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Heavy metal accumulation in water, sediments and fishes of Nallihan Bird Paradise, Turkey

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Abstract: *The accumulation of some heavy metals such as Pb, Cd, Cu and Ni was determined in water, sediment and fish samples (Alburnus escherichii, Cyprinus carpio and Silurus glanis) collected from Nallihan Bird Paradise (NBP) and its vicinity (Sariyar Dam). The results showed that these metals are found widespread throughout the study area, but metal concentrations in the water samples are below the detection limits (BDL). Pb, Cd, Cu and Ni contamination were determined in sediments and in fish tissues (muscle and liver) and it was seen that they were accumulated and biologically magnified in fish tissues. Metal concentration levels in sediment samples were higher than that of water and fish tissues. The highest amount of metal concentrations in sediment samples among seven stations were determined in Usakbuku (Pb: 0.49 ppm), Sakarya River (Cu: 1.12 ppm) and Sariyar (Ni: 0.77 ppm). Unlikely to the other stations, no metal residues were determined in the sediment samples of Aladag Creek Station.*

Key words: *Heavy metals, Water, Sediment, Fish, Nallihan bird paradise*
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Introduction

Human activity has continuously disturbed the natural environment, particularly the aquatic ecosystems. The use of organochlorine insecticides and heavy metals in industry has lead to widespread environmental contamination. Some of these compounds are the object of study on account of their toxicity and ubiquity and moreover, they are known to remain stable in the aquatic environment (Fernandez *et al.*, 1992; Ayas and Kolankaya, 1996; Heiny and Tate, 1997; Samanta *et al.*, 2005; Singh and Singh, 2006).

The Nallihan Bird Paradise (NBP) including the adjacent reservoir of the Sariyar Dam is one of the most significant water resources and important bird areas of the Central Anatolia, where semi arid climate prevails. It is located 180 km northwest of Ankara and has a surface area of 8,400 ha (coordinates: 40° 02' 24" N - 31°36' 36" E) as depicted in Fig. 1.

NBP is an internationally recognized bird area "Important Bird Area No: 45" (Yarar and Magnin, 1997). This area holds breeding population of night heron which breed in poplar plantation on the southern shores, whilst black storks, Egyptian vulture and lanner breed on the cliffs. The "Nallihan Bird Paradise" holds large number of roosting white storks on migration (more than 10000) and ruddy shelduck. Very large number of grey heron, egret, and little egret breeds in mixed the each other. Black kite and peregrine falcons also breed while white tailed eagle is frequently observed and suspected to breed in the sites close surroundings. The "Nallihan Bird Paradise" was declared a Permanent Wildlife Reserve in 1994. Until today, about 250 bird species, most of them being water birds, have been observed in NBP (Perktas and Ayas, 2005). The native fish fauna composed of 13 species including some endemics for Anatolia such as *Capoeta baliki* and *Alburnus escherichii*. The reservoir is lying in a long, narrow, and deep valley surrounded mainly by bare land, small villages and limited agricultural areas due to its topography and soil characteristics. The fishery established in the reservoir has a great importance for the economic well being of locals and after the wet season the end part of the reservoir area is used for agriculture. In addition, the reservoir is being used for irrigation of the nearby agricultural areas. This Dam was built on Sakarya River in 1958, and receives various kinds of pollutants, including domestic and industrial effluents from the settlements located along the upstream of the reservoir, as well as irrigation and surface runoff. Therefore, there has been continuous flow of pollutants into the river and the reservoir, and pollution in these water systems became significant during the last two decades. Although domestic and to a lesser extent industrial wastewater discharges have been worked on by several studies, there are only a few studies on the reservoir and NBP as a receiving environment (Ekmekci and Erkakan, 1989; Ekmekci *et al.*, 2000; Sharma and Agrawal, 2005). This study aims to determine the extent of heavy metal contamination of the aquatic ecosystem covering the NBP and the reservoir. The main objective was to obtain basic and simple information permitting a better understanding of environmental impact of some of the heavy metals used in the basin. This information would be a useful tool for effective management and control of the natural area with respect to input of some metals that are carried and their bioavailability.

