based on the range of estimated total dietary As exposure (WHO 2010). Fish from other studies show on average lower levels of As (1.13 mg kg^{-1} wet weight for conversion, dry weight ratios were assumed 25%) than the fish in this study (2.27 mg kg^{-1} wet weight) (Table 4).

In invertebrate samples, As concentrations reached levels above the values recommended by the Turkish Food Codex (2002) (i.e. 1 mg kg^{-1} wet weight). On the other hand mean As concentrations were comparable for fish and mussels but 10 and 12-fold higher in crustaceans and cephalopods, respectively. For comparison, others have found 30 and 40 mg of As kg^{-1} (2.65 times less than in this study) for crustaceans and cephalopods respectively from the Mediterranean and Black Seas (Topcuoğlu 2005).

Such elevated levels of As in the seafood that were caught near the coasts of the Marmara and Black Seas could be related to agricultural activities employing pesticides and fertilizers, wood manufacturing, smelting, municipal waste inputs, and fossil fuel byproducts (Wang and Mulligan 2006) all of which are present at the Marmara Sea coast.

Cadmium

The highest Cd concentration was in *Sardina pilchardus* from the Marmara Sea (Table 3). Average Cd concentrations in fish muscle were generally lower in

this study compared with other studies (Table 4). On the other hand, in some previous studies Cd concentrations were found to be considerably higher than values recommended by the Turkish Food Codex in *Merluccius merluccius* and *Merlangius merlangus* in the Marmara Sea (Aksu *et al.*, 2011; Balkis *et al.*, 2012b). Experimental and field-based studies have shown that Cd uptake could decrease with increasing salinity due to Cd chlorocomplexation and therefore lower Cd bioavailability, thus it is expected that more Cd accumulation occurs in fish inhabiting less saline waters (Dutton and Fisher 2011). However, in this study, there were not clear Cd concentration differences between same species. Also these differences were not observed in the muscle tissue of demersal or pelagic fishes (Table 3) between the Marmara and Black Seas (i.e. 0.020 mg kg⁻¹ and 0.019 mg kg⁻¹ respectively), probably related with seawater conditions at sampling locations.

Cd in the muscle and liver of Marmara Sea fish was significantly correlated with Pb ($r = 0.92, p < 0.001$ and $r = 0.89, p < 0.01$ respectively) and with Zn ($r = 0.70, p < 0.05$ and $r = 0.84, p < 0.05$, respectively). Such correlations are not unexpected for fish from this region as this region and its watershed is impacted by mining, smelting and refining activities. All of them are known to contribute Cd, Zn and Pb as industrial by-products (UNEP 2010). Except for whiting from the Marmara Sea, Cd was more concentrated in liver than in muscle tissue (Table 3). Probably because even if a non-essential element, Cd has an affinity for proteinaceous tissue (Mathews and Fisher 2009) and its levels rapidly increase in the liver during exposure and can remain high for a long time during depuration when other organs are already cleaned (Jezierska and Witeska 2006). In the edible parts of the invertebrates, Cd was present in 51 and 81-fold higher concentrations (*Mytilus galloprovincialis* and *Ommastrephes sagittatus*, respectively) than in average fish muscle (Table 3). Cd concentration in *M. galloprovincialis* collected from the Southern coast of the Marmara Sea (Ünlü *et al.* 2008) was found 2.3-fold higher than this study. Also higher levels were determined in Aegean (Sunlu 2006) and Black Sea (Topcuoglu *et al.* 2003; Balkis *et al.* 2012) studies in the same species. A crustacean *Palaemon serratus* from the Marmara Sea showed an order of magnitude higher Cd levels (i.e. 1.02 mg kg⁻¹) (Kurun *et al.* 2007) in comparison to Cd levels measured and reported for crustaceans in this study (Table 3).

Table 3. Element concentrations in muscle and liver tissue of seafood (mean \pm standard deviation in mg kg⁻¹ dry weight) harvested from the Marmara and Black Seas

