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DETERMINATION OF HEAVY METALS IN FISH, WATER AND SEDIMENTS OF AVSAR DAM LAKE IN TURKEY

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ABSTRACT

In the present study, some heavy metals (Cd, Cr, Cu, Fe, Ni and Pb) were seasonally determined in water, sediment and some tissues of *Cyprinus carpio* from Avsar Dam Lake, which is an important water source for irrigation and drinking in Turkey. Heavy metal levels in water, sediment and fish samples were analyzed by inductively coupled plasma spectroscopy (ICP/AES). The obtained results showed that the average values of Fe in water samples were higher than the respective reference values for fresh water. Results for levels in water were compared with national and international water quality guidelines, as well as literature data reported for the lakes. The analysis of heavy metals in sediments indicated that among the six heavy metals tested, Fe was maximally accumulated, followed by Ni, Cu, Cr, Pb and Cd. Heavy metal concentrations were found to decrease in sequence of the *Cyprinus carpio* samples, in the muscle and stomach-intestine as Fe > Cu > Pb> Ni > Cr > Cd; in the gill, heart and liver as Fe > Cu > Ni > Pb > Cr > Cd and in the air sac as Fe > Cu > Ni > Pb > Cd >Cr. In the fish samples, cadmium, chromium, nickel and lead concentrations exceeded the tolerable values provided by international institutions.

Key words: Heavy metal, *Cyprinus carpio*, sediment, pollution, environment

INTRODUCTION

The pollution of the aquatic environment with heavy metals has become a worldwide problem during recent years, because they are indestructible and most of them have toxic effects on organisms (MacFarlane and Burchett, 2000). Among environmental pollutants, metals are of particular concern, due to their potential toxic effect and ability to bioaccumulate in aquatic ecosystems (Censi *et al.,* 2006).

Heavy metal concentrations in aquatic ecosystems are usually monitored by measuring their concentrations in water, sediments and biota (Camusso *et al.,* 1995), which generally exist in low levels in water and attain considerable concentration in sediments and biota (Namminga and Wilhm, 1976). Heavy metals including both essential and non-essential elements have a particular significance in ecotoxicology, since they are highly persistent and all have the potential to be toxic to living organisms (Storelli *et al.,* 2005).

Studies on heavy metals in rivers, lakes, fish and sediments (Özmen *et al.,* 2004; Begüm *et al.,* 2005; Fernandes *et al*., 2008; Öztürk *et al*., 2008; Pote *et al.*, 2008and Praveena *et al*., 2008) have been a major environmental focus especially during the last decade. Sediments are important sinks for various pollutants like pesticides and heavy metals and also play a significant role in the remobilization of contaminants in aquatic systems under favorable conditions and in interactions between water and sediment. Fish samples can be considered as one of the most significant indicators in freshwater systems for the estimation of metal pollution level (Rashed, 2001). The commercial and edible species have been widely investigated in order to check for those hazardous to human health (Begüm *et al.,* 2005).

Heavy metals such as copper, iron, chromium and nickel are essential metals since their play an important role in biological systems, whereas

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cadmium and lead are non-essential metals, as they are toxic, even in trace amounts (Fernandes *et al.,* 2008). For the normal metabolism of the fish, the essential metals must be taken up from water, food or sediment (Canlı and Atlı, 2003). These essential metals can also produce toxic effects when the metal intake is excessively elevated (Tüzen, 2003).

The Avsar Dam Lake is located on the West of Turkey and it is included in the National Water Reserves. The Lake was constructed to help alleviate the water problems of the Gediz basin and many inhabitants of the area also carry out fisheries on the Lake. The quality of this ecosystem has been degrading due to agriculture and human activities. To the best of our knowledge, from literature survey, no work has been carried out on the environmental quality of water, sediments and biota of the Lake.

