

## Assessment of Heavy Metal Residues in the Sediment and Water Samples of Uluabat Lake, Turkey

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Environmental pollution is widespread in many industrialized and developing countries and results in contamination of the land, water, sediment, and air with which all living organisms interact. Metal contamination in aquatic environments has received huge concern due to its toxicity, abundance and persistence in the environment, and subsequent accumulation in aquatic habitats. The main sources of these pollutants are industrial mining, domestic and agricultural wastewaters. Several investigations have determined that, heavy metals concentrate in the sediment samples (Nihtingale 1987; Barlas 1999). Once at the sediment –water interface or in the water column, metals are more likely to transport and enter the food web. Atchison et al. (1977) have shown that, sediments contain toxins that may accumulate in fish indirectly through the food web or directly from exposure due to re-suspended sediments. Some trace elements, such as Cu, Mn, Zn, Fe, are necessary in low concentrations for all living organisms, while most of them have toxicity hazards at high concentrations (Merian 1991). Many of them have been detected in several biotas, sediments, and water (Srikanth et al.1993; Tolun et al. 2001; Topçuoğlu et al. 2002; Turgut 2003). Also, a lot of toxic metals such as Cd, Pb, and Hg occur naturally in sea water or lake water. The metals originated from human activities are one of the major source of metal pollution in water.

Toxic metals can alter many physiological processes and biochemical parameters, either in blood or in tissues including structural deformations in aquatic animals (Barlas 1999a; Barlas1999b; Al-Yousuf et al. 2000; Canlı et al. 2001; Cengiz and Ünlü 2002). Being non-biodegradable, they can be concentrated along the food chain, producing their toxic effects at points often far away from the source of pollution (Fernandez et al. 2000; Berzins and Bundy 2002; Kische and Machiwa 2003).

The objectivities of this paper are, to examine the concentration of selected heavy metals in water and sediment samples at different stations and different months in Uluabat Lake, during 2001 November-2002 September. This information would be a useful toll for the effective management and control of the natural area with respect to the input of chemicals and their bioavailability.