Species	Tissue	As	Cd	Co	Cr	Cu	Fe	Hg	Ni	Pb	Se	Zn	
<i>L. ramada</i>	Muscle	2.01 \pm 0.10	0.02 \pm 0.01	0.07 \pm 0.01	1.60 \pm 1.28	2.32 \pm 0.06	55.6 \pm 5.0	0.06 \pm 0.01	0.46 \pm 0.37	0.07 \pm 0.01	1.06 \pm 0.03	17.2 \pm 1.0	
	Liver	4.90 \pm 0.23	0.03 \pm 0.01	0.04 \pm 0.01	1.50 \pm 1.07	2.30 \pm 0.06	84.2 \pm 12	0.33 \pm 0.02	0.31 \pm 0.29	0.05 \pm 0.01	2.27 \pm 0.07	18.0 \pm 1.4	
<i>M. merlangus</i>	Muscle	4.98 \pm 0.04	0.15 \pm 0.02	0.04 \pm 0.01	0.15 \pm 0.06	10.6 \pm 0.52	38.9 \pm 0.5	0.02 \pm 0.01	0.06 \pm 0.05	0.03 \pm 0.01	1.13 \pm 0.02	30.2 \pm 0.3	
	Liver	11.7 \pm 2.38	0.70 \pm 0.08	1.63 \pm 0.08	0.18 \pm 0.01	15.0 \pm 0.98	307 \pm 29	0.32 \pm 0.06	0.21 \pm 0.01	0.07 \pm 0.02	10.8 \pm 0.86	100 \pm 19	
<i>M. barbatus</i>	Muscle	12.7 \pm 1.20	0.02 \pm 0.01	0.05 \pm 0.01	0.33 \pm 0.04	1.00 \pm 0.18	20.2 \pm 0.7	0.47 \pm 0.02	0.05 \pm 0.05	0.02 \pm 0.01	1.05 \pm 0.04	14.6 \pm 1.3	
	Liver	11.7 \pm 2.38	0.70 \pm 0.08	1.63 \pm 0.08	0.18 \pm 0.01	15.0 \pm 0.98	307 \pm 29	0.32 \pm 0.06	0.21 \pm 0.01	0.07 \pm 0.02	10.8 \pm 0.86	100 \pm 19	
<i>M. surmuletus</i>	Muscle	11.7 \pm 0.32	0.01 \pm 0.01	0.09 \pm 0.01	0.74 \pm 0.47	1.77 \pm 0.25	30.4 \pm 0.8	0.29 \pm 0.04	0.17 \pm 0.02	0.04 \pm 0.01	1.08 \pm 0.02	16.5 \pm 1.0	
	Liver	13.6 \pm 2.38	0.44 \pm 0.03	1.70 \pm 0.10	0.22 \pm 0.02	18.2 \pm 2.85	344 \pm 51	0.07 \pm 0.01	0.42 \pm 0.05	0.10 \pm 0.02	8.01 \pm 0.44	58.2 \pm 0.7	
<i>P. salnatris</i>	Muscle	2.87 \pm 0.11	0.02 \pm 0.01	0.02 \pm 0.01	0.61 \pm 0.15	2.29 \pm 0.19	17.2 \pm 2.4	0.11 \pm 0.01	0.13 \pm 0.06	0.01 \pm 0.01	1.61 \pm 0.16	15.3 \pm 1.0	
	Liver	4.16 \pm 0.97	0.08 \pm 0.02	0.16 \pm 0.01	0.21 \pm 0.03	12.7 \pm 1.01	248 \pm 49	0.02 \pm 0.01	0.06 \pm 0.01	0.07 \pm 0.01	5.00 \pm 0.74	61.7 \pm 4.1	
<i>P. maxima</i>	Muscle	5.43 \pm 0.02	0.01 \pm 0.01	0.02 \pm 0.01	0.04 \pm 0.50	0.76 \pm 0.03	17.3 \pm 2.8	0.50 \pm 0.01	0.08 \pm 0.08	0.02 \pm 0.02	2.33 \pm 0.01	21.9 \pm 0.6	
	Liver	4.80 \pm 0.10	0.04 \pm 0.01	0.57 \pm 0.02	0.44 \pm 0.20	10.1 \pm 0.06	339 \pm 9.0	0.16 \pm 0.01	0.07 \pm 0.02	0.05 \pm 0.01	6.81 \pm 0.04	63.1 \pm 1.4	