The aim of this study was to determine the heavy metals concentrations (Cd, Cr, Cu, Fe, Ni, Pb) in water, sediments and in muscle, liver, gill, stomach-intestine, air sac and heart of fish species (*Cyprinus carpio* L., 1758) from the Avsar Dam lake, since this fish is an important component of the human diet in this zone. The results obtained from this study would provide information for background levels of metals in the water, sediment and fish species of the lake, contributing to the effective monitoring of both environmental quality and the health of the organisms inhabiting the lake ecosystem.

MATERIALS AND METHODS

Description of study area

Avsar Dam Lake is on the Gediz River in west Anatolia, Turkey (38° 13' N 28°.33' E - 38° 13' N 28°.37' E). The Maximum lake capacity is 69.000.000 m^3. Lake area is 5.25 km^2 (Anonymous, 1997). The lake is located approximately 120 km from the city of Manisa. It is used for irrigation and fisheries. In this study, surface water and sediment samples were taken from two different sampling sites at Avsar Dam Lake(Fig. 1). *Cyprinus carpio.* samples were also caught from the same localities. The two stations were determined considering the geographical structure of the dam, environmental conditions and sediment structure.

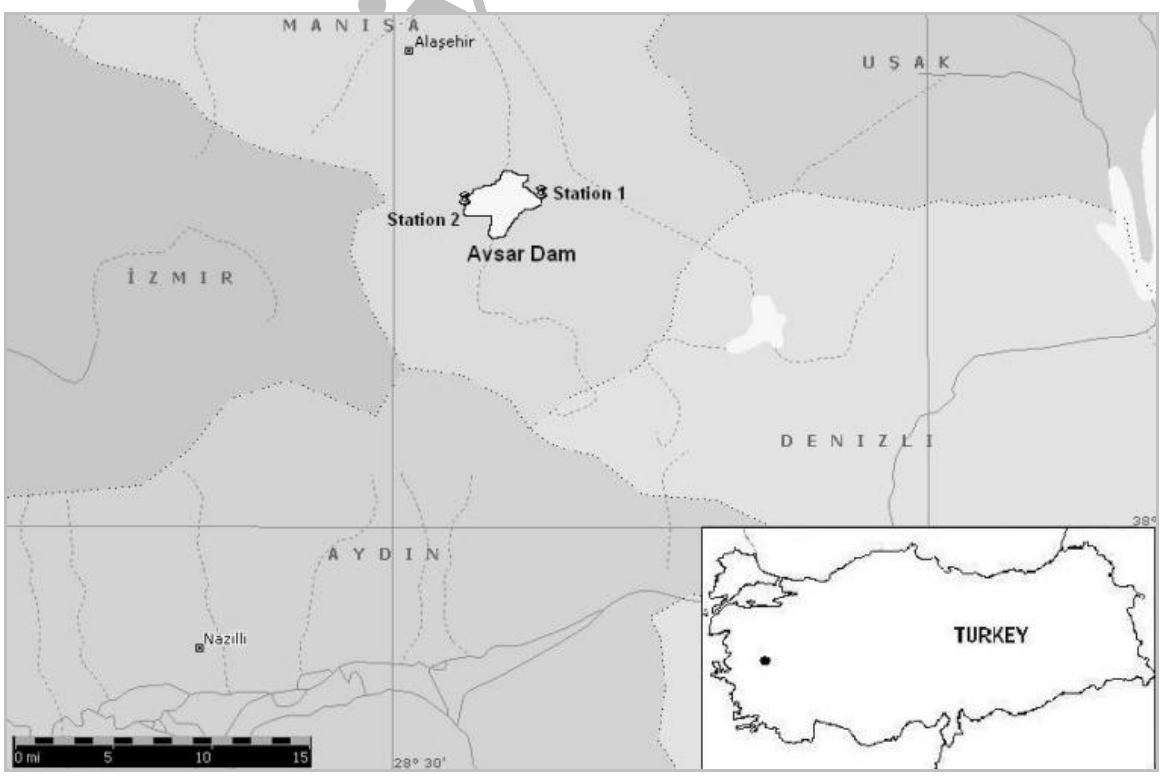

Fig. 1: Avsar Dam Lake and research station.

