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Cadmium, Lead, Mercury and Copper in Fish from the Marmara Sea, Turkey

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Rapid industrialization and the discharge of potentially toxic trace metals into the marine environment has become a serious problem (Gaspic et al. 2002). Marine organisms, including fish, accumulate contaminants from the environment and therefore have been extensively used in marine pollution monitoring programs (Küçüksezgin et al. 2001). Much has also been written about metal levels as a whole in fish, water and sediment in particular areas (Usero et al. 2003; Navarro et al. 2006; Tüzen 2003; Türkmen et al. 2005). A metal such as Cu is an essential metal since it plays an important role in biological systems, whereas Hg, Cd and Pb are non-essential metals, as they are toxic, even in trace amounts. The aim of this work was to determine ranges and variations of potentially toxic trace metals (Cu, Hg, Cd and Pb) in the fish collected from various sampling points of the Marmara Sea since these fish are an important component of the human diet in this zone. The species we tested are commonly consumed by the local population in Turkey, thus we wanted to estimate the health risk for these seafood consumers.

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Materials and Methods

This is a descriptive study. All fish samples were collected from January to December 2005. Fish samples such as witting (*Merlangius merlangus*), grey mullet (*Mugil auratus*), piceral (*Macna smaris*), red mullet (*Mullus barbatus*), mussel (*Elliptio buckleyi* Lea, 1843), Bakalyaro hake (*Merluccius merluccius*), anchovy (*Engraulis encrasicolus*), two banded bream (*Diplotus vulgaris*), striped bream (*Pagellus erythrinus*), common sole (*Solea solea*), blue fish (*Pomatomus saltator*), pilchard (*Sardina pilchardus*), Atlantic mackerel (*Scomber scombrus*), scad (*Trachurus mediterraneus*), chub mackerel (*Scomber japonicus*), gav fish (*Belone belone*), Atlantic bonito (*Sarda sarda*), silverside (*Atherina boyeri*), blue fish (*Pomatomus saltator*), and shrimp are abundant and commercially valuable species in the Marmara Sea.

Fish (100 samples) were purchased from local fisherman and were brought to the laboratory on the same day. Sample preparation and analysis were conducted according to the procedure described by Bernhard (1976). Fish samples were homogenized in a blender and one gram of homogenate was digested. A microwave digestion system (Berghof MWS3+) was used to prepare the samples for analysis. In recent years, microwave digestion processes have been used in numereous studies (Küçüksezgin et al. 2001; Machado et al. 1999; Usero et al. 2003) owing to the advantages of this technique, which include speed of digestion and less possibility of contamination during the process. Samples (without skin) were mixed with 5 ml HNO_3(65%) and 5 ml H_2SO_4 in polypropylene vials. After 10 minutes of mixing, 1 ml H_2O_2 was added and samples were placed in a microwave (1 hour at 105°C). After digestion, the residues were diluted to 25 ml with HNO_3 (0.3%) (Canlı and Atlı 2003; Glumni et al. 1994; Stahr 1977; Sures et al. 1995). Instrument-calibrated standard solutions were prepared from commercial materials. Following acid digestion, all the samples were analyzed for 4 elements (Cu, Pb, Cd, and Hg) by atomic absorption spectrophotometer (AAS). Cu, Cd and Pb were analyzed in a graphite furnace (Perkin Elmer A Analyst 800 with Zeeman Background Corrector) with an autosampler. Detection limits for Cu, Cd and Pb were 0.014 µg/L, 0.002 µg/L and 0.05 µg/L, respectively. Wavelengths for Cu, Cd and Pb were 324.8 nm, 228.8 nm and 283.3nm, respectively. Also hydride-generation technique (detection limit 0.009 µg/L) was used for analysis of Hg. Wavelength was 253.7 nm for Hg. All reagents used for these analyses were of analytical grade. Statistical analysis of data was carried out using SPSS statistical package programs. The quality of data was checked by the analysis of certified reference material (fish:DORM-2, National Research Council, Canada).

