Assessment of Heavy Metals in Fourteen Marine Fish Species of Four Turkish Seas

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Heavy metal concentrations of Cd, Co, Cr, Cu, Fe, Mn, Pb, Ni and Zn in muscles and livers of fourteen fish species from seven stations of four Turkish Seas viz. Mediterranean, Aegean, Marmara and Black Sea, were monitored. Metal concentrations in muscles of fish species were found <0.01-0.43 mg kg\(^{-1}\) for cadmium, <0.01-0.41 mg kg\(^{-1}\) for cobalt, 0.03-2.08 mg kg\(^{-1}\) for chromium, 0.16-10.7 mg kg\(^{-1}\) for copper, 5.31-115 mg kg\(^{-1}\) for iron, 0.07-3.62 mg kg\(^{-1}\) for manganese, 0.01-3.43 mg kg\(^{-1}\) for nickel, 0.15-1.15 mg kg\(^{-1}\) for lead, 4.17-22.4 mg kg\(^{-1}\) for zinc, respectively. All metal concentrations in livers were higher than those of in muscles for the same species. Metal concentrations in the edible parts of fish were assessed for human consumption by comparison with Provisional Tolerable Weekly Intake (PTWI) and Provisional Tolerable Daily Intake (PTDI) values. The values of all metals in muscles of analyzed fish in the present study stayed below the established limit values. Consequently, it might be concluded that these metals in the edible parts of the examined species should not pose any public health problems.

[Key words: Metal contaminations, Fish, Tolerable intakes, Tissues, Turkish seas.]

Introduction

Tremendous portion of contaminants originating from either direct discharges or hydrological and atmospheric processes are ultimately deposited in aquatic ecosystems. Numerous studies have been carried out on metal accumulation in different fish species\(^1\)-\(^4\) from these ecosystems. Biomonitors respond specially to the bioavailable pollutant loads\(^5\). Among biomonitor organisms, fish have been popular targets of heavy metal monitoring programs in marine environments because sampling, sample preparation and chemical analysis are comparatively simpler, more rapid and less expensive than alternative choices such as water and sediments\(^6\).

Turkey is covered by seas on three sides with 8333 km long coastal line and fishing is considerable income sources for the country. The four seas, the Mediterranean, Aegean, Marmara and Black Sea, around Turkey each reflect a different ecological character. Seven sampling stations in the present study were selected from the major fisheries areas of Turkey. These areas support the significant amount in Turkish fish market. Therefore, determination of the metal contaminants in these locations directly concern with Turkish public health. Aim of this study was to determine the metal levels (Cd, Co, Cr, Cu, Fe, Mn, Pb, Ni and Zn) in muscles and livers of fourteen fish species from Turkish seas having different ecological characteristics, and to assess whether these fish acceptable for human consumption.

Materials and Methods

Fish samples were obtained from commercial fishing efforts of local fishermen from seven different sites along the coastal waters of Turkey from December 2004 to July 2005. These sampling sites are the coast and offshore of Sinop (SNP) in Black sea; the coast and offshore of Yalova (YLV) in the Marmara Sea; Northern Aegean Sea (NAS) and Central Aegean Sea (CAS) in Aegean Sea, the coast and of offshore Antalya Bay (AB), offshore and coast of Mersin Bay (MB) and offshore and coast of İskenderun Bay (IB) in northern east Mediterranean Sea (Fig. 1). Fourteen fish species (197 samples) examined in this study are shore rockling (Gaidropsarus mediterraneus L., 1758), so-iuy mullet (Mugil soiuy Basilewsky, 1855), European pilchard (Sardina pilchardus Walbaum, 1792), blotched picarel (Spicara maena L., 1758), tub gurnard (Trigla lucerna L., 1758), comber (Serranus cabrilla L., 1758), white seabream (Diplodus sargus L., 1758), oceanic puffer (Lagocephalus lagocephalus L., 1758), goldband goatfish (Upeneus moluccensis
Bleeker, 1855), brushtooth lizardfish (Saurida undosquamis Richardson, 1848), greater weever (Trachinus draco L., 1758), saddled seabream (Oblada melanura L., 1758), European hake (Merluccius merluccius L., 1758) and marbled spinefoot (Siganus rivulatus Forsskal, 1775). Specimens collected during the sampling period were frozen in prewashed polyethylene bags and frozen samples brought to the laboratory in ice chests. Samples from İskenderun Bay were brought to laboratory in ice chests within the sampling days, because the station is close by the laboratory. Total length and weight of the samples were measured to the nearest millimeter and gram before dissection. Approximately 0.5 gram sample of muscle and liver (the livers of 2-3 samples were pooled when it was lesser than 0.5 gram) from each fish were dissected, washed with distilled water, weighed, packed in polyethylene bags and stored at -18 °C until the performance of chemical analysis.