Sampling and sample preparation

Water, sediment and fish samples were collected 4 times (from July to April) for every 3 months from two sites in the lake. The sampling bottles were pre-conditioned with 5% nitric acid and later rinsed thoroughly with distilled de-ionized water. At each sampling site, the polyethylene sampling bottles were rinsed at least three times before sampling was done. Pre-cleaned polyethylene sampling bottles were immersed about 10 cm below the water surface. About 0.5 L of the water samples were taken at each sampling site. Samples were acidified with 10% HNO_3, placed in an ice bath and brought to the laboratory. The samples were filtered through a 0.45 µm micropore membrane filter and kept at 4 °C until analysis. The samples were analyzed directly.

Sediment samples were collected using grab sampler from two sites. Samples were transported to the laboratory and air-dried in the laboratory at room temperature. Once air-dried, sediment samples were powdered and passed through 160 µm sieve. The samples packed in polyethylene bags and stored below −20°C prior to analysis. Sediments samples were weighed placed into the digestion bombs with 10 mL of HNO_3/HCl (1:3 v/v) and digested in a microwave digestion system. Sediments analysis was carried out according to the procedure described earlier (Binning and Baird, 2001).

A total of 36 samples of mirror carp, *Cyprinus. carpio* species were collected with nets by local fishermen. Fish samples were transported to the laboratory in a thermos flask with ice on the same day. The mean length and weight of the fish were 303.6±12.4 mm and 526.6±32.15 g for *Cyprinus. carpio*. All fish samples were kept at -30°C until analysis. Sample preparation and analysis were conducted according to the procedure described by Bernhard (1976). Before analysis, muscle, liver, gill, stomach-intestine, air sac and heart from *Cyprinus. carpio* were removed. Fish samples were homogenized in a blender and one gram of homogenate was digested. A microwave digestion system (CEM Mars 5 ESP 1500 PLUS) was used to prepare the samples for analysis. In recent years, microwave digestion processes have been used in numerous studies (Machado *et al*., 1999; Kucuksezgin *et al*., 2001; Usero *et al*., 2003) owing to the advantages of this technique, which include speed of digestion and less possibility of contamination during the process. Samples (without skin) were mixed with 5 mL HNO_3 (65%) and 5 mL H_2SO_4 in polypropylene vials. After 10 minutes of mixing, 1 mL H_2O_2 was added and samples were placed in a microwave (1 hour at 105°C). After digestion, the residues were diluted to 25 mL with HNO_3 (0.3%) (Canlı and Atlı, 2003).

Determination of the elements in all samples was carried out by ICP–AES (Varian-Terra Model Liberty II). Detection limits are given in Table 1. The detection limit is defined as the lowest analytical signal to be distinguished qualitatively at a specified confidence level from the background signal (Kackstaetter and Heinrichs, 1997). The accuracy of analytical procedure was checked by analyzing the standard reference materials (water: SRM-143d, National Institute of Standards and Technology; sediment: CRM-277, Community Bureau of Reference; fish: DORM-2, National Research Council). Recovery rates ranged from 79 to 96% for all elements the investigated.

Table 1: Spectral lines used in emission measurements and the instrumental detection limit for the elements measured by using ICP–AES.

Element	Wavelength (nm)	Instrumental detection limit (µg/L)
Cd	228.8	0.001
Cr	267.8	0.007
Cu	324.8	0.014
Fe	259.4	0.07
Ni	231.6	0.05
Pb	220.4	0.05

RESULTS

Table 2 shows the water quality constituents of Avsar Dam Lake water, reference freshwater values and other global published values on Lakes in different continents. In water samples, according to analysis results, the following findings were obtained for the concentration ranges of the metals: Cd: 0.0001 – 0.0012 mg/L; Cr: 0.001 – 0.012 mg/L; Cu: 0.01 – 0.02 mg/L; Fe: 0.28 – 2.39 mg/L; Ni: 0.0004 – 0.012 mg/L and Pb: 0.0003 – 0.019 mg/L were found. Heavy metal concentrations in the lake water were decreased in the sequence of Fe > Cu > Pb > Cr > Ni > Cd.

