Environ Monit Assess (2011) 173:387–395
DOI 10.1007/s10661-010-1394-7

Accumulation of heavy metals with water quality parameters in Kızılırmak River Basin (Delice River) in Turkey

Nuray Emir Akbulut · A. Murat Tuncer

Received: 31 July 2009 / Accepted: 11 February 2010 / Published online: 5 March 2010

Abstract Kızılırmak River has been used as Ankara's drinking water source for approximately 1.5 years. Therefore, this region's water, sediment, and fish samples are measured for detecting the heavy metals. This is important for the current situation as well as the future in terms of potential impact. The amount of heavy metals in drinking water should be within the limited values; otherwise, the accumulation of heavy metals will cause many problems to living organisms. Especially high levels of arsenic, cadmium, nickel, mercury, etc. are very dangerous to freshwater ecosystems as for human if the water is being use as drinking water. In this study, water, sediment samples, muscle, and gills of three fish species (*Capoeta tinca*, *Capoeta capoeta*, *Leuciscus cephalus*) were analyzed for the presence of heavy metals such as (Al, Fe, As, Cd, Ni, Mn, Se, Si) to determine present accumulation levels and possible toxic effect. The accumulation pattern of heavy metals in the water, sediment, and fish tissue follows the sequence: Si > Fe > Al > Mn > As > Ni > Se > Cd, Fe > Al > Mn > Ni > As > Se > Cd, and Fe > Al > Mn > As > Ni > Si > Cd. In addition, the detected concentrations of heavy metals in the Kızılırmak and Delice Rivers are compared with other heavy metal studies in the other main rivers and lakes in Turkey.

Keywords Heavy metal · Bioaccumulation · Water · Sediment · Fish · Water quality · Kızılırmak Basin

N. E. Akbulut (✉)
Department of Biology, Faculty of Science, Hacettepe University, 06800 Beytepe, Ankara, Turkey
e-mail: emir@hacettepe.edu.tr

A. M. Tuncer
Pediatric Hematology Unit, Department of Pediatrics, Medical Faculty, Hacettepe University, 06100 Sıhhiye, Ankara, Turkey

A. M. Tuncer
Cancer Control Department, Ministry of Health of Turkey, İlkiz Street No:4/1, 06100 Ankara, Turkey

Introduction

Most of the metals are taken through drinking water. These metals can be the normal components of both food and pollution, such as the pesticide residue involving metals, the passage of metals to the food chain, or they can be the result of environmental pollution. The metals can pollute air, water, and soil through the natural sources and technological means. Water passing from the mineral beds dissolve the metals here and become harmful.

The toxic effect of metals can change according to the characteristics of metals. Generally, heavy metals create toxic effect by forming complexes with organic compounds. They lose some of their characteristics to provide their molecular functions, and there comes the effected cell death. Industrial wastes are considered critical factors that degrade the natural environment. Composite effluent stained with different heavy metals are major environmental pollutants of varied wetland ecosystem (Cheung et al. 2003; Chatterjee et al. 2006).

Heavy metals such as cadmium is biologically nonessential and demonstrably toxic even at relatively low concentrations, and some elements like iron, iodine, copper, manganese, zinc, cobalt, molybdenum, selenium, and nickel are essential for normal body functions (Alemdaroğlu et al. 2003). Studies from the field and laboratory experiments showed that accumulation of heavy metals in a tissue is mainly dependent upon water concentrations of metals and exposure period, although some other environmental factors such as salinity, pH, hardness, and temperature play significant roles in metal accumulation (Canlı and Atlı 2003; Barlas et al. 2005).

Most of the papers published on organisms as pollution bioindicators including Karadede and Ünlü (2000), Gümgüm et al. (2001), Canlı et al. (2001), Karadede et al. (2004), Yiğit and Altındağ (2002), Altındağ and Yiğit (2005), and Karadede Akın and Unlu (2007) have concentrated on fish. The objective of this study is to determine the concentrations of heavy metals such as Fe, Al, As, Cd, Mn, Ni, Se, and Si in water, sediment, and fish tissues in Kızılırmak River, Delice Stream, and its arms.

Material and methods

The water, sediment, and fish samples were collected from four different stations in February, May, and August 2008. Water samples were taken with 0.5 l precleaned polyethylene bottles. The sediment samples were collected with an Ekman sampler in cleaned 250 ml plastic bottles. Fish samples were collected using electroshock at the selected stations. In this sampling site, three fish species (*Capoeta tinca*, *Capoeta capoeta*, *Leuciscus cephalus*) were collected. For the analyses, four male and four female specimens of similar sizes were selected from each fish species to take gill and muscle samples. In addition, water quality parameters data such as NH4, PO_4, NO_3, NO_2, SO_4, Cl, HCO_3, CO_3, Mg, Ca, K, and Na were taken from the project (Hacettepe University, Project no. 0701601006).

