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Assessment of Heavy Metals (Cadmium and Lead) in Vacuum Packaged Smoked Fish Species (Mackerel, ***Salmo salar*** and ***Oncorhynhus mykiss***) Marketed in Ankara (Turkey)*

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Özet: ***Ankara'daki marketlerde vakum paketli dumanlanmış balık türlerinde (Mackerel, Salmo salar ve Oncorhynhus mykiss) ağır metallerin (kadmiyum ve kurşun) belirlenmesi.*** Ankara'daki marketlerde, ticari olarak satılan dumanlanmış ve vakum paketlenmiş balık türlerindeki kadmiyum (Cd) ve kurşun (Pb) konsantrasyonları değerlendirilmiştir. 2004-2005 yılları arasında Ankara'daki hipermarketlerden toplam 73 adet dumanlanıp paketlenmiş balık fileto örneği temin edilmiştir. İz element konsantrasyonu GFAAS yöntemi ile ölçülmüştür. Cd için sınır değer kuru maddede 0.003-0.034 mg kg $^{-1}$ olarak bulunurken, Pb için bu değer 0.001-0.791 mg kg^{-1} olarak bulunmuştur. Analiz edilen tüm balık örneklerinde kadmiyum konsantrasyonu, Türkiye ve Avrupa Birliği Mevzuatı tarafından 0.05 mg kg^{-1} olarak belirlenen limitlerin altındayken, 27 balık örneğindeki Pb seviyesi Türkiye'deki kabul edilebilir limitleri aşmıştır (0.2 mg kg^{-1}). Buna rağmen, yüksek seviyelerde ölçülen ağır metal konsantrasyonlarında bile, haftada 400 g balık tüketen 60 kg ağırlığında bir yetişkinin tahmini haftalık Pb ve Cd alım miktarı, Joint FAO/WHO Expert Committee tarafından tavsiye edilen geçici tolere edilebilir haftalık alım miktarının (Cd için 7 µg-kg^{-1} ve Pb için 25 µg kg^{-1}) altında olduğu saptanmıştır.

Anahtar Kelimeler: Kadmiyum, Kurşun, Dumanlanmış balık, Graphite Furnace Atomic Absorption Spectrometry.

Abstract: Cadmium (Cd) and lead (Pb) concentrations in vacuum packaged smoked fish species that are commercially sold on the Ankara market were evaluated. A total of 73 smoked fish fillet samples were purchased from Ankara hypermarkets between 2004-2005. Trace metal concentrations were measured by GFAAS. The range found for Cd 0.003-0.036 mg kg^{-1} dry weight, while that for Pb was 0.001-0.791 mg kg^{-1} dry weight. Cadmium concentrations in all fish species analyzed (100%) were below 0.05 mg kg^{-1} the limit specified by Turkish and EU legislation, whereas Pb levels in 27 fish samples (36.9%) exceeded the Turkish acceptable limit of 0.2 mg kg^{-1}. However, at even the highest heavy metal concentrations measured, the estimated weekly intakes of Cd and Pb for a 60 kg adult consuming 400 g of fish per week would be below the provisional tolerable weekly intakes recommended by the Joint FAO/WHO Expert Committee of 7 µg-kg^{-1} body weight for Cd and 25 µg kg^{-1} body weight for Pb.

Key Words: Cadmium, Lead, Smoked fish, Graphite Furnace Atomic Absorption Spectrometry.

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Introduction

Many chemical elements that, are present in seafood are essential for human life at low concentrations, but can be toxic at high concentrations. Other elements such as mercury (Hg), cadmium (Cd) and lead (Pb) have no known essential function in life and are toxic even at low concentrations when ingested over a long period. Therefore many consumers regard any presence of these elements in fish as a hazard to health. (Oehlenschläger 2005). Trace metals are generally released in aquatic environments in different ways and accumulation of these metals is dependent on the concentration of the metal and the exposure period. Levels of heavy metals in fish have been widely reported (Romeo et al., 1999, Edwards et al., 2001, Gaspic et al., 2002, Satarug et al., 2003, Küçüksezgin et al., 2006). Cadmium has not been found to occur naturally in its pure state and its concentration seems to be directly proportional to zinc (Zn) and (Pb) concentrations. Use of Cd in agriculture and industry has been identified as a major source of wide dispersion into the environment and food. The major route of exposure to Cd for the non-smoking general population is via food; the contribution from other pathways to total uptake is small (Goyer 1991). The International Agency for Research on Cancer (IARC) classifies Cd as Class 1 "*The agent (mixture) is carcinogenic to humans*". Certain marine vertebrates contain markedly elevated Cd concentrations (Anon 1993b, Jarup et al., 1998). Lead pollution is multidimensional, including food processing techniques, traffic pollution and other factors. Lead poisoning is generally ranked as the most common environmental health hazard (Goyer 1991). The most common routes of human Pb exposure are inhalation of traffic exhaust fumes, inadvertent ingestion of Pb paint and consumption of Pb contaminated foods (Adekunle and Akinyemi 2004). However, the uptake of Pb through the food chain is of less importance since the concentration of Pb in fish does not increase with trophic level and age but with increasing concentration in the

