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Investigation of Toxic Metal Contamination in Water and Sediments of Gölbaşı Lake (Adıyaman)

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Abstract

Gölbaşı Lake, which forms the most important wetland between the Mediterranean Region and the Southeastern Anatolia Region, is a natural lake and protected as a natural park. Excessive grazing causes damage to the vegetation around the villages and makes the area vulnerable to erosion. Increased agricultural production in the region has also brought pollution problems. Measures must be taken for the sustainability of water and sediment quality of this lake which is from our natural wetlands. For this purpose, in this study, water quality of Gölbaşı Lake and heavy metal rezidues in water and sediment were evaluated. Water and sediment sampling were carried out in two periods, dry (August 2017) and wet (November 2017). Ammonia, nitrite, nitrate, phosphate and biological oxygen requirement values of water quality parameters were examined. Residue quantities of heavy metals such as Pb, Cu, Zn, As, Cr and Cd have been evaluated in lake water. In the lake sediment, 12 types of metal (Pb, Cu, Zn, As, Cr, Cd, Ni, Se, Co, Fe, Al and Mn) were analyzed. Gölbaşı Lake was found to be in the first class according to the classifications of the water quality, physicochemical parameters and elements of Continental Water Surface Water Resources. In general, sediment metal remains are in the order of Fe>Al>Mn>Ni>Cr>Zn>Cu>Pb>Co>As>Se>Cd. The metal concentrations in the

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sediment of the lake are below the limit of sediment quality guidelines determined by USEPA. Nevertheless, in order to ensure the sustainability of the water and sediment quality of Gölbaşı Lake, which is one of our natural wetlands, it is necessary to remove the pollutants that may be a source around the lake or to take precautions about it.

Keywords: Gölbaşı lake, Metal, ICPMS, Sediment, Water quality.

Gölbaşı Gölü (Adıyaman) Su ve Sedimentlerindeki Toksik Metal Kontaminasyonunun Araştırılması

Özet

Akdeniz Bölgesiyle Güneydoğu Anadolu Bölgesi arasında en önemli sulak alanı oluşturan Gölbaşı Gölü, doğal bir göldür ve tabiat parkı olarak koruma altına alınmıştır. Aşırı otlatma özellikle köylerin civarındaki bitki örtüsünün zarar görmesine yol açmakta ve alanı erozyona açık bir hale getirmektedir. Bölgede tarımsal üretimin artması da kirlilikle ilgili sorunları beraberinde getirmiştir. Doğal sulak alanlarımızdan olan bu gölün su ve sediment kalitesi sürdürülebilirliği için tedbirler alınması gerekmektedir. Bu amaçla bu çalışmada, Gölbaşı Gölü'nün su kalitesi ile su ve sedimentinde ağır metal kalıntısı değerlendirilmiştir. Su ve sediment örneklemeleri, kurak (Ağustos 2017) ve yağışlı (Kasım 2017) olmak üzere iki dönemde yapılmıştır. Su kalitesi parametrelerinden amonyak, nitrit, nitrat, fosfat ve biyolojik oksijen ihtiyacı değerlerine bakılmıştır. Göl suyunda örneklerinde ağır metallerden Pb, Cu, Zn, As, Cr ve Cd'nin kalıntı miktarları değerlendirilmiştir. Sediment örneklerinde ise 12 çeşit metalin kalıntı analizi yapılmıştır. Gölbaşı Gölü su kalitesi, fizikokimyasal parametreler ve elementler bakımından Kıtaiçi Yerüstü Su Kaynaklarının sınıflarına göre I. Sınıf kalitede bulunmuştur. Genel olarak sedimentte metal kalıntısı sıralaması Fe>Al>Mn>Ni>Cr>Zn>Cu>Pb>Co>As>Se>Cd şeklindedir. Göl sedimentindeki metal konsantrasyonları, USEPA tarafından belirlenen sediment kalite kuralları sınırının altındadır. Yine de doğal sulak alanlarımızdan olan Gölbaşı Gölü'nün su ve sediment kalitesinin sürdürülebilirliğinin sağlanması için gölün çevresinde kaynak olabilecek kirlilik unsurlarının ortadan kaldırılması veya bununla ilgili tedbirler alınması gerekmektedir.

Anahtar Kelimeler: Gölbaşı gölü, Metal, ICPMS, Sediment, Su kalitesi.