Results and Discussion

A total of 100 fish samples were analyzed. It is well known that fish are able to concentrate heavy metals such as mercury (Hg), cadmium (Cd), copper (Cu), lead (Pb), and many others in their tissues; therefore, they can be used for monitoring heavy metal pollution of the environment. In the present study, four metals were analyzed in muscle tissue of fish collected from different regions of Marmara Sea. The heavy metal (Pb, Cd and Hg) and trace element (Cu) concentrations in fish species are given in Table 1. According to the Turkish Food Codex Regulation (1997), Hg, Pb, Cu and Cd levels of fish should not exceed 0.5, 1.0, 20 and 0.1 mg kg^{-1} (wet mass), respectively. The fish species analyzed are used for human consumption. Cd (1.122 ± 0.0535 mg kg^{-1}) and Hg (1.750 ± 0.0262 mg kg^{-1}) levels in the edible mussel from the Marmara Sea were higher than the maximum permissible value in Turkey. Generally, the overall mercury levels in Bakalyaro hake (0.518 ± 0.0340 mg kg^{-1}) and anchovy (0.550±0.0400 mg kg^{-1}) samples were higher than the maximum permissible value, while the mean mercury content in striped mullet, shrimp, blue fish (25 cm) and two banded bream was slightly lower in comparison to the maximum permissible value. In this study, Turkey maximum levels for Pb and Cu were not exceeded in the muscle of any of the fish analyzed.

Metal contents in mussels were evaluated in some studies (Bat et al. 1999; Çetinkaya 1996; Karadede and Unlu 2000; Kücüksezgin et al. 2001; Sunlu 2002; Şentürk 1993; Topçuoğlu 2002) in Turkey. Bat et al. (1999) determined Cu, Zn, Pb and Cd concentrations in the mediterranean mussel *Myltilus galloprovicialis* Lamarck, 1819from the Sinop Coast of the Black Sea. Seasonal

Table 1 Metal concentration mg kg^{-1} in fish species (expressed as mean concentration ± SD, n = 5)

Fish species	Hg (X±SD)	Pb (X±SD)	Cu (X±SD)	Cd (X±SD)
Witting	0.0352 ± 0.0079	0.207 ± 0.0336	9.487 ± 0.4540	0.054 ± 0.0303
Grey mullet	0.0074 ± 0.0011	0.124 ± 0.0178	1.890 ± 0.0905	0.036 ± 0.0210
Piceral	0.032 ± 0.0057	0.082 ± 0.0391	0.392 ± 0.0378	0.039 ± 0.0196
Red mullet	0.434 ± 0.0127	0.035 ± 0.0336	0.300 ± 0.0171	0.012 ± 0.0054
Mussel	1.750 ± 0.0262*	0.822 ± 0.0966	1.232 ± 0.0873	1.122 ± 0.0535*
Bakalyaro hake	0.518 ± 0.0340*	0.045 ± 0.0217	0.243 ± 0.0358	0.046 ± 0.0370
Anchovy	0.550 ± 0.0400*	0.099 ± 0.0188	3.492 ± 0.0446	0.027 ± 0.0353
Two banded bream	0.378 ± 0.0171	0.052 ± 0.0310	0.298 ± 0.0508	0.017 ± 0.0078
Striped bream	0.290 ± 0.0436	0.269 ± 0.0608	0.234 ± 0.0566	0.025 ± 0.0085
Common sole	0.329 ± 0.0224	0.133 ± 0.0256	0.370 ± 0.0210	0.022 ± 0.0072
Blue fish (15cm)	0.028 ± 0.0079	0.108 ± 0.0501	0.628 ± 0.0427	0.043 ± 0.0407
Pilchard	0.242 ± 0.0333	0.142 ± 0.0453	0.558 ± 0.0251	0.008 ± 0.0032
Atlantic mackerel	0.013 ± 0.0038	0.074 ± 0.0431	0.567 ± 0.0377	0.021 ± 0.0150
Scad	0.053 ± 0.0120	0.074 ± 0.0259	0.381 ± 0.0308	0.010 ± 0.0055
Chub mackerel	0.035 ± 0.0103	0.063 ± 0.0296	0.396 ± 0.0226	0.011 ± 0.0063
Gav fish	0.022 ± 0.0046	0.062 ± 0.0190	0.298 ± 0.0264	0.029 ± 0.0102
Atlantic bonito	0.374 ± 0.0361	0.228 ± 0.0222	0.854 ± 0.0552	0.032 ± 0.0178
Silverside	0.034 ± 0.0115	0.019 ± 0.0167	0.319 ± 0.0538	0.017 ± 0.0079
Shrimp	0.464 ± 0.0403	0.167 ± 0.0211	0.880 ± 0.0587	0.016 ± 0.0090
Blue fish (25cm)	0.421 ± 0.0468	0.270 ± 0.0423	1.104 ± 0.0594	0.012 ± 0.0104