water (Oehlenschläger 2005). Lead and cadmium are most commonly distributed environmental metal poisons and each of these persistent contaminants has been blamed for large-scale poisoning incidents. Several organisations such as Food and Agriculture Organisation (FAO) and the World Health Organisation (WHO) provide guidelines on the intake of trace elements by humans. The provisional tolerable weekly intake (PTWI) recommended by the Joint FAO/WHO Expert Committee for Cd and Pb are 7 µg Cd kg^{-1} body weight per week (Anon 2003) and 25 µg Pb kg^{-1} body weight per week respectively (Anon 1993a). Smoked fish is widely consumed all over the world because of its high protein, low saturated fat, fat soluble vitamins, essential minerals and omega fatty acids known to support good health (Ikem and Egiebor 2005). Heavy metal concentrations in organic samples such as fish products are mostly assayed using atomic absorption spectrometry (Sures et al., 1995, Tüzen 2003, Henry et al., 2004, Mendil et al., 2005, Türkmen et al., 2005). As low concentrations of Cd and Pb can cause serious toxic effects in organisms, it is necessary to determine the heavy metal contents of fish products that are intended for human consumption from the view of public health.

The aim of this study was to determine the concentrations of Cd and Pb in vacuum packaged smoked fish fillets of commercially important fish species consumed in Ankara.

Materials and Methods

A total of 73 vacuum packaged smoked fish samples including *Salmo salar* (48), mackerel (*Scomber scombrus*) (9) and *Oncorhynchus mykiss* (16) species were purchased from 5 different markets of Ankara between July 2004 and March 2005 and analysed in the laboratory. All samples were approximately at the same stage of their shelf-life.

Wet ashing method; all samples were homogenised and 2 g of homogenate were weighed, placed in vessel in the ashing unit with 10 ml 65% HNO_3 (Carlo Erba:7697-37-2), 5 ml 37% HCl (Merck:1.00314) and 2 ml 35% H_2O_2 (Merck:1.08600) and gradually heated (Velp DK-6 Heating Digester) (150°C for 1 h, 200°C for 2 h, 250°C for 1 h, 300°C for 2 hours). The solutions were allowed to cool at room temperature, transferred into 25 mL volumetric flasks and diluted to the mark with ultra-distilled water (Sartorius Arium 611) (Khansari et al., 2005, Tüzen 2003).

Chemical analyses; a graphite furnace atomic absorption spectrometer (GFAAS) Perkin Elmer model 800 equipped with electrodeless discharge lamp (EDL) (for Pb Serial no. 03449 EDL System 2; for Cd Serial no. 02484 EDL System 2) was used to determine the Cd and Pb concentrations of samples. Optimum temperature programmes were used for ashing and atomisation curves. The analyses were performed at 228.8 nm for Cd and 283.3 nm for Pb and a WinLab 32 computer programme was used for the analysis. Quantification was performed using calibration curves of standards.

Calibration standards; for Cd the calibration standards Cal std 1(1 ppb), Cal std 2(5 ppb) and Cal std 3 (10 ppb) were prepared from stock Cd Standard solution (Custom Grade Standard; 1007± 2 µg mL^{-1}, 2% HNO_3 (abs), Lot :X-QCD01106, Density:1.014 g mL^{-1}) with 0.3% of HNO_3. For Pb the calibration standards Cal std1 (10 ppb), Cal std2 (20 ppb) and Cal std3 (40 ppb) were prepared from stock Pb standard solution (Custom Grade Standard; 1006 ±2 µg mL^{-1}, 35% of HNO_3 (abs.), Lot:W-PBO211.4 Density-1.0002 g mL^{-1}) with 0.3% of HNO_3. Analytical blanks were run in the same way as the samples and concentrations were determined using standard solutions prepared in the same acid mixture. One-way analyses of variance (ANOVA) and Tamhane's test were used to determine whether Pb and Cd concentrations varied significantly between species, with values less than 0.01 ($p<0.01$) considered statistically significant. The statistical calculations were performed with SPSS, 11.5 versions (ref no: 651544).

