Preliminary Assessment of Heavy Metals in Water and Some Cyprinidae species from the Porsuk River, Turkey

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Abstract

The presence of manganese, copper, cadmium, lead, nickel, zinc, chromium and iron concentrations was examined between June 2000 and July 2000, in water and some Cyprinidae species (*Barbus plebejus* Bonaparte, 1839*, Capoeta capoeta* (Güldenstadt, 1773)*, Capoeta tinca* (Heckel, 1843) and *Leuciscus cephalus* (Linnaeus, 1758)) from 11 sites within the Porsuk river in the northwest of Turkey suffering inputs from industrial and mining activities. Also, some parameters such as dissolved oxygen, temperature and pH of selected eleven stations in the Porsuk River were measured. The metal concentrations in the river water were found as in the range of 10-100 µg/L for Zn, 20-90 µg/L for Mn, 19-65 µg/L for Fe, 17.8-65.8 µg/L for Ni, 0.09-9.6 µg/L for Pb, 0.01-8.8 µg/L for Cd, 0.18-3.69 µg/L for Cu and 0.0067-0.025 µg/L for Cr. The metal concentrations found in the tissues of the four fish species varied considerably. The accumulation order of heavy metals in fish samples for liver was found to be Zn (*Capoeta tinca*) > Fe (*Leuciscus cephalus*) > Ni (*C. tinca*) > Mn (*C. capoeta*) > Cu (*L. cephalus)* > Cd (*C. tinca*) > Pb (*C. capoeta*) > Cr (*C. capoeta*).; for muscle Zn (*L. cephalus)* > Fe (*L. cephalus)* > Mn (*C. tinca*) > Ni (*C. capoeta*) > Cr (*L. cephalus)* > Pb (*Barbus plebejus)* > Cu (*C. capoeta)* > Cd (*C. capoeta*). The highest mean zinc concentrations (µg/gr wet weight) in liver and muscle were found to be 42.35-36.51 and 30-20.23 µg/g for *Capoeta tinca* and *Leuciscus cephalus,* respectively.

Key words: Heavy metals, fishes, Porsuk River.

INTRODUCTION

Heavy metals are an important group of chemical pollutants in natural waters. The accumulation of metals in an aquatic environment has direct consequences to man and the ecosystem. Heavy metals, of either human or natural origin, entering the aquatic ecosystems are transferred through food-webs to fish, humans and other piscivorous animals [1]. Their sources are mainly from domestic and industrial effluents [2, 3] and weathering of minerals and soil and atmospheric deposition [4, 5]. Chromium, cadmium, copper, lead, nickel and zinc are found in the list of organic and inorganic hazardous pollutants which is prepared by USEPA [6, 7]. Most fish are capable of accumulating heavy metals from their diet and from water through the gills [8]. The concentrations of heavy metals in the organs of fish are determined primarily by the level of pollution of the water and food, and so are indicative of the level of the pollution in the environment.

Cyprinidae is the freshwater fish family, which is widely distributed in the Turkish inland waters. They are the main source of fish food and are economically important in inland fisheries and aquaculture resources in Turkey. Study area, Porsuk River that is one of the most important tributaries of Sakarya River, economically important areas of the northwestern of the Central Anatolia. Although, several studies has been carried out in fish pollution by heavy metals in Turkey, but limited information has been published about metal's bioaccumulation in Upper Sakarya River Basin -Porsuk River and its fish [9,10]. The present study was carried out to determine the levels of some heavy metals (Mn, Cr, Cu, Cd, Zn, Fe, Pb and Ni) in water and in muscle and liver of four Cyprinid species (*Barbus plebejus, Capoeta capoeta, Capoeta tinca* and *Leuciscus cephalus*) from the Porsuk River.

MATERIALS AND METHODS

Description of study area

Sakarya River (824 km) is one of the longest rivers in Turkey. The study area has been carried out along the Porsuk river basin that is one of the biggest tributaries of the Sakarya River (Turkey). The Porsuk basin is one of the most economically important areas of the northwestern of the Central Anatolia. Very different economic activities take place in the area, ranging from agricultural, industrial and urban uses each of which provides different sources of these pollutants. The sampling sites along the rivers and the sources of pollutants effecting the Porsuk River are also shown in Figure 1. The sites were chosen due to easy.

