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Concentrations of some Heavy Metals in Water, Sediment and some Living Organisms from the Zamanti River in Turkey

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Abstract

Water samples, sediments, aquatic plant (*Nasturtium officinale*) and fish species (*Oncorhynchus mykiss, Cyprinus carpio*) from the Zamantı River of Turkey were analyzed quantitatively for the presence of chromium, manganese and cadmium using an Atomic Absorption Spectrophotometer. The samples were collected from three stations. Water quality parameters, such as temperature, pH, dissolved oxygen and electrical conductivity were measured. According to the findings; pH value varied between 8.15-8.6. The gradual order of metals in water, sediment, *Nasturtium officinale* and fish species were given as follow; Mn>Cr>Cd in water, Mn>Cr>Cd in sediment, Mn>Cr>Cd in *Nasturtium officinale* , Mn>Cr>Cd in fish species. In comparison to international standards, low Cd and Cr levels were identified in all of the water, sediment, plant and fish samples. Mn levels were also low in the sediment, plant and fish samples. Only in the water samples were the Mn levels higher in comparison to the EC (Europian Community, 1998) and EPA (Environment Protection Agency, 2002) standard.

Keywords: ***Cyprinus carpio*, heavy metals, *Nasturtium officinale*, *Oncorhynchus mykiss*, Zamantı River.**

INTRODUCTION

Pollutants and environmental pollution can lead to significant problems for both living organisms and societies. The increases in worldwide population, as well as the advances in technology, contribute significantly to environmental pollution [1]. In our day, pollutants are being constantly being released into the air, soil, underground water sources, lakes and rivers [2, 3]. As a type of pollutant, heavy metals can accumulate in aquatic environments and lead to significant toxic effects [4]. In recent years, there has been a considerable rise in the number of problems associated with heavy metal pollution in aquatic environments. Even small quantities of heavy metals can contribute significantly to environmental pollution.

Heavy metals can be classified as toxic, semi-essential and essential [5]. Essential heavy metals can cause toxic effects in organisms when present in excessive quantities [6]. The concentration of certain metals in aquatic environments can increase due to the release of agricultural, domestic and industrial wastes into water sources. Suspended or dissolved heavy metals and other pollutants can be taken up by living organisms, or they can precipitate and accumulate in sediments. Most lakes, rivers and ocean sediments have been contaminated with pollutants. In the past ten years, the number of studies performed to demonstrate the environmental effects of heavy metals in river and lake fish and sediments have increased [7- 10]. The distribution and levels of metals in sediment environments neighboring residential areas can provide evidence on the effect of humans on aquatic environments. Assessing the accumulation of metals in sediments is important for determining these metals' environmental effects on local communities. In rivers, a correlation is observed between the concentration of heavy metals in the bottom sediments and the concentration of heavy metals in water [11].

Fish are in important source of food for humans. They represent a rich source of protein, polyunsaturated fatty acids (particularly omega-3 fatty acids), calcium, zinc (Zn) and iron (Fe) [12]. Fish require certain metals to maintain and sustain their normal metabolic functions [13]. However, excessive intake of these metals can also lead to toxic effects. Heavy metals released as a result of various physicochemical processes can be taken up by other organisms through the food chain [3, 14]. Fish samples are one of the most commonly used indicators for freshwater systems, and are employed to estimate and identify the levels of trace element pollution [15]. For this reason, numerous studies have been published on the measurement of heavy metals in fish [10, 16-18].

All metal ions, even those required for essential functions in plants, are extremely toxic to the metabolism of living organisms if taken in excessive quantities [19]. Metals can lead to oxidative stress in plants through the formation of free radicals [20]. Plants posses various tolerance and resistance mechanisms against metal ions [21, 22]. Every plant species demonstrates a different type of tolerance to different pollutants [23]. Aquatic marcophytes accumulate heavy metals in their tissues. Many studies have been conducted regarding the accumulation of metals in aquatic plants [24-28]. For this reason, these plants can potentially be used for the biological filtering and treatment of certain metals in water [29].