Each fish specimens were measured, tagged, and placed in a sterile plastic bag and kept at −18°C (Bernard 1976). Chemicals and heavy metals were analyzed in Hacettepe University LA-ICP-MS laboratory. The accuracy also was

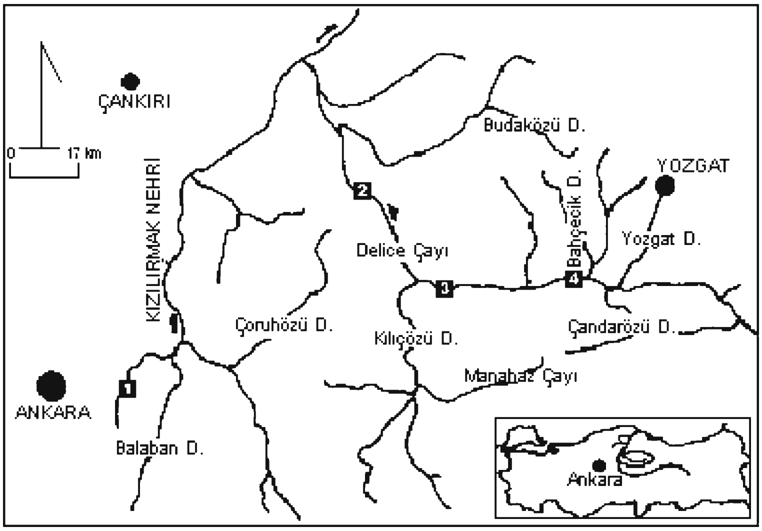

Fig. 1 The map of the study area and sampling locations (modified from Gül and Yılmaz 2002 and Akbulut and Akbulut 2009)

examined by analyzing a blank. During the sampling, EC, pH, temperature, salinity, and dissolved O_2 were measured on the selected stations using Consort C933 model sampler (in situ).

The determined heavy metal contents in the water, sediment, fish muscle, and gill were evaluated statistically using analysis of variance analysis of variance (ANOVA) technique (SPSS software version 15.0 program). The partition coefficient for the metal concentration in water, sediment, and fish tissue samples were normalized and determined as 0.01 and 0.05. The means with same letters (a and b) show no statistically significant differences.

Study area and sampling locations

Kızılırmak River (Red River) is Turkey's longest river with a length of 1355 km. Springing from Kızıldağ, Sivas, it flows across the central Anatolian plain, cuts through the Pontid Mountains, and disembogues the Black Sea near the city of Samsun. Its catchment area is 78.180 km^2. The name—Red River—is derived from the high concentration of suspended clay particles that causes its characteristic reddish color (Akbulut et al. 2009). Delice Stream is the main arm of Kızılırmak River and flows between Çankırı, Yozgat, Kırşehir, and Kırıkkale cities and connected with Kızılırmak near Çankırı (Fig. 1; Gül and Yılmaz 2002).

Results and discussion

Measured physicochemical parameters of water are given in Tables 1 and 2. The residue data of the measured metals in water, sediment, and fish tissue samples have been shown in the Tables 3, 4, and 5, and statistical result have been shown in the Tables 6 and 7.

Physicochemical parameters

According to the table, mean pH ranged between 8.14 and 8.33, mean salinity measurements ranged between 1.3 and 2.4 ppm, water temperature ranged between 13.9°C and 17.6°C, the mean dissolved oxygen changed according to the temperature, and the values ranged between 5.32 and 7.49 ppm. EC measurement ranged between 128 μmhos and 327 mS.

Major anion concentration showed a general trend of Cl > SO_4 > HCO_3 > CO_3 > NO_3 > NO_2; in them, mean sulfate and chloride were very high through the year ranging between 261.9 and 433.3 and 153.5 and 869 ppm, respectively. During the study, hardness changed between 44.64 and 79.88 (French hardness) in the class of hard water (Akbulut and Akbulut 2009).

Heavy metals

Aluminum

In water samples, Al ranged between min. 39.32 μg/l (in August) and max. 628.7 μg/l (in February). Mean values in February, May, and August were 256.3, 142.28, and 77.331. In sediment, Al ranged between min. 468.25 μg/g (in May) and max. 2071.5 μg/g (in August). Mean values in February, May, and August were 1,110.25, 704.68, and 1,537.4, respectively. In the fish muscle min., Al value was 25.396 μg/g (*C. tinca*) in May, and max. value was 296.12 μg/g (*C. capoeta*) in August, whereas in gill min., Al value was 140.71 (*C. capoeta*) in May and max. value was 771.7 (*C. capoeta*) in February.