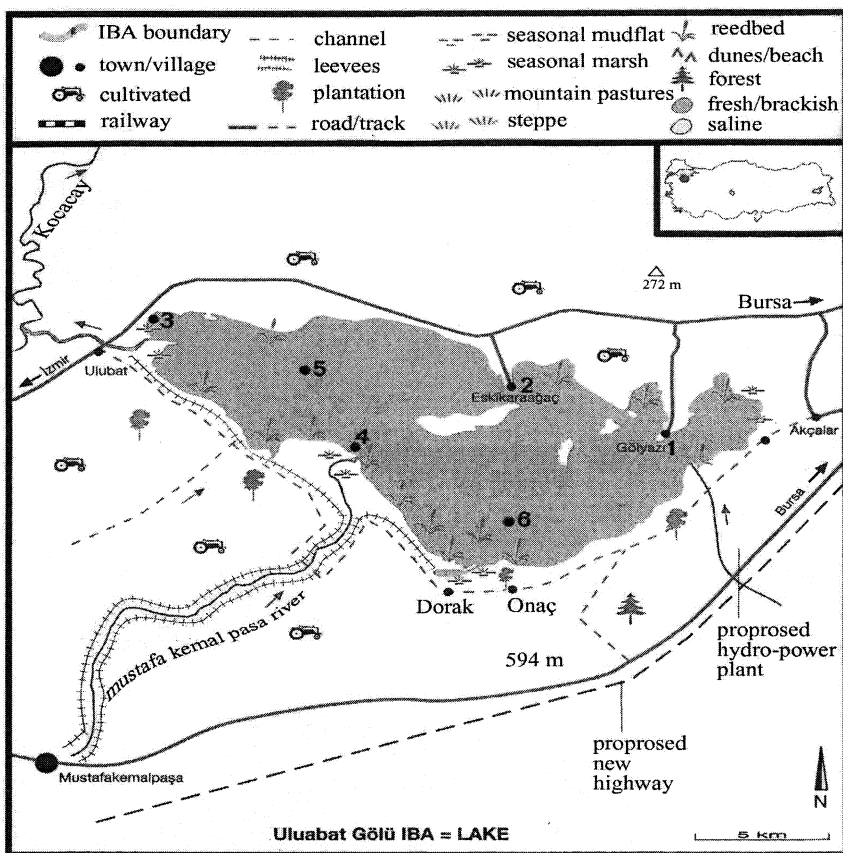
## MATERIALS AND METHODS

Uluabat Lake is located, in the Northwestern part of Turkey. It is a large but shallow (maximally 3m deep) freshwater lake, which covers an area of between 135 and 160 km<sup>2</sup> depending on the lake. The largest island is the Halilbey Island. The lake is principally fed by the Mustafa Kemalpaşa river and its only outlet is in the north-west where it drains into the Kocaçay river (Fig. 1). As the area is one of the most productive agricultural areas in Turkey due to its suitable climatic conditions, high quality soils, and developed irrigation, agricultural lands and industry surround the lake (Magnin and Yazar 1997).

Sampling was done in two months intervals from November 2001-September 2002 to the present at the 6 points shown in figure 1. The selection of sampling locations was biased toward areas of apparent high sediment accumulation and current or historical industrial activity. Water samples were collected 0.5 m below the water surface, in 250 ml pre-cleaned polyethylene bottles. For the trace element analysis, a 200-ml sample was immediately filtered through a Whatman 0.45 µm glass fiber filter and transferred into an acid-cleaned 250 ml polypropylene bottle, and then acidified with concentrated nitric acid to pH less than 2.0. Water temperature, pH, electrical conductivity (EC) and dissolved oxygen (DO) were measured at the sampling site. For Fe, Mn, Cu, Zn, Cr, Pb, Ni and Co determination in water samples an air-acetylene flame was used then analyzed using an Atomic Absorption Spectrophotometer (AAS), Perkin-Elmer 2280 model. The upper 10 cm of sediments collected with an Ekman sampler, in clean 250 ml plastic bottles. Then, all the samples kept at -18 °C until analysis. All glassware used for the analyses were carefully cleaned with nitric acid followed by thorough rinsing with distilled water before use. All reagents used were of analytical reagent grade (Merck, Germany). Deionized water was used throughout the study.

The digestion of sediment samples for determination of some heavy metals was performed with 0.5 g of dried well, homogenized sediment samples. The sediments were accurately weighed on an analytical balance and then transferred into a glass beaker, moistened with a few drops of distilled water and 10ml pure HNO<sub>3</sub> (% 70 w/w). The solution that we added was heated on a hot plate, till it was dry. After cooling about 1 hour, 5 ml of HF (% 40 w/w) and 5 ml HClO<sub>4</sub> (% 60 w/w) were added. The acid mixture was heated on a hot plate at 80-90 °C, inside a fume hood until the dark color disappeared. Since hydrated HF boils at 120 °C, it was heated cautiously at first and the temperature was not allowed to exceed 120 °C until the final traces of HF and HClO<sub>4</sub> were expelled. The residue was completely dissolved in 10 ml HCL (1.0 M) then heated on a hot plate for thirty minutes. After the containers were cooled, the solution was transferred quantitatively to a 50 ml volumetric flask by adding, distilled-deionized water (Yelhseu et al. 2002). The concentrations of Fe, Mn, Cu, Zn, Cr, Pb, Ni, Cd and Co were determined in the supernatant, using an AAS.

All metal concentrations were determined on dry weight basis. All residues are expressed as µg/g. Data analysis (standard deviation, minimum and maximum



**Figure 1.** Study site (Magnin and Yazar 1997).

concentrations) were carried out. According to these methods, the detection limit is  $0.0001\mu\text{g/g}$ . Values below detection limits were assigned as not detectable. Kruskal-Wallis test (SPSS package program) was used to determine differences, in some heavy metal residues in water and sediment samples, sampling stations and seasons (Sokal and Rohlf 1995). The 0.001 level of significance for probability was used as the criterion of statistical significance.