<i>S. sarda</i>	Muscle	1.48 \pm 0.02	0.02 \pm 0.01	0.02 \pm 0.01	1.34 \pm 0.45	2.40 \pm 0.02	41.0 \pm 3.9	0.11 \pm 0.01	0.43 \pm 0.03	0.03 \pm 0.01	1.58 \pm 0.06	12.3 \pm 0.3	
	Liver	3.21 \pm 0.14	0.18 \pm 0.01	0.09 \pm 0.01	0.32 \pm 0.02	5.14 \pm 0.09	70.8 \pm 1.3	0.10 \pm 0.10	0.07 \pm 0.01	0.03 \pm 0.01	8.05 \pm 0.28	68.3 \pm 1.0	
<i>S. solea</i>	Muscle	11.6 \pm 0.14	0.02 \pm 0.01	0.16 \pm 0.02	1.44 \pm 0.67	2.05 \pm 0.06	37.1 \pm 1.5	0.09 \pm 0.02	0.30 \pm 0.06	0.03 \pm 0.01	1.60 \pm 0.01	18.4 \pm 0.6	
	Liver	18.6 \pm 0.77	0.02 \pm 0.01	0.02 \pm 0.01	1.89 \pm 1.64	1.26 \pm 0.11	23.2 \pm 0.5	0.30 \pm 0.02	0.25 \pm 0.15	0.01 \pm 0.01	1.49 \pm 0.06	12.7 \pm 0.4	
<i>S. umbra</i>	Muscle	5.08 \pm 0.12	0.16 \pm 0.02	0.24 \pm 0.01	0.14 \pm 0.02	7.11 \pm 0.07	329 \pm 11	0.01 \pm 0.01	0.06 \pm 0.06	0.04 \pm 0.02	2.15 \pm 0.03	36.9 \pm 0.4	
	Liver	12.2 \pm 1.68	0.02 \pm 0.01	0.04 \pm 0.02	0.43 \pm 0.21	7.80 \pm 3.11	135 \pm 17	1.11 \pm 0.07	BDL	BDL	2.83 \pm 0.06	17.7 \pm 0.5	
<i>A. thazard</i>	Muscle	19.1 \pm 0.94	0.28 \pm 0.01	0.17 \pm 0.02	0.25 \pm 0.02	10.6 \pm 0.47	898 \pm 34	0.63 \pm 0.02	0.01 \pm 0.01	0.13 \pm 0.01	13.0 \pm 0.30	181 \pm 7.9	
	Liver	1.23 \pm 0.14	0.02 \pm 0.01	0.02 \pm 0.01	0.37 \pm 0.02	2.20 \pm 0.13	21.8 \pm 7.9	0.89 \pm 0.07	BDL	0.03 \pm 0.01	0.75 \pm 0.09	22.6 \pm 2.2	
<i>B. belone</i>	Muscle	4.50 \pm 0.14	0.05 \pm 0.01	0.04 \pm 0.01	0.17 \pm 0.02	5.83 \pm 0.04	387 \pm 2.0	0.10 \pm 0.01	0.06 \pm 0.02	0.08 \pm 0.01	1.42 \pm 0.01	4.02 \pm 0.6	
	Liver	10.3 \pm 0.47	0.02 \pm 0.01	0.05 \pm 0.01	0.33 \pm 0.02	2.76 \pm 0.14	26.3 \pm 2.1	0.11 \pm 0.01	0.06 \pm 0.01	0.03 \pm 0.02	0.90 \pm 0.02	24.5 \pm 1.0	
<i>E. encrasicolus</i>	Muscle	12.5 \pm 0.08	0.04 \pm 0.01	0.13 \pm 0.02	3.11 \pm 1.91	1.79 \pm 0.43	36.2 \pm 2.1	0.31 \pm 0.01	0.82 \pm 0.28	0.05 \pm 0.02	1.33 \pm 0.06	18.8 \pm 0.4	
	Liver	2.32 \pm 0.07	0.04 \pm 0.02	0.01 \pm 0.01	0.43 \pm 0.10	3.64 \pm 0.59	26.4 \pm 4.9	0.04 \pm 0.02	0.08 \pm 0.07	0.02 \pm 0.02	0.35 \pm 0.04	14.7 \pm 0.3	
<i>M. merlangus</i> ¹	Muscle	18.4 \pm 0.25	0.02 \pm 0.01	0.02 \pm 0.01	0.48 \pm 0.08	0.67 \pm 0.03	12.1 \pm 0.6	0.52 \pm 0.02	0.03 \pm 0.03	0.05 \pm 0.02	1.29 \pm 0.03	13.6 \pm 0.6	
