Kafkas Univ Vet Fak Derg
16 (1): 119-125, 2010
DOI:10.9775/kvfd.2009.982

RESEARCH ARTICLE

Determination of Heavy Metal Levels in Fish Samples Collected from the Middle Black Sea

Cevat NİSBET * Göknur TERZİ ** Osman PİLGİR *** Neslihan SARAC ***

* Department of Biochemistry, Faculty of Veterinary Medicine, Ondokuz Mayis University, 55139, Samsun - TURKEY
** Department of Food Hygiene and Technology, Faculty of Veterinary Medicine, Ondokuz Mayis University, 55139, Samsun - TURKEY
*** Refik Saydam Hygiene Center Directory of Samsun, 55139, Samsun - TURKEY

Makale Kodu (Article Code): KVFD-2009-982

Summary

The purpose of this study is to determine some heavy metals in muscle tissues of fish collected from the Middle Black Sea Coast of Samsun, Sinop, Terme, Fatsa and Ordu in Turkey. A total of 1650 fish samples including *Trachurus trachurus, Alosa caspia, Pomatomus saltatrix, Mullus barbatus, Spicara smaris, Engraulis encrasicolus, Gobius cephalarges, Sarda sarda, Merlangius euxmus* and *Psetta maxima* were used as material. Metal concentrations in fish samples were measured by atomic absorption spectrophotometry. The average value of metal concentrations in fish samples were determined as follows: 2.38 µg/g for Cu, 5.41 for Mn, 26.06 for Fe, 3.40 for Ni, 25.74 for Zn, 0.77 for Pb and 0.022 for Cd, but Hg was not detected. These values were compared with FAO/WHO standards and metal concentrations in fish samples were found to be lower than the maximum permissible levels, but lead level was found to be higher.

Keywords: *Heavy metal, Atomic absorption spectrometry, Fish*

Orta Karadeniz Bölgesinden Toplanan Balıklarda Ağır Metal Düzeylerinin Belirlenmesi

Özet

Bu çalışma Türkiye'nin Orta Karadeniz kıyılarındaki Samsun, Sinop, Terme, Fatsa ve Ordu yörelerinden toplanan balık kas dokularında bazı ağır metal düzeylerinin araştırılması amacıyla yapıldı. İstavrit, tirsi, çinekop, barbun, izmarit, hamsi, kaya balığı, palamut, mezgit ve kalkan olmak üzere toplam 1650 adet balık örneği materyal olarak kullanıldı. Balıkta metal konsantrasyonu atomik absorbsiyon spektrometresi kullanılarak belirlendi. Balık örneklerinde ortalama ağır metal konsantrasyonları: Cu: 2,38, Mn: 5,41, Fe: 26,06, Ni: 3,40, Zn: 25,74, Pb:0,77 ve Cd: 0,022 µg/g olarak bulundu, Hg ise tespit edilemedi. Elde edilen bu değerler FAO/WHO standartları ile karşılaştırıldığında balık örneklerinin maksimum kabul edilebilir limitleri aşmadığı, fakat kurşun düzeyinin limitlerin üzerinde olduğu belirlendi.

Anahtar sözcükler: *Ağır metal, Atomik absorbsiyon spektrometresi, Balık*

INTRODUCTION

Sea pollution is an indispensable part of environmental pollution. Domestic and industrial wastes, nuclear power stations built for electric generation, erosions, improper coastal fill areas, oil pollution, and marine accidents are significant factors causing sea pollution [1,2].

Main sources of pollution in the Black Sea include the disposal of domestic and industrial wastes of the countries surrounding the Black Sea, as well as of many European countries, directly to the sea through rivers such as Danube, Dnieper, Don [3].

Chemical pollutants in the Black Sea such as oil, pesticides and heavy metals give harm to biologic life and indirectly threaten human health. Heavy metals in water environment bring about balance disorder in

İletişim (Correspondence)
☎ +90 362 3121919/2812
✉ goknurterzi@yahoo.com

ecosystem by causing structural damage in fish at cellular and molecular level; while they, at the same time, cause heavy metal toxicity in humans through the consumption of fish that constitute an important ring in food chain [4,5].

The objectives of this study are: (1) to measure the concentrations of copper (Cu), manganese (Mn), iron (Fe), nickel (Ni), zinc (Zn), lead (Pb), cadmium (Cd) and mercury (Hg) in ten fish species, at five sites in Middle Black Sea in order to determine the extent of any heavy metal contamination; (2) to estimate the seasonal variation of heavy metal loading in these fishes; and (3) to find the correlation between metal concentrations and fish size evaluation.