## RESULTS AND DISCUSSION

Heavy metal analyses were carried out on water and sediment samples from different localities in Uluabat Lake. Occurrence and concentrations of heavy metals were not changed by statistically between the sampling stations. Otherwise, accumulation and biological magnification of heavy metal residues were determined to high levels in sediment samples than water samples. According to these results, table 1 and 2 were prepared using heavy metal residues, monthly. The concentrations (mean  $\pm$ SD) of heavy metals in water samples are given in Table 1, in the monitoring months. Iron is the most abundant of the metals analyzed in water samples, especially in November 2001 and February 2002. Fe

concentrations ranged from  $0.007 \pm 0.01 \mu\text{g/g}$  in July 2002 to  $3.78 \pm 2.94 \mu\text{g/g}$  in November 2001. Manganese is always the most abundant of the trace metals in water with values ranging from  $0.008 \pm 0.001 \mu\text{g/g}$  in July to  $0.25 \pm 0.18 \mu\text{g/g}$  in November. Cd, Co, Cu and Pb levels were always under detection limit of the methodology used (except for Pb and Cu collected in February 2002). In water samples, concentrations of Zn averaged 0.003 to  $0.22 \mu\text{g/g}$  in May and February 2002 respectively. Also, Zn was not detected in July and September 2002. Ni, also demonstrated a decrease concentration in November 2001, February and May 2002 (ranged from 0.02 to  $0.005 \mu\text{g/g}$  in water samples). Heavy metal residues were lower than the maximum allowable levels in drinking water (WHO 1984).

The concentrations (mean  $\pm$ SD) of heavy metals in sediment samples are given in Table 2. Fe concentrations in sediment samples ranged  $18.01 \pm 0.83 \mu\text{g/g}$  in February to  $27.03 \pm 0.78 \mu\text{g/g}$  in May 2002. Fe concentration levels in sediments were consistently higher than other analyzed metals, especially in May, July and September 2002. The highest mean levels of Mn ( $23.92 \pm 2.92 \mu\text{g/g}$ ), Cu ( $1.19 \pm 0.05 \mu\text{g/g}$ ), Cr ( $4.88 \pm 0.30 \mu\text{g/g}$ ), Pb ( $2.39 \pm 0.24 \mu\text{g/g}$ ), Ni ( $8.93 \pm 1.18 \mu\text{g/g}$ ), Cd ( $0.12 \pm 0.006 \mu\text{g/g}$ ) and Co ( $1.81 \pm 0.12 \mu\text{g/g}$ ) were found in May 2002, in sediment samples. The highest concentration of Zn ( $8.36 \pm 0.13 \mu\text{g/g}$ ) was recorded in September 2002. Pb concentration levels in sediments were consistently higher than Cd concentration levels. These results could be explained by the fact that, Cd in sediments is mainly associated with the carbonate fraction and it is readily soluble metal, whereas Pb is mainly associated with the Fe-Mn oxide fraction and has higher retention in sediments (Gonzalez et al. 1994). Chale (2002) reported that, the levels of all the trace metals (Cu, Pb, Fe, Mn, Zn and Cd) in water were very low, but the concentrations in inshore sediments were much higher than, in offshore sediments in Lake Tanganyika. Comparison of the levels of some recorded in this study with samples from other countries (Table 3), revealed that levels of these metals are always lower than any other area.

In Uluabat Lake, heavy metal concentrations were much lower (except in Shing Mun River, Hong Kong (Sin et al. 2001)) than, concentrations found in sediments heavily polluted in Victoria Lake, Tanzania (Kishe and Machiwa 2003), in Danube River, Hungary (Woitke et al. 2003), in Nasser Lake, Egypt (Rashed 2001), in South Western, (Michigan USA) (Gilliland et al. 1993), in Patroon Reservoir, USA (Arnason and Fletcher 2003), and in Southeast Regional Park, Spain (Fernandez et al. 2000). Otherwise, according to Table 2, lead and cadmium concentrations were relatively higher in sediment samples, especially in May, July and September in Uluabat Lake. This is very important because, these metals were accumulated and biologically magnified in the food chain. The high levels of Pb, Cd, Zn and Fe in sediments in Uluabat Lake reflect the presence of lake polluting activities around Uluabat Lake. Domestic and industrial effluents and atmospheric deposition may be the major sources of the observed high level of Pb and Zn. Also, these high results may be due to the low level of water in these months. Barlas (1999a) concluded that concentrations of Cd and Pb in water and sediment samples were higher than permitted values, especially in August and October in Upper Sakarya River Basin, Turkey.