	Liver	2.37 \pm 0.09	0.01 \pm 0.01	0.02 \pm 0.01	0.20 \pm 0.14	5.13 \pm 0.72	72.2 \pm 54	0.08 \pm 0.02	BDL	0.01 \pm 0.02	0.33 \pm 0.02	20.3 \pm 3.1	
<i>M. merlangus</i> ²	Muscle	5.81 \pm 0.16	0.01 \pm 0.01	0.01 \pm 0.01	0.61 \pm 0.08	0.78 \pm 0.02	12.3 \pm 5.3	0.45 \pm 0.04	BDL	0.01 \pm 0.01	1.01 \pm 0.04	16.4 \pm 0.5	
	Liver	13.4 \pm 0.04	0.48 \pm 0.01	0.45 \pm 0.02	0.30 \pm 0.07	73.9 \pm 3.39	388 \pm 13	0.04 \pm 0.01	0.18 \pm 0.12	0.36 \pm 0.02	4.28 \pm 0.02	143 \pm 0.4	
<i>S. pilchardus</i>	Muscle	5.81 \pm 0.40	0.05 \pm 0.02	0.04 \pm 0.01	0.37 \pm 0.04	3.03 \pm 0.45	39.7 \pm 5.3	0.11 \pm 0.02	0.05 \pm 0.01	0.10 \pm 0.01	0.90 \pm 0.10	30.8 \pm 1.2	
	Liver	7.37 \pm 0.20	0.07 \pm 0.02	0.06 \pm 0.01	0.32 \pm 0.09	3.55 \pm 0.09	110 \pm 2.0	0.02 \pm 0.01	0.36 \pm 0.03	0.09 \pm 0.01	2.57 \pm 0.02	55.4 \pm 1.2	
<i>S. scombrus</i>	Muscle	20.1 \pm 1.39	0.01 \pm 0.01	0.04 \pm 0.01	0.72 \pm 0.41	2.05 \pm 0.35	33.6 \pm 3.7	1.31 \pm 0.08	0.27 \pm 0.05	0.01 \pm 0.02	3.25 \pm 0.01	18.6 \pm 0.9	
	Liver	5.57 \pm 0.37	0.02 \pm 0.01	0.07 \pm 0.01	0.58 \pm 0.02	2.14 \pm 0.02	32.3 \pm 5.0	0.14 \pm 0.02	0.05 \pm 0.02	0.04 \pm 0.02	1.58 \pm 0.10	21.5 \pm 1.3	
<i>T. mediterraneus</i>	Muscle	7.54 \pm 0.05	0.01 \pm 0.01	0.02 \pm 0.01	0.71 \pm 0.30	0.99 \pm 0.01	14.8 \pm 0.5	0.29 \pm 0.03	0.06 \pm 0.01	0.02 \pm 0.01	1.89 \pm 0.14	16.5 \pm 0.5	
	Liver	7.39 \pm 1.12	0.05 \pm 0.02	0.47 \pm 0.04	0.08 \pm 0.01	21.8 \pm 1.25	519 \pm 46	0.15 \pm 0.02	-	0.02 \pm 0.01	4.48 \pm 0.11	75.0 \pm 8.1	
<i>Invertebrata</i>	<i>M. galloprovincialis</i>	Edible	8.79 \pm 0.14	1.04 \pm 0.04	0.79 \pm 0.01	3.17 \pm 0.04	5.07 \pm 0.23	436 \pm 5.9	0.08 \pm 0.01	1.72 \pm 0.02	6.83 \pm 0.46	2.80 \pm 0.10	276 \pm 14
		Edible	113 \pm 21.5	0.08 \pm 0.04	0.19 \pm 0.06	3.20 \pm 0.09	186 \pm 12.3	63.1 \pm 6.4	0.26 \pm 0.03	2.33 \pm 0.79	0.36 \pm 0.04	5.82 \pm 0.69	218 \pm 27
		Edible	68.3 \pm 4.96	0.06 \pm 0.01	0.07 \pm 0.01	0.43 \pm 0.11	21.0 \pm 0.08	98.3 \pm 54	0.04 \pm 0.01	0.48 \pm 0.03	0.16 \pm 0.03	1.51 \pm 0.07	37.3 \pm 1.5
		Edible	106 \pm 1.39	1.67 \pm 0.17	0.23 \pm 0.01	1.48 \pm 0.41	76.9 \pm 8.10	36.3 \pm 6.5	1.45 \pm 0.05	0.55 \pm 0.1	0.07 \pm 0.02	2.75 \pm 0.15	55.4 \pm 0.2

