

# Seasonal Changes of Some Heavy Metal Concentrations in Sapanca Lake Water, Turkey

Fatih DUMAN<sup>1</sup>

Göksal SEZEN<sup>2</sup>

Gül NİLHAN TUG<sup>2\*</sup>

<sup>1</sup> Erciyes University, Faculty of Arts and Sciences, Department of Biology, 38039 Kayseri, TURKEY

<sup>2</sup> Ankara University, Science Faculty, Department of Biology, 06100 Ankara, TURKEY

\* Corresponding Author  
e-mail: tug@science.ankara.edu.tr

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## Abstract

Sapanca is one of the few lakes in Turkey, which provides drinking water. Because of its natural beauty and proximity to the metropolitan Istanbul, it is exposed to heavy urbanization. In this study, it was aimed to investigate seasonal changes of some heavy metal (Pb, Cr, Cu, Mn, Ni, Zn and Cd) concentrations and to determine water quality classes of Sapanca Lake water. Ten different stations were chosen as sampling area and water samples were taken from these stations in May 2003, July 2003, November 2003 and February 2004. ICP-OES Sequential device was used for the analysis. It was found that heavy metals concentrations in the water samples were decreased in sequence of Zn > Cr > Ni > Pb > Mn > Cu > Cd. Also, it was determined that Sapanca Lake has 2<sup>nd</sup> class water quality for Pb, Cr and Ni and 1<sup>st</sup> class water quality for Mn, Cu, Zn and Cd. Seasonal highest values of heavy metals were observed as follows; Zn in Spring, Cr and Cu in Summer, Cr, Mn and Ni in Autumn and Cd and Pb in Winter.

**Key words:** Lake Sapanca, seasonal changes, water, heavy metal

## INTRUDUCTION

Lake Sapanca is located at the northeast of the Marmara region of Turkey. This freshwater lake is feeding by several creeks (which are almost dry in summer) and partly by groundwater. This lake is used as a source of drinking and process water by the city of Adapazarı and several important industries in Izmit area. The total population of the basin is estimated to be over 100,000 in 2030 according to the population increase trend [1]. Though there is no direct discharge of waste into the lake, chemical pollutants of industrial, domestic and agricultural origin find their way into the lake through surface-runoff and precipitation. The lake basin is surrounded by motorways (TEM, Trans-European Motorways) and a railway connecting Asia to Europe (Fig. 1).



Figure 1. Map of the study location and sampling site.

A recent study described that the heavy metal concentrations in waters of anthropogenic lakes are as follows (in mg/l): 2.4–12 K, 23–98 Ca, 14–60 Mg, 2–4790 Fe, (in µg/l): 13–65 Co, 130–1480 Mn, 4–55 Ni, 86–751 Zn, 7–198 Cu [2]. Morkoc et al. [3] oligotrophically evaluated the Sapanca Lake at their study. Tanık et al. [1] determined that fertilizers and pesticides

are the principal pollution sources and high amount of these pollutants enter the lake. The surface sediment metal enrichment of Sapanca Lake was investigated by Balkan and Balkas [4] and they found that the lead and cadmium amounts in sediment have increased. In the study performed by Yalcin and Sevinc [5] about the heavy metal pollution at Sapanca Lake showed that there is a risk of pollution in Sapanca Lake and according to the comparisons with the former studies it was reported that while the zinc concentration was relatively stable, there was an important increase in the concentrations of Pb and Fe.

The study on pollution around Sapanca Lake at the roadside, Sisman et al. [6] found that Ni accumulation was below the world's standards but Pb accumulation exceeded the acceptable level [7,8]. At the study done before and after 17 August 1999 Marmara earthquake on the streams flow into the Sapanca Lake, Dundar et al. [9] found that in Istanbul, Mahmudiye and Kurucay streams the Pb and Cd accumulations increased, Cu accumulation matched the standards and Zn and Fe accumulations decreased after the earthquake. In this study, it was aimed to examine the seasonal changes in Pb, Cr, Cu, Mn, Ni, Zn and Cd concentrations of Sapanca Lake water and to study the water quality class of the lake. These findings are important, not only for clarifying the present heavy metal pollution levels of the lake but also for the development of rational management plans.

## MATERIALS AND METHOD

Ten different stations were chosen as sampling area (Fig. 1) and water samples were taken from these stations in May 2003, July 2003, November 2003 and February 2004. Samples of water were collected by hand from a rowing boat by submerging pre-cleaned PE bottles approximately 50 cm beneath the water

surface. Suspended particulate matter was separated by filtering water samples through 0.45- $\mu\text{m}$  preweighed Whatman GF/C filters. Filtered solutions were acidified to 0.5 % (v/v) by using concentrated nitric acid as for the precipitation samples.