**Table 1.** Heavy metal concentrations ( $\mu\text{g/g}$  dry weight) in water samples of the Uluabat Lake.

	November 2001 mean $\pm$ SD	February 2002 mean $\pm$ SD	May 2002 mean $\pm$ SD	July 2002 mean $\pm$ SD	September 2002 mean $\pm$ SD	$\chi^2$	df	Signif
Fe	3.78 $\pm$ 2.94	0.45 $\pm$ 0.05	0.29 $\pm$ 0.09	0.007 $\pm$ 0.01	0.73 $\pm$ 1.61	25.33	4	<0.001
Mn	0.25 $\pm$ 0.18	0.06 $\pm$ 0.04	0.03 $\pm$ 0.009	0.008 $\pm$ 0.001	0.03 $\pm$ 0.01	18.33	4	0.001
Cu	nd	0.01 $\pm$ 0.007	nd	nd	nd	21.27	4	<0.001
Zn	0.01 $\pm$ 0.012	0.22 $\pm$ 0.09	0.003 $\pm$ 0.004	nd	nd	21.26	4	<0.001
Cr	0.15 $\pm$ 0.18	0.009 $\pm$ 0.007	nd	nd	nd	20.97	4	<0.001
Pb	nd	0.04 $\pm$ 0.03	nd	nd	nd	16.37	4	0.003
Ni	0.04 $\pm$ 0.01	0.05 $\pm$ 0.01	0.02 $\pm$ 0.02	nd	nd	19.9	4	0.001
Cd	nd	nd	nd	nd	nd	-	4	-
Co	nd	nd	nd	nd	nd	-	4	-

SD: Standard Deviation

nd: not detected

**Table 2.** Heavy metal concentrations ( $\mu\text{g/g}$  dry weight) in sediment samples of the Uluabat Lake.

	November 2001 mean $\pm$ SD	February 2002 mean $\pm$ SD	May 2002 mean $\pm$ SD	July 2002 mean $\pm$ SD	September 2002 mean $\pm$ SD	$\chi^2$	df	Signif
Fe	18.21 $\pm$ 2.66	18.01 $\pm$ 0.83	27.03 $\pm$ 0.78	26.51 $\pm$ 0.25	25.86 $\pm$ 0.66	24.83	4	<0.001
Mn	6.57 $\pm$ 2.44	6.42 $\pm$ 0.68	23.92 $\pm$ 2.92	19.99 $\pm$ 6.56	20.89 $\pm$ 2.22	22.07	4	<0.001
Cu	0.31 $\pm$ 0.15	0.25 $\pm$ 0.05	1.19 $\pm$ 0.05	1.03 $\pm$ 0.08	0.98 $\pm$ 0.16	24.55	4	<0.001
Zn	0.74 $\pm$ 0.18	0.76 $\pm$ 0.32	3.97 $\pm$ 2.06	5.66 $\pm$ 3.09	8.36 $\pm$ 0.13	23.74	4	<0.001
Cr	0.83 $\pm$ 0.13	0.90 $\pm$ 0.06	4.88 $\pm$ 0.30	4.28 $\pm$ 0.37	3.88 $\pm$ 0.60	24.88	4	<0.001
Pb	0.43 $\pm$ 0.06	0.42 $\pm$ 0.06	2.39 $\pm$ 0.24	2.08 $\pm$ 0.28	1.78 $\pm$ 0.16	24.61	4	<0.001
Ni	1.84 $\pm$ 0.40	1.97 $\pm$ 0.23	8.93 $\pm$ 1.18	7.58 $\pm$ 1.28	6.85 $\pm$ 1.38	23.23	4	<0.001
Cd	0.03 $\pm$ 0.002	0.02 $\pm$ 0.004	0.12 $\pm$ 0.006	0.11 $\pm$ 0.006	0.11 $\pm$ 0.006	22.19	4	<0.001
Co	0.24 $\pm$ 0.03	0.26 $\pm$ 0.02	1.81 $\pm$ 0.12	1.57 $\pm$ 0.13	1.41 $\pm$ 0.15	25.42	4	<0.001

SD: Standard Deviation

Statistical analysis indicated that levels of Fe, Mn, Cu, Zn, Cr, Pb, Ni, Cd and Co in sediment samples, changed significantly ( $P<0.001$ ) with water samples and seasons.