MATERIAL and METHODS

Sampling: A total of 1650 fish samples which include 10 species, namely as *Trachurus trachurus* (n=200), *Alosa caspia* (n=200), *Pomatomus saltatrix* (n=150), *Mullus barbatus* (n=200), *Spicara smaris* (n=150), *Engraulis encrasicolus* (n=200), *Gobius cephalarges* (n=100), *Sarda sarda* (n=150), *Merlangius euxmus* (n=200) and *Psetta maxima* (n=100) were collected from five stations (Samsun, Sinop, Terme, Fatsa and Ordu) in the Middle Black Sea Coasts in 2005-2006. Average fish lenghts were determined as 12.41±1.35 cm for *Trachurus trachurus,* 13.75±0.98 cm for *Alosa caspia,* 13.07±1.04 cm for *Pomatomus saltatrix,* 10.75±0.66 cm for *Mullus barbatus,* 8.87±0.83 cm for *Spicara smaris,* 7.00±1.25 cm for *Engraulis encrasicolus,* for 10.87±0.79 cm *Gobius cephalarges,* 21.75±1.74 cm for *Sarda sarda,* 11.95±1.06 cm for *Merlangius euxmus* and 31.75±1.58 cm for *Psetta maxima*. Fish samples were washed with distilled water and dried at 105°C for 24 h. The dried samples were ground, then homogenized using an agate pestle and stored in polyethylene bottles. All samples were frozen at -20°C until the analysis.

Apparatus: For the analyses of heavy metals, a Shimadzu AA-6701F Atomic Absorption Spectrometer was used. Lead and cadmium concentrations were determined by graphite furnace using argon as inert gas. Other metal measurements were carried out in air /acetylene flame. All reagents used were of analytical reagent grade (Merck, Germany).

Digestion procedures: Dry ashing: One gram of fish sample was put into porcelain crucible. The furnace temperature was slowly increased from room temperature to 450°C in 1 h. The samples were ashed until a white or grey ash residue was obtained. Approximately fourteen hours later, 5 mL of HNO_3 (25% v/v) was added on the residue and the mixture, when necessary, was heated slowly to dissolve the residue. Then the solution was transferred to 25 mL volumetric flask and made up to volume. A blank digest was carried out in the same way [6,7]. The heavy metal concentrations were determined by an atomic absorption spectrophotometer (Shimadzu, AA-6701F). All metals were determined against standards.

Data analysis: Statistical analysis of data was carried out using SPSS statistical package programs. All experimental results were means ± standard error of three paralel measurements. The results were evaluated by using one-way ANOVA and any significant differences further evaluated using the Tukey multiple-comparison test. The level of significance was set at $P<0.05$. Pearson correlation test and linear regression analysis was used to check for significant relationships between heavy metal concentrations and fish size. The seasonal comparisons were performed using t- test .

RESULTS

In this study, the concentrations of metals in fish muscle tissue are given in *Table 1*. The concentration of metals in the samples are dependent on the species of fish. Some species accumulated the metals at high ratio. When metal levels in the muscle tissue of

Table 1. *Metal concentrations (µg/g dry wt) in some fish collected from Turkish coast of the Middle Black Sea (Mean±SE)*

Tablo 1. *Orta Karadeniz Bölgesinin Türkiye kıyılarından toplanan bazı balık örneklerinde metal konsantrasyonları (µg/g kuru ağırlık) (Mean±SE)*

Fish samples	Metal concentrations							
	Cu	Mn	Fe	Ni	Zn	Pb	Cd	Hg
Trachurus trachurus	1.79±0.12	10.72±0.88	21.17±1.14	4.68±0.72	27.70±1.00	0.60±0.07	0.012±0.002	ND
Alosa caspia	2.62±0.58	2.50±0.21	33.78±7.93	1.60±0.17	30.87±7.11	0.86±0.16	0.022±0.002	ND
Gobius cephalarges	2.72±0.69	8.56±1.45	26.17±1.35	4.75±0.79	23.30±1.01	0.51±0.10	0.020±0.007	ND
Psetta maxima	2.13±0.21	3.26±0.32	21.72±0.83	3.22±0.47	24.83±1.71	0.73±0.21	0.022±0.007	ND
Sarda sarda	1.74±0.18	3.53±0.48	25.96±2.73	3.04±0.24	19.55±1.20	0.90±0.11	0.025±0.005	ND
Pomatomus saltatrix	2.86±0.58	5.14±0.56	23.81±1.72	1.91±0.17	25.51± 0.92	1.26±0.21	0.025±0.002	ND
Merlangius euxmus	3.72±0.59	6.92±0.71	28.84±1.69	3.78±0.38	31.34±1.61	0.58±0.03	0.002±0.000	ND
Mullus barbatus	3.14±0.31	6.96±1.05	29.17±2.18	2.47±0.17	23.71±0.71	0.92±0.12	0.020±0.002	ND
Engraulis encrasicolus	2.73±0.21	3.93±0.76	26.06±2.14	3.12±0.37	26.25±1.67	0.70±0.07	0.035±0.005	ND
Spicara smaris	0.35±0.10	2.60±0.14	23.89±3.06	5.77±0.43	24.35±1.96	0.67±0.10	0.035±0.002	ND
Mean	2.38±0.36	5.41±0.65	26.06±2.47	3.40±0.39	25.74±1.88	0.77±0.12	0.022±0.003	ND