1. Introduction

The main criteria that determine contamination in aquatic environments are physicochemical and biological factors. Biodiversity, nutrient chain, water quality and the cleanliness of water from the biological front have a great significance in living aquatic life. It is necessary to determine the purpose of using the lakes, to make measurements suitable for these purposes and to periodically monitor the selected parameters. In contrast to increased water demand, the availability of freshwater resources requires the conservation and improvement of the quality of existing water resources. For our watershed-based lakes and wetlands, a detailed inventory study is needed primarily for "conservation-use" based management. In this context, the ecological structures of our lakes and wetlands, the purposes of use, the pressures and effects and the causes of these pressures need to be presented. Without all these factors in place, it will not be possible to define the management strategy, the effective protection of our lakes and wetlands, and the formulation of viable and correct decisions [12].

Gölbaşı Lake, which is located in the district of Adıyaman's Gölbaşı and gives its name to the county, is located in the district center. The 1687 hectare area, including the Gölbaşı Lake, the İnekli Lake and the Azaplı Lake, is a wetland ecosystem. These lakes area was declared as "Gölbaşı Lakes Nature Park" on 28.06.2008 according to the 3rd article of the National Parks Law no. 2873. Gölbaşı Lakes, which has a rich biological diversity with freshwater ecosystem, is located on the migration route used by migratory birds flying between Africa and Europe. However, Gölbaşı Lakes are exposed to some misuse hazards. In particular, in the 1970s and 1980s, some places in the vicinity of the lakes were dried by the local people and benefiting from the Gölbaşı lake waters as drinking and using water affect the ecosystems they have with the lakes in a negative way [5]. Heavy metal pollution worldwide; is an ongoing environmental problem for developed and developing countries. A number of trace elements showed significant increase in aquatic aquamarine input from terrestrial and atmospheric environments [11]. Heavy metals are permanent and they can bioaccumulate, so they pose a high risk to ecosystems [3]. Mining, industrial wastes, use of pesticides and the other anhropogenic activities are sources of heavy metals [2]. Despite differences in toxic effects of the metals, environmental conditions, exposure time and concentration are important indicators of ecosystem health [7]. Lake sediments are significant reservoirs of metals in the aquatic environment [1]. The metal residues may accumulate in rivers, sediments, aquatic flora, fauna, and microorganisms, due to they may enter into the food chain, they can be a threat to the human health [10]. Sediments can act as a storage for heavy metal in aquatic environment, but metals cannot fix in sediment forever. With the periodic change of physico-chemical conditions of the water, a portion of these metals is involved in the water column again and become available to living organisms [6]. It is important to learn about the types of trace metals in sediments and determine their main sources in order to avoid river pollution [9]. Therefore we aimed to assess the current status of metal contamination in the waters and sediments at different sample points of Gölbaşı Lake. This evaluation can help to effective protection of Gölbaşı Lake.

2. Materials and Methods

2.1 Sampling Points

Figure 1. The map of the study area

Water and sediment samples were collected at three stations:

1: From the part of the N 37º 47.90' – E 37º 39.66' coordinate of the road to Malatya-Gaziantep,

2: Gölbaşı Dede Korkut Street part of the N 37º 48.05' – E 37º 38.25' coordinate,

3: Gölbaşı Dede Korkut Street part of the N 37º 47.76' – E 37º 38.49' coordinate (Figure 1). The sampling points were chosen based on pollution in the wastewater discharge point of Adıyaman basins of the Gölbaşı Lake.

2.2 Sample Collection

Water and sediment samples were taken between August and November 2017. The water samples were collected using a Ruttner water sampler (Hydro-Bios 2 L, 0.5 m long) and placed in glass bottles of 1 L capacity. Some physico-chemical parameters of water were measured at each sampling point. The water samples were carried to laboratory in dark-colored bottles with cold chains for chemical analyses. The sampling of sediments were performed with a Eckman grab sampler which has surface area of 0.185 m^2 (Hydro-Bios, Kiel, Germany).

2.3 Water Quality Analyses

Water temperature, dissolved oxygen concentrations, conductivity and pH were recorded in the field using portable meters. BOD, ammonium, nitrate, nitrite and phosphate values were determined by the spectrophotometer DR/2010 model Hachlange.

