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Trace Metal Contents in Fish Species from Ataturk Dam Lake (Euphrates, Turkey)

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Abstract

The Zn, Cu, As, Cd, Hg and Pb levels of the popular species (*Silurus triostegus, Acanthobrama marmid*, *Aspius vorax, Capoeta trutta*, *Carasobarbus luteus*, *Chalcalburnus mossulens* and *Cyprinus carpio*) of Ataturk Dam Lake (Euphrates, Turkey) were studied to estimate the risk of human consumption and pollution of Euphrates River which is important for Turkey, Syria and Iraq. Trace metal amounts differed between the species ($P<0.05$) even they were living in similar habitats. The variations of measured heavy metals (mg/kg d.w.) were 10.27-19.74 for Zn; 0.101-2.785 for Cu, 0.164-0.279 for As; ND (Not determined)-0.649 for Hg; ND-0.236 for Pb. Cd was not determined during the study. Regarding the Zn, Cu, Cd, and As contents, the samples were safe for human consumption. Mercury and lead were not detected in some of the samples, but their amounts exceeded the limits in *S. triostegus* and *A. marmid*, respectively. It was concluded that the fish from Ataturk Dam Lake are not heavily burdened with metals, but they should be controlled periodically to avoid excessive intake of trace metals by human, and to monitoring the pollution of aquatic environment.

Keywords: Fish, heavy metal, seafood, freshwater.

Atatürk Baraj Gölü (Fırat, Türkiye) Balıklarındaki İz Element Miktarının Belirlenmesi

Özet

Türkiye, Irak ve Suriye için önem taşıyan Fırat Nehri'ndeki kirliliğin ve buradaki yaygın balık türlerinin insan tüketimi açısından riskinin belirlenmesi amacıyla Atatürk Baraj Gölü'ndeki (Fırat, Türkiye) *Silurus triostegus, Acanthobrama marmid, Aspius vorax, Capoeta trutta*, *Carasobarbus luteus*, *Chalcalburnus mossulens,* ve *Cyprinus carpio*'te Zn, Cu, As, Cd, Hg ve Pb seviyeleri tespit edilmiştir. Farklı türlerin içerdiği iz elementlerin miktarı benzer ortamlarda yaşamalarına karşın farklılık ($P<0,05$) göstermiştir. Analiz edilen iz elementlerin miktarları Zn için 10,27-19,74; Cu için 0,101-2,785, As için 0,164-0,279; Hg için TE (Tespit edilmemiş)- 0,649; Pb için TE-0,236 (mg/kg) arasında değişmektedir. Çinko, Cu, Cd ve As miktarları bakımından örnekler insan tüketimi açısından güvenlidir. Cıva ve kurşun ise bazı örneklerde tespit edilmemiş, ancak Hg miktarı bazı *S. triostegus* örneklerinde; kurşun ise bazı *A. marmid* 'lerde sınırları aşmıştır. Atatürk Baraj Gölü'ndeki balıkların ağır metalle önemli düzeyle kontamine olmadıkları, ancak insanların tüketim yoluyla aşırı ağır metal almasını önlemek için bunlarda düzenli kontrollerin yapılması ve su kirliliğinin gözlenmesi gerektiği anlaşılmaktadır.

Anahtar Kelimeler: Balık, ağır metal, su ürünü, tatlısu.

Introduction

Ataturk Dam Lake on the Euphrates River (Turkey) has 81,700 hectares of surface area, 48,700,000,000 m^3 of total water deposit, and it is the largest dam lake of Turkey (Oymak *et al*., 2001). Besides the dense population, industry and agriculture also developed around this lake; and therefore, the contamination of Ataturk Dam Lake increased in recent years. The probable pollution is important either for Turkey or for Syria and Iraq due to the route of Euphrates River (Karadede *et al*., 2004).