ND: *Not determined,* ***Mean±SE:*** *Mean ±Standart Error*

Table 2. *The seasonal changes of metal concentrations (µg/g dry wt) in of some fish collected from Turkish coast of the Middle Black Sea (Mean±SE)*

Tablo 2. *Orta Karadeniz Bölgesinin Türkiye kıyılarından toplanan bazı balık örneklerinde metal konsantrasyonlarının mevsimsel değişimi (µg/g kuru ağırlık) (Mean±SE)*

Season	Fish samples	Metal concentrations							
		Cu	Mn	Fe	Ni	Zn	Pb	Cd	Hg
Winter	*Trachurus trachurus*	1.31±0.16	11.2±0.76	22.51±1.02	6.14±0.34	25.40±3.18	0.56±0.08	0.002±0.001	ND
	Alosa caspia	2.70±0.26	2.56±0.17	33.56±1.80	1.32±0.11	30.34±1.92	0.71±0.11	0.018±0.004	ND
	Gobius cephalarges	2.75±0.34	9.44±1.88	25.00±1.60	5.96±1.08	21.40±4.13	0.50±0.14	0.016±0.009	ND
	Psetta maxima	2.01±0.27	2.64±0.27	22.94±1.92	2.54±0.61	25.62±2.14	0.86±0.09	0.021±0.007	ND
	Sarda sarda	1.02±0.27	2.87±0.57	22.92±2.50	3.54±0.38	15.32±5.10	1.15±0.17	0.024±0.004	ND
	Pomatomus saltatrix	2.78±0.27	4.48±0.73	26.56±2.73	1.89±0.23	23.48±5.75	1.24±0.05	0.020±0.004	ND
	Merlangius euxmus	3.70±0.26	7.33±0.83	29.93±1.91	3.88±0.45	30.60±2.68	0.54±0.04	0.001±0.001	ND
	Mullus barbatus	3.40±0.43	8.92±1.38	30.83±3.22	2.43±0.15	23.47±5.10	0.72±0.10	0.017±0.005	ND
	Engraulis encrasicolus	2.78±0.21	3.89±0.14	22.92±3.06	3.60±0.15	26.59±1.95	0.57±0.04	0.039±0.008	ND
	Spicara smaris	0.30±0.98	2.67±0.25	23.78±3.06	7.68±0.18	25.00±2.63	0.64±0.10	0.036±0.007	ND
	Mean	2.27±0.34	5.61±0.69	26.13±2.28	3.80±0.36	25.00±3.45	0.75±0.09	0.019±0.005	ND
Spring	*Trachurus trachurus*	2.27±0.20	10.24± 0.78	19.83±1.25	3.22±0.37	30.00±1.48	0.63±0.09	0.023±0.002	ND
	Alosa caspia	2.54±0.18	2.47±1.04	33.56±0.91	1.88±0.25	31.38±0.66	1.01±0.03	0.026±0.000	ND
	Gobius cephalarges	2.69±0.23	7.68±0.62	27.34±2.11	3.54±0.10	25.20±0.90	0.52±0.07	0.024±0.000	ND
	Psetta maxima	2.25±0.17	3.88±0.61	20.05±3.24	3.89±0.53	24.04±3.10	0.60±0.08	0.023±0.000	ND
	Sarda sarda	2.46±0.17	4.20±0.77	29.00±2.19	2.54±0.25	23.68±0.98	0.65±0.04	0.026±0.005	ND
	Pomatomus saltatrix	2.94±0.34	5.80±0.85	21.06±1.33	1.92±0.19	27.54±1.66	1.28±0.20	0.030±0.001	ND
	Merlangius euxmus	3.74±0.46	6.51±0.77	27.75±1.08	3.67±0.22	32.00±0.71	0.62±0.06	0.003±0.001	ND
	Mullus barbatus	2.88±0.30	5.00±0.12	27.51±1.00	2.50±0.43	23.95±0.95	1.12±0.20	0.023±0.003	ND
	Engraulis encrasicolus	2.68±0.25	3.97±0.92	22.92±3.24	2.63±0.22	25.91±0.71	0.83±0.08	0.031±0.003	ND
	Spicara smaris	0.40±0.13	2.65±0.84	24.00±0.71	3.86±0.18	23.70±0.89	0.70±0.07	0.034±0.009	ND
	Mean	2.48±0.24	5.21±0.73	25.97±1.70	2.90±0.27	26.80±1.20	0.79±0.09	0.024±0.002	ND