†: Over the limit value (FAO, 1983; TPC, 2002), 1: Short average length, 2: Long average length, BDL: Below detection limit, -: Not measured

Lead

S. pilchardus had the highest Pb concentration, while Pb was below the detection limit for *Auxis thazard* (Table 3). Fish tissue Pb concentrations in this study were generally lower than in the same species from elsewhere (Table 4). There was a positive correlation between Pb and Zn in analysed fish that originated from the Marmara Sea ($r = 0.63, p < 0.05$). Correlation between Pb and Zn in environmental samples could be related to contamination from the industries that use Pb-Zn ores (UNEP, 2010). Within this study, mean Pb concentration for fish from the Marmara Sea was slightly higher than for fish from the Black Sea (Table 4). In general higher concentrations for Pb were found in liver than in the muscle except for *Merlangius* and *Sardine* species (Table 3). Other significant correlations were found for Pb and Ni ($r = 0.94, p < 0.01$), and Pb and As ($r = 0.82, p < 0.05$) in the livers of fish from the Black Sea, and Pb and Cu ($r = 0.89, p < 0.01$) in the livers harvested from Marmara Sea fishes. These results probably related temporal elemental variations in the regions.

Lead concentration in *M. galloprovincialis* was 198-fold higher than in average fish muscle (Table 3). Concentration of Pb in invertebrates in this study from the Marmara Sea was below the limit established by Turkish Food Codex (2002); however, in mussel tissue it was higher than other studies in the Marmara (Ünlü *et al.* 2008), Aegean (Sunlu 2006) and Black Sea (Topcuoglu *et al.* 2003; Balkis *et al.* 2012). In surface waters residence times of biological particles containing lead have been estimated at two to five years, so it is difficult to explain interactions between environmental conditions and lead concentrations in the field study. In Turkey to date the biggest contribution of Pb is petroleum related. Besides the biggest petroleum refinery on the coast of Izmit Bay, Pb arrives in the surface waters via atmospheric deposition from automobiles and probably ship derived exhaust fumes.

Mercury and Selenium

Scomber scombrus from the Marmara Sea had the highest Hg concentration in its muscle (Table 3). Other studies have shown that fish caught from the Marmara and Black Seas had generally comparable levels of Hg, except those from the Adriatic Sea (Bilandžić *et al.* 2011), which had an order of magnitude higher Hg than this study (Table 4). Just as for Hg, the highest Se concentration was in the muscle of *S. scombrus* (Table 3). In previous studies from the Marmara and Black Seas, Se was generally found in lower concentrations than this study, except one Black Sea study (Alkan *et al.* 2012) for the same fish species (Table 4). As previously reported Hg and Se can be correlated in biota and it has been concluded that Se has a protective effect against Hg, because of their high binding affinity for each other (Paulsson and Lundbergh 1991). In this study, it is also shown that Hg and Se in fish muscle tissue were significantly

correlated in both the Marmara ($r = 0.70, p < 0.05$) and Black Seas ($r = 0.67, p < 0.05$). Correlation coefficients were also determined as significant for Hg and Se in liver tissue of the Marmara and Black Sea fishes ($r = 0.79, p < 0.05$, and $r = 0.92, p < 0.01$, respectively). Thereby, significant correlations possibly indicate detention of Se by Hg or vice versa. It is noteworthy that Hg was 2 to 30 fold higher in muscle than liver tissue (Table 3). The possible reason for the higher concentration of Hg in muscle is due to its very slow efflux out of the muscle. Thus, Hg accumulation in muscle tissue is expected and a significant correlation between total body length and Hg concentrations ($r = 0.61, p < 0.01$) support time dependent Hg build-up in older and therefore larger fish. Also Hg concentrations in whiting that have different average length from the Marmara Sea (Table 3) support this finding.

Among the invertebrates, while the highest Hg concentration was found in *O. sagittatus*, the highest Se level was found in *P. serratus* (Table 3). Since there are very limited studies present of invertebrates in the Marmara and Black Seas, comparison of Se results is difficult. However, in average Se concentrations were given in the Marmara marine environments as 3 mg kg^{-1} , 4 mg kg^{-1} , and 3 mg kg^{-1} for mussel, crustacean and cephalopod species respectively (Topcuoğlu 2005) that coincide with our results.

Nickel and Chromium

Although generally found in lower levels, concentrations of Ni in fish muscle were comparable to previously published Ni concentrations in fish from the Marmara and Black Seas (Table 4). Fish muscle Ni concentrations correlated with Cr for both the Marmara ($r = 0.97, p < 0.001$) and Black Seas ($r = 0.76, p < 0.05$) fishes. Although average Cr and Ni levels were found higher in the Black Sea, *M. merlangus* from the Marmara Sea had the highest concentrations (i.e. 3.11 mg kg^{-1}) (Table 3). Different from Ni, Cr reached their higher levels in muscle tissue than liver in almost all fish species (Table 3).

