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Investigation of Sediment Pore Water Heavy Metal (Cu and Pb) Geochemistry in Deriner Dam Lake, Artvin, Turkey

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Research Article

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Abstract

The aim of this study was to determine metal pollution and ecological risk in the limnetic sediment pore water around Deriner Dam Lake. The Deriner Dam Lake is located in the Coruh Basin (Artvin) in northeastern Anatolia in Turkey. Cu and Pb concentrations were determined in a total of 7 stations, 4 of which were in the lake and 3 of which in the stream that was lake feeding. The samples were collected a range of 1.5-60 m depth, as October 2016. Metal concentrations were determined using an inductively coupled plasma-mass spectrometer (ICP-MS) analysis in ACME. Mean values of Cu and Pb in limnetic sediment pore water were higher than reference value pore water chemistry (WQC). According to sediment guidance values (SGV), mean values of Cu and Pb were determined as class B- moderately contaminated. According to stations, the metal concentrations in sampling area decrease in the order A1, A3, A2, D3, D1, D2, D4. Based upon the results from the present study Cu and Pb can be considered as the contributor to toxicity around the Deriner Dam Lake.

Keywords: Geochemistry, Heavy metal, Pore water, Ecosystem, ICP-MS

Deriner Baraj Gölü Ekosisteminde Sediment Gözenek Suyu Ağır Metal (Cu ve Pb) Jeokimyasının İrdelenmesi, Artvin, Türkiye

Özet

Bu çalışmanın amacı, Deriner Baraj Gölü'nde sediment gözenek suyundaki metal kirliliği ve ekolojik riski belirlemektir. Deriner Baraj Gölü, Türkiye'nin kuzeydoğu Anadolu bölgesinde Çoruh Havzasında (Artvin) yer alır. Metal konsantrasyonlarını belirlemek için toplam 7 istasyon belirlenmiştir. Bu istasyonların 4 tanesi göl ortamından, 3 tanesi bu gölü besleyen akarsu kolundan seçilmiştir. Örnekler, Ekim 2016'da 1.5-60 m derinlik aralığında toplanmıştır. Metal konsantrasyonları, ACME analitik kimya laboratuarında ICP-MS yöntemi ile tespit edilmiştir. Sediment gözenek suyundaki Cu ve Pb'nin ortalama değerleri, literatürde yaygın olarak kullanılan gözenek suyu kimyası değerlerinden (WQC) daha yüksek bulunmuştur. Elde edilen metal değerleri sediment gözenek suyu kalite değerleri (SGV) ile kıyaslandığında Cu ve Pb'nin ortalama değeri orta derecede kontamine (B sınıfı) olarak tespit edilmiştir. İstasyonlara göre örnekleme alanındaki metal konsantrasyonları, A1, A3, A2, D3, D1, D2, D4 sırasına göre azalmaktadır. Bu çalışmanın sonuçlarına dayanarak, Cu ve Pb elementlerinin deriner baraj gölü için toksik etki gösterebileceği söylenebilir.

Anahtar kelimeler: Jeokimya, Ağır metal, Gözenek suyu, Ekosistem, ICP-MS

INTRODUCTION

The Deriner Dam Lake, construction began in 1988, is located on the Coruh basin in the center of the Artvin city, including the area where many incinerators such as industrial and domestic waste are discharged. Despite having a small area with an area of 7436 km, Artvin province is exposed to considerable floods during certain periods, especially spring months, of the year due to both the heavy rainfall, especially the coastal part, and its topography is steep and rough. Floods, which are seen to be significant, cause high erosion in the region. The sediment brought by Coruh River annually is 5.8 million m^3. For this reason, the river basin is one of the most exposed to sediment deposition areas in Turkey (Hasimoglu, 2015).Deriner dam is the highest dam in Turkey and the 6th in the world with 249 meter body height. Besides, Deriner dam is Turkey's highest double-curved concrete arch dam (Konakoglu and Gokalp, 2018). These characteristics of the dam lake provide a total of 1 billion 970 million m^3 of water (Hasimoglu, 2015). As well as, the study area is naturally a very rich area by mineral deposits. There are two active Cu and Au mine in the region.

Considering the environmental impact of mines, it is known that wastewater that flows to the waterways from mining operations changes the natural characteristics of surface water and forms layers of different sediments in the aquatic environment, which adversely affects the aquatic ecosystem. In addition, there are many anthropogenic pollutant such as concrete plants, fuel stations, aquculture activity in the study area (Ozseker and Eruz, 2017).