The aim of this study was to determine the concentration of certain heavy metals in water, sediment, plant (*Nasturtium officinale*) and fish (*Oncorhynchus mykiss* and *Cyprinus carpio*) samples from the Zamantı River, and to provide information regarding the heavy metal levels of these samples. Furthermore, this study will allow us to obtain information on the overall health of the abovementioned organisms in this river ecosystem.

MATERIALS AND METHODS

The headwater of the Zamanti River, which is the subject of the study, is located in the village of Serefiye, Uzunyayla in the Pınarbası district of the province of Kayseri, at an elevation of 1637 meters. The Zamantı River then unifies with the Göksu River at about 80 km from Adana and they form the Seyhan River, which flows into the Mediterranean Sea. The Seyhan River is 560 km long and its basin area is 20,100 km^2. The Zamantı River is made up of quite a number of creeks and brooks. The part of the Zamanti River examined in this study is between the location of its headwaters (Serefiye Village) and Bahcelik Dam Lake (Pınarbaşı), where it flows first. Three stations equally distributed in the specified area were determined during the study.

Some environmental parameters were studied at each station during the field study using a multiparameter device. The water samples were taken in accordance with the sampling rules from the stations located on the river [30]. The pH, temperature, dissolved oxygen and electrical conductivity values of the water samples were measured in the field using a WTW Multi 3400i device.

The water samples that were brought to the laboratory were filtered using a membrane filter of 0.45 µm pore diameter in order to detect the dissolved elements. The water samples taken from the filtrate was buffered using nitric acid. An appropriate volume of nitric acid was added. The sample was prepared for analysis by sealing and mixing the tube. The contents of the dissolved elements were measured using an ICP-OES device in compliance with relevant standards.

The sediment samples were put into colored glass boxes. After the water was completely removed from the samples using a drying oven, 1 g was taken from each sample and put into microwave solvation tubes. 5 mL HNO_3 and 1 mL H_2O_2 was added on top of each tube and solvated in a microwave oven. After this process, the tubes were cooled to room temperature and the solution in the tubes was transferred into 25 mL polypropylene volumetric flasks. The solutions in the volumetric flasks were diluted to 25 mL using distilled water [31]. The metal analysis of the samples was carried out in the ICP-OES device.

The plant samples (*N. officinale*) were brought to the laboratory in colored boxes. The ion escape and electrical conductivity change in the plants were measured [32]. A 0.5 g plant sample was taken and left in a beaker containing 100 mL deionized water for 24 hr. The electrical conductivity of the water was measured using a WTW Multi 3400i brand conductometer. For the heavy metal analyses, a part of the samples were taken and dried at 70°C in a drying oven. A 0.5 g sample was taken from the dried samples and their metal contents were determined using the ICP-OES device. The samples were analyzed three times.

O. mykiss and *C. carpio* samples were brought to the laboratory and their lengths and weights were measured. The branchia tissues were dissected using pincers and scalpel, then 0.5 g of each was taken by weighing them on an analytical balance and put into microwave. They were left to cool down the solvation process and transferred into volumetric flasks after dilution. The prepared samples were analyzed using the ICP-OES device.

The presence or absence of significant differences between the Mn, Cd and Cr levels measured in Plant-root, Plant-body, water, sediment and fish samples from different stations was tested with the Kruskal Wallis test, which is a nonparametric test. For each heavy metal parameter, the mean and standard deviation of triplicate measurements was calculated. All statistical analyses were performed using SPSS 15.0 statistical software. The results were considered significant in the case of $p < 0.05$.