Among the invertebrates, Ni and Cr reached highest concentrations in *P. serratus* (Table 3) and were higher than their average concentrations in fish muscle (i.e., 0.22 mg kg^{-1} for Ni and 0.96 mg kg^{-1} for Cr). Concentrations of Ni in *P. serratus* are within the range of previously reported results from the Marmara Sea (e.g. 4.8 mg kg^{-1} in average) (Kurun *et al.* 2007). Significant correlation was also determined between Ni and Cr ($r = 0.98, p < 0.05$) in edible tissue of invertebrates. Since the Eastern Marmara Sea sediments were documented as moderately or heavily polluted with Ni and Cr (Pekey *et al.* 2004), this sediment contamination could contribute to elevated body burdens in the investigated invertebrates.

Cobalt, Copper, Iron and Zinc

While the highest Co and Fe concentrations were determined in *M. merlangus* and *A. thazard* respectively, the highest Cu and Zn concentrations were determined in *S. pilchardus* muscle tissue in the Marmara Sea (Table 3). Comparisons of these metals based on their average levels are discussed below. Co concentrations were found lower than other studies (Table 4). Even though Co levels were comparable with the Marmara and Black Sea Studies, its concentration was 72 fold higher (i.e., 1.43 mg kg⁻¹ wet weight.) (Uysal *et al.* 2008) than this study in *Liza ramada* from the Western Mediterranean Sea. Fe concentrations were comparable to previous studies except one that was 7 fold higher than this study from the Marmara Sea (Ozden *et al.* 2010) (Table 4). However, in this same study Fe concentrations were similar for *M. merlangus* in the same sampling season and the Cu concentrations were comparable with Black Sea studies. Studies from the other seas reported up to 9 fold higher results such as from the Eastern Mediterranean Sea (Türkmen *et al.* 2008) (Table 4). Zn concentrations were also comparable with previous studies from other seas except one Black Sea study where Zn levels reached 16 fold higher concentrations in average (Tuzen 2009) (Table 4). In the same study Zn concentrations were found 11, 16, 19 and 23-fold higher than this study for *Psetta maxima*, *M. merlangus*, *Mullus barbatus* and *Pomatomus saltatrix* respectively. As an important constituent of micronutrients the elements mentioned above can be found in the cytoplasm of marine phytoplankton (Fisher and Reinfelder 1995) and the major intake for marine organisms in the food web is by ingestion. However, their accumulation in the tissue of the fishes depends on different factors such as abundance in the environment (Luoma and Rainbow 2005), mobility in the tissue or the exchange speed of the metal (Luoma 1983). Thus, lower or higher concentrations in muscle tissue are expected in particular marine environments for fishes. Depend on results of this study, it was determined that an element which has slow mobility (i.e., Hg and Cr) tends to be accumulated in muscle tissue, while others (i.e., Co, Cu, Fe and Zn) in the liver with exception some of these elements in *M. merlangus* (Table 3). From a different viewpoint, Co, Cu, Fe, and Zn are known as micronutrients and the human diet must include these elements at trace levels. Although no exact value is known as the minimum dietary intake for Co and Fe, WHO suggested 1.01 and 2.5 mg kg⁻¹day⁻¹ for Cu and Zn, respectively (1996) also the US EPA (2000) suggested 0.055 mg kg⁻¹day⁻¹ for Se. Based on present results, those seafood-derived micronutrients can be assumed a good sources for the human diet.

Among invertebrates, while Cu concentrations in *P. serratus* reached levels above the values recommended by the Turkish Food Codex (2002), the highest Co, Fe and Zn levels were determined in *M. galloprovincialis* (Table 3). In the Marmara Sea, while average Cu and Zn were found in lower concentrations (i.e., 39.9 and 37.7 mg kg⁻¹ in wet weight), Fe was found in higher

concentrations (i.e., 24.6 mg kg⁻¹ in wet weight) (Kurun *et al.* 2007) in *P. serratus*. In *M. galloprovincialis* while Co and Cu were found in higher concentrations (i.e., 1.4 and 5.36 mg kg⁻¹ respectively), Fe and Zn were found lower (i.e., 82.3 and 78.2 mg kg⁻¹ respectively) than this study by Culha *et al.* (2011) in the same season. However in the Aegean and Black Seas, while average Zn concentrations were found lower (i.e., 23.31 mg kg⁻¹wet weight and 69.1 mg kg⁻¹ respectively), Cu concentrations were found higher (i.e., 1.48 mg kg⁻¹ wet weight and 9.1 mg kg⁻¹ respectively) than this study in *M. galloprovincialis* (Topcuoglu *et al.* 2003; Sunlu 2006).