One of the most important sources of heavy metal pollution in aquatic environments is terrestrial erosion. In this way the metal compounds enter the water column and accumulate in the sediment layer after sedimentation. These pollutants with different roots accumulating in the sediments can migrate back to the water column after sedimentation by physical, chemical and biological processes. Thus, sediments are a source of environmental pollutants in aquatic environment. Therefore, the role of sediment analysis is great in determining the pollution that exists in aquatic environments (Abrahim and Parker, 2008). Also, the sediments are indicators of aquatic pollution, and the metal concentration in sediments and sediment pore water can reflect the aquatic pollution level (Selvaraj et al., 2004). With this aim, sediments for heavy metals are used to toxicity identification, sediment quality assessment and digenetic studies (Shaw et al., 1990; Chester et.al., 1993).

Metals are directly or indirectly affected by some of the reactions during storage in the sediment layer. During these reactions, the participations are occur to pore water from solid sediment surface or the deposity take place from pore water. Pore water is an important intermediate layer that controls the movement between sediment and water layer. The geochemistry of the bottom sediments affects the water column chemistry in this way and heavy metals stored in the polluted sediments therefore form a toxic effect not only on the benthic organisms but also on the living environment in the water column. For these reasons, it is important to examine the metal content of pore water especially in limnetic ecosystems.

Lake sediments can be considered as the ultimate density place of toxic metals. Over time, the sediment accumulating at the bottom of a lake is in contact with water and is in transition with the water column. Due to this transition, metals affect the benthic ecosystem such as absorbed by organisms (Salomons and Förstner, 1984; Calmano, 1989; Ozseker and Eruz, 2017). Since the metal accumulation capacities of the sediments are limited, the metals that accumulate in the sediment layer in a dense amount first migrate to the sediment pore water and then to the water column from this intermediate layer. At this point, sediment pore water is a key role in providing the passage of metals between the sediment layer and the water column. The metals, such as copper (Cu) and lead (Pb) are regarded as serious pollutants of aquatic ecosystems because of their environmental persistence, toxicity, and ability to be incorporated into food chains (Förstner and Wittman, 2012).

In this study, the metal concentrations measured in the sediment pore water of Deriner Dam Lake were compared with suitable reference values, such as sediment guidance values for freshwater (SGV) and pore water chemistry (WQC) which are commonly used guidance to determine the pollution load in sediment layer of aquatic environment (US EPA, 2002; Heredia and Cirelli, 2009; Ozseker and Eruz, 2017). These guidance were used to determine the level of pollution around Deriner Dam Lake.The goal of this research was to determine the spatial changes in the natural and anthropogenic heavy metal pollution in sediment pore water around Deriner Dam Lake.

MATERIAL and METHODS

This study was a survey of heavy metal pollution in the southwestern Black Sea region of Artvin province. In this context, the research was carried out in two different areas, Deriner Dam Lake and Ardanuç Stream, which is a branch of the Coruh river that feeds this lake (Figure 1). Metal concentrations (Cu and Pb) were determined in a total of 7 stations, 4 of which were lake and 3 of which stream that was lake feeding (Table 1).

Table 1. The coordinates of study area

Stations	**Deriner Dam Lake**		**Stations**	**Ardanuç Stream**	
	Latitude	**Longitude**		**Latitude**	**Longitude**
D1	41°10'03,87"	41°52'42,46"	A1	41°07'27,38"	42°03'41,40"
D2	41°09'30,06"	41°53'40,30"	A2	41°07'57,14"	42°02'50,97"
D3	41°08'23,53"	41°53'44,47"	A3	41°09'37,98"	41°58'20,39"
D4	41°07'10,88"	41°52'24,80"			