It is known that heavy metals are the most important forms of pollution and they may accumulate in the tissues of fish which are often at the top of the aquatic food chain. Fish may concentrate large amounts of metals from the water and they might be toxic for human consumption (Papagiannis *et al*., 2004). The effects of trace metals on human health are of great interest today, especially for

aquatic food products. Therefore estimation of the trace metals in fish became important to estimate freshwater pollution and the risk potential of human consumption (Dural *et al*., 2007; Göksu *et al*., 2003). Likewise, many studies have been published on the trace metals in freshwater fish (Alam *et al*., 2002; Ay *et al*., 1999; Chi *et al*., 2007; Farkas *et al*., 2000; Gumgum *et al*., 1994; Yang *et al*., 2007). There are a few studies on trace metals in some of the fish caught from Ataturk Dam Lake (Karadede and Unlu, 1998; 2000; Karadede *et al*., 1997; Karadede *et al*., 2004). In recent years, data on trace metals in the fish caught from Ataturk Dam Lake became very important due to the petroleum leakage to Atatürk Dam Lake by a breakdown of Batman–Yumurtalık pipeline (BOTAŞ) on 13th April, 2005 (Anonymous, 2005).

Zinc, copper, arsenic, cadmium, mercury and lead are considered to be harmfull for human when their amount is over the limits in fish muscle (Anonymous, 2002). It is known that *Silurus triostegus*, *Acanthobrama marmid*, *Aspius vorax, Capoeta trutta*, *Carasobarbus luteus, Chalcalburnus mossulensis* and *Cyprinus carpio* are the most common species, and they are considered to be an essential part of the diet in the region (Kuru, 1978; Karadede and Unlu, 2000). The aim of this study is to determine the Zn, Cu, As, Cd, Hg and Pb levels of the most popular species from Ataturk Dam Lake, therefore to estimate the pollution of Euphrates River, which is important for Turkey and for Syria and Iraq.

Materials and Methods

Fish samples were caught from Ataturk Dam Lake on Euphrates River (Figure 1), Turkey during the catching season (February-March) of 2008. The temperature, pH, and dissolved oxygen (DO) values of Ataturk Dam Lake were 15.90±1.15°C, 8.27±0.12, and 7.86±0.82 mg/L, respectively. Gill-nets of various mesh sizes were used for catching. The sex, ages, length and weight of the samples were shown in Table 1. Samples were iced in straphore boxes, transferred to the laboratory, and their lengths and weights were measured immediately. Then, the muscles were grounded and stored as frozen in plastic cups until time for analysis.

The Ethos D (Type Ethos plus 1) microwave lab station purchased from Milestone Inc. (Monroe, Ct, USA) was used to digest fish samples prior to metal analysis. Thermo electron X7 inductively coupled plasma mass spectrometry (ICP-MS), model X series; UK was used to analyze digested samples for total metals. The following elements were measured using the ICP-MS: Mercury (Hg), Zinc (Zn), Cooper (Cu),

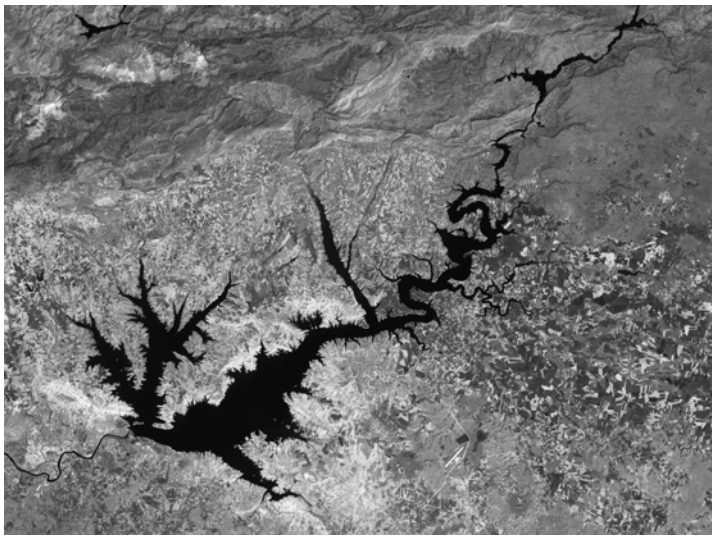

Figure 1. The map of Ataturk Dam Lake, on the Euphrates River (Turkey).