Determinations of the elements in all samples were carried out by Varian ICP-OES. The samples were analyzed in triplicate. SPSS 11.5 statistical program was used to calculate standard deviations, minimum, maximum and mean concentrations. In this study,  $\alpha$  was chosen to be 0.05. Results of testing were considered significant if calculated  $p$ -values were  $\leq 0.05$ . For comparison of means, ANOVA test and Post Hoc. Duncan test were used.

## RESULTS

### Lead

Annual mean heavy metal concentrations of water samples taken from each station of Sapanca Lake are given on Fig. 2.

**Table 1.** Seasonal mean concentrations of heavy metals ( $\mu\text{g L}^{-1}$ ) in water samples together with minimum, maximum and standart deviation values

|    | Season        | Mean                | Std. Deviation | Minimum | Maximum |
|----|---------------|---------------------|----------------|---------|---------|
| Pb | Spring        | 28.29 <sup>a</sup>  | 8.14           | 8.49    | 38.57   |
|    | Summer        | 26.72 <sup>a</sup>  | 9.31           | 6.18    | 43.37   |
|    | Autumn        | 29.58 <sup>a</sup>  | 10.06          | 19.0    | 55.21   |
|    | Winter        | 58.09 <sup>b</sup>  | 11.04          | 28.68   | 65.04   |
|    | <b>Annual</b> | <b>35.67</b>        |                |         |         |
| Cr | Spring        | 63.95 <sup>b</sup>  | 1.67           | 60.07   | 65.76   |
|    | Summer        | 65.61 <sup>b</sup>  | 0.41           | 64.99   | 66.49   |
|    | Autumn        | 65.47 <sup>b</sup>  | 0.60           | 64.45   | 66.81   |
|    | Winter        | 52.85 <sup>a</sup>  | 21.33          | 11.89   | 66.19   |
|    | <b>Annual</b> | <b>61.97</b>        |                |         |         |
| Cu | Spring        | 12.74 <sup>a</sup>  | 5.21           | 6.31    | 19.82   |
|    | Summer        | 45.58 <sup>b</sup>  | 60.80          | 8.49    | 22.65   |
|    | Autumn        | 10.40 <sup>a</sup>  | 8.92           | 5.63    | 36.38   |
|    | Winter        | 4.08 <sup>a</sup>   | 3.87           | 1.79    | 15.26   |
|    | <b>Annual</b> | <b>18.20</b>        |                |         |         |
| Mn | Spring        | 26.24 <sup>b</sup>  | 1.69           | 23.40   | 28.76   |
|    | Summer        | 27.11 <sup>b</sup>  | 20.19          | 3.74    | 67.64   |
|    | Autumn        | 17.88 <sup>a</sup>  | 16.56          | 1.14    | 60.31   |
|    | Winter        | 19.05 <sup>a</sup>  | 5.61           | 11.10   | 27.18   |
|    | <b>Annual</b> | <b>22.57</b>        |                |         |         |
| Ni | Spring        | 54.69 <sup>b</sup>  | 6.89           | 40.53   | 63.61   |
|    | Summer        | 59.41 <sup>c</sup>  | 3.94           | 53.07   | 66.30   |
|    | Autumn        | 62.99 <sup>d</sup>  | 1.63           | 60.60   | 65.65   |
|    | Winter        | 8.67 <sup>a</sup>   | 6.92           | 0.10    | 20.80   |
|    | <b>Annual</b> | <b>46.44</b>        |                |         |         |
| Zn | Spring        | 203.24 <sup>c</sup> | 173.68         | 27.40   | 636.95  |
|    | Summer        | 24.21 <sup>a</sup>  | 21.33          | 8.09    | 81.09   |
|    | Autumn        | 11.90 <sup>a</sup>  | 5.93           | 2.97    | 20.75   |
|    | Winter        | 114.72 <sup>b</sup> | 97.42          | 2.88    | 274.43  |
|    | <b>Annual</b> | <b>88.52</b>        |                |         |         |
| Cd | Spring        | 2.40 <sup>a</sup>   | 0.47           | 1.79    | 3.27    |
|    | Summer        | 2.45 <sup>a</sup>   | 0.44           | 1.75    | 3.12    |
|    | Autumn        | 2.62 <sup>a</sup>   | 0.34           | 2.16    | 3.37    |
|    | Winter        | 4.44 <sup>b</sup>   | 2.8            | 0.18    | 8.26    |
|    | <b>Annual</b> | <b>2.98</b>         |                |         |         |

For a given metal, mean concentrations followed by the same letter are not significantly different ( $p < 0.05$ ).