Results and Discussion

The concentrations of Cd and Pb measured in fish samples (Table 1) varied from 0.003 to 0.036 mg kg^{-1} with a mean of 0.01367 mg kg^{-1} for Cd, and 0.001 to 0.791 mg kg^{-1} with a mean of 0.17710 mg kg^{-1} for Pb. Current Turkish legislation specifies the maximum heavy metal limits in fish meat as 0.05 mg kg^{-1} for Cd and 0.2 mg kg^{-1} for Pb, (Anon 2002) which are in line with the corresponding EU regulations (Anon 2005). Cadmium concentrations in all samples analysed (100%) were below the Turkish and EU limit of 0.05 mg kg^{-1}, whereas Pb levels in 27 of 73 samples (36.9 %) exceeded the Turkish and EU acceptable limit of 0.2 mg kg^{-1}. The Cd and Pb concentrations varied in the fish species analysed. The variations in Cd concentration (Fig. 1) among the different species were not statistically significant $F_{0,05}$ (2;72)=3,15, F_{Cd}= 0,916 ($p>0.05$), whereas those in the Pb concentration (Fig. 2) were statistically significant $F_{0,05}$ (2;72)=3,15, F_{Pb}= 5,188 ($p<0.01$). Four of 16 (25%) homebred smoked *Oncorhynchus mykiss* and 23 of 48 (47%) imported smoked *Salmo salar* samples were found to contain high concentrations of Pb. Whereas Pb concentrations in all mackerel samples were below the critical value. Using FAO/WHO (Anon 2003), values the provisional tolerable weekly intake of Cd and Pb for a 60 kg adult was estimated to be 420 and 1500 µg $person^{-1}$ $week^{-1}$ respectively. The maximum Cd level found in this study was 0.036 mg kg^{-1} and therefore a 60 kg adult could safely consume 58 meals (200 g portions) of fish per week. The maximum Pb concentration observed was 0.791 mg kg^{-1} and thus consumption of more than 9 meals of fish per week represents the tolerable weekly intake of lead. Heavy metal concentrations found in this study were considerably higher than those found previously found in fish Cd: 0.10-10 µg kg-1 and Pb: 0.10-491 µg kg^{-1} in Izmir Bay (Küçüksezgin et al., 2006). Eboh et al., (2006) reported Pb in the muscle, gills and liver tissue of fish at a range of 0.001-0.002 mg kg^{-1} but did not find any heavy metal residues in salmon and mackerel species. On the other hand, the mean concentrations of Cd (0.37-0.79 µg g^{-1}) and Pb (4.27-6.12 µg g^{-1}) reported by Canlı and Atlı (2005) in muscle tissues of six different fish species are higher than our results. The cadmium concentrations in tuna fish