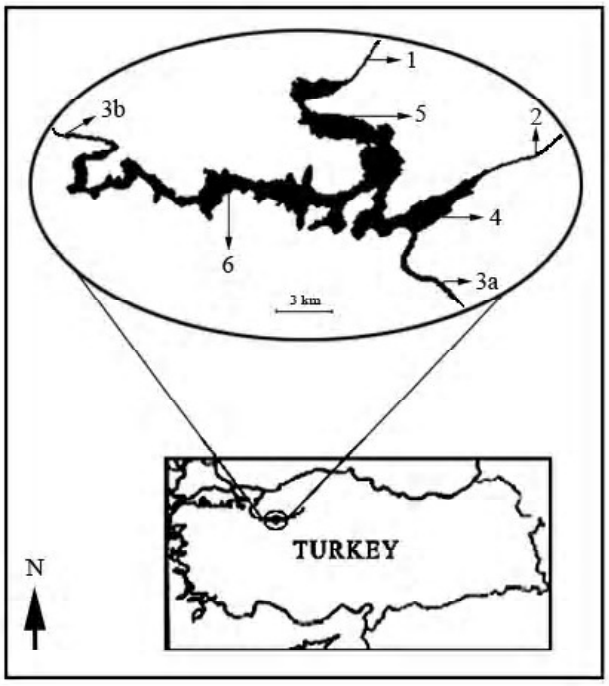

Fig. 1: Map showing sampling stations in Nallihan Bird Paradise (1 = Alada Creek, 2 = Kirmir Creek, 3a = Sakarya River-entry, 3b = Sakaraya River-exit 4 = Usakbuku, 5 = Cayirhan and 5 = Sariyar)

Materials and Methods

Study area and sampling stations: Samples were collected from the stations marked on the Fig. 1. On the neighborhood of Aladag Creek, there were no urban or industrial areas and this creek represented a non-polluted area. Kirmir Creek and Sakarya River flow along the Sakarya Basin receiving urban, industrial and agriculture based pollutants, which also include heavy metals, and have high pollution loads. Naturally, these rivers bring these pollutants, including heavy metals, to the Nallihan Bird Paradise. Cayirhan, Usakbuku and Sariyar sampling stations were selected in the reservoir in order to represent the lentic (lake) environment, where fishing is intensive and pollution load brought by the rivers flowing into the lake can accumulate. Another reason for selecting these locations as sampling stations is the convenience of catching all three of the fish species of concern for this study. Water and sediment samples were collected from seven different sites in NBP and its tributaries. These are Aladag and Kirmir Creeks (1 - 2), Sakarya River-entry and Sakarya River-exit (3a - 3b), Usakbuku, Cayirhan and Sariyar (4 - 5 and 6). Fish samplings were performed from four different locations as follows: Aladag Creek (1), Usakbuku, Cayirhan and Sariyar (4 - 5 and 6).

Sample collection, storage and analyses:

Water: Water samples were collected seasonally throughout 1998 and 1999 (summer and autumn in 1998, winter and spring in 1999). Water and sediment sampling was performed in seasonal basis annually throughout 1998 (summer - autumn) and 1999 (winter - spring). Water samples were collected from 0.1 m below the water surface, into glass bottles that were pre-cleaned by distilled water and acidified with concentrated nitric acid to pH less than 2.0 than stored in polyethylene bottles at 4°C until the analyses. All water samples were immediately brought to the laboratory and were filtered through 0.45 µm millipore filters and acidified with concentrated nitric acid (1:1 v/v) per liter to pH less than 2.0. Analyses were performed according to APHA, 1995.

Sediments: The upper 10 cm of the bottom layer sediment samples were taken with Ekman grab. Each sediment core was packed separately in acid-soaked clean polyethylene packets and brought to the laboratory in ice buckets. In the laboratory the sediment samples were dried at 105°C to constant weight, ground and the fraction passing a BS20 sieve was stored in clean acid-soaked polyethylene packets at 20°C. Analyses were performed according to APHA, 1995.