ND: *Not determined,* ***Mean±SE:*** *Mean ±Standart Error*

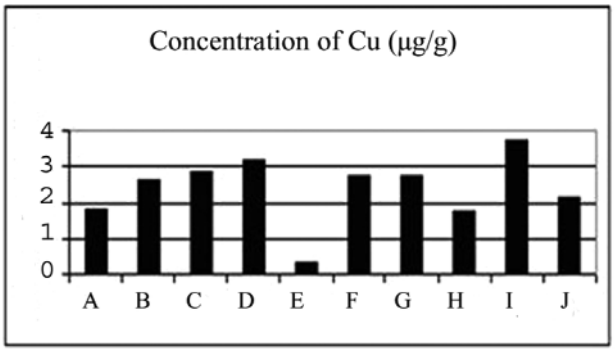

Fig 1. Distribution of Cu content in fish species. ***A:*** *Trachurus trachurus,* ***B:*** *Alosa caspia,* ***C:*** *Pomatomus saltatrix,* ***D:*** *Mullus barbatus,* ***E:*** *Spicara smaris,* ***F:*** *Engraulis encrasicolus,* ***G:*** *Gobius cephalarges,* ***H:*** *Sarda sarda,* ***I:*** *Merlangius euxmus,* ***J:*** *Psetta maxima*

Şekil 1. Balık türlerine göre Cu miktarının dağılımı. ***A:*** *Trachurus trachurus,* ***B:*** *Alosa caspia,* ***C:*** *Pomatomus saltatrix,* ***D:*** *Mullus barbatus,* ***E:*** *Spicara smaris,* ***F:*** *Engraulis encrasicolus,* ***G:*** *Gobius cephalarges,* ***H:*** *Sarda sarda,* ***I:*** *Merlangius euxmus,* ***J:*** *Psetta maxima*

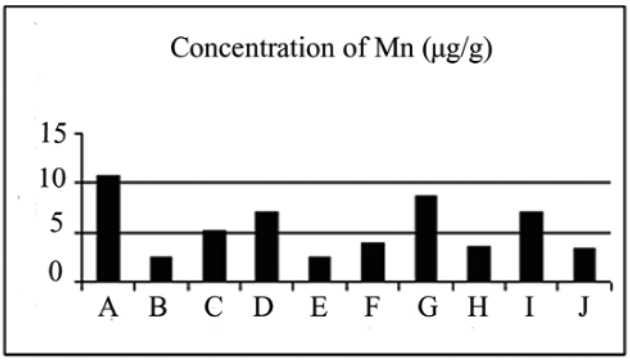

Fig 2. Distribution of Mn content in fish species. ***A:*** *Trachurus trachurus,* ***B:*** *Alosa caspia,* ***C:*** *Pomatomus saltatrix,* ***D:*** *Mullus barbatus,* ***E:*** *Spicara smaris,* ***F:*** *Engraulis encrasicolus,* ***G:*** *Gobius cephalarges,* ***H:*** *Sarda sarda,* ***I:*** *Merlangius euxmus,* ***J:*** *Psetta maxima*

Şekil 2. Balık türlerine göre Mn miktarının dağılımı. ***A:*** *Trachurus trachurus,* ***B:*** *Alosa caspia,* ***C:*** *Pomatomus saltatrix,* ***D:*** *Mullus barbatus,* ***E:*** *Spicara smaris,* ***F:*** *Engraulis encrasicolus,* ***G:*** *Gobius cephalarges,* ***H:*** *Sarda sarda,* ***I:*** *Merlangius euxmus,* ***J:*** *Psetta maxima*

fish were statistically compared, disparity between fish species (ANOVA, P<0.05) was considered to be significant.

Significant seasonal variations were detected in the heavy metal load of fish for all elements analyzed. The metal concentrations of tissues, manganese, nickel and iron were decreased from winter to spring, while the copper, lead, zinc and cadmium load increased. According to the t-test these differences in nickel and cadmium were statistically significant (P<0.05) but no significance was observed for other metals *(Table 2).*

Results of correlation analysis between the element concentrations of fish tissues and the size showed in *Table 3.* There was no statistically significant relationship between the metal content of the tissues and the fish length for all species (P>0.05).

Table 3. *The relationship between the length and heavy metal concentration of some fish species*
Tablo 3. *Bazı balık türlerinde ağır metal konsantrasyonu ile balık büyüklüğü arasındaki ilişki*