Chemical Analyses:
Tissues were homogenized and digested with 10 ml of HNO₃ (analytical grade) in Teflon vessels in microwave oven (CEM MARS-5 Closed Vessel Microwave Digestion System) using the following microwave digestion program: pressure 200 psi, ramp time 25 min., temperature 210 °C, maximum power 300 W, hold time 10 min. After cooling, residue was transferred to 25 ml volumetric flasks and diluted to level with deionized water. Before analysis, the samples were filtered through a 0.45 μm membrane filter. Sample blanks were prepared in the laboratory in a similar manner to the field samples. All metal concentrations were determined on wet weight basis as mg kg⁻¹. All samples were analyzed three times for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn by inductively coupled plasma optical emission spectrometer (ICP-OES, VARIAN VISTA-MPX OES). Standard solutions were prepared from stock solutions (Merck, multi element standard). A Dorm-2 certified dogfish tissue was used as the calibration verification standard. Recoveries between 88% and 113% were accepted to validate the calibration. Results showed good agreement between the certified and the analytical values, the recovery of elements being partially complete for most of them. Extraction and analyses of samples were performed in the Food Quality Control Laboratory of Hatay.

Statistical Analyses:
A logarithmic transformation was done on the data to improve normality. To test the differences among species, one way ANOVA was performed. Post hoc test (Tukey) was applied to determine statistically significant differences following ANOVA. Possibilities less than 0.05 were considered statistically significant (p<0.05). All statistical calculations were performed with SPSS 13.0 for Windows.

Results and Discussion
Muscles and livers were chosen as target organs for assessing metal accumulation since, the concentrations of metals in muscles reflect the metal concentration in waters, whereas the concentrations in liver represent storage of metals by fish. The concentrations of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn found in the muscle and liver tissues of fourteen fish species from seven stations along the Turkish seas are presented in Table 1 and 2, together with their means and standard errors, respectively. Metal levels in the muscles of examined species were generally lower than those in livers for the same species within the same sites. Increased metal concentrations in liver may represent storage of sequestered products in this organ. Iron was the highest, and cadmium and cobalt were generally the lowest in both muscle and liver of analyzed fish species in the present study. Similar situations were reported by many researchers.
Cadmium concentrations in examined fish ranged from <0.01 mg kg\(^{-1}\) in both *M. soiuy* (SNP) and *S. maena* (NAS) to 0.39 mg kg\(^{-1}\) in *S. undosquamis* (MB) for muscles, and from 0.03 mg kg\(^{-1}\) in *T. luctera* (YLV) to 1.53 mg kg\(^{-1}\) in *M. merlucius* (IB) for livers. In the literature, cadmium levels have been reported as 0.008-1.13 mg kg\(^{-1}\) for muscles of fish from Marmara Sea\(^{12}\), 0.02 mg kg\(^{-1}\) for muscles of fish from Mumbai, India\(^{13}\), 0.02-1.32 mg kg\(^{-1}\) for muscles of fish from Indian fish markets\(^{14}\), <0.02-0.24 mg kg\(^{-1}\) for muscles of fish from Black Sea coast\(^{15}\), 0.09-0.48 mg kg\(^{-1}\) for muscles of fish from middle Black Sea coast\(^{6}\).