In the overall assessment, higher average regression coefficient were found in muscle than liver tissue ($r^2 = 0.80$, $n = 19$ and $r^2 = 0.44$, $n = 14$ respectively) based on biserial calculations between all fish muscle and between all fish liver element concentrations from the Marmara and Black Seas. This coefficient reached 0.99 ($n = 19$) in fish muscle for As, Cd, Hg and Pb, that are known as non-essential elements. These results indicate that most elements, especially non-essentials, are accumulated consistently in the fish muscle tissue however liver represents temporarily alterations probably related with metabolic processes and environmental factors. Also it should be noted that total concentrations of metals were examined in this study and ionic forms of the metals show different binding affinities. Although there were no meaningful differences between benthic and pelagic fishes or benthic fishes and metal accumulation, invertebrate species that fed on the benthic habitat, accumulated elements more efficiently. Among invertebrates with the exception of *M. galloprovincialis* which accumulated Co, Fe, Pb and Zn at the highest concentrations, *P. serratus* which accumulated As, Cr, Cu, Ni and Se and *O. sagittatus* which accumulated Cd and Hg at the highest levels can be suitable organisms for metal biomonitoring studies.

Table 4. Average metal concentrations in fish muscle tissue (mg kg^{-1}) from various marine environments (Half of detection limit were used for average metal concentrations calculation if given data have been indicated as “below detection limit”. Dry to wet weight conversion based on Table 1 are also presented for this study).

Location	Dry / Wet	As	Cd	Co	Cr	Cu	Fe	Hg	Ni	Pb	Se	Zn
Average Black Sea ^{TS}	Dry	8.06	0.019	0.05	1.16	1.85	37.2	0.25	0.24	0.03	1.70	16.3
	Wet	1.98	0.005	0.01	0.28	0.47	8.97	0.06	0.06	0.01	0.42	4.02
Average Marmara Sea ^{TS}	Dry	9.97	0.022	0.05	0.77	2.42	36.4	0.52	0.19	0.04	1.57	20.1
	Wet	2.52	0.01	0.01	0.18	0.68	10.1	0.14	0.04	0.01	0.42	5.50
Average Total ^{TS}	Dry	9.06	0.02	0.05	0.96	2.15	36.8	0.39	0.22	0.03	1.63	18.3
	Wet	2.27	0.01	0.01	0.23	0.58	9.54	0.10	0.05	0.01	0.42	4.80
Eastern Black Sea ¹	Dry	-	0.23	-	-	2.23	-	-	-	1.66	-	17.3
Eastern Black Sea ²	Dry	9.80	0.03	0.08	0.71	1.07	-	0.08	0.23	0.09	3.58	25.1
Western, Central & Eastern Black Sea ³	Wet	0.19	0.22	-	1.04	1.46	-	0.06	2.04	0.53	0.43	65.9
Marmara Sea ⁴	Wet	-	0.02	0.04	0.11	0.72	7.46	-	0.02	1.13	-	4.49
Marmara Sea ⁵	Wet	0.36	0.04	0.15	1.27	1.05	70.9	0.42	0.79	0.27	0.40	16.6
Eastern Aegean Sea ⁴	Wet	-	0.05	0.11	0.15	3.70	38.9	-	0.58	0.51	-	8.60
Eastern Aegean Sea ⁶	Wet	-	0.00	-	-	-	-	0.09	-	0.13	-	-
Eastern Mediterranean Sea ⁴	Wet	-	0.21	0.23	1.01	5.11	23.9	-	2.25	0.70	-	7.92
Eastern Mediterranean Sea ⁷	Wet	-	0.07	-	0.05	1.46	1.29	-	0.17	0.22	-	2.71
Western Mediterranean Sea ⁸	Wet	-	-	0.27	0.10	2.45	5.53	-	-	-	-	7.04
Adriatic Sea ⁹	Wet	2.83	0.65	-	-	4.13	-	2.18	-	0.01	-	-
Threshold effect levels-FAO ¹⁰ and TFC ^{11,12}	Wet	1.0	0.05	-	-	20.0	-	1.0	-	0.30	-	50

