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Concentration of heavy metals in water and chub, *Leuciscus cephalus* (Linn.) from the river Yildiz, Turkey

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Abstract: *The concentration of heavy metals (Cu, Fe and Zn) were determined by atomic absorption spectrophotometry in the river water and the edible muscle tissues of chub, Leuciscus cephalus, from river Yildiz, Turkey, and in the waste water. The following results were found in the water of the river Yildiz: Cu 0.03-0.53, Fe 0.91-1.96 and Zn, 0.53-1.49 μgl^{-1}, in the waste water: Cu 0.20-0.52, Fe 1.22-2.29 and Zn 0.92-1.46 μgl^{-1} and in the edible muscle of chub: Cu 1.00-3.79, Fe 7.21-17.04 and Zn 4.12-18.33 $\mu g\, g^{-1}$ wet weight respectively. Among the heavy metals studied Pb, Cd, Co, Cr, Ni and Mn were not detected in the river water, waste water and chub samples. Heavy metal contents in these samples were evaluated and the highest concentrations of Cu, Fe and Zn were found in the muscle tissue. The levels of the heavy metals were detected in decreasing order as iron > zinc > copper. All the samples contained comparatively lower amounts of metals as suggested by international and national regulatory bodies. Thus, we recommend periodic monitoring of these metals in the fish consumed by local people.*

Key words: *Heavy metals, River water, Waste water, Fish, River Yildiz*
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Introduction

Increasing population, urbanization and industrialization in the past century have resulted in increased domestic and industrial effluent being discharged into the aquatic system (Ajmal *et al*., 1988; Ekpo and Ibok, 1999). These wastes are a potential source of heavy metal pollution in the aquatic environment (Pfeiffer *et al*., 1986; Unlu *et al*., 1996; Muley *et al*., 2007). In recent years, programmes for the monitoring river pollution, including the monitoring of heavy metals, have been initiated in Turkey (Gey, 1985; Goksu *et al*., 2003; Karadede *et al*., 2004; Tezcan and Ozbay, 1984).

All heavy metals are potentially harmful to most organisms at certain level of exposure and absorption (Yilmaz, 2003; Ozdilek *et al*., 2007). As distinct from organic substances, they can migrate and accumulate in different components of natural ecosystems (water, soil, bottom deposits and living organisms). Most heavy metals are supposed to accumulate in aquatic animals and pass their toxic effects onto the upper links of the trophic chain, including human beings (Karadede and Unlu, 2000; Sindhe and Kulkarni, 2005; Yigit and Altindag, 2006). The contamination of a river with heavy metals may have a devastating effect on the ecological balance of the aquatic environment with the diversity of aquatic organisms becoming limited in accordance with the extent of the contamination (Canli *et al*., 1998; Samanta *et al*., 2005).

The river Yildiz is one of the major tributaries of the river Kizilirmak, which is the largest river in Turkey. In the province of central Anatolia, this river drains and receives effluent water discharged from hot spring water located in a recreational area. This may increase the magnitude of environmental pollution in the near future. The effects of the hot spring water on the river Yildiz have not yet been clearly identified and little attention has been paid to pollution control in relation to the possible impact of metals on the environment.

The aim of this study was to determine the concentration of heavy metals in the river water and the edible muscle tissues of chub, *Leuciscus cephalus* from the river Yildiz, Turkey and in the wastewater discharged hot spring water.

Materials and Methods

Study area: The study area is located in the city of Sivas, central Anatolia. The river Yildiz runs from the Yildiz mountain to the river Kizilirmak, and is about 140 km long. A total of 6 sites were selected as representative regions of the river and are shown in Fig. 1: locality (loc.) 1: below Zengi village; loc. 2: Cigil Creek; loc. 3: upper Hayranli village; loc. 4: Hot spring water; loc. 5: below Yildiz site; loc. 6: Incesu village. The sites were chosen according to the location of principal sources of pollution. For example, locality 5 receives effluent discharged from hot spring water. The other locations receive domestic, agricultural effluents and sewage water from areas surrounding the river.

Sample collection: The main fish species of the river Yildiz are *Barbus plebejus, Leuciscus cephalus, Capoeta capoeta, Capoeta tinca* and *Cyprinus carpio*. Of them, *Leuciscus cephalus* (Family: Cyprinidae) was selected for the present study and caught in each of the four seasons from February to November 1993 from four (1, 3, 5 and 6) localities (Fig. 1) in the river Yildiz, where these species are widely distributed in the aquatic environment and has commercial importance. These fishes have omnivorous nature (Geldiay and Balik, 1988).