Manganese

Mn values ranged between min. 1.355 μg/l (in May) and 233.5 μg/l (in February), and mean values in February, May, and August were 81.62, 3.117, and 43 μg/l, respectively. In sediment, Mn values ranged between 161.7 (in May) and 1,760 μg/g (in August), and mean values in February, May, and August were 508.2, 313, 1,224.5 μg/g, respectively. In fish muscle, Mn value was min 4.40 (*L. cephalus*) in February and max. 80.94 μg/g (*C. tinca*) in May; in gill, Mn was detected as min 51.36 (*C. capoeta*) in February and max. 345.3 μg/g (*C. capoeta*) in May.

Iron

Fe values ranged between min. 51.1 and max. 2819 μg/l in August, and mean values were 386.7,

Table 1 Measured physicochemical parameters on the sampling stations (in situ)

	pH	Temperature (°C)	Salinity (%)	Dissolved O_2 (mg/l)	EC (mS)
1. Station mean	8.26 ± 0.425	13.9 ± 6.1	1.6 ± 0.291	5.32 ± 2.796	280 ± 457
Min.–max.	7.81–9.26	4.2–21.8	0.9–2	0.16–8.81	100–1,500
2. Station mean	8.33 ± 0.166	17.6 ± 10.1	2.4 ± 1.16	7.49 ± 2.14	327.7 ± 210
Min.–max.	8.13–8.68	1.6–32	1–5	3.39–10.12	110–700
3. Station mean	8.25 ± 0.187	15.7 ± 8.53	1.3 ± 0.27	7.48 ± 3.04	139.7 ± 42.6
Min.–max.	8.05–8.5	2.83–29	0.9–1.6	0.86–10.5	80–210
4. Station mean	8.14 ± 0.182	14.2 ± 7.24	1.4 ± 0.182	6.67 ± 2.67	128 ± 38.3
Min.–max.	7.9–8.42	2.73–24.9	0.9–1.5	1.03–9.63	75–170

Table 2 Determined major anions and cations on the sampling stations (mg/l)

	Ca	K	Cl	CO_3	HCO_3	Mg
1. Station mean	116 ± 8.775	6.96 ± 2.164	217.3 ± 22.91	6.59 ± 9.654	206.4 ± 85.97	39.4 ± 2.31
Min.–max.	104.6–125.1	5.18–10.68	189.1–241.6	0–21.31	130.2–343.7	37.3–43
2. Station mean	167.31 ± 64.37	8.23 ± 2.783	869 ± 828	22.43 ± 19.11	371.88 ± 56.15	72 ± 26.51
Min.–max.	113.695–259.431	5.473–11.987	275.433–2,075.0315	0–46.60	314.342–440.694	44.581–108.007
3. Station mean	116.1 ± 19.38	34.52 ± 64.42	173 ± 66.50	17.48 ± 11	329.8 ± 51.34	54.28 ± 16.51
Min.–max.	95.6592–142.257	4.592–149.758	104.021–282.8746	0–30.457	275.584–393.956	36.641–81.5849
4. Station mean	114.3 ± 15.86	5.47 ± 1.46	153.5 ± 27.76	30.56 ± 8.0	349.7 ± 51.1	46.9 ± 8.23
Min.–max.	97.16–128.53	3.87–7.18	113.37–175	11.65–76.99	278.07–398.3	35.77–53.48

	Na	NH_4	NO_2	NO_3	PO_4	SO_4
1. Station mean	175.5 ± 9.559	9.314 ± 5.967	0.708 ± 0.273	2.35 ± 2.05	0.245	306.5 ± 30.86
Min.–max.	165.4–191.2	4.05–15.8	0.514–0.902	0.51–5.77	0–1.227	268.11–346.9
2. Station mean	597.7 ± 462.1	5.639 ± 3.785	0.783 ± 0.574	16.22 ± 9.47	nd	433.02 ± 195.7
Min.–max.	236.4–1,266.19	1.96–9.51	0.28–1.281	8.048–29.2368		249.047–707.0924
3. Station mean	187.8 ± 65.43	13 ± 15.48	0.796 ± 0.555	11.51 ± 2.96	2.9 ± 3.61	332.9 ± 166
Min.–max.	99.958–284.507	2.7–35.94	0.403–1.18	8.20–16.34	0.34–5.467	165.863–610.8372
4. Station mean	164.8 ± 45.97	4.84 ± 2.54	0.687	14.36 ± 14.36	nd	261.9 ± 62.45
Min.–max.	102.38–210.03	3.04–6.64	0–2.766	6.22–24.75		172.06–316.65

Mean values and ± standard deviation (the data are taken from 0701601006 project of Hacettepe University BAB)

Table 3 Mean, minimum, and maximum heavy metal concentration in water and sediment samples