Table 1. Biometric parameters of the samples

Species	Sex	Ages	FL/TL (mm)	Weight (g)
Silurus triostegus	1♂/1♀	7–8	717.5 ±31.8	2309.0 ± 75.4
Aspius vorax	2♀	7–9	537.5 ±60.1	1476.5±598.9
Cyprinus carpio	3♂/2♀	5–7	340.6 ±101.0	701.4 ± 605.4
Cyprinus carpio	2♂/1♀	3–4	268.3 ±28.4	292.3 ±97.3
Carasobarbus luteus	2♂/3♀	4–5	269.0 ±43.6	256.8 ± 133.9
Capoeta trutta	2♂/4♀	5–8	371.7 ±68.1	538.8 ±306.8
Chalcarburnus mosulensis	7♂/5♀	2–4	202.6 ±13.8	48.3 ±9.3
Acanthobrama marmid	3♂/3♀	3–5	210.2 ±43.5	94.0 ±58.7

Cadmium (Cd), Lead (Pb) and Arsenic (As). For each sample, between 0.3 and 0.5 g of fish muscle (wet weight) was weighed and placed in a Teflon digestion vessel with 7 ml of concentrated (65%) nitric acid (HNO_3) and 1 ml 30% hydrogen peroxide (H_2O_2). The sample in the vessel containing concentrated nitric acid was then subjected to a microwave program as follows: Step 1: 25-200°C for 10 min at 1000W; Step 2: 200°C for 10 min at 1000 W. Digests were finally made up with deionised water to 25 ml in acid washed standard flasks. The concentrations of mercury, zinc, cooper, cadmium, lead, and arsenic in the fish digests were measured with the ICP-MS. The instrument detection limits on the ICP-MS were 50 ppt for Hg, 2 ppt for Cd, 10 ppt for Pb, 20 ppt for Cu, 100 ppt for Zn, and 25 ppt for As. Calibration standards were purchased from High-Purity Standards (P.O. Box 41727 Charleston, SC 29423, USA): Hg:1000±3 µg/mL in 2% HNO_3 catalogue no: 100033-1, Cd:1000±3 µg/mL in 2% HNO_3 catalogue no: 10008-1, Pb: 1000±3 µg/mL in 2% HNO_3 catalogue no: 100028-1, Cu:1000 ± 3 µg/mL in 2% HNO_3 catalogue no: 100014-1, Zn: 1000±3 µg/mL in 2% HNO_3 catalogue no: 100068-1, As:1000±3 µg/mL in 2% HNO_3 catalogue no: 10003-1. The standards were appropriately dilute and used to calibrate the ICP-MS before metal determinations in samples (EPA, 1994). ICP-MS operating conditions: Nebulizer gas flow 0.91 L/min, Radio frequency (RF) 1200 W, Lens voltage 1.6 V, Cool Gas 13.0 L/min, Auxiliary Gas 0.70 L/min. The observed and certified values of trace metal concentrations were presented in Table 2 (catalogue no. ERMI-CE278, LGC Promochem, Middlesex, UK).

The descriptive statistics (mean, standard deviation,) and one –way analysis of variance (ANOVA) were conducted using the SPSS 11.0 software. Significance was established at $P<0.05$ (Sümbüloğlu and Sümbüloğlu, 2002).

Results and Discussion

It is known that arsenic, mercury, lead and cadmium are the most commonly distributed environmental metal poisons (Reilly, 2002). They are accumulated in human tissues and may be the cause of some diseases (Rodríguez *et al*., 2003; Yilmaz *et al*., 2007). It is also known that fish consumption is the only significant source of methyl mercury for the public (Rice *et al.,* 2000). The maximum levels of As, Cd, Hg and Pb were proposed as 1.0 mg/kg d.w., 0.05 mg/kg d.w.w, 0.50 mg/kg d.w. and 0.20 mg/kg d.w., respectively for muscle meat of fish (Turk Gida Kodeksi, 2002; EU 2005). The Codex Alimentarius (2002) reported the limit value for lead in fish as 0.20 mg/kg d.w., and FDA (2001) proposed 1 mg/kg d.w. for Hg.