When the average seasonal lead concentration in water samples of Sapanca Lake were investigated (Table 1), it was found that the highest lead accumulation occurred in winter. Annual mean lead concentration was measured as 35.67  $\mu\text{g L}^{-1}$ . The highest lead level was measured at station 2 (Fig. 2). According to the lead pollution, Sapanca Lake has 2<sup>nd</sup> class water quality (Table 2). In this study Pb concentration in water samples from Sapanca Lake were found higher than these values especially in winter.

### Chromium

In water samples of Sapanca Lake, Cr concentration with the value of 52.85  $\mu\text{g L}^{-1}$  in winter was lower than the other seasons (Table 1). Mean annual Cr concentration was determined as 61.97  $\mu\text{g L}^{-1}$ . Cr concentrations of station 8 and station 9 were found lower than the other stations. Sapanca Lake has a 2<sup>nd</sup> class water quality in terms of Cr concentrations (Table 2).

**Table 2.** Quality criterias of inland water resources (TSE-266) and standarts of WHO and EPA [15, 16]

| Metals (mg/L) | Water Quality Class (TSE-266) |                      |             |                    | WHO  | EPA  |
|---------------|-------------------------------|----------------------|-------------|--------------------|------|------|
|               | 1. High Quality               | 2. Slightly Polluted | 3. Polluted | 4. Highly Polluted |      |      |
| Lead          | 0.01                          | 0.02                 | 0.05        | >0.05              | 0.1  | 0.05 |
| Chromium      | 0.02                          | 0.05                 | 0.2         | >0.5               | 0.1  | 0.1  |
| Copper        | 0.02                          | 0.05                 | 0.2         | >0.2               | -    | 1.3  |
| Manganese     | 0.1                           | 0.5                  | 3           | >3                 | 0.5  | 0.05 |
| Nickel        | 0.02                          | 0.05                 | 0.2         | >0.2               | 0.2  | -    |
| Zinc          | 0.2                           | 0.5                  | 2           | >2                 | -    | 5    |
| Cadmium       | 0.003                         | 0.005                | 0.01        | >0.01              | 0.01 | 0.01 |

### Copper

Cu concentrations of Sapanca Lake reached the highest level in summer and in autumn and decreased gradually in winter (Table 1). Mean annual copper concentration in water samples of Sapanca Lake was found as  $24.61 \mu\text{g L}^{-1}$  and water quality class of Sapanca Lake was 1<sup>st</sup>. The highest Cu concentration was measured at station 7 (Fig. 2).

### Manganese

It was found that Mn concentration is higher in spring and summer than autumn and winter. Mean annual Mn concentration was found as  $22.57 \mu\text{g L}^{-1}$  and the water quality class was 1<sup>st</sup>. According to the annual averages the highest Mn concentration was observed in station 6 (Fig. 2).

### Nickel

It was found that Ni concentration is higher in autumn with respect to other seasons. Mean annual Ni concentration in Sapanca Lake was measured as  $46.44 \mu\text{g L}^{-1}$ . There is no difference between the stations according to the mean annual concentrations (Fig. 2). Sapanca Lake has 2<sup>nd</sup> class water quality according to the Turkish standards institution criterions (Table 2).

### Zinc

The highest Zn value in Sapanca Lake was measured in spring. Mean annual Zn concentration determined as  $88.52 \mu\text{g L}^{-1}$ . The highest Zn concentration in the lake was observed in station 1 (Fig. 2). Sapanca Lake is a 1<sup>st</sup> class lake in terms of Zn concentration.