Data	Cu	Mn	Fe	Ni	Zn	Pb	Cd
Mullus barbatus							
R value	0.264	0.136	0.264	-0.085	-0.148	0.034	0.068
P value	0.143	0.457	0.143	0.643	0.418	0.850	0.708
Equation	Y=31.20+ (0.25525)X	Y=31.42+ (0.09868)X	Y=31.09+ (0.03011)X	Y=31.94+ (-0.05676)X	Y=31.91+ (-0.00669)X	Y=31.60+ (0.29695)X	Y=31.72+ (1.04452)X
Model P value	0.289	0.538	0.6273	0.593	0.824	0.663	0.8611
Pomatomus saltatrix							
R value	-0.035	-0.016	-0.184	0.086	-0.090	-0.101	0.179
P value	0.829	0.918	0.253	0.594	0.579	0.531	0.267
Equation	Y=13.19+ (-0.05209)X	Y=13.08+ (-0.00227)X	Y=13.25+ (-0.00764)X	Y=12.91+ (0.08120)X	Y=13.74+ (-0.02644)X	Y=13.29+ (-0.32946)X	Y=12.80+ (9.85622)X
Model P value	0.729	0.962	0.624	0.596	0.365	0.417	0.308
Engraulis encrasicolus							
R value	0.037	0.004	-0.313	0.044	-0.093	0.126	-0.040
P value	0.862	0.985	0.136	0.837	0.663	0.555	0.852
Equation	Y=6.90+ (0.03385)X	Y=7.05+ (-0.01360)X	Y=7.936+ (-0.03593)	Y=6.96+ (0.00811)X	Y=7.51+ (-0.01979)X	Y=6.90+ (0.14199)X	Y=6.83+ (4.24779)
Model P value	0.895	0.850	0.152	0.956	0.544	0.848	0.782
Trachurus trachurus							
R value	-0.166	-0.186	-0.148	-0.083	0.203	0.034	-0.014
P value	0.257	0.204	0.313	0.572	0.166	0.816	0.922
Equation	Y=12.80+ (-0.211580)X	Y=12.87+ (-0.05711)X	Y=12.88+ (-0.02193)X	Y=12.58+ (-0.04559)X	Y=11.88+ (0.01922)X	Y=12.44+ (-0.04614)X	Y=12.44+ (-1.69381)X
Model P value	0.336	0.284	0.385	0.680	0.503	0.920	0.888
Spicara smaris							
R value	-0.478	-0.529	-0.365	-0.188	-0.554	0.163	-0.109
P value	0.230	0.177	0.373	0.654	0.153	0.698	0.797
Equation	Y=9.50+ (-1.77920)X	Y=11.95+ (-1.18058)X	Y=9.45+ (-0.02434)X	Y=9.02+ (-0.02642)X	Y=10.72+ (-0.07576)X	Y=8.81+ (0.08718)X	Y=9.02+ (-4.16667)X
Model P value	0.118	0.141	0.545	0.927	0.203	0.943	0.789
Psetta maxima							
R value	0.264	0.136	0.264	-0.085	-0.148	0.034	0.068
P value	0.143	0.457	0.143	0.643	0.418	0.850	0.708
Equation	Y=31.20+ (0.25525)X	Y=31.42+ (0.09868)X	Y=31.09+ (0.03011)X	Y=31.94+ (-0.05676)X	Y=31.91+ (-0.00669)X	Y=31.60+ (0.29695)X	Y=31.72+ (1.04452)X
Model P value	0.289	0.538	0.6273	0.593	0.824	0.663	0.8611
Gobius cephalarges							
R value	0.291	0.201	0.245	-0.357	-0.148	0.125	0.114
P value	0.166	0.344	0.248	0.086	0.584	0.559	0.595
Equation	Y=10.53+ (0.16558)X	Y=10.81+ (0.00650)X	Y=10.28+ (0.02251)X	Y=10.92+ (-0.01128)	Y=11.41+ (-0.02332)X	Y=10.79+ (0.14146)X	Y=10.83+ (1.83342)X
Model P value	0.261	0.787	0.382	0.798	0.500	0.683	0.730
Merlangius euxmus							
R value	0.041	-0.128	0.144	-0.046	-0.059	0.119	-0.017
P value	0.777	0.382	0.325	0.754	0.686	0.420	0.907
Equation	Y=11.96+ (-0.00097)X	Y=11.98+ (-0.00456)X	Y=11.59+ (0.01259)	Y=11.98+ (-0.00778)	Y=12.00+ (-0.00139)	Y=11.59+ (0.61527)X	Y=11.95+ (1.51515)X
Model P value	0.991	0.879	0.339	0.888	0.917	0.277	0.932

Y *is metal concentration (µg/g) and* ***X*** *is fish lenght (cm),* ***R value:*** *Pearson correlation coefficients,* ***P values:*** *Levels of significance*

Table 3. *(Continue))*

Tablo 3. *(Devam)*

Data	Cu	Mn	Fe	Ni	Zn	Pb	Cd
Sarda sarda							
R value	0.091	0.682	0.160	-0.347	-0.014	0.059	0.036
P value	0.617	0.341	0.379	0.051	0.935	0.745	0.843
Equation	Y=21.42+ (0.18607)X	Y=21.31+ (0.12324)X	Y=21.42+ (0.01252)X	Y=22.50+ (-0.24723)X	Y=22.19+ (-0.02300)X	Y=21.41+ (0.40427)X	Y=21.75+ (-0.22136)X
Model P value	0.540	0.288	0.544	0.282	0.625	0.449	0.985
Alosa caspia							
R value	-0.003	-0.060	-0.286	0.007	0.057	-0.130	-0.068
P value	0.986	0.741	0.111	0.966	0.753	0.475	0.709
Equation	Y=13.72+ (0.01247)X	Y=13.90+ (-0.06247)X	Y=14.36+ (-0.02390)X	Y=13.76+ (-0.00940)X	Y=13.52+ (0.00924)X	Y=13.90+ (-0.21492)X	Y=13.85+ (-4.57143)X
Model P value	0.948	0.682	0.273	0.959	0.827	0.589	0.750

Y *is metal concentration (µg/g) and* ***X*** *is fish lenght (cm),* ***R value:*** *Pearson correlation coefficients,* ***P values:*** *Levels of significance*