Table 2: The heavy metal concentrations in the Avşar Dam Lake's water and comparison with guidelines and different literature Mean (±SD) (mg/L).

Guidelines/Locality	Cd	Cr	Cu	Fe	Ni	Pb	References
TSE-266	0.005	0.05	2	0.2	0.02	0.01	TSE-266, 2005
WPCL	0.003	0.02	0.02	0.3	0.02	0.01	WPCL, 2004
CIW	0.01	0.1	0.2	5	0.2	5	Anonymous, 1997
WHO	0.01	0.05	2	-	0.02	0.05	WHO, 1993
EPA	0.01	0.05	1.3	0.3	-	0.05	EPA, 2002
EC	5	50	2	0.2	20	10	EC, 1998
Avsar Dam Lake St.1	0.0007±0.002	0.005±0.005	0.01±0.001	0.9±0.4	0.004±0.002	0.01±0.007	This study
Avsar Dam Lake t.2	0.001±0.012	0.006±0.004	0.01±0.003	0.9±0.95	0.006±0.006	0.005±0.007	This study
Demirköprü Dam Lake	0.001	0.006	0.02	0.26	0.016	0.02	Öztürk *et al.*, 2008
Gediz River	0.0036	0.099	0.034	0.121	0.062	0.218	Uzunoğlu, 1999
Lapland Lakes	0.00002	0.0002	0.0003	0.087	0.0003	0.0003	Mannio *et al*., 1995
Siberian Pond	<0.001	0.002	0.002	0.29	0.002	0.002	Gladyshev *et al.*, 2001
Atatürk Dam Lake			0.22	0.062	0.015		Karadede and Ünlü, 2000
Hazar Lake			0.002	0.43	0.012		Özmen *et al*., 2004

Table 3 shows the total extractable metals from Avsar Dam Lake water sediments and other global published values for Lake sediments. The concentrations in sediment samples were as follows: Cd: 0.34 – 1.23 mg/L; Cr: 9.41 – 19.9 mg/L; Cu: 18.2 – 38.4 mg/L; Fe: 19680 – 28560 mg/L; Ni: 19.8 – 39.4 mg/L and Pb concentration 0.64 – 6.35 mg/L were found. Heavy metal concentrations in the lake sediments decreased in the sequence of Fe > Ni > Cu > Cr > Pb > Cd.

Table 3: The heavy metal concentrations in the Avşar Dam Lake's sediment and comparision with Sediment Quality Guideline and different literature Mean (±SD) (mg/kg dry weight).

Locality	Cd	Cr	Cu	Fe	Ni	Pb	References
LEL (Lowest Effect Level)	0.60	26.0	16.0	%2	16.0	31.0	NOOA, 2009
TEC (Threshold Effect Concentration)	0.99	43.4	31.6	-	22.7	35.8	NOOA, 2009
PEC (Probable Effect Concentration)	4.90	111.0	149.0	-	48.6	128.0	NOOA, 2009
SEL (Severe Effect Level)	10.00	110.0	110.0	%4	75.0	250.0	NOOA, 2009
Avsar Dam Lake St.1	0.76±0.4	14.48±4.4	29.98±4.7	25268±920	29.99±8.4	2.44±2.2	This study
Avsar Dam Lake St.2	0.76±0.2	13.33±2.2	23.47±9.9	22734±4084	28.25±6.9	4.04±2.1	This study
Demirköprü Dam Lake	0.82	6.75	15.1	15681	14.3	6.5	Öztürk *et al.*, 2008
Gediz River	0.64	140	257	5066	60.5	18.9	Uzunoğlu, 1999
Atatürk Dam Lake	-	-	22.70	19265	139.69	-	Karadede and Ünlü, 2000
Hazar Lake	-	-	6.4	30000	130	-	Özmen *et al*., 2004
Lake Victoria	7.0	12.9	26.1	-	-	54.6	Kishe and Machiwa, 2003
Lake Texoma	2	30	38	19393	17	10	An and Kampbell, 2003
Lake Geneva	18.4	337	727	40.6	87	620	Pote *et al.*, 2008
Wielkie Lake	1.20	1.15	2.05	30.2	1.60	9.7	Szymanowska *et al*, 1999
Boszkowo Lake	1.80	1.85	2.95	98.9	2.95	13.4	Szymanowska *et al.*, 1999
Dominickie Lake	1.25	1.30	2.65	44.1	2.05	12.9	Szymanowska *et al*, 1999