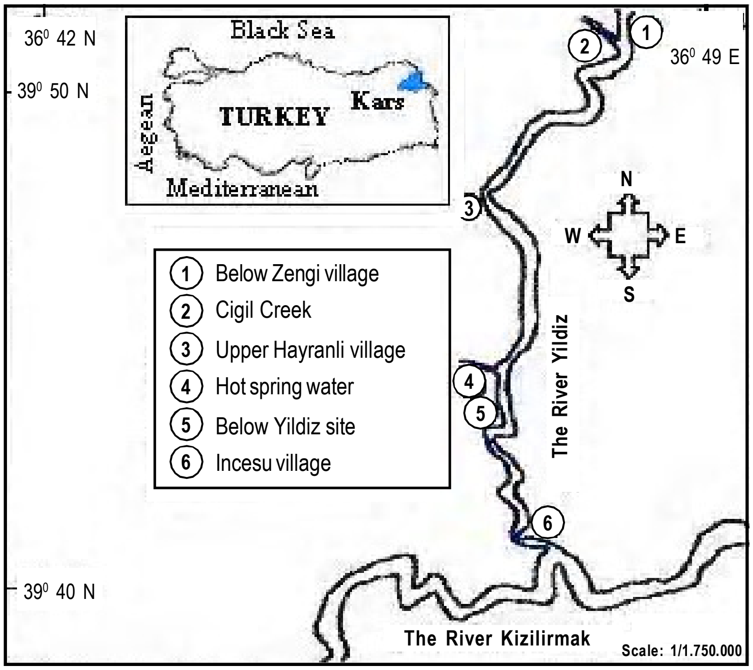

Fig. 1: Map of the river Yildez, Turkey, showing locations of study area

A total of 25 chub were caught from the river Yildiz by net and electro-fishing. Their size and weight were immediately measured and estimated as 13.34±3.93 (7.0-19.2) cm and 25.97±18.83 (2.26-59.06) g respectively. The fish samples were transported daily to the laboratory in an ice-box and were kept in deep freeze at -21°C until analysis.

Water samples were taken from the same localities as the fish (Fig. 1). Samples were collected manually from the middle of the river stream, 10 cm below the surface using polyethylene bottles. One liter of each sample was preserved with 10 ml of 6N nitric acid and stored at 5°C.

The water samples for heavy metal analysis were either filtered through Whatman filter paper No.1, and 1000 ml of the filtered samples were acidified to pH 2 with 20 ml of 6 N HNO_3, or after extraction in methyl-isobutyl-ketone (MIKB). Standard solutions for Fe, Zn, Cu, Pb, Co and Cd were prepared according to the analytical methods for atomic absorption spectrophotometry (Kalfakakou and Akrida-Demertz, 1987; Mathis and Cummings, 1973).

Analytical procedure: For analysis, muscle samples were taken (approximately 3-5 g) from the dorso-lateral surface of each fish and weighed. After being individually transferred to previously weighed 50 ml glass vials and dried in an oven for 24 hr at 105°C, they were digested on a hot plate by adding nitric acid and hydrogen peroxide (1:1) v/v according to FAO Fisheries Technical Paper No. 158 **(**Bernhard, 1976)**.** The digested samples were diluted to 50 ml with deionized water.

Analysis of the heavy metals in both the water and the fish samples was carried out using a flame atomic absorption spectrophotometry (Perkin Elmer model 603) to determine the levels of iron, zinc and copper. Heavy metal concentration in water is presented in $\mu g\ l^{-1}$, and in the edible muscle tissues of the chub as $\mu g\ g^{-1}$ of the wet weight.

Statistical procedure: Statistical analysis of the results was carried out by one-way analysis of variance (ANOVA) (Ozdamar, 1999). The Duncan-test for independent samples was used to determine significant differences. The level of significance was taken as $p<0.05$.