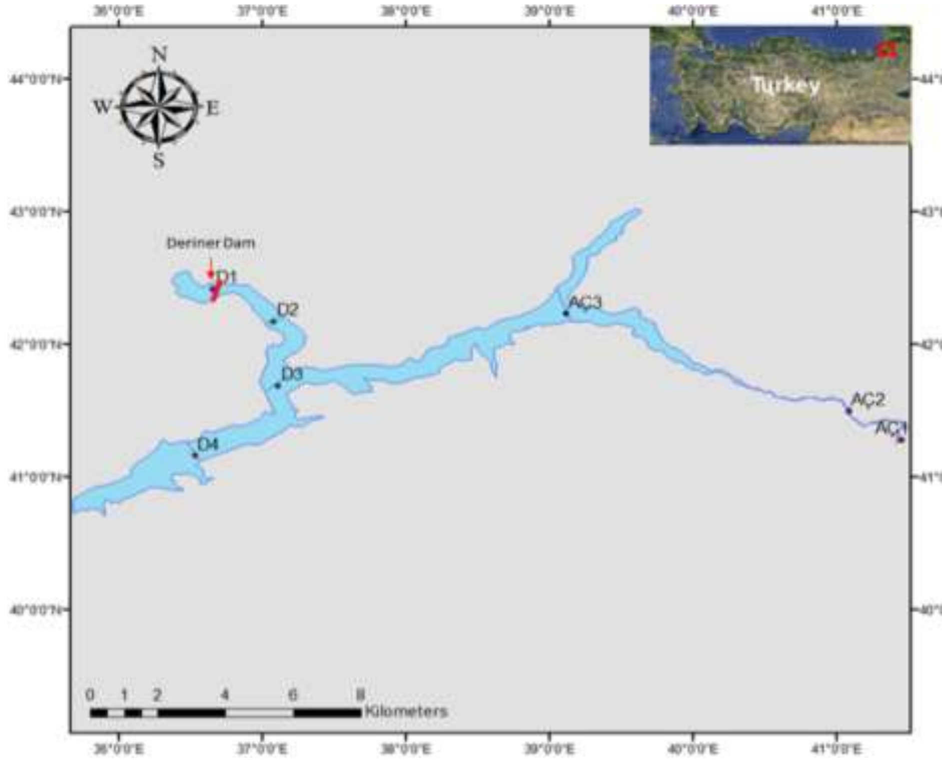

Figure 1. Map of the study area

The samples were collected a range of 1.5-60 m depth, as October 2016. A sediment core sampler, having replaceable transparent sampling tubes with 5 cm mouth diameter and 50 cm length and made of stainless steel with manual controllable,was used to collect sediment samples from 7 different stations. The stations were chosen so as to cover the metal pollution affected area. The samples were placed in polyethylene bags using a clean plastic spatula to prevent contamination. After collection, all samples were placed in refrigerator, and transported to the laboratory where they were stored at – 18 ˚C until being analyzed (Csuros and Csuros, 2016). Prior to analysis, samples were dried at 45 ˚C. For general physical properties of the sediment around Deriner Dam Lake, sediment samples were separeted in two categories as by means of wet analysis method with sieve 0.63 micron. The material under the sieve was evaluated as clay. The material remaining on the sieve was dried and divided into different material sizes with the help of AS 200 Vibratory Sive Shaker. After than, the mass and total percentage values of material fractions were determined by combination of clay and other dimensional materials (Retsch, Germany) (Aytekin, 2004).

Sediment size analysis was performed using wet sieve analysis method. For metal analysis, sediment samples were sieved to pass <63 µm because metals exhibits usually a higher affinity to small grains (Morillo et al., 2004). Pore waters were separated from the sediment layers by centrifugation at 10,160 rcf x g for 30 min at +4 ˚C and filtered through 0.45 µm cellulose acetate membranes. Filtration and subsequent manipulation of the samples were carried out in a glove box under argon atmosphere in avoid alteration of the initial conditions (Santos-Echeandia et al., 2009). Pore water samples were acidified with suprapure HCL (pH < 2).

Metal concentrations were determined using an inductively coupled plasma-mass spectrometer (ICP-MS) analysis in ACME Lab. (Vancouer, BC. Canada). The accuracy of the analysis was ranged from 95.81% to 130.50%. The volume fraction of porosity (n) can be defined as the reaction of void space (VV) relative to the apparent total bulk volume (VT) of the sample. Porosity is described in percentage (Klobes et al., 2006).

$n=(VV/VT)*100$

Physicochemical parameters such as pH and oxygen, which are directly related to the mobility of the metals, were determined *in situ* and measured using a Hach Lange HQ40D multi meter. Pore waters were separated from the sediment layers by centrifugation at 10,160 rcf x g for 30 min at +4 ˚C and filtered through 0.45 µm cellulose acetate membranes pore water samples were acidified with supra pure HCL (pH < 2). Determining the level of pollution, pore water chemistry (WQC) and Sediment guidance values (SGV) for fresh water sediment were applied.

The one-way analysis of variance (ANOVA), followed by Duncan's test, was used to identify the significance ($p<0.05$) of local differences (Kim et al., 2014). Statistical analyses were performed using SPSS 15.0 (IBM, Armonk, NY, USA).