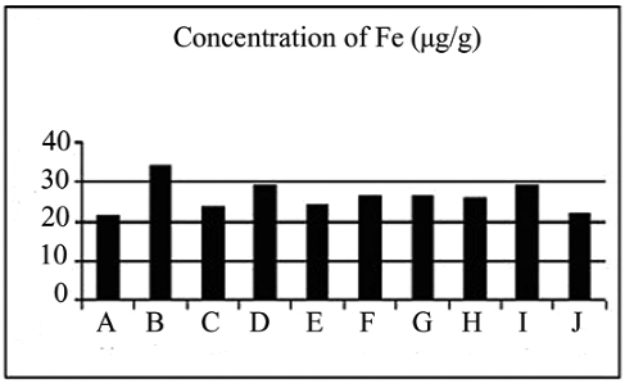

Fig 3. Distribution of Fe content in fish species. ***A:*** *Trachurus trachurus,* ***B:*** *Alosa caspia,* ***C:*** *Pomatomus saltatrix,* ***D:*** *Mullus barbatus,* ***E:*** *Spicara smaris,* ***F:*** *Engraulis encrasicolus,* ***G:*** *Gobius cephalarges,* ***H:*** *Sarda sarda,* ***I:*** *Merlangius euxmus,* ***J:*** *Psetta maxima*

Şekil 3. Balık türlerine göre Fe miktarının dağılımı. ***A:*** *Trachurus trachurus,* ***B:*** *Alosa caspia,* ***C:*** *Pomatomus saltatrix,* ***D:*** *Mullus barbatus,* ***E:*** *Spicara smaris,* ***F:*** *Engraulis encrasicolus,* ***G:*** *Gobius cephalarges,* ***H:*** *Sarda sarda,* ***I:*** *Merlangius euxmus,* ***J:*** *Psetta maxima*

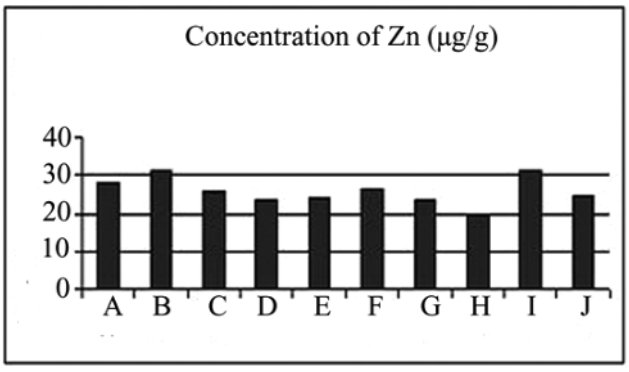

Fig 5. Distribution of Zn content in fish species. ***A:*** *Trachurus trachurus,* ***B:*** *Alosa caspia,* ***C:*** *Pomatomus saltatrix,* ***D:*** *Mullus barbatus,* ***E:*** *Spicara smaris,* ***F:*** *Engraulis encrasicolus,* ***G:*** *Gobius cephalarges,* ***H:*** *Sarda sarda,* ***I:*** *Merlangius euxmus,* ***J:*** *Psetta maxima*

Şekil 5. Balık türlerine göre Zn miktarının dağılımı ***A:*** *Trachurus trachurus,* ***B:*** *Alosa caspia,* ***C:*** *Pomatomus saltatrix,* ***D:*** *Mullus barbatus,* ***E:*** *Spicara smaris,* ***F:*** *Engraulis encrasicolus,* ***G:*** *Gobius cephalarges,* ***H:*** *Sarda sarda,* ***I:*** *Merlangius euxmus,* ***J:*** *Psetta maxima*

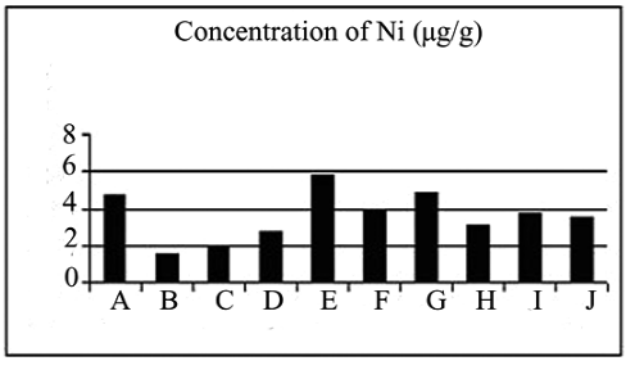

Fig 4. Distribution of Ni content in fish species ***A:*** *Trachurus trachurus,* ***B:*** *Alosa caspia,* ***C:*** *Pomatomus saltatrix,* ***D:*** *Mullus barbatus,* ***E:*** *Spicara smaris,* ***F:*** *Engraulis encrasicolus,* ***G:*** *Gobius cephalarges,* ***H:*** *Sarda sarda,* ***I:*** *Merlangius euxmus,* ***J:*** *Psetta maxima*