	Water (μg/l)			Sediment (μg/g)		
	February 2008	May 2008	August 2008	February 2008	May 2008	August 2008
Al	256.3 ± 149.8	142.28 ± 13.77	77.331 ± 75.23	1,110.25 ± 170.6	704.68 ± 150.8	1,537.4 ± 521.5
	61.84–628.7	131.2–180.3	39.32–301.1	979–1,335.25	468.25–864.77	1,279.5–2,071.5
Mn	81.62 ± 92.9	3.117 ± 2.27	43 ± 63.25	508.2 ± 73	313 ± 111.7	1,224.5 ± 396.7
	8.19–233.5	1.355–9.596	19.51–232.7	462.1–663.6	161.7–472.4	686.5–1,760
Fe	386.7 ± 159.2	129.78 ± 36.86	393.53 ± 310.05	1,245.7 ± 41.13	903.3 ± 273.7	5,011 ± 3,669.6
	73.77–805.8	84.93–186.9	51.1–2,819	1,190.4–1,302.9	426.25–1,137.5	4,663.5–14,560
Ni	12.88 ± 10.94	9.50 ± 8.89	0.0445	62.1 ± 29.73	31.74 ± 3.711	237.3 ± 274
	0.978–42.52	0–26.79	0–0.445	24.56–104.35	26.98–36	57.95–711
As	13.17 ± 4.16	6.178 ± 2.41	8.411 ± 2.53	44.28 ± 4.40	34.24 ± 10.49	44.42 ± 8.55
	7.843–16.23	0.518–8.882	3.305–11.54	39.17–51.2	17.68–46	35.03–57.9
Cd	0.440 ± 0.53	0.287 ± 0.202	nd	0.616 ± 0.237	0.656 ± 0.512	0.5243 ± 0.08
	0.063–1.477	0.093–0.614		0.320–0.954	0.191–1.472	0.4082–0.6237
Si	22,390 ± 7,944	2,056.4 ± 202.39	9,652.3 ± 5,192.9	nd	nd	nd
	11,760–30,720	1,784–2,307	7,097–24,640			
Se	8.156 ± 4.3	5.226 ± 2.73	5.578 ± 2.27	1.175 ± 0.439	nd	3.6 ± 1.06
	0.04–14.56	0–5.743	2.841–8.771	0–1.02		2.67–5.4

nd not detected

Table 4 Mean, minimum, and maximum heavy metal concentration in the fish samples (muscle)

	Capoeta tinca (μg/g)			*Capoeta capoeta* (μg/g)			*Leuciscus cephalus* (μg/g)		
	February 2008	May 2008	August 2008	February 2008	May 2008	August 2008	February 2008	May 2008	August 2008
Al	79.18	44.19	164.2	162.58	69.2	184.5	78.4	60.04	788.33
	66.65–91.71	25.396–62.996	129.7–211.9	76.101–211.3	58.43–80.00	72.88–296.12	75.80–81	35.52–84.56	
Mn	14.34	32.47	16.92	18.56	4.443	14.47	9.452	13.21	32.93
	6.82–28.53	5.98–80.94	18.17–19.38	6.433–32.14	8.046–20.84	5.087–23.87	4.40–14.505	10.7–15.73	
Fe	172.5	788.2	345	166.26	52.35	185.86	97.45	85.28	585.83
	70.89–389.8	19–2,319.7	65.61–572.3	73.72–215.80	21.97–82.74	90.58–281.14	91.74–97.17	37.86–132.7	
Ni	nd	44.81	0.122	7.62	5.222	nd	0.22	9.91	11.62
		1.627–130	0–0.366	0–19.87	2.201–8.243		0–0.441	4.41–15.41	
As	27.86	13.87	20.27	39.12	14.34	18.06	19.46	11.49	58.83
	8.109–75	6.46–26.46	13.93–29.32	11.92–75.23	6.871–23.457	7.75–28.38	16.70–22.23	6.00–16.99	
Cd	8.96	5.42	0.836	13.43	0.48	1.086	8.8	2.761	5.645
	7.938–13.31	0.005–15.95	0.190–1.679	1.02–27.44	0.151–1.058	0.503–1.669	1.391–16.21	0.873–4.65	
Si	nd	nd	nd	–	–	–	–	–	–
Se	nd	0–0–0.0351	1.934	nd	0.56	0.91	nd	nd	2.703
			0.765–3.438		0–0.139	0.649–1.171			

Table 5 Mean, minimum, and maximum heavy metal concentration in the fish samples (Gill)