Sampling and Analyses

Fish samples (*Barbus plebejus, Capoeta capoeta, Capoeta tinca* and *Leuciscus cephalus*) were caught using electroshock at selected stations shown in Figure 1, from the Porsuk River, between June 2000 and July 2000. The samples were transported in iceboxes to the laboratory on the same day. Random three fish samples belonging to each species were chosen and fresh fish samples were weighted. Fork lengths of the species were measured in terms of millimeter. The weight of the fish was calculated with a Ohaus balance (W±0.5g). Age was determined by the examination of the scales due to the practicality and reliability of this method. The age

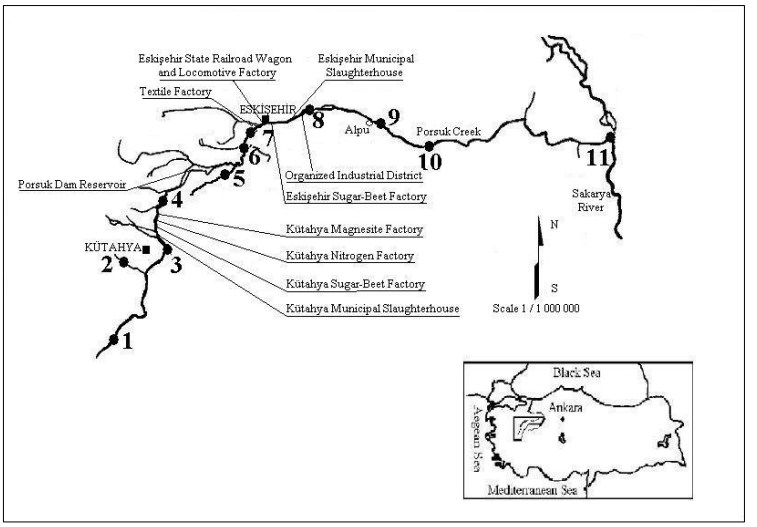

Figure 1. Location map of the study area, sampling stations and sources of pollutants effecting the Porsuk River basin.accessibility and they also reflect different activities in the catchments, which may affect the quality situation in the river. Samples were taken between June 2000 and July 2000.

determination was performed by removing approximately 30 scales from the body between the lateral line and dorsal fin of each fish. [11]. The age, weight and fork length of fish sample were caught are shown in Table 1. Fish samples were kept at -20°C until analysis. Before analysis, a bit of muscle, the whole livers from each fish were removed. Samples of tissues from each fish were weighed 1 g well homogenized tissue samples were wet digested with the mixture of 1 ml HNO_3/5 ml $HClO_4$. Completely digested samples were filtered and solution diluted to 20 ml by deionized water. Analysis of Mn, Cr, Cu, Cd, Zn, Fe, Pb and Ni were performed by Hitachi 180-70, polarized Zeeman Atomic Absorption Spectrophotometer.

Water samples were collected from the same area 30 cm below the water surface in 300 ml sterilized glass bottles from the Porsuk River according to the standard procedures described in the sampling guide [12,13]. Samples for metal analyses were acidified with concentrate nitric acid to pH less than 2.0. The samples after collection were kept at about 4°C until analyzed. Water temperature, pH and dissolved oxygen (DO) were measured in loco with multilane F/SET 3 from 0.3 m depth. Levels of heavy metals in water samples from the Porsuk River with other physical parameters are shown in Table 2. Classification of psychochemical parameters was performed according to the criteria of inland water quality that is commonly used in Turkey [14].

In addition, Npar and Kruscal-Wallis test systems were used for the evaluation of results. The Kruscal–Wallis test for statistical comparison of tissue Mn, Cr, Cu, Cd, Pb, Ni, Zn and Fe, between fish species was applied [15].

RESULTS

River water

The some parameters determined in the river are summarized in Table 2. The temperature varied between 12-23.8 °C; the pH between 7.7-8.8; the dissolved oxygen between 0.55 – 11.82 mg/L. The accumulation order of heavy metals was found as Zn > Mn > Fe > Ni > Pb > Cd > Cu > Cr in water samples. The highest concentration was recorded for Zn (100 µg./L) and the lowest for Cr (0,025 µg./L) (Table 2). Barlas [9, 10] reported lead, cadmium, nickel, copper and manganese concentrations from 0.013 µg./L to 4.41 µg./L; 0.03 µg./L to 1.532 µg./L 0.552 µg./L to 13.48 µg./L; from trace to16.72 µg./L; from 3.985 µg./L to 14.57 µg./L respectively from Upper Sakarya River basin water between 1995-1996. Our findings were parallel with this study except manganese maximum value when compared with the values found in this study.