* Higher than the maximum permissible value

differences were also evaluated in the same study and the levels of metals found were generally lower than the permitted levels by Bat et al. (1999). Sentürk (1993) studied Hg, Cd and Pb concentrations in mussels AAS. In that study, mussels were collected from different areas of the Marmara Sea. Hg, Cd and Pb contents for Anadolu Kavagı were 0.34 ppm, 0.15 ppm and 0.85 ppm, respectively; for Yenikapı 0.63 ppm, 0.70 ppm and 0.81 ppm respectively. Pb, Cd, Hg and Cu contents were 0.29–1.1, 0.08–0.46, 0.02–0.07 and 1.1–4.9 ppm, respectively, in mussels. Sunlu (2002) determined heavy metal levels in *M. galloprovincialis* Lamarck, 1819for the Bay of Izmir: Pb, Cd and Cu contents for five different parts of the Bay were 0.58–1.82, 0.04–1.12 and 0.32–3.25 ppm, respectively. Compared to our study, these Pb and Cu levels are higher, while the Cd levels are similar. Furthermore, the levels of Cu and Pb we observed are lower than those reported by Catsiki et al. (2004), where they found Cu and Pb levels of 4.10–6.94 and 0.59–3.26 ppm, respectively. Glynn et al. (2003) investigated trace metal concentrations in shellfish from Irish waters. Cd, Cu, Pb and Hg levels in mussel tissue were found to be 0.263, 8.33, 1.95 and 0.182 ppm, respectively. These findings were higher for Cd and Hg and lower for Pb and Cu than our findings. Maximum levels for Hg, Pb and Cd in foodstuffs, including bivalve mussels were evaluated in EU Commission Regulation 466/2001/EEC (as amended by Regulation 221/2002/EC). Standard levels for Cd, Pb, and Hg are 0.05 mg/kg, 0.2 mg/kg, and 0.5 mg/kg, respectively; in our study, Cd and Hg levels in Marmara Sea mussels were higher than the standard level dictated by EU regulation (2003).

Filazi et al. (2003) found muscle tissue in grey mullet collected from Black Sea contained Cu, Pb and Cd at 0.30–1.00, 0.57–1.12 and 0.10–0.40 μg kg $^{-1}$, respectively. In our study, we found higher levels of Cu, Pb and Cd than Filazi et al. (2003). Gaspic et al. (2002) have reported muscle tissue in hake collected from the Adriatic Sea to contain 4.1–29 μg kg^{1} Cd and 49–158 μg kg $^{-1}$ Pb: Cd and Pb levels in our study were higher. Türkmen et al. (2005) reported Cd, Pb and Cu in the muscle tissue of red mullet collected from the northeastern Mediterranean Sea at levels of 0.831 mg kg^{-1}, 1.808 mg kg^{-1}, 2.201 mg kg^{-1}, respectively. In our study, Cd, Pb and Cu were observed at lower concentrations than the Türkmen et al (2005) study. Canlı and Atlı (2003) found Cd, Pb and Cu concentrations higher than our study in the muscle tissue of silverside, grey mullet, chub mackerel and pilchard collected from the Mediterranean Sea. Compared to the results of Mormede and Davies (2001), slightly higher levels of Cd were found in whiting and hake in our study; lower median concentrations of Cu in whiting and Pb in whiting and Bakalyaro hake were observed in our study. In other studies, the highest concentrations of Hg, Pb, Cu and Cd were found in liver, showing the detoxification and accumulation role of that organ. There were very low levels of these metals in the muscle tissue. However, muscle is commonly analyzed because it is the main fish part consumed by humans and therefore has health risk implications (Henry et al. 2004). The concentrations of heavy metals observed in muscle tissue in our study are all below the Turkish Food Codex limits for human consumption. Mussels are recognized as a pollution bioindicator organism as they accumulate pollutants in their tissues at elevated levels in relation to pollutant biological availability in the marine environment (Bat et al. 1999; Machado et al. 1999). These heavy metals are introduced to the Marmara Sea by rivers, direct discharge of industrial wastes, and agricultural and municipal usage. In addition, the metal levels in the marine environment have increased due to oil pollution and airborne contaminants. Deep-water fisheries are becoming more and more important, and there is a paucity of chemical monitoring of these fisheries (Mormede and Davies 2001).

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