Fishes: Three fish species; bleak (*Albumus escherichii*), common carp (*Cyprinus carpio*) and wels (*Silurus glanis*), which are consumed by local people and water birds are selected to determine the heavy metal accumulation. These species were selected due to their differences of niche and habitat preferences. Wels is a benthic fish, which has a piscivorous diet. According to stomach content analysis, the diet of wels depends mainly on bleak (Ekmekci *et al.*, 2000). Fish specimens from the reservoir were provided from the local fisherman, which were caught by gill nets. Fish specimens of creeks were captured by pulsed DC electro fishing equipment. Bleaks were sampled from Cayirhan, Usakbuku and Sariyar Stations and from Aladag Creek. Carps and wels were sampled only at Cayirhan, Usakbuku and Sariyar Stations. Fish samples were selected from the same age group as far as possible. Sampled carps were 2+ years old, while 1+year-old wels and bleak were used. The fish were anesthetized in 100 mg/l MS 222 containing plastic gallon and these samples were transferred to laboratory in ice-boxes. Fish samples were dried at 102°C to constant weight. The exoskeleton of fishes was removed and the muscle and liver were removed and cut into pieces and than were stored in polyethylene packet at 20°C.

Concentrations of metals in all the samples were measured by atomic absorption spectrophotometer (Jarrel Ash-850) at the Middle East Technical University Environmental Engineering Laboratory. Pb was measured at wave length 283.3 nm, Ni at 232.0 nm, Cd at 222.8 nm and Cu at 365.4 nm. The minimum concentrations of metals that could be detected were 0.02 ppm for each metal. Calibration was made with standard solutions. The precision and accuracy of determination was checked by repeated analyses of the sub-samples of the standards and by recovery tests. Results were presented on the dry-weight basis in order to avoid errors associated with varying moisture levels in soft tissues (Adrian and Stevens, 1979). Values below detection limits were assigned as "BDL" on the tables and geometric means were reported for residue data.

Statistical analyses: Metal contents determined in water, sediment and fish tissue samples were evaluated statistically using analysis of variance (ANOVA) technique. The metal concentration values determined in sediments and fish tissue were normalized. The partition coefficient for metal concentrations in water and sediment environments and in fish tissue was determined as 0.05.

Results and Discussion

Metal concentration in water, sediments and fish samples are shown in Table 1 and 2. Metal concentration of the water samples were found to be below the detection limits (BDL). Pb, Cd, Cu and Ni contamination were determined in sediments and fish samples and the levels of heavy metals in fishes were found to be higher than that of both, sediments and water, they live.

In sediment samples, the highest metal concentration among seven stations were determined in Usakbuku (Pb: 0.49 ppm), Sakarya River (Cu: 1.12 ppm) and Sariyar (Ni: 0.77 ppm) stations. Unlike other stations, no metal residues were determined in the sediment samples taken from Aladag Creek. The highest value for Pb and Cu in sediments were in the station located in Sakarya River just in the entrance of the dam lake. These concentrations decrease at the point where Sakarya River leaves the dam lake. Cd was not found in water or sediment samples in any of the stations, but it was detected in the liver tissue of wels that was caught in some of the sampling stations.

Fishes (bleak, carp and wells) were caught at four locations in the NBP (Aladag Creek, Usakbuku, Cayirhan and Sariyar). The results showed that metal accumulation in fish tissues (liver and

Table - 1: Concentrations (ppm) of Pb, Cd, Cu and Ni in water and sediments from different sampling stations

Stations no.		Pb		Cd		Cu		Ni	
(locations)		Water	Sediment	Water	Sediment	Water	Sediment	Water	Sediment
1	Aladag Creek	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
2	Kirmir Creek	BDL	0.27	BDL		BDL	0.18	BDL	0.34
3a	Sakarya River (enter)	BDL	0.7	BDL	BDL	BDL	1.12	BDL	0.63
3b	Sakarya River (exit)	BDL	0.2	BDL	BDL	BDL	0.28	BDL	0.11
4	Usakbuku	BDL	0.49	BDL	BDL	BDL	0.36	BDL	0.66
5	Cayirhan	BDL	0.18	BDL	BDL	BDL	0.24	BDL	0.3
6	Sariyar	BDL	0.25	BDL	BDL	BDL	0.23	BDL	0.77