Table 1. The age, size and weight of fish sample were measured (n: number of fishes; FL ± fork length (mm); S.D. ± standard deviation (minimum and maximum values are given in parentheses).

Species	n	Age interval	FL. ± S.D. (min-max)	BW. ± S.D. (min-max)
Barbus plebejus	40	1-4	18.61±6.01 (10.5-30.5)	49.42±40.37 (7.5-214)
Capoeta capoeta	20	1-4	17.55±5.12 (10.8-25.6)	96.12±31.56 (50.5-152)
Capoeta tinca	40	1-4	16.61±3.63 (9.7-24.4)	38.24±20.98 (9.5-81.5)
Leuciscus cephalus	60	1-7	21.16±5.37 (11-42)	102.37±98.76 (22-496.5)

River fish, muscle and liver, metal concentrations

Metal levels were detected in the muscle and liver tissues from four Cyprinidae species of Porsuk River and results are presented in Table 3.

According to our results zinc levels in muscle are significantly different between species (Kruscall–Wallis= 16.327, p< 0.05) and in the following order, *Leuciscus cephalus*> *Capoeta tinca* > *Capoeta capoeta* > *Barbus plebejus.* In liver tissue significant differences are also found between species (Kruscall–Wallis= 28.483, p< 0.05) and in the following order *Capoeta tinca* > *Leuciscus cephalus* > *Capoeta capoeta* > *Barbus plebejus*.

Manganese concentrations detected in muscle tissues present significant differences between species (Kruscall–Wallis = 35.613, p< 0.05). Lower concentrations were found in *Barbus plebejus* while higher concentrations were recorded for the *Capoeta tinca.* Mangenese–liver concentrations appear significantly higher in *Capoeta capoeta* compared to *Leuciscus cephalus*.

Chromium and iron levels in liver are significantly different between species (Kruscall–Wallis for Cr= 24.663, p< 0.05; Kruscall–Wallis for Fe= 30.395, p< 0.05;). Lower concentrations of Cr were found in *Barbus plebejus* while higher concentrations were detected for *Capoeta capoeta.* The highest Fe levels found in *Leuciscus cephalus* while the lowest Fe concentrations were recorded for *Capoeta capoeta.* In muscle tissue Fe concentrations were shown no significant differences between species (Kruscall–Wallis= 25.818, p>0.05) while Cr concentrations significant differences between species (Kruscall–Wallis= 19.892, p< 0.05). The order-row for species according to Cr-muscle concentrations goes as follows: *Leuciscus cephalus* > *Capoeta capoeta* > *Barbus plebejus* > *Capoeta tinca.*

Copper and lead levels in muscle or liver samples reveal significant differences between species (Kruscall–Wallis for Cu (muscle)= 35.515, p: p< 0.05; Kruscall–Wallis for Cu (liver)= 25.026, p< 0.05; Kruscall–Wallis for Pb (muscle)= 21.507, p< 0.05 and Kruscall–Wallis for Pb (liver)= 30.148, p< 0.05); however, Cu liver concentrations in all species were higher than Cu–muscle concentrations.

In similar way, nickel liver concentrations in all species were higher than Ni–muscle concentrations. Ni concentrations detected in muscle tissues present significant differences between species (Kruscall–Wallis= 20.867, p< 0.05). Lower concentrations were found in *Capoeta tinca* while higher concentrations were recorded for the *Capoeta capoeta.* In liver tissue high nickel concentrations were detected compared the muscle and significant differences are also found between species (Kruscall–Wallis= 36.747, p< 0.05) and in the following order *Capoeta tinca* > *Capoeta capoeta* > *Barbus plebejus* > *Leuciscus cephalus.*

Cadmium levels in muscle or liver samples reveal significant differences between species (Kruscall–Wallis (muscle) =39.683, p< 0.05; Kruscall–Wallis (liver)= 35.023, p< 0.05). Lower concentrations of Cd in muscle were found in *Leuciscus cephalus* while higher concentrations were detected for *Capoeta capoeta.* The highest Cd levels in liver found in *C. tinca* while the lowest Cd concentrations were recorded for *Leuciscus cephalus.*

Table 2. Levels of heavy metal concentrations (µg./L) in water samples from the Porsuk River with other parameters between June 2000 and July 2000 (Ss: sampling site, t: temperature, DO: dissolved oxygen; Roman numbers in parentheses are indicated classes of the water quality in the stations).