Cobalt concentrations ranged from <0.01 mg kg\(^{-1}\) in *M. soiuy* (SNP) to 0.41 mg kg\(^{-1}\) in *U. moluccensis* (MB) for muscles, and from 0.07 mg kg\(^{-1}\) in *G. mediterraneus* (SNP), *S. pilchardus* (NAS), *S. undosquamis* (AB and IB) to 1.77 mg kg\(^{-1}\) in *U. moluccensis* (MB) for livers. Cobalt concentrations in the literature have been reported as 0.07 mg kg\(^{-1}\) for muscles of fish from Mumbai, India\(^{13}\), 0.02-0.67 mg kg\(^{-1}\) for muscles of fish from Indian fish markets\(^{12}\), 0.03-0.44 mg kg\(^{-1}\) for muscles and 0.11-1.45 mg kg\(^{-1}\) for livers of fish from four Turkish seas\(^{3}\). Our cobalt levels were approximate with literature values.
Chromium concentrations in analyzed fish ranged from 0.11-0.46 mg kg\(^{-1}\) for muscles of fish from the İskenderun Bay, Turkey\(^5\), 0.59-1.69 mg kg\(^{-1}\) for muscles of fish from the Black and Aegean seas, Turkey\(^6\), 0.15-5.06 mg kg\(^{-1}\) for muscles of fish from western coast of United Arab Emirates\(^7\), 0.234-9.49 mg kg\(^{-1}\) for muscles fish from Marmara sea\(^8\), 0.09-0.49 mg kg\(^{-1}\) for muscles of fish from Black and Aegean seas, Turkey\(^9\).

Copper levels ranged from 0.16 mg kg\(^{-1}\) in *M. soiuy* (SNP) to 10.7 mg kg\(^{-1}\) in *M. merluccius* (CAS) for muscles, and from 1.24 mg kg\(^{-1}\) in *T. lucerna* (YLV) to 26.7 mg kg\(^{-1}\) in *S. rivulatus* (IB) for livers. In the literature, copper have been reported as 2.19-4.41 mg kg\(^{-1}\) for muscles and 18.2-203 mg kg\(^{-1}\) for livers of fish from Mediterranean Sea\(^9\), 3.4-8.3 mg kg\(^{-1}\) for muscles and 20.8-260 mg kg\(^{-1}\) for livers of fish from Yumurtalık coast of İskenderun Gulf\(^10\), 1.63-24.9 mg kg\(^{-1}\) for muscles of fish from western coast of United Arab Emirates\(^7\), 0.234-9.49 mg kg\(^{-1}\) for muscles fish from Marmara sea\(^8\), 0.15-5.06 mg kg\(^{-1}\) for muscles of fish from Black and Aegean seas, Turkey\(^9\), 18.5-72.3 mg kg\(^{-1}\) for muscles of fish from Black and Aegean seas, Turkey\(^9\), 0.49-3.9 mg kg\(^{-1}\) for muscles of fish from the Black and Aegean seas, Turkey\(^6\), 0.09-0.49 mg kg\(^{-1}\) for muscles of fish from Black and Aegean seas, Turkey\(^9\).
manganese concentrations were generally in agreement with literature.

Manganese concentrations ranged from 0.07 mg kg\(^{-1}\) in \textit{T. lucerna} (YLV) to 3.62 mg kg\(^{-1}\) in \textit{S. pilchardus} (CAS) for muscles, and from 0.39 mg kg\(^{-1}\) in \textit{S. maena} (YLV) to 7.61 mg kg\(^{-1}\) in \textit{T. lucerna} (IB) for livers. In the literature, manganese concentrations have been reported in the range of 0.092-9.23 mg kg\(^{-1}\) for muscles of different fish species from coastal waters of Caspian Sea\(^{23}\), 11.1-72.9 mg kg\(^{-1}\) for muscles of fish from Turkey\(^{24}\), 0.14-3.36 mg kg\(^{-1}\) for muscles of fish from Indian fish markets\(^{14}\), 0.11-1.20 mg kg\(^{-1}\) for muscles and 2.17-24.2 mg kg\(^{-1}\) for livers of fish\(^{25}\), 0.18-2.78 mg kg\(^{-1}\) for muscles and 0.47-9.90 mg kg\(^{-1}\) for livers\(^{26}\). Manganese levels in the present study were generally within the range of literature.