2.4 Microwave Digestion of Sediments

The sediment samples were digested with an acid mixture using a Berghof microwave digestion system according to EPA 3051. The weighted sediment samples (0.5 g to 1,0 g) were feed into the digestion vessel and operated by the following steps to extract appropriate species gradually. Step 1, Adding 3 mL of nitric acid (HNO_3 65 %), 9 ml of hydrochloric acid (HCl 37 %) and shaking the mixture carefully or stir with a clean teflon or a glass bar. Step 2, Waiting at least 2 min before the vessel is closed. Step 3, Heating in the microwave oven with the following program:

Step	3
T (°C)	175
P (bar)	40
Power (%)	80
Ta (min.)	1
Time (min)	10

2.5 Quantification of Metal Residues in the Samples

The certain heavy metals (Pb, Cu, Zn, As, Cr ve Cd) were analyzed in the water and sediment samples. The research was carried out using an inductively coupled plasma mass spectrometer NexION 350X with a universal cell technology (UCT) (PerkinElmer, USA) and model solutions. The main ICP-MS instrumental operating conditions are shown in Table 1. The model solutions were prepared using standard solutions (PerkinElmer, USA) and deionized water. The analytical signal of elements was measured in standard/KED and collision modes. The choice of the effective correction conditions of the polyatomic interferences was made by the determination of the optimal helium flow rate in the range from 0.5 to 3.5 ml/min.

Table 1. ICP-MS instrumental operating conditions

Component / Parameter	Type / Value / Mode
Nebulizer	Mainhard (concentric)
Spray Chamber	Glass Cyclonic
Triple Cone Interface Material	Nickel
Plasma Gas Flow	18.0 L/min
Auxiliary Gas Flow	1.2 L/min
Nebulizer Gas Flow	0.84 L/min
Sample Uptake Rate	1 mL/min
RF Power	1150 W
Integration Time	600 ms
Replicates per Sample	3
Mode of Operation	STD/KED Mode Collision (using He gas)

2.6 Statistical Analysis

The software package SPSS 22 (USA) was used for all statistical analysis. Data normality was determined using the Shapiro-Wilk test ($p < 0.05$). The Kruskal-Wallis test was used to compare the biochemical parameters between groups. If any significant difference was detected between groups, the Bonferroni Mann-Whitney U test was performed. $p < 0.05$ was considered as statistically significant.

3. Results and Discussion

The data related to the water quality parameters of Gölbaşı Lake are shown in Table 2. In terms of all the values in the analysis results, Gölbaşı Lake is a lake with first class water quality when compared to "Quality Criteria According to Continuous Internal Surface Water Resources".

Table 2. Some water quality parameters of Gölbaşı Lake during the study period

Sampling points	**Seasons**	Diss O_2 (ppm)	Temp (°C)	Conduct (IS/cm)	pH	NH_4 (ppm)	NO_2 (ppm)	NO_3 (ppm)	PO_4^{-3} (ppm)	BOD
St-1	Dry	8.45	22.6	336	10.99	ND	0.05	1.35	ND	5.5
St-2	Dry	7.72	25	394	10.95	0.04	0.05	1.42	0.004	10
St-3	Dry	7.46	23.2	337	10.95	ND	0.05	1.37	ND	5.6
St-1	Wet	7.86	17.6	326	11.12	ND	0.045	0.993	ND	3.1
St-2	Wet	7.65	17	327	11.41	ND	0.043	1.08	ND	2.6
St-3	Wet	7.47	17.1	326	11.53	ND	0.041	1.03	ND	2.6

The results of metal content in water samples taken from Gölbaşı Lake during dry and wet times are given in Table 3. If concentration order of the elements in the water of Gölbaşı Lake is done on a seasonal basis followed this decreasing order Zn>Cr>Cu>As>Pb>Cd in the dry season and Cr>As>Zn>Pb>Cu>Cd in the wet season. When the three regions are sorted by the average of the metal concentration in the water samples were followed this decreasing order Zn>Cr>As>Cu>Pb>Cd. If the regions are compared with respect to the whole metal content of the water samples, the most polluted region is determined as the second region, and the metal contents of the first and third regions are found very close to each other. In all three regions, it was determined that the metal with the highest concentration in both dry and rainy periods was chromium. In general, the total amount of metal in the water was found to be higher in the dry period than in the wet season. A statistically significant difference was found for the three regions in terms of chromium and zinc concentrations between dry and rainy periods ($p<0.05$). Regarding the arsenic concentration, no statistically significant difference was observed between regions and seasons ($p>0.05$) (Table 3). The metal concentrations in water were found below the maximum permissible concentrations (mg/L) of heavy metals in drinking water set by USEPA, 2001 (Table 4) [4].