	Capoeta tinca (μg/g)			*Capoeta capoeta* (μg/g)			*Leuciscus cephalus* (μg/g)		
	February 2008	May 08	August 2008	February 2008	May 08	August 2008	February 2008	May 08	August 2008
Al	645.98	149.8	418.5	617.8	337	506.5	492.1	276	474.63
	555.27–759.5	148–151.7	343.03–464.7	502.54–771.7	140.71–533.36	431.61–581.5	341.88–642.42	196–356.1	
Mn	122.4	89.25	90.2	14.4	119.85	131.6	95.27	166.4	43.62
	65–199.12	54–124.5	71.50–103.23	51.36–118.21	54.41–345.37	79.85–183.48	94.11–96.43	130–202.8	
Fe	1,099.9	239.5	459.52	754.3	551.3	795.18	742.2	510.8	381.88
	643–2,064.8	170–308.69	377.86–551.27	320.52–1,080.1	259.65–843.14	494.11–1,096.26	701.76–782.82	406.1–615.5	
Ni	nd–50.88	17	1.9	31.41	38.63	2.9	1.25	40.85	6.5362
		12.66–21.48	0–5.7	0–91.25	14.859–62.42	0–8.71	nd–2.41	24.27–57.44	
As	102.74	30.9	39.23	133.8	95.97	42.27	111.4	84.26	43.22
	57.46–199.18	24.42–37.41	28.12–46.32	75.50–241	26.60–183.70	34.50–50.04	103.25–119.58	57.7–110.83	
Cd	10	1.28	1.444	3.518	6.06	1.07	9	5.969	3.485
	3.216–13.46	0.575–2.07	0.712–1.558	1.809–6.937	1.512–6.581	1.01–1.131	3.381–14.63	2.05–9.888	
Si	nd	nd	nd	nd	–	–	–	–	–
Se	nd	0–1.585	4.155	nd	nd	6.62	nd	nd	8.652

Table 6 Statistical result of water, sediment, and fish samples

Metals	February	May	August	*F* value ANOVA	Probability
Water					
Al	256.3 ± 149.8a	142.28 ± 13.771a	77.331 ± 75.232b	20.853	0.000 < 0.05
Mn	82.675 ± 92.997a	3.117 ± 2.275b	43 ± 63.257a	27.149	0.000 < 0.01
As	13.179 ± 4.166a	6.178 ± 2.417b	8.441 ± 2.530b	10.706	0.000 < 0.05
Sediment					
Al	1,110.2 ± 170.6a	704.68 ± 150.8a	1,914.12 ± 521.5b	10.530	0.004 < 0.05
Fe	1,245.72 ± 41.137a	878.33 ± 273.7a	8,614.6 ± 3,669.6b	40.869	0.000 < 0.05
Mn	508.22 ± 73a	313 ± 111.75a	1,227 ± 396.7b	14.907	0.001 < 0.05

The means with same letters (a and b) show no statistically differences

129.78, and 393.53 throughout sampling period in water. In sediment, Fe ranged between min. 426.25 and max. 14,560 μg/g in August, and mean values were 1,245.7, 903.3, and 5,011 throughout sampling. Fe ranged min. 19 μg/g (*C. tinca*) and max. 2,319.7 μg/g (*C. tinca*) in fish muscle in May, whereas in gill samples, it was min. 170 μg/g (*C. tinca*) in May and max. 2,064.8 μg/g (*C. tinca*) in February.

Nickel

Ni ranged between min. 0–0.445 in August and max. 42.52 μg/l in February. The mean values were 12.88, 9.50, and 0.0445 μg/l, respectively. In sediment, Ni ranged between 24.56 in February and 711 in August. The mean values were 62.1, 31.74, and 237.3 μg/g, respectively. Ni value was under detection level in some months in fish muscle samples, but it ranged between 0.366 and 130 μg/g in (*C. tinca*). It was also under detection level in some months also in the gill, but it ranged between 2.41 and 57.44 μg/g (*L. Cephalus*) in February and May samples.

Arsenic

Arsenic was measured min. 0.518 μg/l in May and 16.23 in February. Mean values were 13.17, 6.178, and 8.411 μg/l. In sediment, arsenic was measured min. 17.68 μg/g in May and 57.9 in August. Mean values were 44.28, 34.24, and 44.42 μg/g. In muscle samples, As level was min. 6.00 μg/g (*L. cephalus*) in May and 75.23 μg/g (*C. capoeta*) in February. In gill samples, As level was min 24.42 μg/g (*C. tinca*) in May and 241 μg/g (*C. capoeta*) in February.

Cadmium

Cadmium values were measured between 0.063 and 1.477 μg/l (in February), and in August, it was under the detectable level. The mean values were 0.440 and 0.287 μg/l in February and May sampling. Cadmium values ranged between 0.191 and 1.472 μg/g in the sediment samples in May and mean values were 0.616, 0.656, 0.5243 μg/g. Cd was min. 0.005 μg/g (*C. tinca*) in May and max. 27.44 μg/g (*C. capoeta*) in muscle in February samples. The gill samples were detected to contain

Table 7 Statistical result of water, sediment, and fish samples

Fish	*Leuciscus cephalus*	*Capoeta tinca*	*Capoeta capoeta*	*F* value ANOVA	Probability
Muscle					
Ni	8.739 ± 4.142a	−3.26 ± 1.175b	−3.343 ± 4.57b	52.536	0.000 < 0.01
Gill					
Al	329.35 ± 92ab	582.7 ± 108.8a	591 ± 120.7b	7.679	0.007 < 0.05
Fe	520.34 ± 122.2a	900.1 ± 541.7ab	883.3 ± 242.8b	5.157	0.024 < 0.05

The means with same letters (a and b) show no statistically differences

0.575 μg/g (*C. tinca*) Cd in May and 14.63 μg/g (*L. cephalus*) in February.