RESULTS AND DISCUSSION

Certain physical parameters of the Zamantı River were measured at three different stations; a comparative evaluation of these physical parameters is shown in Table 1. The average water temperature of the Zamanti River during the course of the study was dedected as 8.6 ^oC. The highest temperature was measured at the 1st station (10.1 ^oC); and the lowest temperature was measured at 2nd station (6.2 ^oC). The pH values did not differ much among the stations and were determined to be 8.49 on the average. The lowest dissolved oxygen levels were measured at the 1st station (86 %) and the highest dissolved oxygen levels were measured at the 2nd station (108 %). The electrical conductivity values were measured to be 340, 438, and 440 microsiemens/cm at the 1^{st}, 2^{nd}, and 3^{rd} stations respectively (Table 1). The results acquired from some environmental parameters of the Zamanti River are shown in Table 1. Although the pH values differ according to some environmental parameters measured at all of the stations, the water was found to be 1^{st} class quality in terms of temperature and dissolved oxygen levels. However, the lightly alkali nature of the water stems mostly from the presence of bicarbonate ions. The temperature measurements were found to be low. Since the water temperature is significant in fish life, the fish were classified as cold water, mild and warm water fish [33]. The water from the river provides optimum conditions for cold water fish. The dissolved oxygen values were also found to be the lowest at the stations where the measured temperature was found to be the highest. However, the dissolved oxygen concentration measured in the surface water during the study was generally adequate for biological life (7.4 - 10.8 mg/L).

In this study, the levels of heavy metals absorbed by the *N. officinale, O.mykiss,* and *C. carpio* species were compared with the levels of heavy metals found in the water and sediment samples collected from the Zamantı River.

The Mn, Cd and Cr levels measured in the water samples were 0.050309-0.172763 ppm, 0.00685-0.00751 ppm and 0.04974-0.05736 ppm respectively. According to their average levels, these metals can be ranked as Mn > Cr > Cd in terms of concentration. Based on these results, it was determined that the Mn, Cd and Cr levels in the water samples varied from one station to another ($p>0.05$) (Tablo 2). No correlation was observed between the Cr and Cd levels measured in the water samples ($r = 0,072$ $p>0.05$). On the other hand, a low and negative correlation was observed between the Mn and Cr levels (r = -0.212

p>0.05). In other words, an increase in Mn levels was accompanied by a decrease in Cr levels, while a decrease in Mn levels was accompanied by an increase in Cr levels. However, this correlation was not significant. A low and negative correlation was identified between the Cd and Mn levels(r = -0.139 p>0.05). In other words, an increase in Cd levels was accompanied by a decrease in Mn levels, while a decrease in Cd levels was accompanied by an increase in Mn levels. However, this correlation was also not significant (Table 9). Comparison of the quantities of heavy metals detected in the water samples. All three metals were found in low quantities in the water samples. The levels of certain heavy metals in our water samples were different than the levels observed in other aquatic environments (Table 3) [34-36].

The Mn, Cd and Cr levels measured in the sediment samples were 1.52635-5.86636 ppm, 0.00253-0.00563 ppm and 0.35261-0.94301 ppm respectively. According to their average levels, these metals can be ranked as Mn > Cr > Cd in terms of concentration. Based on the study results, the Mn, Cd and Cr levels measured in the sediment samples varied from one station to another (p<0.05) (Table 2). For all three heavy metals, the levels measured at the second station were higher than the levels observed in the other stations. All three metals were found in low quantities in the sediment samples. The Cr and Mn levels in the sediment samples were higher than the levels observed in the water samples. This could be due to the precipitation of heavy metals from the water into sediments. A moderate and positive correlation was identified between the Mn and Cd levels (r = 0.527 p>0.05). In other words, an increase in Mn levels was accompanied by an increase in Cd levels, while a decrease in Mn levels was accompanied by a decrease in Cd levels. However, this correlation was not significant. A high and positive correlation was identified between the Mn and Cr levels (r = 1.000 p<0.01). In other words, an increase in Mn levels was accompanied by an increase in Cr levels, while a decrease in Mn levels was accompanied by a decrease in Cr levels. This correlation between the Mn and Cr levels was significant. A moderate and positive correlation was identified between the Cd and Cr levels (r = 0.527 p>0.05). In other words, an increase in Cd levels was accompanied by an increase in Cr levels, while a decrease in Cd levels was accompanied by a decrease in Cr levels. However, this correlation was not significant (Table 8). The heavy metal levels measured in the sediment samples was higher than the levels measured in the plant and water samples. Many studies have reported greater heavy metal accumulation in sediments [37, 38]. The level of certain heavy metals in our sediment samples was different than the levels observed in other aquatic environments (Table 4) [34-36, 39, 40].