BDL = Below the Detection Limit

Table - 2: Concentrations (ppm) of Pb, Cd, Cu and Ni in liver and musscle of wels, carp and bleak from different sampling stations

Stations no.			Wels (N = 6) *Silurus glanis*		Carp (N = 6) *(Cyprinus carpio)*		Bleak (N = 9) *(Alburnus orontis)*	
(location)		Metals	Liver	Muscle	Liver	Muscle	Liver	Muscle
1	Aladag Creek	Pb	*	*	*	*	BDL	BDL
		Cu	*	*	*	*	BDL	BDL
		Cd	*	*	*	*	BDL	BDL
		Ni	*	*	*	*	BDL	BDL
4	Usakbuku	Pb	0.779	0.067	0.321	0.062	BDL	BDL
		Cu	0.605	BDL	BDL	BDL	BDL	BDL
		Cd	0.056	BDL	BDL	BDL	BDL	BDL
		Ni	0.127	0.042	BDL	BDL	BDL	BDL
5	Cayirhan	Pb	BDL	BDL	0.501	BDL	BDL	BDL
		Cu	BDL	BDL	BDL	BDL	BDL	BDL
		Cd	0.032	BDL	BDL	BDL	BDL	BDL
		Ni	0.114	BDL	BDL	BDL	BDL	BDL
6	Sariyar	Pb	0.167	0.077	0.439	0.135	BDL	BDL
		Cu	BDL	BDL	BDL	BDL	BDL	BDL
		Cd	0.355	BDL	BDL	BDL	BDL	BDL
		Ni	0.187	0.095	BDL	BDL	BDL	BDL

* = residue analyses couldn't be done because of no fish in the stations

muscle) is relatively higher than in sediments In addition, metal accumulation in liver of the fishes were found to be higher than in muscles. Among the fishes, maximum bioaccumulation was found in wels liver. The level of accumulation showed an increase in fish samples caught at Usakbuku (Pb: 0.779; Cu: 0.605 ppm), when compared with other stations. The levels of metal residues in bleak are lower than carp and wels (Table 2). Although, reservoir water is not used for drinking, fishery in the reservoir has a commercial importance and locals consume considerable amount of fish caught in the reservoir (Ekmekci *et al*., 2000). In addition, the NBP is important for aquatic and terrestrial wildlife in this area. Sakarya River is one of the most polluted rivers of Turkey, since it receives the sewage and industrial effluents of Kutahya, Eskisehir and Ankara cities before flowing into reservoir. The pollutants from heavy industries and agriculture areas in the region are transported to the downstream parts of the Sakarya basin by heavy rains. Metal contamination in the upstream region of Sakarya River was reported by Barlas (1999) who found that Sakarya Basin was significantly polluted with Cd, Pb, Cu and Ni and these heavy metals, especially Cd and Pb, were accumulated in sediments and fishes (*Cyprinus carpio* and *Barbus plebejus*). We found similar results and Pb, Cu and Ni levels are particularly higher in the sediments and liver tissues of fish samples.