Nickel concentrations in fish ranged from 0.03 mg kg\(^{-1}\) in \textit{T. lucerna} (YLV) to 3.43 mg kg\(^{-1}\) in \textit{S. rivulatus} (IB) for muscles, and from 0.16 mg kg\(^{-1}\) in \textit{T. lucerna} (YLV) to 10.1 mg kg\(^{-1}\) in \textit{U. moluccensis} (MB) for livers. In the literature nickel levels were reported as 1.89-6.07 mg kg\(^{-1}\) for muscles and 1.70-11.2 mg kg\(^{-1}\) for livers of fish from Northeast Mediterranean Sea\(^{27}\), 0.03-0.69 mg kg\(^{-1}\) for muscles of fish from Indian fish markets\(^{14}\), 0.02-4.22 mg kg\(^{-1}\) for muscles and 0.40-9.70 mg kg\(^{-1}\) for livers of fish from coastal waters of Turkey\(^{8}\), 1.92-5.68 mg kg\(^{-1}\) for muscles of fish from Black and Aegean seas\(^{11}\). Nickel concentrations in the present study were generally within the range of literature.

Lead contents ranged from 0.15 mg kg\(^{-1}\) in \textit{M. merluccius} (IB) to 1.15 mg kg\(^{-1}\) in \textit{M. merluccius} (CAS) for muscles, and from 0.33 mg kg\(^{-1}\) in \textit{S. rivulatus} (AB) to 5.80 mg kg\(^{-1}\) in \textit{S. undosquamis} (MB) for livers. In the literature lead levels have been reported in the range of 2.98-6.12 mg kg\(^{-1}\) for muscles and 8.87-41.2 mg kg\(^{-1}\) for livers of fish from Mediterranean Sea\(^{9}\), nd-0.40 mg kg\(^{-1}\) for muscles and 0.03-1.73 mg kg\(^{-1}\) for liver fish from Adriatic and Ionian seas\(^{5}\), 1.26-2.09 mg kg\(^{-1}\) for muscles of fish\(^{4}\), 0.04-1.31 mg kg\(^{-1}\) for muscles and 0.86-1.53 mg kg\(^{-1}\) for livers of fish from Turkish seas\(^{18}\), 0.19-0.47 mg kg\(^{-1}\) for muscles and 0.52-0.71 mg kg\(^{-1}\) for livers of fish from Yelkoma Lagoon, northeastern Mediterranean\(^{10}\). Lead concentrations in the present study have showed similarities with the literature values.

Zinc levels in fish ranged from 3.74 mg kg\(^{-1}\) in \textit{O. melanura} (CAS) to 22.4 mg kg\(^{-1}\) in \textit{T. lucerna} (NAS) for muscles, and from 11.5 mg kg\(^{-1}\) in \textit{T. draco} (IB) to 69.2 mg kg\(^{-1}\) in \textit{M. merluccius} (CAS) for livers. In the literature zinc levels have been reported in the range of 12.5-201 mg kg\(^{-1}\) for muscles of different fish species from coastal waters of Caspian Sea\(^{23}\), 4.36 mg kg\(^{-1}\) for muscles of fish from İskenderun Bay, Turkey\(^{9}\), 3.71-122.8 mg kg\(^{-1}\) for muscles of fish from western coast of United Arab Emirates\(^{21}\), 4.49-11.2 mg kg\(^{-1}\) for muscles and 26.2-43.5 mg kg\(^{-1}\) for livers of fish from Turkish seas\(^{18}\). Zinc concentrations in the present study have the similar levels with the literature values.

One way ANOVA performed to test the differences between species and sites (Table 1 and 2). In livers, the differences among the metal levels by both species and sites were statistically significant with the exception of manganese. On the other hand, in muscles, the differences were statistically significant for all metals (p<0.05).