Silisium

Silisium ranged between min. 1,784 in May and 30,720 μg/l in February in water. The mean values were 22,390, 2,056.4, and 9,652.3 μg/l, respectively. Silisium was under detectable level in sediment, fish gill, and fish muscle samples.

Selenium

It was 0.0351 μg/g (*C. tinca*) in May and 3,438 μg/g in (*C. tinca*) in August in muscle samples. Se was accumulated 1.585 μg/g (*C. tinca*) in May and 6.629 μg/g in (*C. capoeta*) in August in the gill of fish.

Statistical result

1. There is no difference in terms of values of Al in water between February and May, and there is a difference between other months.
2. There is no difference in terms of values of Mn in water between February and August, and there is a difference between other months.
3. There is no difference in terms of values of As in water between May and August, whereas there is a difference between the other months.
4. There is no difference in terms of Al, Fe, and Mn values in sediment between February and May, but there is a difference between other months.
5. Only *C. capoeta* and *C. tinca* fish species do have not different values in terms of Ni in muscles. Among other fish species, the differences are evident.
6. Only *C. capoeta* and *C. tinca* fish species display differences in Al values in terms of gill, and among other fish species, there is no difference.
7. Only *L. cephalus* and *C. capoeta* fish species display differences in Fe values in terms of gill, and among other fish species, there is no difference.

Kızılırmak River receives many important nutrient inputs such as wastewater of many cities through the river and its arms, as well as agricultural and industrial pollutants. The measured sulfate, nitrite, nitrate, and chloride concentrations exceeded the limit values in the study area (TKB Water Contamination Regulation 2004).

In this study, Al, Fe, As, and Cd were detected at higher levels in Delice River Basin especially in the sediment samples. These metals were accumulated and biologically magnified in the food chain. Kızılırmak River Basin consisted of many pollutant factors such as industrial, agricultural, and domestic wastes of cities. These heavy metals might have accumulated in the fish tissue through the resuspended sediments.

The toxic effects of metals can change according to the structure of metals. Generally, heavy metals create toxic effect by forming complexes with organic compounds. The solubility of the metals primarily depends on the pH, dissolved oxygen, and hardness (Barlas 1999). An increase in pH generally decreases the solubility of toxic heavy metals (Hellawel 1988). In the current study, pH ranged between 7.81 and 9.26 and mean dissolved oxygen ranged between 5.32 and 7.49, but in some periods, this value decreased to 0.16 due to the input of heavily polluted wastewaters through the river. The hardness of the river water ranged between 42 and 75 Fr. These conditions are not favorable for the solubility of metals. In addition, metals were settled and accumulated in the sediment. According to inland water source classification, water quality of the Kızılırmak River may fall in categories III and IV (TKB 2004).

The accumulation level of heavy metals was higher in gill compared to muscle samples. Al and Fe in muscle and gill samples were as follows: Al min. 25.396 (*C. tinca*) in May, max. 296.12 (*C. capoeta*) in August; Fe min. 19 μg/g (*C. tinca*) in May, max. 2,319.7 μg/g (*C. tinca*) in May. In the gill samples, Al. is min. 140.71 (*C. capoeta*) in May and max. 771.7 (*C. capoeta*) in February; Fe min. 170 μg/g (*C. capoeta*) in May, max. 2,064.8 μg/g (*C. tinca*) in February. The concentration of these values exceeded the limit values of inland water sources classification (TKB 2004).

When we look at the EPA (2006) drinking water criteria, the values are 0.3 mg/l for Fe and 0.05–0.2 mg/l for Al. There is an accumulation of these metals at the fish species living in Kızılırmak River. These values were 6.38–200.86 mg/kg at the fish in Atatürk Dam Lake on the Euphrates River (Karadede et al. 2004), 327.7 mg/kg at the *Capoeta barroisi* in Ceyhan River, and 4.58–5.27 mg/l in Yeşilırmak River (Mendil et al. 2005).

Arsenic is one of the most toxic metals and As level was min 6.00 μg/g in (*L. cephalus*) in May and 75.23 μg/g (*C. capoeta*) in February in fish tissue. The As level in gill tissue was min. 24.42 μg/g in (*C. tinca*) in May and max. 241 μg/g (*C. capoeta*) in February. While the amount that should be at the drinking water standards is 10 μg/l, there was a significant accumulation in fish tissues.