				Parameters							
Ss	**t (^{o}C)**	**pH**	**DO**	**Mn**	**Cr**	**Cu**	**Cd**	**Zn**	**Fe**	**Pb**	**Ni**
1	17.1	7.9	7.52	20	0.0098	0.25	0.015	10	29	0.090	19.1
	(I-II)	(I)	(II)	(I)	(I)	(I)	(I)	(I)	(I)	(I)	(I)
2	17.8	7.8	5.29	90	0.0078	0.18	0.012	10	35	0.25	17.8
	(I-II)	(I)	(III)	(I)	(I)	(I)	(I)	(I)	(I)	(I)	(I)
3	18.3	7.8	5.22	10.7	0.0067	0.47	0.070	20	62	1.20	23.2
	(I-II)	(I)	(III)	(I)	(I)	(I)	(I)	(I)	(I)	(I)	(II)
4	18.2	7.7	3	57	0.014	2.08	3.70	100	65	4	44
	(I-II)	(I)	(III)	(I)	(I)	(I)	(II)	(I)	(I)	(I)	(II)
5	12.0	8.4	5.57	89	0.025	1.54	0.24	90	39	1.39	24.4
	(I-II)	(II)	(III)	(I)	(I)	(I)	(I)	(I)	(I)	(I)	(II)
6	17.5	7.9	7.16	22	0.021	1.54	0.58	10	19	1.39	29.9
	(I-II)	(I)	(II)	(I)	(I)	(I)	(I)	(I)	(I)	(I)	(II)
7	23.8	8.2	11.82	37	0.019	1.23	2.65	30	64	2.72	30.2
	(I-II)	(II)	(I)	(I)	(I)	(I)	(I)	(I)	(I)	(I)	(II)
8	22.9	8.8	0.99	37.8	0.017	1.78	2.89	20	39	3.48	38.6
	(I-II)	(I)	(IV)	(I)	(I)	(I)	(I)	(I)	(I)	(I)	(II)
9	22.6	8.2	0.79	56	0.019	2	3.69	40	48	2.85	28.9
	(I-II)	(II)	(IV)	(I)	(I)	(I)	(II)	(I)	(I)	(I)	(II)
10	23.5	8.4	0.55	51	0.013	2.85	4.40	50	43	9.60	65.8
	(I-II)	(II)	(IV)	(I)	(I)	(I)	(II)	(I)	(I)	(I)	(III)
11	22.5	7.9	2.67	57.4	0.011	3.69	8.80	90	39	7.40	65.5
	(I-II)	(I)	(IV)	(I)	(I)	(I)	(III)	(I)	(I)	(I)	(III)

Table 3. The mean ± SD heavy metal concentrations in different tissue of four Cyprinidae species from the Porsuk River. (Minimum and maximum values are given in parentheses; units for water µgr l^{-1}, units for tissue µg./g)*.

* : (± S.D : standard deviation ;T: tissue; L: liver; M: muscle).