The tolerable daily and weekly intakes were estimated by means of references for economically important fish species consumed by adult people in Turkey (Table 3). Average daily fish consumption in Turkey is 20 g per person\(^{28}\). This is also equivalent to 140 g per person per week. EWI (estimated weekly intake) and EDI (estimated daily intake) values presented in Table 3 were estimated by assuming that a 70-kg person will consume 20 g fish/day which is equal to 140 g fish/week. EWI values of metals for an adult (\(µg/70\) kg body weight) consuming 140 g fish/week were estimated using the maximum metal levels in Table 1 for each species [EWI (\(µg/70\) kg body weight/week)=Maximum levels of metal (\(µg/kg\)) multiplied by fish consumption (kg/70 kg body weight/week)]. Then, EDI values were calculated from EWI values. Table 3 also compares the estimated EWI and EDI to recommended values (PTWI and PTDI). As can be seen in Table 3, the estimated EWI and EDI values for economically important fish examined in the present study were below the recommended values\(^{29-30-31}\) (Table 3).
**Conclusion**
Statistically significant differences were determined among the mean metal values obtained from fish species investigated along the Black Sea, Marmara Sea, Aegean Sea and Mediterranean Sea. For muscles, Zn in *T. lucerna* from NAS, Mn in *S. pilchardus* and Cu, Fe and Pb in *M. merluccius* from CAS, Cd in *S. undosquamis* and Cr in *S. pilchardus* from MB, Ni in *S. rivulatus* from IB were higher than other species and sites. Elevated Cr levels in both MB and IB stations might be the result of natural chromium mines through the Northeastern Mediterranean. Results of this study supply valuable information about metal contents in sampled fish species along the Turkish seas, and consequently, indicate the environmental contamination along the coastal areas. Moreover, these results are important to evaluate both the chemical quality of fish and the possible risk associated with their consumption. Because PTWI and PTDI values estimated for examined fish and metals were below the established values by various authorities,** it may be concluded that consumption of these species is not a problem on human health.

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**References**

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**Table 3** — The comparison with recommended values and the estimated daily and weekly intakes for some economically important fish species examined in this study.

<table>
<thead>
<tr>
<th>Metal</th>
<th>PTWI a</th>
<th>PTDI b</th>
<th>EWI c</th>
<th>M. soiuy d EWI d (EDI)</th>
<th>S. pilchardus EWI (EDI)</th>
<th>M. merluccius EWI (EDI)</th>
<th>S. undosquamis EWI (EDI)</th>
<th>S. cabrilla EWI (EDI)</th>
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<tbody>
<tr>
<td>Cd</td>
<td>7</td>
<td>490</td>
<td>70</td>
<td>-</td>
<td>50.4 (7.2)</td>
<td>30.8 (4.4)</td>
<td>51.8 (7.4)</td>
<td>28.0 (4.0)</td>
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<tr>
<td>Cu</td>
<td>3500</td>
<td>245000</td>
<td>35000</td>
<td>22.4 (3.2)</td>
<td>671 (95.8)</td>
<td>1498 (214)</td>
<td>168 (24.0)</td>
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<td>Fe</td>
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<td>392000</td>
<td>56000</td>
<td>6020 (860)</td>
<td>13608 (1944)</td>
<td>16100 (2300)</td>
<td>6720 (960)</td>
<td>11228 (1604)</td>
</tr>
<tr>
<td>Ni</td>
<td>35</td>
<td>2450</td>
<td>350</td>
<td>165 (23.6)</td>
<td>409 (58.4)</td>
<td>84 (12.0)</td>
<td>442 (63.1)</td>
<td>157 (22.4)</td>
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<tr>
<td>Mn</td>
<td>980</td>
<td>68600</td>
<td>980</td>
<td>71.4 (10.2)</td>
<td>507 (72.4)</td>
<td>204 (29.1)</td>
<td>111 (15.8)</td>
<td>202 (28.8)</td>
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<td>25</td>
<td>1750</td>
<td>250</td>
<td>32.3 (4.6)</td>
<td>126 (18)</td>
<td>161 (23.0)</td>
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<td>7000</td>
<td>490000</td>
<td>70000</td>
<td>788 (113)</td>
<td>1526 (218)</td>
<td>1372 (196)</td>
<td>1205 (172)</td>
<td>1086 (155)</td>
</tr>
</tbody>
</table>

**Notes:**
- PTWI for 70 kg adult person (µg/week/70 kg body weight).
- PTDI, Permissible Tolerable Daily Intake (µg/day/70 kg body weight).
- EWI, Estimated Weekly Intake in µg/week/70 kg body weight.
- EDI, Estimated Daily Intake in µg/day/70 kg body weight.
- WHO recommends a TDI (Tolerable Daily Intake) of 5 µg/day/kg body weight, i.e. 350 µg/day for a 70-kg person.
- EPA recommends a RfD (Reference Dose) of 0.14 mg/day/kg body weight, i.e. 9800 µg/day for a 70-kg person.
- Provisional Tolerable Weekly Intake (PTWI) in µg/week/kg body weight
- Mean weekly fish consumption in Turkey is 0.14 kg per person.


28 FAO., Fisheries and Aquaculture, Turkey (2008).

29 EPA., Manganese compounds (2008).