Table 4: The heavy metal concentrations of *Cyprinus carpio* samples from the Avşar Dam Lake (Mean±S.D, mg/kg wet weight).

Heavy metals	Muscle	Gill	Stomach-intestine	Air sac	Heart	Liver
Cd	0.17±0.07	0.15±0.14	0.15±0.20	0.72±0.24	0.49±0.34	0.79±0.33
Cr	1.18±0.73	1.61±0.73	1.77±1.16	0.42±0.49	1.27±0.38	0.83±0.53
Cu	3.85±2.18	3.94±0.87	5.80±3.86	8.88±3.26	12±5.92	9.73±4.03
Fe	16.55±6.99	203.7±106.9	396.9±128.2	71.3±30.9	118.05±34.19	94.27±54.85
Ni	1.27±1.18	3.52±3.33	3.23±3.04	1.05±1.20	3.99±3.82	7±1.94
Pb	2.14±2.09	3.11±2.50	3.61±0.37	1.00±1.03	1.62±1.03	3.42±3.23

The mean concentrations of heavy metals in the muscle, liver, heart, stomach-intestine, air sac and gills of *Cyprinus carpio* samples are given in Table 4. Heavy metal concentrations in the fish samples decreased in the sequence for the muscle as Fe > Cu > Pb > Ni > Cr > Cd, for the gill as Fe > Cu > Ni > Pb > Cr > Cd, for the stomach-intestine as Fe > Cu > Pb > Ni > Cr >Cd, for the air sac as Fe > Cu > Ni > Pb > Cd >Cr, for the heart as Fe > Cu > Ni > Pb > Cr >Cd and for the liver as Fe > Cu > Ni > Pb > Cr > Cd.

DISCUSSION

The Cd, Cr, Cu, Fe, Ni, Pb concentrations in lake water in the two sampling sites were compared with international standards. The obtained results showed that, with the exception of Fe, the heavy metal concentrations in water did not exceed WHO (World Health Organization, 1993), EC (Europian Community, 1998), EPA (Environment Protection Agency, 2002), WPCL (Water Pollution Control Legislation, 2004), CIW (Anonymous, Criterions of the Irrigation Water, 1997) and TSE-266 (Turkish Standards, 2005) guidelines (Table 2).

In the criterions of the irrigation water report (CIW) given as a result of "Gediz River Basin Study", maximum heavy metal concentrations allowed in irrigation waters were stated (Anonymous, 1997). These values and our results were compared and it was found as low heavy metal concentrations. In this case, the water taken from Avsar Dam Lake is proper for irrigation.

The heavy metal levels of water in Avsar Dam Lake were lower compared to the metal levels in Gediz River (Uzunoğlu, 1999) and Atatürk Dam Lake(Karadede and Ünlü, 2000) with the exception of Fe. Meanwhile Cu and Fe concentrations were higher than the Hazar Lake (Özmen *et al*., 2004) and Fe concentration was higher than the Demirköprü Dam Lake(Öztürk *et al*., 2008). Also, all heavy metal concentrations of water in Avsar Dam Lake were higher than the reported values for Lapland Lakes and Siberian Pond (Mannio *et al*., 1995; Gladyshev *et al*., 2001), (Table 2).