Table 3. Seasonal concentration of metals (µg L^{-1}; mean±SD) in water of sampling points

Stations	Seasons	Cr	Cu	Pb	Zn	As	Cd
St-1	Dry	$1.95±0.06^{2}$	0.55±0.08	0.015±0.01	$1.73±0.17^{2}$	0.57±0.05	0.013±0.003
	Wet	$0.86±0.03^{*}$	$0.27±0.02^{*}$	$0.42±0.018^{2,3,*}$	$0.31±0.02^{*}$	0.53±0.03	$0.004±0.003^{*}$
St-2	Dry	$1.46±0.1^{1,3}$	$0.83±0.19^{3}$	0.046±0.03	$3.95±0.14^{1,3}$	0.53±0.07	0.012±0.007
	Wet	$0.85±0.03^{*}$	$0.26±0.04^{*}$	$0.23±0.01^{1,*}$	$0.45±0.11^{*}$	0.59±0.02	0.009±0.005
St-3	Dry	$2.1±0.1^{2}$	$0.38±0.13^{2}$	0.063±0.03	$1.93±0.3^{2}$	0.57±0.04	0.019±0.005
	Wet	$0.90±0.07^{*}$	0.28±0.09	$0.21±0.03^{1,*}$	$0.28±0.19^{*}$	0.59±0.06	$0.004±0.002^{*}$

Statistical differences that were found between St-1, St-2 and St-3 at the same season are shown as a superscript that 1,2,3 respectively ($p < 0.05$)

*: Statistical differences were found between dry and wet seansons at the same site ($p < 0.05$)

Table 4. Maximum permissible concentrations (mg/L) of heavy metals in drinking water (EPA, 2001)

Elements	EPA
Pb	0.02
Zn	5.0-15.00
Cu	0.05-1.50
Cd	0.003
Cr	0.05
Mn	0.5
Fe	-

The results of the metal residues in the sediment samples were shown in Table 5. The order of sediment metal concentration was almost the same in dry and wet periods. The average metal concentration of dry and wet periods in sediment is as follows:

Fe>Al>Mn>Ni>Cr>Zn>Cu>Pb>Co>As>Se>Cd and their average concentrations were Fe: 9306.4 Al: 8438.5 Mn: 2461.05 Ni: 45.49 Cr: 30.18 Zn: 25.34 Cu: 11.91 Pb: 9.89 Co: 6.69 As: 3.85 Se: 0.21 Cd: 0.085 mg/kg. When compared in terms of zones, the highest metal concentration in sediment was determined in the third zone, followed by the first and second zones, respectively. In all three regions, the most concentrated metal was Fe and the lowest was Cd in both dry and wet seasons. Among the toxic metals, Ni and Cr were detected in the dry period at the maximum of the 69.31±0.81 and 41.25±2.43 concentrations respectively in the 3 rd regions, while Pb was detected in the wet period with the average concentration of 13.94 ± 0.08 in the 2 rd region. It was observed that Cu, Ni, Co, Cr, Fe, Al and Mn were higher in the wet period and Pb, Zn, As, Cd and Se were higher in the dry period when evaluated according to the seasons. A statistically significant difference was observed in the three regions in terms of Cu concentration ($p<0.05$) (Table 5). The Pb, Zn and Ni residues showed a statistically significant difference according to the seasons and regions ($p<0.05$) (Table 5). Co, Cr and Fe residues showed a significant difference compared to only seasons ($p<0.05$) (Table 5).

Table 5. Seasonal concentration of metals in sediment (mg kg^{-1}; mean±SD) of sampling points

Stations	Seasons	Cu	Pb	Zn	As	Ni	Cd
St-1	Dry	$6.92±0.30^{2,3}$	$6.49±0.10^{2,3}$	$13.02±1.52^{2,3}$	3.60±0.17	$50.31±1.31^{2,3}$	$0.060±0.01^{3}$
	Wet	$7±0.57^{2,3}$	$8.84±0.32^{2,3*}$	$21.41±1.11^{2,3*}$	$4.65±0.27^{2*}$	$41.78±2.16^{2,3*}$	$0.215±0.01^{2,3*}$
St-2	Dry	$11.07±0.59^{1,3}$	$9.2±0.44^{1}$	$29.21±1.71^{1,3}$	3.45±0.14	$27.47±1.55^{1,3}$	$0.045±0.01^{3}$
	Wet	$11.76±0.55^{1,3}$	$13.94±0.08^{1.3*}$	$32.74±0.72^{1,3*}$	$3.67±0.13^{1}$	$61.64±0.68^{1,3*}$	$0.14±0.02^{1,3*}$
St-3	Dry	$19.91±0.45^{1,2}$	$9.82±0.53^{1}$	$26.61±0.63^{1,2}$	3.60±1.14	$69.31±0.81^{1,2}$	$0.004±0.004^{1,2}$
	Wet	$14.77±1.76^{1,2*}$	$11.04±0.67^{1.2*}$	$29.02±1.53^{1,2*}$	$4.1±0.32^{*}$	$22.43±1.51^{1,2*}$	$0.045±0.01^{1,2*}$