Results and Discussion

The results for overall metal burdens are summarized in Table 1, 2, 3 and 4 respectively. Copper concentrations were observed lower in the river water than in waste water and in the muscle of *Leuciscus cephalus*. However, iron levels were found higher in the muscle of chub , *Leuciscus cephalus* comparatively than in the waste water and river water (Table 1 and 4). Zinc values were not high among the examined samples. Although iron in all the samples was higher than the zinc and copper. Significant differences were found between iron, copper and zinc levels in the water ($p<0.05$). The concentration of the heavy metals was determined to be in the order iron >zinc >copper. A highly significant correlation between the elements in the edible muscle tissue of chub, *Leuciscus cephalus* analyzed was observed statistically and shown in Table 2 and 3. There was a positive relationship ($r=0.78$, $p<0.05$) between the copper and zinc concentrations. There was no clear difference in the levels of the metals tested when factors such as length, age and weight were compared. No significant differences ($p>0.05$) were observed between the water and the muscle tissues. While lead, cadmium, cobalt, chromium, nickel and manganese were not present at detectable levels in the water and muscle.

Table - 1: The mean concentrations of copper, iron and zinc determined in the water and waste water collected from the monitoring sites along the river Yildiz

Heavy metals	Months	Localities					
		1	2	3	4**	5	6
	February	0.44 ±0.10	0.23±0.02	0.38±0.10	0.23± 0.11	0.23±0.10	0.19±0.03
Copper	May	0.53± 0.21	0.15± 0.07	0.15±0.03	0.52±0.08	0.26±0.03	0.19±0.02
(Cu)	August	0.30±0.03	0.07±0.01	0.03±0.01	0.20±0.04	0.07±0.02	0.26±0.01
	November	0.41±0.01	0.36±0.10	0.24 ±0.02	0.38±0.02	0.41±0.21	0.16±0.04
	February	1.59±0.60	1.44 ±0.15	1.16±0.23	1.96±0.36	150±0.26	1.38±0.24
Iron	May	1.44±0.42	1.38 ±0.12	1.38±0.32	2.14±0.62	1.96±0.34	1.38±0.16
(Fe)	August	1.38±0.13	1.27±0.26	1.27±0.52	1.22±0.24	1.41±0.22	1.66±0.33
	November	1.36± 0.21	1.30±0.32	0.91±0.10	2.29±0.42	1.23±0.09	1.10±0.32
	February	0.53±0.12	0.64±0.21	0.65±0.22	1.02±0.06	1.00±0.08	1.12±0.13
Zinc	May	0.76±0.09	0.54±0.14	0.62±0.12	1.05±0.10	1.05±0.07	1.41±0.21
(Zn)	August	0.60±0.08	0.72±0.23	0.68±0.15	0.92±0.08	0.74±0.04	0.77±0.09
	November	1.44±0.22	1.32±0.36	1.46±0.13	1.46±0.36	1.49±0.22	1.21±0.20

*All values in µg l^{-1} (Mean values±S.E.)
**Waste water locality

Table - 2: The average concentration of the heavy metals in the muscle tissues of the chub caught from the monitoring sites along the river Yildiz

Sites	N	Cu		Fe		Zn	
		X S.E.	Min Max	X S.E.	Min Max	X S.E.	Min Max
1	9	1.82±0.77	1.06-2.87	12.40±3.18	9.13-16.68	11.41±4.00	7.65-16.15
3	5	1.49±0.32	1.19-1.81	12.64±3.77	8.48-15.82	12.08±2.78	10.08-15.26
5	5	1.31±0.27	1.01-1.50	12.42±3.64	10.26-16.63	8.67±3.49	4.78-11.53
6	6	1.98±1.22	1.12-3.79	11.66±4.12	7.21-17.04	12.31±6.00	4.12-18.38
p value		N.S		N.S		N.S	

All values in µg g^{-1} [Mean values (X)±S.E]
N = Total number of fish analysed
NS = Non significant
a, b = Indicates statistical differences among the mean within the same row ($p<0.05$)

Table - 3: Monthly variation of mean heavy metal concentrations detected in the muscle tissues of the chub from the river Yildiz

Months	N	Cu		Fe		Zn	
		X S.E.	Min Max	X S.E.	Min Max	X S.E.	Min Max
February	6	2.47±1.07^{a}	1.42-3.79	11.82±1.42^{ab}	10.26-13.63	15.32±2.83^{a}	11.53-18.33
May	4	1.70^{a}±0.23^{ab}	1.53-1.86	16.86±0.26^{a}	16.68-17.04	13.06±0.30^{a}	12.85-13.27
August	7	1.10±0.07^{b}	1.01-1.19	12.20±4.73^{ab}	7.21-16.63	7.09^{b}±3.2 1^{b}	4.12-10.91
November	8	1.50±0.00^{ab}	1.49-1.50	10.41±1.64^{b}	8.48-12.48	10.34±2.63^{ab}	7.65-13.94
p value		<0.05		<0.05		<0.05	