Şekil 4. Balık türlerine göre Ni miktarının dağılımı ***A:*** *Trachurus trachurus,* ***B:*** *Alosa caspia,* ***C:*** *Pomatomus saltatrix,* ***D:*** *Mullus barbatus,* ***E:*** *Spicara smaris,* ***F:*** *Engraulis encrasicolus,* ***G:*** *Gobius cephalarges,* ***H:*** *Sarda sarda,* ***I:*** *Merlangius euxmus,* ***J:*** *Psetta maxima*

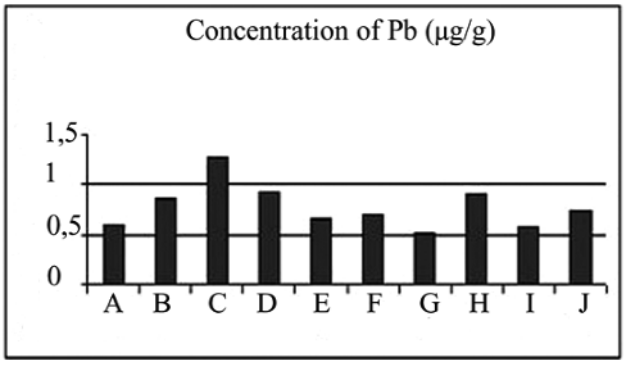

Fig 6. Distribution of Pb content in fish species ***A:*** *Trachurus trachurus,* ***B:*** *Alosa caspia,* ***C:*** *Pomatomus saltatrix,* ***D:*** *Mullus barbatus,* ***E:*** *Spicara smaris,* ***F:*** *Engraulis encrasicolus,* ***G:*** *Gobius cephalarges,* ***H:*** *Sarda sarda,* ***I:*** *Merlangius euxmus,* ***J:*** *Psetta maxima*

Şekil 6. Balık türlerine göre Pb miktarının dağılımı ***A:*** *Trachurus trachurus,* ***B:*** *Alosa caspia,* ***C:*** *Pomatomus saltatrix,* ***D:*** *Mullus barbatus,* ***E:*** *Spicara smaris,* ***F:*** *Engraulis encrasicolus,* ***G:*** *Gobius cephalarges,* ***H:*** *Sarda sarda,* ***I:*** *Merlangius euxmus,* ***J:*** *Psetta maxima*

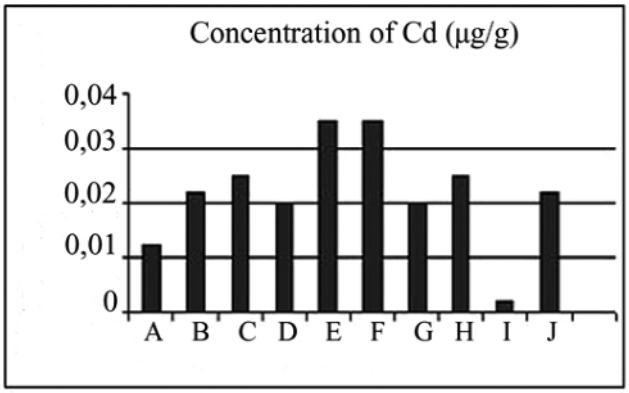

Fig 7. Distribution of Cd content in fish species ***A:*** *Trachurus trachurus,* ***B:*** *Alosa caspia,* ***C:*** *Pomatomus saltatrix,* ***D:*** *Mullus barbatus,* ***E:*** *Spicara smaris,* ***F:*** *Engraulis encrasicolus,* ***G:*** *Gobius cephalarges,* ***H:*** *Sarda sarda,* ***I:*** *Merlangius euxmus,* ***J:*** *Psetta maxima*

Şekil 7. Balık türlerine göre Cd miktarının dağılımı ***A:*** *Trachurus trachurus,* ***B:*** *Alosa caspia,* ***C:*** *Pomatomus saltatrix,* ***D:*** *Mullus barbatus,* ***E:*** *Spicara smaris,* ***F:*** *Engraulis encrasicolus,* ***G:*** *Gobius cephalarges,* ***H:*** *Sarda sarda,* ***I:*** *Merlangius euxmus,* ***J:*** *Psetta maxima*

DISCUSSION

Heavy metals, which constitute a considerable part of water and sea pollution, are among inseparable causes of environmental pollution. Heavy metals in sea creatures, though in small amounts, may accumulate and gradually reach levels causing toxic effect. On the other hand, although minerals are a basic requirement for sea creatures, excessive increase in their amount causes organic pollution. In this study, metal levels in the muscle tissue of fish was considered to be significant between different fish species (ANOVA, P<0.05). Similarly, Canli and Atli [8], and Kalay et al.[5] have also detected different values in metal levels in fish species. Metal levels in fish differ in their nutrition, the difference between the metabolic activities among fish species, surface width formed by gills, and ecological needs [5].

