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Heavy metal levels in several fish species from Turkey

Schwermetallgehalte verschiedener Fischarten aus der Türkei

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Summary

In this research, heavy metal (lead, arsenic, mercury, and cadmium) levels in edible muscle tissues of four different species of fish (flathead grey mullet [*Mugil cephalus* L., 1758], European pilchard [*Sardina pilchardus* W. 1792], gilt-head [sea] bream [*Sparus aurata* L., 1758], and European seabass [*Dicentrarchus labrax* L., 1758]) caught from Izmir Bay, open (Aegean) sea, and Karaburun fish farm (Izmir Bay) were determined. Mean heavy metal levels of all species of fish ranged below the upper limits as established by the Turkish Food Codex except Cd for three samples, and merely 2 % percent of all samples exceeded the corresponding thresholds. Values recorded in this study were markedly lower than most data from the literature from other areas of Turkey.

Keywords: arsenic, mercury, lead, cadmium, heavy metal, fish, contamination

Zusammenfassung

In dieser Studie wurden Schwermetalle (Blei, Arsen, Quecksilber und Cadmium) aus Muskelgewebe vier verschiedener Fischarten (Großkopfmeeräsche [*Mugil cephalus* L., 1758], Europäische Sardine [*Sardina pilchardus* W. 1792], Goldbrassen [*Sparus aurata* L., 1758] und Wolfsbarsch [*Dicentrarchus labrax* L., 1758]) bestimmt. Die Fische stammten aus der Bucht von Izmir (offene See und Fischzucht). Die mittleren Schwermetallgehalte lagen unterhalb der Obergrenzen des türkischen Lebensmittelkodexes. Bei drei Proben wurde die Obergrenze von Cadmium überschritten. Lediglich 2 % aller Proben überschritten die entsprechenden Grenzwerte. Die in dieser Studie erfassen Daten lagen deutlich niedriger als die in der Literatur angegeben Daten aus früheren Erhebungen aus anderen Gebieten der Türkei.

Schlüsselwörter: Arsen, Quecksilber, Blei, Cadmium, Schwermetall, Kontamination

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Introduction

Metals play an important role in living organisms. On one hand, they are in need of trace elements like Fe (iron), Co (cobalt), Zn (zinc), Mn (manganese), Cr (chrome), Mo (molybdenum), Se (selenium), Ni (nickel) and Sn (tin) for enzyme activity (Özan, 2005). However, exceeding amounts of these trace elements in cells may cause toxicity by effecting adversely the physiologic functions of the body (Çalta and Canpolat, 2002; Sivaperumal et al., 2007). On the other hand, Cd (cadmium), Hg (mercury), Pb (lead) and As (arsenic) are known as heavy metals which, when ingested, cannot be excreted from the body by natural physiological mechanisms and may cause toxicity in living organisms by accumulating in the body. As a result of the accumulation of these metals in seas or lakes, fish and other aquatic organisms may die. In fact, people's lives could be in danger if they consume these types of seafood (Çalta and Canpolat, 2002).

Generally, the toxic effects of heavy metals are originated from the complex structures formed among organic compounds and heavy metals. When these metals bind to O, S or N groups, they may disrupt the activity of important enzyme systems or may affect the structure of proteins. Consequently and in order to fulfill their functions, biological molecules may lose their number of properties and ultimately death of the cells may take place (Sütbeyaz et al., 2008).

Heavy metal levels in fish tissues are related to heavy metal concentration in the sea in where the animals live (Canpolat and Çalta, 2001). Temperature, oxygen concentration, composition and pH value of sea water, climatic conditions, general physichological and feeding behaviour of fish are the main factors affecting those heavy metal levels (Ekici and Yarsan, 2009).

Muscular tissue, livers and kidneys of fish are used to determine heavy metal contamination in fish and sea water (Olsvik, 2001). The highest heavy metal contamination level was determined for liver tissue of the common pandora *(Pagellus erythrinus)* living in the Aegean Sea (Katalay et al., 2005).

In a communication for fishery products released by the Food, Agriculture and Husbandry Ministery of Turkey, limits for several heavy metals were established. According to it, maximum limits for Cd, Hg, As and Pb amount to 0.05 µg/g, 0.50 µg/g, 1.0 µg/g, and 0.30 µg/g, respectively (Kayhan et al., 2006; Tüzen 2009).