In the *O. mykiss* samples, the Mn, Cd and Cr levels were measured as 0.06236-0.07013 ppm, 0.00597-0.00651 ppm and 0.04106-*0.04669* ppm, respectively; while in the *C. carpio* samples, the Mn, Cd and Cr levels were measured as 0.03753-0.04391 ppm, 0.00663-0.00706 ppm and 0.04265-0.04702 ppm, respectively. Based on their average levels, these metals can be ranked as Mn > Cr > Cd for the *O. mykiss* samples, as Cr > Mn > Cd for the *C. carpio* samples in terms of concentration (Table 5). No significant differences were identified between the Mn, Cd and Cr levels measured in the *O. mykiss* and *C. carpio* samples (p>0.05). The heavy metal levels measured in the fish samples were relatively low [36-39].

Chlorophyl and EC values were measured for the plants taken from each of the three stations (*N. officinale*). EC levels for the plants collected from the 1st, 2nd and 3rd stations were measured to be 23, 22, and 24 microsiemens/cm, respectively. The Mn, Cd and Cr levels measured in the plant-root samples were 0.04323-5.90832 ppm, 0.00593-0.00702 ppm and 0.00702-0.04272 ppm respectively. According to their average levels, these metals can be ranked as Mn > Cr > Cd in terms of concentration. Based on the study results, it was determined that the Mn, Cd and Cr levels in the plant root samples varied significantly from one station to another (p<0.05). The Mn levels measured in the plant root samples from the second station were higher than the levels measured in samples from the other stations. On the other hand, the Cr levels measured in the plant root samples from the first station were higher than the levels measured in samples from the other stations. However, Cd levels in the plant root samples did not vary significantly from one station to another (p>0.05) (Tablo 2). There was no relationship or correlation between the Mn and Cd levels in the plant root samples (r = 0.043 p>0.05) . A moderate and negative correlation was identified between the Mn and Cr levels(r = -0.502 p>0.05). In other words, an increase in Mn levels was accompanied by a decrease in Cr levels, while a decrease in Mn levels was accompanied by an increase in Cr levels. However, this correlation was not significant. A moderate and negative correlation was identified between the Cd and Cr levels (r = -0.502 p>0.05). In other words, an increase in Cd levels was accompanied by a decrease in Cr levels, while a decrease in Cd levels was accompanied by an increase in Cr levels. However, this correlation was also not significant (Table 6).

The Mn, Cd and Cr levels measured in the plant-body samples were 0.55326-13.91324 ppm, 0.00436-0.00687 ppm and 0.002630-0.03631 ppm respectively. According to their average levels, these metals can be ranked as Mn > Cr > Cd in terms of concentration. Based on the study results, it was determined that the Mn and Cr levels in the plant body samples varied from one station to another (p<0.05). Similar to the observations with the plant root samples, higher Mn levels were measured in plant body samples from the second station in comparison to the samples from the other stations. On the other hand, the Cr levels measured in the plant body samples from the first station were higher than the levels measured in samples from the other stations. However, Cd levels in the plant body samples did not vary significantly from one station to another (p>0.05) (Table 2). No correlation was observed between the Mn and Cd levels measured in the plant body samples (r = -0.062 p>0.05). On the other hand, a moderate and negative correlation was identified between the Mn and Cr levels (r = -0.458 p>0.05). In other words, an increase in Mn levels was accompanied by a decrease in Cr levels, while a decrease in Mn levels was accompanied by an increase in Cr levels. However, this correlation was not significant. A moderate and negative correlation was identified between the Cd and Cr levels (r = -0.343 p>0.05). In other words, an increase in Cd levels was accompanied by a decrease in Cr levels, while a decrease in Cd levels was accompanied by an increase in Cr levels. However, this correlation was also not significant (Table 7).