Determination of the concentrations of Cu and Zn in fish is another important subject both with respect to nature management and human consumption of fish (Amundsen *et al*., 1997). Turk Gida Kodeksi, (2002) sets the maximum limit for Zn as 50 mg/kg d.w., and for Cu as 20 mg/kg d.w. in the muscles of fish. Papagiannis *et al.* (2004) studied the copper and zinc levels in freshwater fish from Lake Pamvotis (Greece), and reported Cu and Zn levels for *C. carpio* as 3.08 mg/kg d.w. and 52.81 mg/kg d.w., respectively. They mentioned that there are no guidelines on acceptable levels of Cu and Zn in fish suggested by EEC or FAO/ WHO.

In our study Zn was the highest value among the metals studied, and *C. luteus* was containing Zn (19.74 mg/kg d.w.) higher than the other species. However, this value was still below the limits. The amount of Cu was between 0.101-2.785 mg/kg d.w. and As was between 0.164-0.279 mg/kg d.w. during the study, and samples were in the safety permissible levels for human consumption. Cadmium was not detected in any fish species studied. Mercury and lead were also not detected in some of the samples, but their amounts exceeded the limits in *S. triostegus* and *A. marmid*, respectively. As it was shown in (Table 3), the amounts of trace metals differ between the species ($P<0.05$) even they were living in similar habitats. Likewise, different heavy metal levels were observed between various species of fish in similar studies (Karadede *et al*., 2004; Karadede and Unlu, 2007). It was mentioned that heavy metal levels in different species depend on biometric properties of the fish (Linde *et al*., 1998; Al-Yousuf *et al.*, 2000), and their feeding habits (Amundsen *et al*., 1997; Romeoa *et al*., 1999; Mormede and Davies, 2001; Watanabe *et al*., 2003).

Karadede and Unlu (2000) studied the concentrations of some trace metals in various species from Ataturk Dam Lake (Euphrates, Turkey). They did not determine Cd, Hg and Pb in the fish muscles, and reported lower amounts of Zn and Cu than the

Table 2. Observed and certified values of trace metal concentrations, as mg/kg d.w., in standard reference materials (n = 3)

Elemental Concentrations (mg/kg d.w.)	Certified value	Uncertainty	Observed value
Hg	0.196	0.009	0.198
Cd	0.348	0.007	0.476
Cu	9.45	0.13	9.66
Zn	83.11	1.70	84.68
Pb	2.00	0.04	2.03
As	6.07	0.13	6.41

Table 3. The trace metal concentrations (mg/kg d.w.) in the muscles of fish, caught from Ataturk Dam Lake (Euphrates, Turkey)

	Zn	Cu	As	Cd	Hg	Pb
Silurus triostegus	12.38±0.21 [a]	0.101±0.003 [a]	0.264±0.005 [a]	ND*	0.649± 0.007 [a]	ND*
Aspius vorax	10.46±0.18 [b]	0.215±0.002 [b]	0.272±0.007 [ab]	ND	0.315± 0.005 [b]	ND
Cyprinus carpio (common)	17.45±0.39 [c]	0.385±0.006 [c]	0.176±0.005 [c]	ND	ND	ND
Cyprinus carpio (mirror)	10.85±0.13 [d]	0.414±0.023 [d]	0.207±0.011 [d]	ND	ND	0.018±0.001 [a]
Carasobarbus luteus	19.74±0.37 [e]	0.258±0.001 [e]	0.196±0.001 [e]	ND	0.056±0.000 [c]	ND
Capoeta trutta	10.27±0.10 [b]	0.241± 0.003 [e]	0.192±0.009 [e]	ND	ND	ND
Chalcalburnus mossulensis	13.72±0.20 [f]	0.465±0.020 [f]	0.164±0.001 [f]	ND	0.287±0.001 [d]	ND
Acanthobrama marmid	16.94±0.30 [g]	2.785±0.030 [g]	0.279±0.009 [b]	ND	0.056±0.000 [c]	0.236±0.001 [b]

*ND= Not Determined

[a, b, c,d,e,f,g] = Different letters in the same column show significant differences among samples($P<0.05$)

limits similar to those in our study.