	T.	Mn	Cr	Cu	Cd	Zn	Fe	Pb	Ni
Water		37.9±27 (20-90)	0.015±0.006 (0.0067-0.025)	1.601±1.07 (0.18-3.69)	2.4±2.7 (0.01-8.8)	42±34.9 (10-100)	41±14 (19-65)	3.1±2.9 (0.09-9.6)	35.2±16.1 (17.8-65.8)
B. plebejus	L.	0.38±0.45 (0.145-1.06)	0.028±0.005 (0.021-0.031)	0.23±0.16 (0.11-0.46)	0.066±0.11 (0.0068-0.24)	10.61±0.66 (9.68-11.25)	3.25±2.34 (2.04-6.78)	0.12±0.018 (0.11-0.15)	0.74±0.34 (0.23-0.92)
	M.	0.23±0.16 (0.14-0.48)	0.14±0.035 (0.12-0.19)	0.088±0.085 (0.021-0.21)	0.042±0.047 (0.016-0.11)	8.27±1.34 (6.78-9.94)	0.51±0.051 (0.46-0.57)	0.14±0.12 (0.072-0.32)	0.42±0.25 (0.04-0.56)
C. capoeta	L.	1.13±1.1 (0.3-1.9)	0.22±0.24 (0.057-0.39)	0.42±0.065 (0.37-0.47)	0.146±0.162 (0.031-0.261)	13.31±5.24 (9.6-17.02)	5.82±1.66 (4.65-7)	0.31±0.31 (0.094-0.53)	1.71±0.01 (1.7-1.7)
	M.	0.53±0.3 (0.31-0.75)	0.23±0.013 (0.22-0.24)	0.26±0.069 (0.21-0.31)	0.126±0.132 (0.032-0.22)	8.92±2.43 (7.2-10.65)	1.08±0.014 (1.07-1.09)	0.14±0.1 (0.072-0.22)	0.68±0.065 (0.64-0.73)
C. tinca	L.	0.83±0.52 (0.19-1.46)	0.069±0.021 (0.046-0.097)	0.36±0.07 (0.31-0.44)	0.176±0.287 (0.027-0.608)	42.35±24.24 (11.7-71)	8.08±1.77 (6.20-10.43)	0.3±0.15 (0.17-0.5)	0.77±0.81 (0.14-1.97)
	M.	0.82±1.21 (0.11-2.6)	0.037±0.08 (0.03-0.05)	0.13±0.062 (0.067-0.18)	0.04±0.055 (0.0064-0.123)	30.03±16.24 (16.73-52.4)	0.48±0.13 (0.36-0.67)	0.16±0.069 (0.08-0.25)	0.33±0.04 (0.3-0.39)
L. cephalus	L.	0.241±0.25 (0,11-0,74)	0.097±0.071 (0.064-0.24)	0.21±0.20 (0.073-0.0623)	0.0159±0.014 (0.0033-0.042)	36.51±21.09 (14.86-65.30)	5.1±3.15 (3.19-11.5)	0.13±0.04 (0.1-0.21)	0.71±0.2 (0.32-0.89)
	M.	0.58±0.74 (0.17-2.04)	0.18±0.25 (0.036-0.673)	0.13±0.097 (0.054-0.301)	0.0282±0.019 (0.0058-0.047)	20.23±19.84 (1.69-59.03)	2.24±1.1 (0.97-3.63)	0.14±0.071 (0.05-0.27)	0.35±0.12 (0.26-0.57)

DISCUSSION

The concentrations of heavy metals detected in µg/g in muscle and liver (minimum, maximum and average) of *Barbus plebejus, Capoeta capoeta, Capoeta tinca* and *Leuciscus cephalus* are summarized in Table 3. In the study, especially zinc had the highest concentrations in the liver and muscle, followed by iron, nickel, manganese, copper, lead, cadmium and chromium. In *Barbus plebejus, Capoeta capoeta, Capoeta tinca* and *Leuciscus cephalus* mean Zn and Fe concentrations appear considerably higher in the liver than muscle (Table 3). The highest mean zinc concentrations in liver were found to be from 42.35 and 36.51 µg/g in *Capoeta tinca* and *Leuciscus cephalus* respectively. In addition, the highest mean zinc concentrations in muscle were found to be 30.03-20.23 µg./g in the same species. It is known that variability of heavy metal levels in different species depends on feeding habits [16], ecological needs, metabolism [17] age, size and length of the fish [18]. However, zinc and iron concentrations were also found in high quantities in water samples. This result is very significant because metals were accumulated and biological magnified in the food chain. These high results may be due to our study area consist of many pollutant factors such as discharge of effluents from factories (ceramic, engine), agricultural and industrial wastes (Figure 1). The results show high levels of zinc and iron in the edible fish tissues (muscle) as a result of the industrial wastes, which introduce to the river body and contain high levels of zinc and iron. We compared our average values of zinc with the range of international standards (40–100 µg./g) and Turkish acceptable limits (50 µg./g) [19] in edible parts of fish (muscle). The comparison showed that our value (30 µg g^{-1}) is lower than the guidelines. However, in *Copeota tinca* and and *Leuciscus cephalus* maximum value of zinc concentrations (52.4 µg./g and 59.03 µg./g respectively) appear considerably higher in the edible parts (muscle) of fish and this value higher than Turkish acceptable limits.

Zinc is essential elements and is carefully regulated by physiological mechanisms in most organisms; accumulate in porphyrins and enzymes. However, they are regarded as potential hazards that can endanger both animal and human health. Knowledge of its concentrations in fish is therefore important both with respect to nature management and human consumption of fish [20].

As conclusion this study was carried out to provide information on heavy metal concentrations in four Cyprinidae species from Porsuk River. All results were below the limits for fish proposed by EU [21] and TFC [19]. Although, levels of heavy metals are not high, a potential danger may emerge in the future depending on the domestic wastewaters and agricultural activities in this region.

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