Kerrison et al. (1988) reported that Cd accumulates in the sediment slowly. In the muscle tissue, cadmium values were measured between 0.005 μg/g (*C. tinca*) in May and 27.44 μg/g (*C. capoeta*) in February; in gill, it was 0.575 μg/g (*C. tinca*) in May and 14.63 μg/g (*L. cephalus*) in February. TKB (2004) gives the Cd amount for fish as 0.05 mg/kg. Cd values measured at the fish tissue; the accumulation is clearly over the standards. Barlas (1999) recorded that Cd value at the fish species living in Sakarya River basin was 0.039–0.301 mg/kg; Göksu et al. (2003) recorded it in Seyhan River as 0.25–0.55 mg/kg. Mendil et al. detected the muscle tissue of *C. tinca* to contain 0.37–1.5 mg/kg in 2005 in Yeşilırmak River. USEPA determined the maximum concentration level of cadmium in drinking water as 0.005 mg/l. The values detected in Kızılırmak water are below the limit value. Yiğit and Altındağ (2002) detected Cd level in water 0.103–0.129 mg/l, in sediment 11.3–13.4 μg/g, in fish muscle 0.585–0.675 μg/g, and in fish gill 0.580–0.670 μg/g in Burdur Lake. Chen et al. (2000) suggested that the highest concentration of Cd in a lake may be attributed to land use variables and high percentage of agricultural area. Altındağ and Yiğit (2005) observed that Cd is found to be above the permissible level of drinking water in international criteria like WHO, EU, and EPA (USA). They found the Cd level 110 μg/l in water, 13.05 μg/g in sediment, and 0.578 μg/g in *L. cephalus* muscle tissue in Beyşehir Lake.

When we look at the Ni value, it was under detection level in some months, but it ranged between 0.366 and 130 μg/g (*C. tinca*) in muscle and between 2.41 and 57.44 μg/g (*L. cephalus*) in gills in February and May. Barlas (1999) found it between 0.006 and 5.6 mg/kg in Sakarya Basin while Mendil et al. (2005) found it to be 1.2–5.4 mg/kg at the fish species living in Yeşilırmak River. In Ceyhan River, max. nickel value was recorded as 14.36 mg/kg and min. 0.18 mg/kg (Akbulut A., unpublished data). There is also accumulation in terms of Ni in Kızılırmak River fish species.

When we look at the statistical analysis results: According to the sampling dates, there is a significant accumulation and difference in Al, Mn, and As in water, while there is a difference for Al, Fe, and Mn in sediment. When the fish species are evaluated in terms of heavy metal accumulation at muscle tissue while there is a difference for Ni, there is no difference detected in Al and Fe accumulation at gill tissue between the sampling dates.

According to the Water Contamination Control Regulation 2004, Delice Stream has II and III class water quality in terms of Fe, Al, Mn, and As when evaluated within the framework of quality criteria for territorial water resource classes. When these parameters are evaluated in terms of sediment, there is quite a high amount of accumulation. There is also an important amount of Fe, Al, As, and Cd accumulation in fish tissue due to food chain and feeding from the bottom. Physicochemical changes that can occur in Kızılırmak River, for instance a change in pH due to fluctuations in the decomposed oxygen and carbonate concentration, will cause an increase in the dissolvability of these metals, thereby their inclusion in the water and accumulation in fish tissue will increase, too. In this regard, the discharges that blend into the water should be refined first, and the water should be continuously monitored.

Acknowledgements The authors would like to thank to Dr. Sibel Atasagun and Dr. Cevher Özeren' helps for the laboratory studies. Thanks to Dr. Serpil Aktas for the help to evaluate statistical result. The field study has been done during the Project of 0701601006 H.U. BAB and major chemical data are taken from this project report.

References

Akbulut, A., & Akbulut, N. (2009). The study of heavy metal pollution and accumulation in water, sediment and fish tissue in Kızılırmak River Basin in Turkey. *Environmental Monitoring and Assessment*. doi:10.1007/s10661-009-1069-4.

Akbulut, E. N., Bayarı, S., Akbulut, A., & Şahin, Y. (2009). Rivers of Turkey. In K. Tockner, C. T. Robinson, & U. Uehlinger (Eds.), *Rivers of Europa* (pp. 643–672). New York: Academic.

Alemdaroğlu, T., Erten, O., & Erk'akan, F. (2003). Trace metal levels in surficial sediments of lake Manyas, Turkey and Tributary Rivers. *International Journal of Environmental Studies, 60*, 287–298.

Altındağ, A., & Yiğit, S. (2005). Assessment of heavy metal concentrations in the food web of lake Beyşehir Turkey. *Chemosphere, 60*, 552–556.

Barlas, N. (1999). A pilot study of heavy metal concentration in various environments and fishes in the Upper Sakarya River Basin. *Environmental Toxicology, 14*(3), 367–373.