All values in µg g^{-1} [Mean values(X)±S.E]
N = Total number of fish analysed
NS = Non significant.
a, b = Indicates statistical differences among the mean within the same row ($p<0.05$)

Table - 4: Mean, minimum and maximum heavy metal concentrations in the water, waste water and *Leuciscus cephalus* in the river Yildiz

Cu mean (Min – Max)	Fe mean (Min – Max)	Zn mean (Min - Max)
The river Yildiz water (µg l^{-1})		
0.25 (0.03 - 0.53)	1.38 (0.91 - 1.96)	0.94 (0.53 - 1.49)
Wastewater (µg l^{-1})		
0.33 (0.20 - 0.52)	1.90 (1.22 - 2.29)	1.11 (0.92 - 1.46)
L. cephalus (muscle) (µg g^{-1})		
1.69 (1.00 - 3.79)	12.24 (7.21 - 17.04)	11.22 (4.12 - 18.33)

The range and mean values of Cu, Fe and Zn in the river water, waste water and the muscle of chub, *Leuciscus cephalus*, were found very low. This may be probably a reflection of the geological and pedological structure of the region. The heavy metals considered in the present study generally occur in trace concentrations under natural conditions. The waste water coming from hot spring water directly is discharged to the river Yildiz without any remediation. Singh *et al*. (1990) measured the concentrations of heavy metals in effluents water of Hindusthan Copper Limited (HCL) and Uranium Corporation of India Limited (UCL). But the level of heavy metals found in the river water in this study were very much lower than values reported from the river water in other point source-contamination sites such as the river Subernarekha by Singh *et al*. (1989) and in the river Calabar by Ekpo and Ibok (1999). This may be directly related to the contamination of the rivers, Subernarekha and Calabar, by Hindusthan Copper Limited.

The concentrations of Cu, Fe and Zn were higher in the muscle tissue than in the river water and in the waste water. This is probably due to the metabolic activities, feeding habits, ecological needs, living modes as well as the different aquatic geochemistry of the heavy metals. Similar results were also reported for a number of different fish species (Davies, *et al*., 2006; Demirak *et al*., 2006). Among the metals monitored, Fe was found in the highest concentration (17.04 µg g^{-1}), and Cu in the lowest concentration (1.00 µg g^{-1}) in the muscle tissue. Kress *et al*. (1999) also found low Cu levels in the fish muscle. These findings were already expected, because Fe is used to transport oxygen throughout the aquatic organisms (Bajc *et al*., 2005). Zn is an essential trace element for living organisms and is important for nucleic acid synthesis and also occurs in many enzymes. Copper also is responsible for hemocyanine synthesis, oxygen transport and a good indicator of urban effluents discharge (Carvalho *et al*., 2000). However, copper and zinc are regarded as potential hazards that can endanger both animal and human health. Knowledge of their concentrations in fish is therefore important for both nature management and human consumption of fish (Yilmaz *et al*., 2007). Muscle is not an active tissue regarding the accumulation of metals such as gill and liver (Bajc *et al*., 2005; Ekpo and Ibok, 1999; Filazi *et al*., 2003). In contrast to this, the results found in the present work were the highest bioaccumulation of analyzed metals in the muscle tissue, but the concentrations of metals in this tissue were lower than the maximum permitted concentrations proposed by the National Research Council (NRC, 1989) and the Turkish Food Codes (TFC, 2002). A comparison of these concentrations with our data clearly showed that the lowest background values were present in the river Yildiz. The concentrations of the heavy metals in water and fish were found to decrease in the order iron >zinc >copper, in agreement with the literature (Ekpo and Ibok, 1999; Gey and Mordogan, 1988; Turkmen *et al*., 2004).

A highly significant correlation between the elements in the edible muscle tissue of *Leuciscus cephalus* analyzed was observed statistically. There was a positive relationship ($r = 0.78$, $p<0.05$) between the copper and zinc concentrations. Demirak *et al*. (2006); Gey (1985), reported that Zn and Cu were found to have relatively higher positive correlation coefficients. In addition, this finding can show that some heavy metals can be related to geochemical structure of the vicinity. There was no clear difference in the levels of the metals tested when factors such as length, age and weight were compared. These findings are similar to those in previous reports (Demirak *et al*., 2006; Gey, 1988). No significant differences ($p>0.05$) were observed between the water and the muscle tissues.