Stations	Seasons	Se	Co	Cr	Fe	Al	Mn
St-1	Dry	0.173±0.08	$6,03±0.24^{3}$	$35,61±1.49^{2,3}$	$8345,47±100.4^{3}$	$9356,55±72.21^{2,3}$	$2283,32±158.08^{3}$
	Wet	$0,562±0.31^{2,*}$	$6,99±0.13^{3,*}$	$26,75±1.09^{3,*}$	$2645,8±2.61^{3,*}$	$9402,5±117.65^{2}$	$8078,8±36.98^{2,3,*}$
St-2	Dry	0.097±0.11	$5.52±0.58^{3}$	$32.24±1.49^{1,3}$	$8388,163±188.78^{3}$	$6240,91±81.39^{1,3}$	$2170,691±265.54^{3}$
	Wet	$0,06±0.013^{1}$	$6,96±0.16^{3,*}$	$24,06±2.96^{*}$	$2403,5±265.7^{*}$	$8873,4±476.5^{1,*}$	$10280,8±598.3^{1,3,*}$
St-3	Dry	0,197±0.11	$9,36±0.4^{1,2}$	$41,25±2.43^{1,2}$	$12177,4±252.12^{1,2}$	$11343,7±137.3^{1,2}$	$3052,5±141.4^{1,2}$
	Wet	0,140±0.14	$5,24±0.53^{1,2,*}$	$21,14±1.54^{1,*}$	$2210,6±103.02^{1,*}$	$8651,5±861.5^{*}$	$5330,2±581.5^{1,2,*}$

Statistical differences that were found between St-1, St-2 and St-3 at the same season are shown as a superscript that 1,2,3 respectively ($p < 0.05$)

*: Statistical differences were found between dry and wet seansons at the same site ($p < 0.05$)

The metal concentrations in the sediment of Gölbaşı Lake are below the limit of sediment quality guidelines determined by USEPA (Table 6) [8].

Table 6. Sediment quality guidelines determined by USEPA* (Ahmad and Shuhaimi-Othman, 2010)

Elements	Unpolluted	Slightly polluted	Seriously polluted	Average concentration in Earth's crust
Pb	<40	40-60	>60	16
Cd	-	-	>6	0.2
As	-	-	-	-
Cu	<25	25-50	>50	70
Zn	<90	90-200	>200	80
Fe	<17000	17000-25000	>25000	50000

* Concentration in mg/kg dry weight

Gölbaşı Lake is a wetland ecosystem property declared as "Gölbaşı Lakes Nature Park". It is an area of ovulation, frying and seasonal living for many native and migratory bird species. At the same time, these lakes also contain fish species and aquatic creatures, as well as algae and water birds. Therefore, the ecological value of this lake for sustainability the continuous monitoring studies must be carried out on bioaccumulation and biomagnifications of metals and their effects on aquatic organisms in the lake.

4. Recommendations

- There is a park which is opened to the use of the people at Gölbaşı Lake. Here, picnic etc. the social needs of the people are eliminated. Therefore, waste collection units should be put in place in order to prevent the disposal of pollutants.
- Beginning from the western side of the lake towards the north, the new road must be closed to vehicles, designed as walking tracks or bicycle tracks and those who will use it should be informed about the disposal of various pollutants that may cause environmental pollution and therefore pollution and necessary waste collection facilities.
- There are agricultural activities around the lake. Metals involved in fertilization and pesticide application mix with rains and rainwater, as well as water used for irrigation purposes. Since it is necessary to adjust the dose and time of the fertilizer in

order to prevent this pollution or to minimize its effect, the people of the region should be encouraged to go through organic farming and be informed about this issue.

- It should be ensured that the fuels used in the settlements next to the lake, especially during the winter months, are of good quality or that natural gas is used to prevent the heavy metal pollution that will arise from these areas.
- Drainage canals should be constructed at the edge of the lake to prevent contamination of the settlements around the lake by rainwater.

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