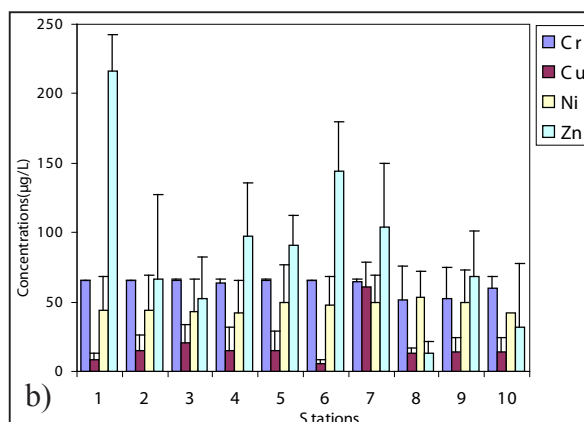
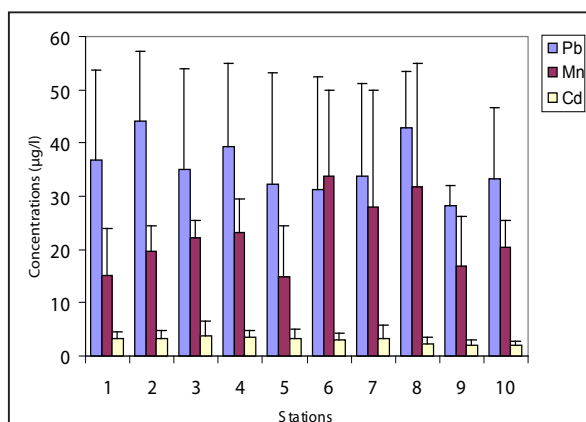
### Cadmium

The highest Cd value was observed in winter (Table 1). Mean annual Cd concentration of Sapanca Lake was  $2.97 \mu\text{g}$

$\text{L}^{-1}$  and Sapanca had 1<sup>st</sup> class water quality. According to mean averages the highest value was observed in station 3.

## DISCUSSION

Main source of the lead is the alkyl derivatives in petroleum [10]. Also it comes from other sources like metal manufacturing, sewages, paints, fertilizers, pesticides and ashes. Leaded gasoline was in use in Turkey until recently. This is probably the most efficient mechanism of anthropogenic Pb contributions into the lake. Especially in winter nearly in all the stations from where samples were taken, Pb levels exceed the limits and 3<sup>rd</sup> class water quality was observed. Yalcin et al. [5] determined the Pb concentration of motorway's wastewater drainage passes round the south of Sapanca Lake between  $10$  and  $50 \mu\text{g L}^{-1}$ . Dunder et al. [9] measured Pb concentrations of samples taken from Sapanca Lake and Sakarya city drinking water as  $36 \mu\text{g L}^{-1}$  and  $22$ - $33 \mu\text{g L}^{-1}$  respectively. The most important factors that cause chromium accumulations in water are plastic wastes, sewages and septic tank wastes. In fresh waters, Cr concentration is in between  $0.1$ - $117 \mu\text{g/L}$  [11]. Copper participates in the ecosystem from many sources like household tools, wood and metal manufacturing, pesticide applications, fertilizers and septic tanks wastes [12]. Yanik stream carries important amount of copper into the lake. Dunder et al. [9] determined average Cu concentration of streams running into Sapanca Lake as  $10$ - $37.6 \mu\text{g L}^{-1}$ . In this study close values were obtained. Although manganese is basically a soil originated element, there are also many other sources like sewages, fertilizers, pesticide applications and metal manufacturing that cause pollution. Being an electron acceptor and receptor in redox potential, it plays an important role in aquatic



**Figure 2.** Annual mean a) Pb, Mn and Cd b) Cr, Cu, Ni and Zn concentrations of Sapanca Lake water together with standart deviation bars.

ecosystems [12]. Ni mainly comes from metal manufacturing and septic tanks. In lakes and streams, Ni concentration is low. Sisman et al. [6] reported that there is not any Ni pollution in the soils taken from auto way that passes round Sapanca Lake. But it is possible to mention about Ni pollution in lake. There are many sources of zinc like fossil fuels, metal manufacturing and fertilization. It is an essential mineral for organisms. It has a critical role in the structural and functional integrity of the cells. It takes role in gene expression and growth. Toxicity is low [13]. As a result of a study performed by Yalcin and Sevinc [14] between 1991 and 1999 in Sapanca Lake water, it was reported that Zn concentration was below the limits. Our results match this report. Cadmium originates from many sources like plastic, fossil fuels, metal manufacturing, fertilizers and sewage. Cd, which is not an essential element, causes inhibition of taking up essential elements like Zn [15]. It is easily taken up and enters the food web [16]. Dundar et al. [9] measured the average Cd concentrations between 6.4-15.6  $\mu\text{g L}^{-1}$  in streams flow into the lake. In this study mean Cd concentration was found low.