Consequently, in terms of ecological, fish are irreplaceable bio-indicators of the degree of damage to the water environment. Moreover, it is also important to monitor the contamination of fish with heavy metals, because frequent consumption of the contaminated fish presents a very serious health risk. The results of the present study enabled us to determine the background concentrations of these metals in both the water and the fish. These data will constitute a reference to future studies on the evolution of contamination in this area**.** On the other hand, a potential danger may occur in the future depending on the agricultural, recreational activities and the effluents of the thermal therapy hospital in this region.

Therefore, the levels of metals accumulated in the fish, which are commonly consumed by public, should be monitored periodically.

References

Ajmal, M., Razi Uddin and Ahsan Ulah Khan: Heavy metals in water, sediments, plants and fish of Kali Nadi U.P. (India). *Environ. Int*., **14**, 515- 523 (1988).

Bajc, Z., K.S. Gacnik, V. Jenci and D.Z. Doganoc: The content of Cu, Zn and Mn in Slovenian freshwater fish. *Slov. Vet. Res*., **42**, 15-21 (2005).

Bernhard, M.: FAO fisheries technical paper no. FIRI/158, Rome (1976).

Canli, M., O. Ay and M. Kalay: Levels of heavy metals (Cd, Pb, Cu, Cr and Ni) in tissue of *Cyprinus carpio, Barbus capito* and *Chondrostoma regium* from the Seyhan river, Turkey. *Tr. J. Zool.*, **22**, 149-157 (1998).

Carvalho, G.P. de, P.R.S. Cavalcante, A.C.L. de, Castro and M.O.A.I. Rosaj: Preliminary assesment of heavy metal levels in *Mytella falcate* (Bivalvia, Mytilidae) from Bacanga river estuary, Sao Luis, State of

Maranhao, Northeastern Brazil. *Rev. Bras. Biol.*, **60**, 1-7 (2000).

Davies, O.A., M.E. Allison and H.S. Uyi: Bioaccumulation of heavy metals in water, sediment and periwinkle (*Tympanotonus fustacus var radula*) from the Elechi Creek, Niger delta. *African J. Biotechnol.,* **5**, 968-973 (2006).

Demirak, A., F. Yilmaz, A.L. Tuna and N. Ozdemir: Heavy metals in water, sediment and tissues of *Leuciscus cephalus* from a stream in southwestern Turkey. *Chemosphere*, **63**, 1451-1458 (2006).

Ekpo, B.O. and U.J. Ibok: Temporal variation and distribution of trace metals in freshwater and fish from Calabar river, S. E. Nigeria. *Environ. Geochem. Hlth.*, **21**, 51-66 (1999).

Filazi, A., R. Baskaya, C. Kum and S.E. Hismiogullar: Metal concentrations in tissue of the Black sea fish *Mugil auratus* from Sinop-Icliman, Turkey. *Human Exp. Toxicol.*, **22**, 85-87 (2003).

Geldiay, R. and S. Balik: Freshwater Fishes of Turkey. E.U., Science Fac. Book Series, Izmir (1988).

Gey, H.: Accumulation levels of the trace elements (Cu, Mn, Zn, Fe, Pb, Co, Cr, Cd) in the tissues and organs of the Bass (*Dicentrarchus labrax* L.) and Soles (*Solea vulgaris* QUENSEL) caught in the gulf of Izmir. V. Natl. Spectrosc. Symp. Sivas, Turkey. pp. 188-199 (1985).

Gey, H.: The research on the concentration levels of some trace elements in the Bass (*Dicentrarchus labrax* L.) and Sole (*Solea vulgaris* QUENSEL) caught by the Aegean Sea coast of Turkey. IX. Natl. Biol. Congr., Sivas, Turkey, 2, 449-456 (1988).

Gey, H. and H. Mordogan: Concentrations of various heavy metals in near shore sediments of inner bay and in some marine organisms in the bay of Izmir. *Doga, TU. Zool.*, **12**, 216-224 (1988).

Goksu, M.Z.L., F. Cevik, O. Findik and E. Sarihan: Investigation of Fe, Zn and Cd in mirror carp (*Cyprinus carpio* L., 1758) and pike pearch (*Stizostedion lucioperca* L., 1758) from Seyhan dam Lake. E.U. *J. Fish. Aquat. Sci.,* **20**, 69-74 (2003).

Kalfakakou, V. and A. Akrida-Demertz: Transfer factors of heavy metals in aquaticorganisms of different trophic levels. The First Biol. Intern. Conf. May 6-10, Athens (1987).