Based on this, the present survey sought to to determine the heavy metal contents of several fish species living in Izmir Bay and in Aegean Sea. Turkey is surrounded, on three coast lines, by sea, i. e. the Black Sea to the north, the Cilician Sean to the south, and the Aegean Sea with the the Izmir Bay to the west, and all seas are important for the fishing industry. Since aquaculture has become increasingly important in Turkey, it comprises both free-ranging and cultured specimens.

Materials and Methods

In this research, daily caught fresh fish samples were purchased from Izmir Fish Bazaar. Tissues from flathead grey mullets (*Mugil cephalus;* FGM), European pilchards (*Sardina pilchardus;* EP), gilt-head (sea) breams (*Sparus aurata;* GHB) and European seabasses (*Dicentrarchus labrax;* ES) were used in the research. While for all fish species, samples were caught both from Izmir Bay (B) and from open sea (Aegean Sea; OS), sea breams and seabasses were also obtained from a fish farm in Karaburun, Izmir (F). Thus, there were ten different types of materials in this research according to their species and fishing area (i. e. FGM-OS, EP-OS, GHB-OS, ES-OS, FGM-B, EP-B, GHB-B, ES-B, GHB-F, and ES-F). Samples were brought to the laboratory immediately in thermoboxes at 4 ± 1 °C. Fish samples were washed under tap water for one minute, and then head, skin, internal organs, and fishbone were removed. In this way, the edible muscle tissue was used for heavy metal analysis.

Heavy metal analysis

0.5 g of fish samples were weighted in digestion tubes for microwave and then, 5 ml of nitric acid and 2 ml of hydrogen peroxide were added to each sample. Tubes were replaced in the microwave digestion unit (Berghof MWS-3) and samples were digested for 40 minutes at 200 °C under 40 psi pressure. After digestion finished, tubes were let to settle for 20 minutes for the samples to cool down. Then, digested samples were transferred into sample containers, completing the total volume of 10 ml by adding water for analysis of Pb, Cd and Hg. Regarding As analysis, 3 ml of HCl, 1 ml of KI and water were added to complete the total volume of 20 ml, whereas for Hg analysis, 1 ml of $KMnO_4$ was added to each sample before measuring in an atomic absorbtion spectrophotometer.

Pb, Cd, Hg and As levels in fish tissues were determined at wavelengths 220.353, 228.802, 253.652 and 193.696 nm, respectively. A nebulizer was used for Pb and Cd analysis whereas a hydrur system was applied for As and Hg analysis. All analyses were performed with a Perkin Elmer ICP-OES Optima 2100 DV model atomic absorbtion spectrophotometer.

Research was repeated three times, and findings were evaluated by SAS (Statistical Analysis System) programme. Statistic evaluation comprised variance analyses Duncan tests (SAS, 2001), and the model was CR (i. e., completely randomized).

Results and Discussion

Lead (Pb)

As seen from Table 1, highest Pb content (0.14 ± 0.07 µg/g) of open sea sea samples was determined in pilchards, followed by sea breans, while no Pb was found in mullets and seabasses. All Izmir Bay samples ranged below the the detection limit (<0.08 µg/g), and average Pb levels in sea bream and seabass samples caught in the Karaburun Fish Farm were ≤0.15 ± 0.01 µg/g. According to the Turkish Food Codex and Coomunication for Fishery Products (Anon., 2008), the highest acceptable limit for Pb in fish samples is 0.3 µg/g. From that point of wiew, Pb levels of all samples complied with this highest acceptable limit.

This data contrasts to results of previous studies obtained at different localisations. According to Topçuoğlu et al. (2002), average Pb levels in fish caught from Black Sea, Turkey, was 0.6 µg/g. Also Tüzen (2003) reported that average Pb level in Black Sea samples was higher (0.85 µg/g) than the acceptable limit. Aygün and Abanoz (2011) determined that average Pb levels in anchovy *(Engraulis encrasicolus)* and whiting *(Merlangius merlangus euxinus)* samples amounted to 0.4 µg/g and 0.9 µg/g, respectively.

Yılmaz (2003) reported that average Pb level of mullet samples from Iskenderun Bay (Cicilian Sea) was extremely high (7.45 µg/g). It is thought that this high Pb level was because of one of the biggest shipyards and the metal industry is located just near the bay. According to Türkmen et al. (2009), average Pb level in muscle tissues of sea bream was 2.314 µg/g. The same researchers discovered that the Pb concentration in muscle tissues of fish samples from the Aegen Sea was, on average, 0.65 µg/g. On the other hand, Aközcan (2009) reported that average Pb level in edible muscle tissues of Aegean pilchard samples was 1.6 µg/g. This suggests an improvement of the fish quality for this area.