TS(This Study), 1-*Merlangius euxinus*, *Spicara smaris*, *Mugil cephalus* (Topcuoglu *et al.* 2003), 2-*M. Merlangus euxinus*, *Mullus barbatus ponticus* (Alkan *et al.* 2012), 3-*Psetta maxima*, *Scomber scombrus*, *M. merlangus*, *M. barbatus*, *M. cephalus*, *Pomatomus saltor*, *Sarda sarda*, *Trachurus trachurus*, *Engraulis encrasicolus*, *Clupea sprattus* (Tuzen 2009), 4-*Trigla gurnardus*, *Scorpaena porcus*, *Sarpa salpa*, *Sparus aurata*, *Boops boops*, *Diplodus vulgaris*, *D. Puntazzo*, *Sphyaena sphyraena*, *Ophidion barbatum*, *Remora australis*, *Sciaena umbra* (Türkmen *et al.* 2008), 5-*Solea solea*, *Mullus surmuletus*, *M. merlangus* (Ozden *et al.* 2010) 6-*M. barbatus* (Kucuksezgin *et al.* 2001), 7-*S. aurata*, *Chelidonichthys lucernus*, *Upeneus molluccensis*, *Solea solea*, *M. merluccius*, *Saurida undosquamis* (Ersoy and Çelik 2010), 8-*Lithognathus mormyrus*, *Liza aurata*, *Chelon labrasus*, *M. cephalus*, *S. aurata*, *L. ramada* (Uysal *et al.* 2008), 9-*E. encrasicolus*, *Scomber japonicus*, *M. surmuletus*, *S. smaris* (Bilandžić *et al.* 2011), 10- (FAO 1983), 11-(TFC 2002), 12-(TFC 2011)

Conclusion

This study dealt with the metal concentrations for considerable amount of economic seafood items that harvested from the Marmara and Black Seas. Present results fill a gap on element levels in some species for the first time in the region. It is noteworthy that As concentrations that were above acceptable limits were found in most of the fish species from the Marmara and Black Seas. Also the Cu concentration above the acceptable limit was found in *P. serratus*. Various factors effect metal concentrations in marine environment and liver tissue can reflect temporarily alterations. However results show that non-essential elements are accumulated consistently in the fish muscle. Similar with other aquatic organisms, fishes can accumulate metals via aqueous and mainly dietary exposure. Therefore, in the future studies besides psychochemical features and complementary analysis in other ecosystem components, it will be beneficial to thoroughly evaluate metal concentrations in organism in the food web of marine fish.

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Marmara ve Karadeniz deniz ürünlerinde elzem olmayan elementlerin ve mikrobesein elementlerin konsantrasyonlarının değerlendirilmesi.

Özet

Kontaminantların bulunduğu çevrelerde yaşayan deniz canlılarında olası toksik elementlerin varlığının belirlenmesi insan sağlığı için önemlidir. Bu çalışmada Marmara ve Karadeniz'den alınan balıkların kas ve karaciğer dokularındaki ve omurgasızların yenilebilir kısımlarındaki As, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, Se ve Zn konsantrasyonları

ICP-MS ile ölçüldü. 18 balık türünün 14'ünde (*Mullus barbatus*, *Mullus surmuletus*, *Psetta maxima*, *Solea solea*, *Sciaena umbra*, *Auxis thazard*, *Engraulis encrasicolus*, *Merlangius merlangus*, *Diplodus puntazzo*, *Sardina pilchardus*, *Scomber scombrus*, *Trachurus mediterraneus*, and *Trigla lyra*) ve 4 omurgasız türünde (*Mytilus galloprovincialis*, *Palaemon serratus*, *Penaeus* sp., ve *Ommastrephes sagittatus*) As ve *Palaemon serratus*'da Cu konsantrasyonlarının Gıda ve Tarım Örgütü (1983) ve Türk Gıda Kodeksi (2002) tarafından tavsiye edilen değerleri aştığı belirlendi. Karaciğer dokusu daha çok geçici değişiklikleri yansıtırken, elzem olmayan elementler balık kas dokusunda birikim gösterdi. Mevcut sonuçlar diğer çalışmalarla karşılaştırıldığında, Marmara denizinden alınan balık örneklerinin kas dokularındaki As ve Se konsantrasyonlarının Marmara'dadaha önceki çalışmalarda belirlenen değerlerden, Karadenizden alınan balık örneklerinin kas dokularındaki Fe ve Hg konsantrasyonlarının ise Karadeniz'de daha önceki çalışmalarda belirlenen değerlerden yüksek olduğu bulundu. Diğer element konsantrasyonlarının, bazı istisnalar dışında, genellikle karşılaştırılabilir seviyede ya da daha düşük düzeyde olduğu belirlendi.

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