The Mn, Cr and Cd levels measured in water samples from the river stations were compared with the international standards. In this context, it was determined that the heavy metal concentrations did not exceed the levels indicated in the WHO [41] and WPCL [42] guidelines (Table 2). However, the Mn levels were higher than the standards described in the EC [43] and EPA [44] guidelines. The high water pH levels can decrease the concentration of the heavy metals; this is because heavy metals cannot dissolve at high pH values; metals bonded to the particles suspended in water or found in sediments can become free only if the water is acidic. In comparison to other studied aquatic environments; the Cd levels measured in the Zamantı River was higher than the levels measured in the Ganga River, Gediz River and Avşar Dam Lake, but lower than the levels measured in the Okumeshi River. The Cr levels, on the other hand, were higher than the levels measured at the Ganga River and Avşar Dam Lake, but lower than the levels measured at the Gediz River and Okumeshi River. Finally, the Mn levels were higher than the levels measured at the Ganga River, but lower than the levels measured at the Okumeshi River (Table 3) [34-36].

The metal concentrations measured in the sediment samples were compared with the standards of the Sediment Quality Guideline. This comparison showed that the concentrations of our samples did not exceed the probable effect concentrations (PECs) [45] . It was also determined that the Mn, Cd and Cr levels in the Zamantı River sediment samples were lower than the levels measured in sediments samples from the Ganda River, Gediz River, Okumeshi River and Avşar Dam Lake (Table 4) [34-36, 39].

The levels of heavy metals measured in the trout and carp samples were compared with the international standards. In this context, it was determined that Mn, Cd and Cr levels were lower than levels described by the international standards [46-48]. In comparison to samples from fish in other aquatic environments, the fish muscle tissue samples collected during the current study had lower levels of heavy metals (Table 5).

Numerous studies have been conducted to date on the accumulation of heavy metals in *N. officinale*, and on the potential use of this species in remediation [26-27]. For this reason, it is inevitable for heavy metals in aquatic environments to be also found and detected in this plant species. Consequently, *N. officinale* seems particularly suitable for use in the phytoremediation of moderately and heavily polluted aquatic ecosystems [29]. In our study, heavy metal levels in *N. officinale* were measured as being relatively low.

Tabel I. The values of environmental parameters for the river.

Stations	Temperature (℃)	pH	O_2 %	Conductivity(μS/cm)
1	10.1	8.6	86	340
2	6.2	8.7	108	478
3	9.5	8.15	88	440

Tabel II. Comparison of heavy metal levels measured in plant, sediment and water samples from different stations

Analysis material		Stations	Cd	Cr	Mn
Plant	*N. officinale* Root	1	0.0063±0.0006	0.0417±0.0012 *	0.0437±0.0012
		2	0.0063±0.0006	0.0073±0.0006	5.4137±0.6488 *
		3	0.0067±0.0006	0.0060±0.0001	0.1940±0.0272
	N. officinale Body	1	0.0053±0.0012	0.0287±0.0067 *	0.5733±0.0222
		2	0.0053±0.0006	0.0173±0.0045	12.3630±1.8173*
		3	0.0060±0.0010	0.0030±0.0001	2.6280±0.5758
Sediment		1	0.0037±0.001	0.3677±0.014	1.7057±0.182
		2	0.0053±0.001	0.846±0.097	5.179±0.671
		3	0.0031±0.001	0.5823±0.069	2.4837±0.242
Water		1	0.007±0.001	0.054±0.002	0.052±0.001
		2	0.007±0.001	0.0537±0.004	0.165±0.008
		3	0.0073±0.001	0.0537±001	0.0513±0.001

*Significant Difference ($p<0.05$)

Tabel III. The trace metal concentration in Zamanti River Water and comparison with water quality guidelines (mg/L).