Sapanca Lake has 2<sup>nd</sup> class water quality for Pb, Cr and Ni, and 1<sup>st</sup> class water quality for Mn, Cu, Zn and Cd. Generally, heavy metal concentrations in the water samples were decreased in sequence of Zn > Cr > Ni > Pb > Mn > Cu > Cd. Seasonal highest values of heavy metals and in which seasons these values were observed were as follows; Zn in Spring, Cr and Cu in Summer, Mn and Ni in Autumn and Cd and Pb in Winter. The concentrations of heavy metals in water change thorough the year. Therefore, in heavy metal pollution studies, it is important to be careful about the sampling time. There was a difference between the heavy metal concentrations of the stations. This means that heavy metals are carried into the lake from different sources. It was found that the highest heavy metal concentrations measured in station 1, 2, 3, 6 and 7 are Zn, Pb, Cd, Mn and Cu respectively.

The highway waste water drainage canal in Sapanca Lake is not adequate. Also drainage waters given into the lake are not treated with any refinement processes. Drainage canal should be constructed around the lake and drainage waters must be refined physically and chemically. Sewages are drained into the lake without any treatment. There should be enough care and authorized offices should control this situation continuously. Pollutants of streams, where the waste waters are drained, should be removed via simple and cheap processes. Interventions should be made to reduce anthropogenic discharges in the lake basin; otherwise, increase heavy metals may result in the elevated concentration in fish and humans.

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## REFERENCES

- [1] Tanik A, Beler Baykal B, Gonenc E, Meric S, Oktem Y. 1998. Effect and control of pollution in catchment area of Lake Sapanca, Turkey. *Environmental Management*. 22:407-414.
- [2] Samecka-Cymerman A, Kempers AJ. 2001. Concentrations of heavy metals and plant nutrients in water, sediments and aquatic macrophytes of anthropogenic lakes (former open cut brown coal mines) differing in stage of acidification. *The Science of The Total Environment*. 281: 87-98.
- [3] Morkoc E, Tugrul S, Ozturk M, Tufekci H, Egesel L, Tufekci V, Oya S, Legovic T. 1998. Trophic characteristics of the Sapanca Lake (Turkey). *CCACAA* 71: 303-322.
- [4] Bakan G, Balkas TI. 1999. Enrichment of metals in the surface sediments of Sapanca Lake. *Water Environment Research*. 71: 71-74.
- [5] Yalcin N, Sevinc V, Turker ES. 1994. The statistical analysis of water quality in Sapanca Lake and the effect of motorway on water quality. *Turkish Journal of Engineering and Environmental Sciences* 18: 431-439.
- [6] Sisman I, Imamoglu M and Aydin AO. 2002. Determination of heavy metals in roadside soil from Sapanca area highway, Turkey. *International Journal of Environment and Pollution*. 17: 306-311.
- [7] WHO (1993). *Guidelines for drinking water quality. Recommendations*, vol. 1, 2<sup>nd</sup> ed. World Health Organization, Geneva.
- [8] EPA. <http://www.epa.gov/safewater/standards.html>
- [9] Dundar MS, Altundag H, Boz V, Akaya K, Sayin M. 2003. Sapanca golune akan derelerdeki bazı eser elementlerin 17 Agustus 1999 Marmara depremi oncesi ve sonrasi karsilastirmali analizi. *A.U. Bilim ve Teknoloji Dergisi*. 4: 205-210.
- [10] Singh RP, Tripathi RD, Sinha SK, Maheshwaril R, Srivastava HS. 1997. Response of higher plants to lead contaminated Environment. *Chemosphere*. 34: 2467-2493.
- [11] Shanker AK, Cervantes C, Loza-Tavera H, Avudainayagam S. 2005. Chromium toxicity in plants. *Environment International*. 31: 739-753.
- [12] Markert B. 1993. *Plant as biomonitors: Indicators for heavy metals in the terrestrial environment*, B. Markert (Ed), (VCH Weinheim, New York/Basel/Cambridge).
- [13] Clearwater SJ, Farag AM, Meyer JS. 2002. Bioavailability and toxicity of dietborne copper and zinc to fish. *Comparative Biochemistry and Physiology Part C, Toxicology & Pharmacology*. 132: 269-313.
- [14] Yalcin N and Sevinc V. 2001. Heavy metal contents of Lake Sapanca. *Turkish Journal of Chemistry* 25: 521-525.
- [15] Charles S, Yunus S, Dubois F, Vander Donckt E. 2001. Determination of cadmium in marine waters: on-line preconcentration and flow-through fluorescence detection. *Analytica Chimica Acta*. 440: 37-43.
- [16] Jain CK. 2004. Metal fractionation study on bed sediments of River Yamuna, India. *Water Research*. 38: 569-578.