The metal concentrations obtained from the sediment samples were compared with Sediment Quality Guideline which showed that these concentrations did not exceed the probable

Table 5: The tolerable values of some heavy metals in the fish (mg/kg)

	Cd	Cr	Cu	Fe	Ni	Pb	References
UNEP	0.3	-	-	-	-	0.3	UNEP, 1985
IAEA-407	0.18	0.73	3.28	146	0.60	0.12	Wyse et al., 2003
TFC	0.05	-	20	-	-	0.2	TFC, 2002
Directive 2005/ 78/EC	0.05	-	-	-	-	0.2	EC, 2005

effect concentration (PEC) levels. The average concentrations of Cd and Fe were higher than those reported in Gediz River. Also, Cr, Cu, Fe and Ni concentrations were higher than the Demirköprü Dam Lakeand Cu concentration was higher than the Hazar Lake. Ni concentration was lower than the Atatürk Dam Lake (Table 3). Generally, the average Cd and Pb concentrations in Avsar Dam Lake were found to be lower than the other studies but Ni and Fe were higher. Differences between our data and the literature probably originate from variations in geological mining history of localities and urban and domestic activities.

When the values obtained in the *Cyprinus carpio* samples were compared with the tolerable values, it has been determined that the pollution has reached to hazardous levels for the health of human (Table 5). Cd, Cr, Ni and Pb values were higher than tolerable values.

The results confirmed the differences of accumulation of heavy metals in different tissues. The highest concentrations of Cr, Fe, and Pb were found in the stomach-intestine. Although, the highest level of Cu was found in the heart. Moreover, Cu accumulation in *Cyprinus carpio* was found to be the highest level in liver (Yaramaz, 1986).

Papagiannis *et al.,* (2004) have determined the level of Cu in various tissues of the *Cyprinus carpio* species in Pomvatis Lake ,Greece they reported the highest level of Cu in the liver and the lowest level of Cu in the muscle. In this study, the level of Cu in the liver was found to be higher than the muscle.

Fe, Cu and Pb accumulation in the muscle of *Cyprinus carpio* samples of Avsar Dam Lake were higher than the carps of Atatürk Dam Lake and Gölcük Lake (Uysal *et al*., 1986). According to the analysis of the results, the heavy metal levels in muscles showed that Fe had the highest and Cd had the lowest concentrations(Table 4). Similar results were reported from a number of fish species which shows that muscle is not an active tissue in accumulating heavy metals (Khan *et al.,* 1989; Karadede and Ünlü, 2000).

Öztürk *et al.,* (1995) found the highest level of Fe and the lowest level of Cd in the muscle, gill, air sac, stomach-intestine and liver of *Cyprinus carpio* samples in Altınkaya Dam, respectively. Also, Öztürk *et al.,* (2008) determined the highest level of Fe and the lowest level of Cd in all studied tissues of *Cyprinus. carpio* samples in Demirköprü Dam Lake. The result of our study was similar to the above studies.

Alam *et al*. (2002) has reported the concentrations of elements in the muscle, liver, intestine, kidney and gonads of cultured and wild carps caught in Lake Kasumigaura, Japan. They reported that the metal concentrations were lowest in muscle, and did not exceed the established quality standards for fish. In this study, the heavy metal levels in fish were found to be high. The high heavy metal levels in *Cyprinus carpio* would pose health hazards to the consumers.

Consequently, it can be concluded that the concentrations of heavy metals in water from Avsar Dam Lake are lower than the TSE-266, WPCL, CIW, WHO, EPA and EC standards, with the exception of Fe. The average concentration of Fe in the lake water was higher than the TSE-266, WPCL, EPA and EC standards. The concentrations of Cr, Cu, Fe and Pb in sediments from Avsar Dam Lake were lower than the sediment samples obtained from Gediz River, which is known as a polluted site. There were high levels of heavy metals in fish. It was determined that the pollution has reached hazardous levels for the health of human. Also, a potential danger may exist in the future, depending on the agricultural development in this region. As the Avsar Dam Lake is also used for agricultural irrigation purposes, performance of pollution researches at certain periods is of significance for both environment and public health.

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