Guidelines/Locality	Cd	Cr	Mn	References
WPCL	0.003	0.02	-	42
WHO	0.01	0.05	0.5	41
EPA	0.01	0.05	0.02	44
EC	5.0	50.0	0.05	43
Zamantı River	0.0071±0.0003	0.0537±0.002	0.0894±0.0568	This study
Ganga River	0.0001-0.0005	0.0015-0.0688	0.0038-0.00973	34
Avsar Dam Lake St.1	0.0007±0.002	0.005±0.005	-	35
Okumeshi River	0.03	0.09	0.13	36

Tabel IV.. The trace metal concentration in the sediment and comparison with sediment quality guidelines (mg/kg dry weight).

Locality	Cd	Cr	Mn	References
LEL (Lowest Element Level)	0.60	26.0	-	45
TEL (Threshold Element Level)	0.99	43.4	-	45
PEC(Probable Effect Concentration)	4.90	111.0	-	45
SEC (Severe Effect Level)	10.0	110.0	-	45
Zamantı River	0.004±0.0011	5.5986±0.216	3.1227±1.6208	This study
Avsar Dam Lake St.1	0.76±0.4	14.48±4.4	-	35
Ganga River	0.70-7.90 µg/g	6.105-20.595 µg/g	134.915-320.45 µg/g	34
Okumeshi River	1.32	0.87	2.76	36
Yeşilırmak River/ (max. Conc.)	0.55	-	446	39
Tigris River (max. Conc.)	7.90	158.35	1681.84	40

Tabel V.. The tolerable values of some trace metals (mg/kg dry weight)

Source	Cd	Cr	Mn	References
UNEP	0.30	-	-	46
IAEA-407	0.18	0.73	11.0	47
Directive 2005/78/EC	0.05	-	-	48.
Oncorhynchus mykiss	0.006±0.001	0.044±0.003	0.066±0.004	This study
Cyprinus carpio	0.007±0.001	0.045±0.002	0.041±0.003	This study
Okumeshi River/ *Tilapia nilotica*	0.62	0.06	1.97	36
Okumeshi River/ *Chrysichthys nigrodidatatus*	0.45	0.04	1.89	36
Yeşilırmak River/ *Cyprinus Carpıo* /autumn	0.15 + 0.02 (µg/g)		1.1 + 0.1 (µg/g)	39

Tabel VI a. Correlation analysis between the heavy metal levels measured in different plant root samples

Materyal		Mn	Cd	Cr
Plant -Root	Mn	1.000		
	Cd	0.043	1.000	
	Cr	-0.502	-0.355	1.000

Tabel VI b. Correlation analysis between the heavy metal levels measured in different plant body samples.

Materyal		Mn	Cd	Cr
Plant -Body	Mn	1.000		
	Cd	-0.062	1.000	
	Cr	-0.458	-0.343	1.000

Tabel VI c. Correlation analysis between the heavy metal levels measured in different sediment samples.

Materyal		Mn	Cd	Cr
Sediment	Mn	1.000		
	Cd	0.527	1.000	
	Cr	1.000**	0.527	1.000

Tabel VI d. Correlation analysis between the heavy metal levels measured in different water samples.

Materyal		Mn	Cd	Cr
Water	Mn	1.000		
	Cd	-0.139	1.000	
	Cr	-0.212	0.072	1.000

CONCLUSION

In conclusion, it was determined that the Cd and Cr levels measured in the water, sediment and fish samples from our study area were lower than the levels described by all international standards. The Mn levels in the sediment and fish samples were also found to be lower than the levels described by the international standards. Although the Mn levels measured in our water samples were higher than the standards set by the EPA and EC, they were nevertheless within the normal levels described by the WHO and SON. The Zamantı River is a river that is extensively used for agricultural purposes, and which also has many fish farms. It is therefore of great importance for human health and the environment to periodically measure and monitor the heavy metal levels in this river.

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