The more or less, uniform concentrations of Ni, Cr and Cu in lake sediment reflect their natural background levels in the local soils. Nickel results were similar to those obtained by Ayaş and Kolankaya (1996) and Barlas (1999a). These researchers reported that, a high nickel level was found in water, sediment, and soil samples in Göksu delta and Upper Sakarya River basin, Turkey. Cu, Mn, Ni and Co have less toxic effects on freshwater organisms, like fish but high quantities of these metals have toxic properties in tissue. In our study, Mn and Fe concentrations were measured high quantities in sediment samples, especially in May, July and September 2002.



**Table 3.** Comparison of mean concentrations of heavy metals in sediment samples from Uluabat Lake and other literature values, reported on a dry weight basis.

Study Area	Cu	Zn	Cr	Pb	Cd	References
Victoria Lake* (Tanzania)	21.6±2.4	36.4±1.8	11.0±1.4	29.6±1.6	2.5±0.5	Kishe and Machiwa, 2003
Danube River* (Hungary)	65.7±12	187±25	64.0±6.5	46.3±6.8	1.2±0.4	Woitke et al. 2003
Shing Mun River (Hong Kong)	0.207 ±1.66	0.032 ±2.2	0.013 ±0.3	0.126 ±0.35	0.022 ±0.04	Sin et al. 2001
South Western * Michigan (USA)	7.2	18	61	9.9	0.27	Gilliland et al.1993
Nasser Lake (Egypt)*	109±2.6	143±2.9	79±2.0	NA	NA	Rashed, 2001
Patroon Reservoir USA (mg/kg)	NA	NA	NA	3600	25	Arnason and Fletcher 2003
Southeast Regional Park, Spain*	NA	NA	NA	1.24	0.54	Fernandez et al. 2000
Uluabat Lake Turkey*	0.75 ±0.05	3.89 ±0.25	2.95 ±1.04	1.42 ±0.28	0.078 ±0.1	This study

NA : Not Analyzed

\* : µg/g dry weight

• : mg/g dry weight

**Table 4.** Mean physical parameters of selected stations in Uluabat Lake between November 2001 September 2002.

Station No.	DO (mg/L) (Min/Max) Mean	Temperature(°C) (Min/Max) Mean	EC (µS/cm) (Min/Max) Mean	pH (Min/Max) Mean
1	8.9-14.7 10.06	8-29 19.32	460-671 531.4	8.24-8.72 8.49
2	8.87-15.3 11.05	8.2-28.4 18.66	478-664 552.8	8.16-8.84 8.48
3	4.60-13.53 8.84	7.3-28.7 18.9	466-671 551.2	7.99-8.77 8.32
4	5.76-11.4 11.13	9.8-28.3 19.9	507-614 568.6	7.86-8.46 8.18
5	5.75-14.78 10.63	7.9-28.4 18.9	443-625 535.8	7.98-8.8 8.3
6	5.74-12.5 8.66	9.4-29.2 20.44	478-634 562.4	8.44-8.01 8.30

However, in water samples Cd, Co, Cr and Cu were found below the limit of detection. The more concentrated metals, such as Fe and Mn are components of biological systems and/or sediments; therefore, the high concentrations are not alarming.

Physical properties of water samples for selected stations are given in Table 4. The temperature of water ranged between 18.9-20.44 °C and the mean pH 8.18-8.49. The variation of pH was random and no seasonality was observed at any sampling point. pH values were within the range of WHO recommendation of, 7-8.5 for drinking water. Conductivity values ranged, between 531.4-568.6 µS/cm, dissolved oxygen values changed from 8.66-11.13mg/L. Hellawell reported that (1988) heavy metal toxicity is affected by temperature, dissolved oxygen concentrations and pH. Cd is very toxic to fish and other aquatic organisms, however, temperature, pH and water hardness are factors that influence its toxicity and uptake by fish (Hontela et al. 1996). In Uluabat Lake, all physical parameters varied in a normal range.

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