Karadede, H., S.A. Oymak and E. Unlu: Heavy metals in mullet, *Liza abu*, and catfish, *Silurus triostegu*s, from the Atatürk dam Lake (Euphrates), Turkey. *Environ. Int*., **30**, 183-188 (2004).

Karadede, H. and E. Unlu: Concentrations of some heavy metals in water, sediment and fish species from the Ataturk dam Lake (Euphrates), Turkiye. *Chemosphere*, **41**, 1371-1376 (2000).

Kress, N., B. Heart, E. Shefer and H. Hornung: Trace element level in fish from clean and polluted coastal marine sites in the Mediterranean Sea, Red sea and North sea. *Helgol. Mar. Res*., **53**, 163-170 (1999).

Mathis, B.J. and T.F. Cummings: Selected metals in sediments water and biota in the Illinois river. *J. Water Pollut. Contr. Fed*., **45**, 1573-1583 (1973).

Muley, D.V., D.M. Karanjkar and S.V. Maske: Impact of industrial effluents on the biochemical composition of fresh water fish, *Labeo rohita. J. Environ. Biol.*, **28**, 245-249 (2007).

NRC.: Recommended Dietary Allowances. 10^{th} Edn., DC Natl. Res. Counc., Washington (1989).

Ozdamar, K.: Biostatistic with SPSS. Kaan Book Co., Eskisehir (1999).

Ozdilek, Hasan Goksel, Paul P. Mathisen and Don Pellegrino: Distribution of heavy metals in vegetation surrounding the Blackstone River, USA: Considerations regarding sediment contamination and long term metals transport in freshwater riverine ecosystems. *J. Environ. Biol.*, **28**, 493-502 (2007).

Pfeiffer, C.W., M. Fiszman, O. Malm and J.M. Azcue: Heavy metal pollution in the Paraiba Do Sul River, Brazil. *Sci. Total Environ.*, **58**, 73-79 (1986).

Samanta, S., K. Mitra, K. Chandra, K. Saha, S. Bandopadhyay and A. Ghosh: Heavy metals in water of the rivers Hooghly and Haldi at Haldia and their impact on fish. *J. Environ. Biol.*, **26**, 517-523 (2005).

Sindhe, V.R. and R.S. Kulkarni: Fecundity of the freshwater fish, *Notopterus notopterus* (Pallas) in natural and heavy metal contaminated water. *J. Environ. Biol.*, **26**, 287-290 (2005).

Singh, N.K., G.R. Dutta, M. Singh and K. Kishore: Assesment of water quality of the river Subernarekha at ghatsila with reference to heavy metal pollution. *J. Freshwater Biol.,* **1**, 113-120 (1989).

Singh, N.K., M.C. Warma and J.S. Datta Munshi: Accumulation of copper, zinc, lead, iron and cadmium in certain freshwater fishes of river Subernarekha. *J. Freshwater Biol.,* **2**, 189-193 (1990).

Tezcan, R. and Y. Ozbay: Heavy metal concentrations in Tohma Creek. Natl. Environ. Symp., Adana. pp. 439-447 (1984).

Turkish Food Codes (TFC): Official Gazette, September 23 (2002).

Turkmen, A., M. Turkmen, Y. Tepe and M. Naz: The correlations between the heavy metal concentrations and temperature, salinity, pH and oxygen parameters of the sea water in Iskenderun Bay. Natl. Water Days. pp. 400-407 (2004).

Unlu, E., O. Akba, S. Sevim and B. Gumgum: Heavy metal levels in mullet, *Liza abu* (Heckel, 1843) (Mugilidae) from Tigris river, Turkey. *Fresen. Environ. Bull*., **5**, 107-112 (1996).

Yigit, Sibel and Ahmet Altindag: Concentration of heavy metals in the food web of Lake Egirdir, Turkey. *J. Environ. Biol.*, **27**, 475-478 (2006).

Yilmaz, A. B.: Levels of heavy metals (Fe, Cu, Ni, Cr, Pb and Zn) in tissue of *Mugil cephalus* and *Trachurus mediterraneus* from Iskenderun bay, Turkey. *Environ. Res*., **92**, 277-281 (2003).

Yilmaz, F., O. Nedim., A. Demirak and A.L. Tuna: Heavy metal levels in two fish species *Leuciscus cephalus* and *Lepomis gibbosus. Food Chemistry*, **100**, 830-835 (2007).