There are various studies on the trace metal levels in *C. carpio* from different inland waters. Mendil and Uluozlu (2007) studied the trace metal levels in *C. carpio* from 6 different lakes in Tokat, Turkey and estimated Pb values between 0.8-2.8 mg/kg d.w., and Zn as 18.4-48.6 mg/kg d.w. The Cd level of *C. Carpio*, caught from Lake Beyşehir (Turkey) was reported as 0.543 mg/kg d.w., Pb content as 0.303 mg/kg d.w. and Hg 0.022 mg/kg d.w. by Altindag and Yigit (2005). The trace metals in *C. carpio* from Taihu Lake, China were represented as 0.021 mg/kg d.w. Cd, 0.177 mg/kg d.w. Pb, and 25 mg/kg d.w. Zn (Chi *et al.*, 2007). In this study, Zn, Cu and as levels of common carp were estimated as 17.45 mg/kg d.w., 0.385 mg/kg d.w. and 0.176 mg/kg d.w. respectively. The amount of Zn was 10.85 mg/kg d.w., Cu was 0.414 mg/kg d.w. and As was 0.207 mg/kg d.w. for mirror carp. Cadmium or mercury were not determined in the muscles of these fish. Even the muscles of common carp was not containing Pb, a low amount of this metal (0.018 mg/kg d.w.) was determined in mirror carp. It is clear that, the metal levels in *C. carpio* from various inland waters are higher than that of our study.

Karadede and Unlu (2007) did not determine Pb in the muscle of *S. triostegus*, caught from the Tigris River, Turkey. They also reported the average Cu content as 3.05 mg/kg d.w., and Zn content as 8.76 mg/kg d.w.. The amount of Cu and Zn in the muscle of *Silurus triostegus*, caught from Ataturk Dam Lake were reported as 4.27 mg/kg d.w.and 10.94 mg/kg d.w., respectively by Karadede *et al.* (2004). As it was presented in 4, Zn and Cu contents in *S. triostegus* were 12.38 mg/kg d.w., and 0.101 mg/kg d.w., respectively. It was seen that our samples containing lower Cu, but higher Zn than the former literatures.

In another study, Turkmen and Ciminli (2007) determined the trace metal levels in the muscles of *Carasobarbus luteus* from the Lake Golbasi (Turkey). They reported lower amounts of Zn and Cu, but higher Cd and Pb than our results determined for the same species.

Karadede and Unlu (2000) reported the amounts of Cu and Zn for *A. marmid, C. trutta* and *C. mossulensis*, caught from Ataturk Dam Lake (Euphrates) as 0.81 mg/kg d.w.and 8.71 mg/kg d.w., 1.68 mg/kg d.w.and 5.32 mg/kg d.w., 2.41 mg/kg d.w.and 17.96 mg/kg d.w., respectively. These results were below the limits similar to those in our study.

Conclusions

The results of this study show that trace metal contents of the samples, caught from Ataturk Dam Lake (Euphrates, Turkey) were generally below the limits. However, Hg content in *S. triostegus* and Pb content in *A. marmid* slightly exceeded the limits, probably due to the petroleum leakage to Atatürk Dam Lake by a breakdown of Batman–Yumurtalık pipeline (BOTAŞ) on 13th April, 2005 (Anonymous, 2005). Therefore, it was concluded that the fish are not heavily burdened with metals, but a danger must be considered depending on the agricultural and industrial developments in this region. The fish from Ataturk Dam Lake should be controlled periodically to avoid excessive intake of trace metals by human, and to monitor the pollution of aquatic environment.

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