The concentrations of heavy metals in water samples from all the stations were found to be below detection limits. This is the result of adsorption and accumulation of metals by suspended solids and the concentration of metals in bottom sediments were found higher than in the water column above the sediments. The solubility of metals is primarily a function of the pH and dissolved oxygen concentrations of water (Chapman, 1992). During our sampling studies, the dissolved oxygen was found to be very low at the deep parts of the stations; especially the values measured in autumn were between 1.0 - 5.2 mg/l in the reservoir. Also, in all the stations pH of the water was measured to be alkaline (Ekmekci *et al*., 2000). As these oxygen and pH conditions are not favorable for the solubility of metals, it was not expected to find metals in water samples. The reservoir is a narrow and long artificial lake formed by relatively small lakes connected to each other with narrow straits as a result of the land topography (Fig.1). After the construction of Sariyar Dam, the sediments carried by Sakarya River was deposited in Sariyar Reservoir. The sediment analysis indicated that metals transported to the reservoir since 1956 were dispersed in the lake depending on the flow direction. In addition, metals were settled and accumulated in the sediments especially at Usakbuku, Cayirhan and Sariyar localities, where the reservoir is comparatively deep. Since more than 50% of the total metals present (and up to 99.9%) in water are usually adsorbed onto suspended particles (Chapman, 1992), heavy metal residues were detected in sediment samples, but not in water samples. The sediments of Sakarya River, just before flowing into the Sariyar Reservoir have higher Pb and Cu residue levels than the other stations in our study area. Even Ni concentration of Sakarya River was found to be very close to the value obtained in Usakbuku station, which is the point where Sakarya River flows into the Dam Lake. When we compare the sediment amounts of Sakarya River before (upstream) and after (downstream) the Dam Lake, it can be clearly seen that the residue levels of all the metals decrease after the Dam Lake. Therefore, it can be concluded that sediments containing the adsorbed metals may deposit especially in the stretch of the Sakarya River flowing into the Reservoir. It is can be said that residue levels in sediments decrease due to sedimentation caused by shore erosion. There is very poor vegetation along the dam lake and erosion is another important factor for increased sedimentation. Erosion subsequently transfers the sediments or soil particles from their point of origin into freshwater systems. As it was stated by Chapman (1992), sediments may then be re-suspended and transported further until it comes to its ultimate resting point or sink where active sediment accumulation occurs. Transportation occurs as a direct function of water movement. According to the results obtained for all stations, Pb and Cu in sediments of Sakarya River are higher than that of the Dam Lake and water running out of the dam lake to Sakarya River.

Three fish species used for monitoring, bleak, wels and carp, were caught from three different locations in the NBP and its vicinity. The results indicated that metal accumulation mainly takes place in the liver tissues of the fish species. Bioaccumulation of metals in fishes takes place directly, from the water by gills and indirectly from food (Barron, 1990). Particulate pollutants may also become soluble within the digestive tract of organisms due to the acidic conditions (Chapman, 1992). Although no significant metal concentration was found in water, some metal residues were found in liver and muscle tissues of wels and carp caught from the reservoir. The accumulation of heavy metals was found to be higher in wells than the other fish species. This result is apparently due to the benthic niches of wells. Also it should be noted that young fishes were used in this study that has an age of 2, so it may be expected to find more accumulation in older fishes.

The results revealed that there were no detectable amounts of heavy metals either in water and sediments or in fish tissue samples of Aladag creek. Therefore, metal residues in the water, sediment and fish samples of this station (Aladag Creek) may be used as a reference in comparison and evaluation of the findings obtained from other sampling stations. Also, the results showed that main sources of metal contamination in the reservoir are Sakarya River and Kirmir Creek. Metal accumulation levels in fish samples vary with the species and the sampling station. The results of metal analysis in bleak revealed that there is no metal contamination in this species. However, bleak is known to feed on *Daphnia*, adult ephemeras, and mosquito pupas, which feed on mostly on zooplankton (Muus and Dahlstrom, 1981; Wooton, 1994). However, metal accumulation in wels is higher than carp and bleak. This can be explained with the fact that metal accumulation is higher in the piscivorus (fish-eating) organisms, such as wels because of their feeding habits (Larsson *et al.,* 1992). This is due to the omnivorous feeding habits (generally with invertebrates, though they prefer plants) of carp

and its habitat (benthos zone). In addition, organisms living in the benthos are more exposed to these contaminants (Schlautman and Morgan, 1993). It is widely accepted that metal contaminants are compounds that adversely affect water and food quality of the aquatic ecosystems (Landrum *et al.*, 1996). Thus, metals in the NBP and reservoir adversely affect fish species as well. Metal compounds are known to harm especially fish tissues and cells and recess growth and breeding.

In conclusion, metal pollution in the NBP and reservoir is not at a level to affect the human health directly, but it may adversely affect the aquatic life and associated wildlife. According to the results, the heavy metals were deposited in the sediments of the dam lake and accumulated in fishes. It should be remarked that *Capoeta baliki* and *Alburnus escherichii* are endemic fish species and have a special importance in means of biodiversity. Pollution levels in the water resources discharging into the NBP have a potential threat on birds and the wildlife in the region.

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