Barlas, N., Akbulut, N., & Aydoğan, M. (2005). Assessment of heavy metal residues in the sediment and water samples of Uluabat Lake, Turkey. *Bulletin of Environmental Contamination and Toxicology, 74*, 286–293.

Bernard, M. (1976). *Sampling analysis of biological material. Manual of methods in aquatic environment research, FAO Fısheries Technical Paper* (p. 121). FIRI/158.

Canlı, M., & Atlı, G. (2003). The relationships between heavy metal (Cd, Cr, Cu, Fe, Pb, Zn) levels and the size of six Mediterranean fish species. *Environmental Pollution, 121*(Issue 1), 129–136.

Canlı, M., Kalay, M., & Ay, O. (2001). Metal (Cd, Pb, Cu, Fe, Cr, Ni) concentrations in tissues of a fish *Sardina pilchardus* and a prawn *Paeanus japonicus* from three stations on the Mediterranean Sea. *Bulletin of Environmental Contamination and Toxicology, 67*, 75–82.

Chatterjee, S., Chattopadhyay, B., & Mukhopadhyay, S. K. (2006). Trace metal distribution in tissues of Cıchlıds (*Orechromıs niloticus* and *O. mossambicus*) collected from wastewater fed fishponds in East Calcutta Wetlands a Ramsar site. *Acta Ichthyologica et Piscatoria, 36*(2), 119–125.

Chen, C. Y., Stemberger, R. S., Klaue, B., Blum, J. D., Pickhard, C., & Folt, C. L. (2000). Accumulation of heavy metals in food web components across a gradient of lakes. *Limnology and Oceanography, 45*(7), 1525–1536.

Cheung, K. C., Poon, B. H. T., Lan, C. Y., & Wong, M. H. (2003). Assessment of metal and nutrient concentration in river water and sediment collected from the cities in the Pearl River Delta, South China. *Chemosphere, 52*, 1431–1440.

EPA (2006). *National recommended water quality criteria* (25 pp.). Washington: Office of Water, Office of Science and Technology.

Göksu, M. L. Z., Çevik, F., Fındık, Ö., & Sarıhan, E. (2003). Seyhan baraj gölündeki Aynalı sazan (*Cyprinus carpio* L., 1758) ve sudak (*Stizostedion lucioperca* L., 1758) larda Fe, Zn, Cd düzeylerinin belirlenmesi. *E.U. Journal of Fisheries & Aquatic Sciences, 20*(1–2), 69–74.

Gül, A., & Yılmaz, M. (2002). Kızılırmak Nehri Delice Irmağı'nda yaşayan Capoeta tinca (Heckel, 1843)nın büyüme özellikleri. *G.Ü. Gazi Eğitim Fakültesi Dergisi, cilt 22*(sayı 1), 13–24.

Gümgüm, B., Ünlü, E., Akbaba, O., Yıldız Abdunnasır, & Namlı, O. (2001). Copper and zinc contamination of the Tigris River (Turkey) and its wetlands. *Arch. Für. Nat. Lands, 40*, 233–239.

Hellawel, M. J. (1988). Toxic substances in rivers and streams. *Environmental Pollution, 50*, 61–85.

Karadede, H., & Ünlü, E. (2000). Concentrations of some heavy metals in water, sediment and fish species from Atatürk Dam Lake (Euphrates) Turkey. *Chemosphere, 41*, 1371–1376.

Karadede Akın, H., & Ünlü, E. (2007). Heavy metal concentration in water, sediment, fish and some benthic organisms from Tigris River, Turkey. *Environmental Monitoring and Assessment, 131*, 323–337.

Karadede, H., Oymak, S. A., & Ünlü, E. (2004). Heavy metal in mullet, Liza abu and catfish, *Silurus triostegus* from Atatürk Dam Lake (Euphrates) Turkey. *Environment International, 30*, 183–188.

Kerrison, P. H., Annonsi, D., Zerrini, S., Ravera, O., & Moss, B. (1988). Effects of low concentrations of heavy metals on plankton community dynamics in a small shallow, fertile lake. *Journal of Plankton Research, 10*, 779–812.

Mendil, D., Tüzen, M., Sarı, H., Suiçmez, M., & Hasdemir, E. (2005). Trace metal levels in tissues of fishes (Capoeta tinca) from the River Yeşilırmak in Tokat, Turkey. *Fresenius Environmental Bulletin, 14*, 960–965.

TKB (2004). *Tarım ve Köyişleri Bakanlığı, Su kirliliği Kontrol Yönetmeliği, Kıta içi su kaynaklarının sınıflarına göre kalite kriterleri, su kirliliği kontrolü yönetmeliği, 31 December official gazete, no. 25687, 51 s* (in Turkish).

Yiğit, S., & Altındağ, A. (2002). Accumulation of heavy metals in the food web components of Burdur lake, Turkey. *Fresenius Environmental Bulletin, 11*(12a), 1048–1052.