In this study, the metal concentrations of tissues, manganese, nickel and iron were decreased from winter to spring, while the copper, lead, zinc and cadmium load increased. Farkas et al.[9] were informed that Cd, Cu, Pb and Zn concentrations of fish have been decreased from autumn to spring, while Hg load increased. There is no statistically significant relationship between the metal content of the tissues and the fish length for all species (P>0.05). Similarly, Allen-Gil et al.[10] defined that there is no significant relationship between the heavy metal concentrations and fish size in Arctic charror burbot. The metal concentration and fish size correlations depend on several factors. Specific metabolism of the metal in the fish and the tissue type is one of the reasons and the other effect is opposing effects of ageing and tissue growth. On account of these reasons it was though that the metal concentration of fishes were originated from nutritional aspect and environment pollution more than fish size for that study.

The concentration of trace elements in water show disparities at different depth levels distinct separation of oxic and anoxic waters throughout depth affects redox potential in the environment. This change affects the distribution of trace metals throughout depth. Supporting these findings, in this study Fe level was found to be high in *Alosa caspia, Merlangius euxmus* and *Mullus barbatus* fished in middle and deep waters. Gulten and Atayener [11] found that Cu concentrations in deep waters were higher than the values in surface waters. Similar to this study, we have also detected in our research that Cu concentration was higher in *Merlangius euxmus* caught in deep waters. Copper is required for hemoglobin synthesis, cellular respiration, proper cardiac function, connective tissue development, keratinization, and tissue pigmentation [12].

The level of Cu in the fish samples ranged from 0.35 to 3.72 with mean of 2.38 µg/g *(Fig. 1) (Table 1).* The lowest and highest values of this element were observerd in *Spicara smaris* and *Merlangius euxmus,* respectively. The Cu levels are in agreement with literature values [10]. Mn concentration obtained ranged from 2.50 to 10.72 with mean of 5.41 µg/g *(Fig. 2).* The highest Mn levels were obtained for *Trachurus trachurus.* These values are similar to those reported by Usero et al.[13]. These levels were higher than other research [2,14].

The concentrations of Fe ranged from 21.17 to 33.78 µg/g *(Fig. 3).* The lowest and highest values of this element were observerd in *Trachurus trachurus* and *Alosa caspia,* respectively. Similar to study findings, Tuzen [2] has determined the Fe levels in *Clupea sprattus* as 25.48 µg/g. The concentrations of Ni, which is another element investigated in this study, has been detected to be approximately 3.40 µg/g in fish, and the highest and lowest amounts were found to be 5.77 µg/g and 1.60 µg/g in *Spicara smaris* and *Alosa caspia,* respectively *(Fig. 4).* Literature values for nickel were reported as 1.2-3.4 µg/g [15]. Zinc is an essential element for fish, as for other living groups; and it exists in the structure of many enzymes. Moreover, it is acknowledged that it has significant functions in protecting membrane structure. Since it is an essential element, fish have a capability of tolerating zinc [16]. The lowest zinc concentrations obtained were in *Sarda sarda* (19.55 µg/g) and the highest zinc levels were obtained in *Merlangius euxmus* (31.34 µg/g) *(Fig. 5).* In a previous study, the concentrations of zinc were 9.50 and 37.39 µg/g [2,8].

In our research, the approximate Pb level in fish was found to be 0.77 µg/g, while the highest and lowest values were detected in *Pomatomus saltatrix* (1.26 µg/g) and *Gobius cephalarges* (0.51 µg/g) respectively *(Fig. 6).* The study findings were similar to those reported by

Uluozlu et al.[17] that showed the lead concentration in fish samples was much higher than the recommended legal limits for human consumption.

Cadmium, which is a highly toxic metal, causes necrosis by accumulating especially in liver and kidney [18]. In our study, the highest amount of cadmium was detected in *Spicara smaris* and *Engraulis encrasicolus* (0.035 µg/g), while the lowest amount was found in *Merlangius euxmus* (0.002 µg/g) *(Fig. 7)*. Cadmium content in fish of the present study is in agreement with previous studies [19,20]. The European Community EC 21 has established the maximum permitted concentration of cadmium 0.1 µg/g. The values determined in our study results were below this limit.

Mercury, another toxic heavy metal, is of coal and pesticide origin, and it causes destruction of nerves and death in cases of intoxication. In this study, mercury was not detectable. Khansari et al.[19] found the Hg level in Thunnus spp as 0.011 µg/g, while Altindag and Yigit [22] detected the same level as 0.012 µg/g in Leuciscus cephalus and as 0.022 µg/g in *Cyprinus carpio*. Although the Cd and Hg levels in fish were found to be below the permitted limits at the end of our study, these heavy metals pose a risk for the environment due to their accumulation in fish.

Turkish legislation establishes maximum levels for four of the metals studied, above which human consumption is not permitted: 0.1 mg/kg for Cd, 20 mg/kg for Cu, 0.5-1 mg/kg for Hg and 0.4 mg/kg for Pb [23]. The concentrations of these metals measured in the muscle of the ten species studied were generally lower than the levels issued by (FAO/WHO) [24] standards and Turkish legislation. But lead concentrations in the fish tissues were higher than the maximum levels set by law.

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