samples from the gulf area of Iran (Khansari et al., 2005) were reported as 0.0046-0.0720 µg g^{-1} with a mean of 0.0223 µg g^{-1} which is similar to our results, whereas the lead concentrations in canned tuna samples were found to be 0.0162-0.0726 µg g^{-1} with a mean of 0.0366 µg g^{-1} (Khansari et al., 2005) i.e. lower than our results. Cadmium concentrations found in the present study varied from 0.003 to 0.036 mg kg^{-1} and were consistent with the findings of Gaspic et al., (2002) who determined 0.004-0.029 mg kg^{-1} in fish fillets belonging to two different fish species. The mean Cd concentrations found in our study are lower than those of (Munoz et al., 2005) who reported a mean of 0.277 mg kg^{-1} for Cd but our mean Pb concentrations are higher than those reported by the same researchers for fish and shellfish. The Pb concentration measured in this study varied from 0.001 to 0.791 mg kg^{-1} which is lower than the 0.156-0.284 mg kg^{-1} measured by Ersoy et al., (2006) in sea bass fillets, whereas it is similar to results presented by Gaspic et al., (2002) who determined 0.049-0.158 mg kg^{-1} in fish fillets belonging to two different fish species. Türkmen et al., (26) studied heavy metals concentrations in three commercially valuable fish species from Iskenderun Bay in the Mediterranean Sea, while Dalman et al., (2006) studied heavy metals (Cd, Pb) in sediments and fish in the south-eastern Aegean Sea (Turkey) in 2006. The present results generally are lower than theirs for Cd and Pb concentrations. Altındağ and Yiğit (2005), determined the heavy metal concentrations of fish species in Lake Beyşehir (Turkey) and found very high. Cd and Pb concentrations in muscle tissue of fish species compared to our findings. Furthermore, our Cd and Pb results in fish species are lower than those of Mendil et al., (2005), who reported the range 0.1-1.2 µg g^{-1} for Cd and 0.7-2.4 µg g^{-1} for Pb in seven fish species obtained from some lakes in Tokat, Turkey. These differences may be due to direct contamination of water by the metals concerned, the geochemical structure of different marine environments, differences in fish species, analytical methodology and other factors. This comparison of Cd and Pb concentrations in smoked fillets of *S. salar*, *O. mykiss* and mackerel fish species with Turkish statutory limits indicated that fish meat is a minor source of cadmium. The Cd levels found in this study do not constitute a risk factor for human health and were consistently below the Turkish acceptable limits, whereas the lead concentrations of 27 of 73 (36.9%) fish samples exceeded these limits. The estimated provisional tolerable weekly intake of Cd and Pb for an 60 kg adult is 420 and 1500 µg $week^{-1}$ respectively. According to our results, a person would be required to consume more than 58 portions (200g) of the monitored fish species per week to reach that limit for Cd and more than 9 portions for Pb, which is far more than the Turkish average weekly consumption of fish.

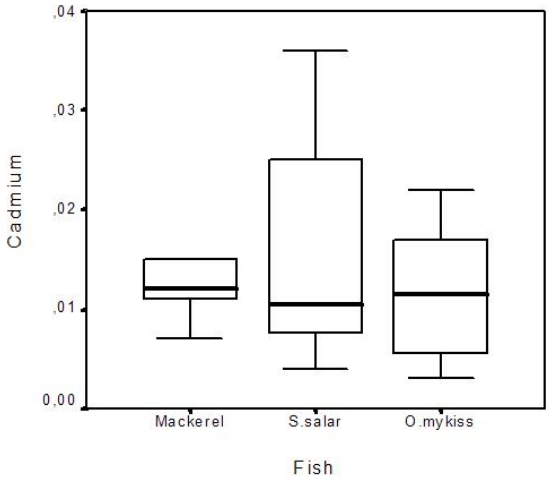

Fig 1. Cadmium concentrations in mackerel (*Scomber scombrus*), *Salmo salar* and *Oncorhynus mykiss* fish samples.

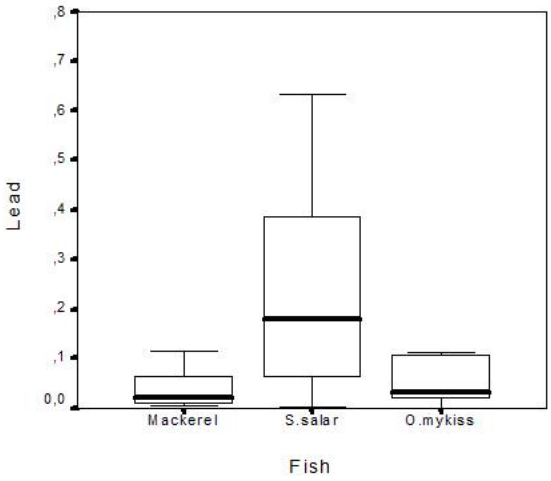

Fig 2. Lead concentrations measured in mackerel (*Scomber scombrus*), *Salmo salar* and *Oncorhynus mykiss* fish samples.

Table 1. Cadmium and lead concentrations (mg kg^{-1}) of the fish species analysed with range and means

		n	$\overline{X} \pm S_{\bar{x}}$	Min	Max	P Value	
Cd	Mackerel	9	0.01289±0.001306	0.07	0.021	(p>0.05)	a
	S. salar	48	0.01458±0.001370	0.04	0.036		a
	O. mykiss	16	0.01138±0.001589	0.03	0.022		a
	Total	73	0.01367±0.000984	0.03	0.036		
Pb	Mackerel	9	0.05033±0.020067	0.05	0.181	(p<0.01)	a
	S. salar	48	0.22331±0.026131	0.02	0.632		b
	O. mykiss	16	0.10975±0.049475	0.01	0.791		a
	Total	73	0.17710±0.021707	0.01	0.791		

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