Cadmium (Cd)

Cd was not detected in seabasses, regardless their origin (Tab. 1). Besides, the same was true for GHB-OS and FGHM-B. The highest average Cd levels were recorded for open sea pilchards and Izmir Bay sea breams.

It was determined that the fishing area had no significant effect on the Cd contents of fish samples (P>0.05), whereas the type of the fish did (P<0.05). On the other hand, Cd levels of sardines and sea basses were significantly different from each other (P<0.05).

According to Turkish Food Codex and Communication for Fishery Products (Anon., 2008), highest acceptable limit for Pb in fish samples in general is 0.05 µg/g, but a different limit (0.1 µg/g) was set for for pilchards. Thus, Cd levels of all samples ranged below the highest acceptable limit except for the samples EP-OS, GHB-B and GHB-F.

As with Pb, Cd contents in fish from other localisations reportedly ranged above the established thresholds, e. g. 0.35 to 0.48 µg/g in the Black Sea (Topçuoğlu et al., 2002; Tüzen, 2009; Mendil et al., 2010) and 0.20 µg/g in Iskenderun Bay (Ersoy and Çelik, 2010).

Mercury (Hg)

All samples contained Hg, with open sea and Izmir Bay seabrasses displaying the highest levels. All other mean values ranged <0,1 µg/g.

The effects of both fishing area and fish type on the Hg levels of fish samples were not siginificantly important (P>0.05).

Since the Turkish Food Codex and Communication for Fishery Products (Anon., 2008) established a threshold of 0.5 µg/g, most samples (98%) complied with this requirement. These results support the observation of Ulutarhan and Küçüksezgin (2007) who measured an average Hg concentration of 0.41 µg/g in Aegean samples, and of Gonül (2006) who recorded values between 0.05 µg/g and 0.22 µg/g for the Izmir Bay. Almost 20 years ago, Izmir bay fish still contained markedly high (0.91 µg/g) levels of Hg (Konta?, 1997). The recent data provided in this study and in the literature shows an improvement.

Arsenic (As) levels in edible muscle tissues of fish samples

Arsenic was not detected in any fish sample (Tab. 1).

TABLE 1: *Heavy metal levels in edible muscle tissues of fish samples [µg/g].*

	Sample		Pb (0.3)*	Cd (0.05)*	Hg (0.5)*	As (1.00)*
Open sea						
	Mullet	FGHM-OS	ND	0.03±0.02	0.04±0.03	ND
	Pilchard	EP-OS	0.14±0.07	0.06±0.02	0.07±0.01	ND
	Seabass	ES-OS	ND	ND	0.32±0.08	ND
	Sea bream	GHB-OS	0.10±0.07	ND	0.09±0.09	ND
Izmir Bay						
	Mullet	FGHM-B	ND	ND	0.02±0.00	ND
	Pilchard	EP-B	ND	0.03±0.01	0.05±0.01	ND
	Seabass	ES-B	ND	ND	0.15±0.08	ND
	Sea bream	GHB-B	ND	0.06±0.03	0.07±0.06	ND
Fish farm						
	Seabass	ES-F	0.11±0.01	ND	0.04±0.01	ND
	Sea bream	GHB-F	0.15±0.01	0.04±0.03	0.47±0.06	ND

* maximum residue level as permitted by the the Food, Agriculture and Husbandry Ministery of Turkey; ND = not detected

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According to Tüzen (2009), As levels of different species of fish samples caught from Black Sea were between 0.11 µg/g and 0.32 µg/g, i. e. below the Turkish threshold (1.0 µg/g). The average As level in mussel samples from Izmir Bay was 1.03 µg/g (Esen, 2006) whereas As levels of mussels from the Mediterrenean Sea were between 0.019 µg/g and 0.098 µg/g (Kayhan et al., 2006).

Conclusion

Fish growing in the Aegean Sea areals close to resp. in Izmir Bay generally yielded low levels of heavy metals. In fact, most samples ranged well below the national requirements. A comparison with data from previous surveys of the same area, and of surveys performed in other areas surrounding Turkey showed that contamination levels have improved in the Aegean Sea, while they eventually remain high for certain elements in other regions.

Conflict of interest

The authors declare that no conflicts of interest exist.

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