RESULTS

General properties were given in Table 2 in sediment and pore water around Borçka Dam Lake and Ardanuç Stream. In this study, sediment material fractions were evaluated in eight categories as gravel (16-32 mm), fine gravel (8-16 mm), very large sand (1-2 mm), coarse sand (0.5-1 mm), medium sand (0.25-0.5 mm), fine sand (0.125-0.25 mm), very fine sand (0.063-0.125 mm) and clay (< 0.063 mm). The sand fractions were generally dominant (>60%) in the surface sediments (Figure 2). Also, values of porosity, pH, temperature, salinity and oxygen were ranged from 35.5 to 57%, from 7.10 to 8.14, from 12.2 to 14.7 ˚C, from 6.45 to 8.35 mg/L, respectively (Table 2).

Table 2. General properties of sediment and pore water around Deriner Dam Lake

	Physical properties						**Chemical properties**		
Area	**Depth m**	**Gravel %**	**Sand %**	**Clay %**	**Porosity %**	**Temperature ˚C**	**pH**	**Oxygen %**	**Oxygen mg/L**
D1	34	1.7	72.6	25.7	40.0	14.4	7.47	65.4	8.05
D2	43	3.5	69.3	27.2	43.0	12.2	8.14	77.3	8.50
D3	55	5.8	78.1	16.1	33.5	13.7	7.41	71.3	7.38
D4	60	1.7	65.6	32.7	56.0	13.2	7.29	65.7	6.45
A1	1.5	7.1	84.8	8.1	57.0	14.1	7.43	75.4	8.35
A2	2.7	7.8	79.4	12.8	53.5	14.4	7.10	73.1	8.11
A3	2.4	8.9	68.7	22.4	51.5	14.7	7.17	70.6	8.08

The meteorological values which were directly related to the physical and chemical properties of sediment and pore water were shown in the Table 3 (Anonymous, 2016). The meteorological values in October were higher than the average for the year. These results indicated high erosion in the region during the study period.

Table 3. Meteorological values in the study area

2016 year	**Wind speed (NNW)**	**Temperature °C**	**Rainfall (kg/m^2)**	**Relative mousture (%)**
October	1.3	16.9	141.0	70.8
Annual average	1.55	12.6	65.96	64.3

Considering the distribution of the material in general, the gravel was founded 1-1%, the fine gravel was founded 2-2%, the very large sand was founded 2-2%, the coarse sand was founded 7-7%, the medium sand was founded 9-9%, the fine sand was founded 38-40%, the very find sand was founded 16-16% and the clay was founded 25-23% in the study area (Figure 2).

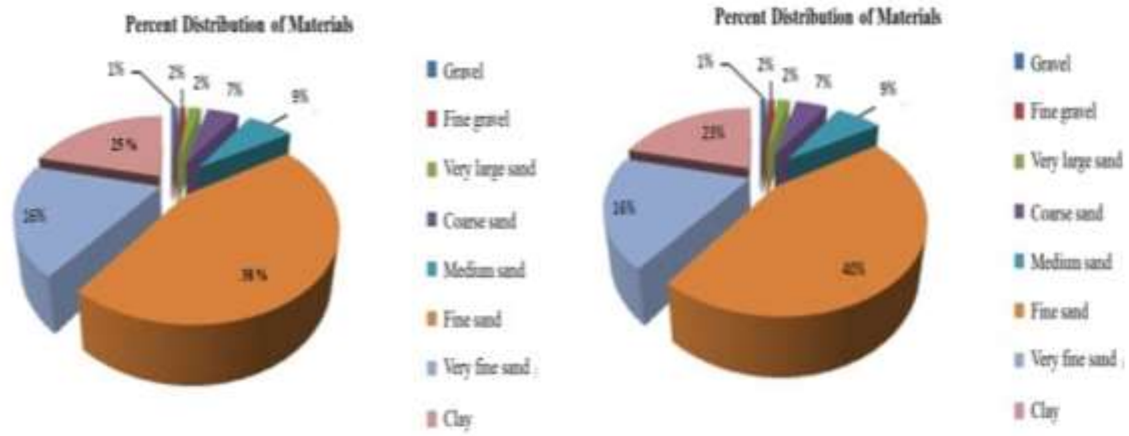

Figure 2. The proportional material in Deriner Dam Lake (left) and Ardanuc Steam (right)

The spatial distribution of sediment material distribution was plotted on the map of the study area and the difference between the accumulation characteristics of the heavy metals in the sediment layer and the distribution of materials directly related to each other was settled (Figure 3).

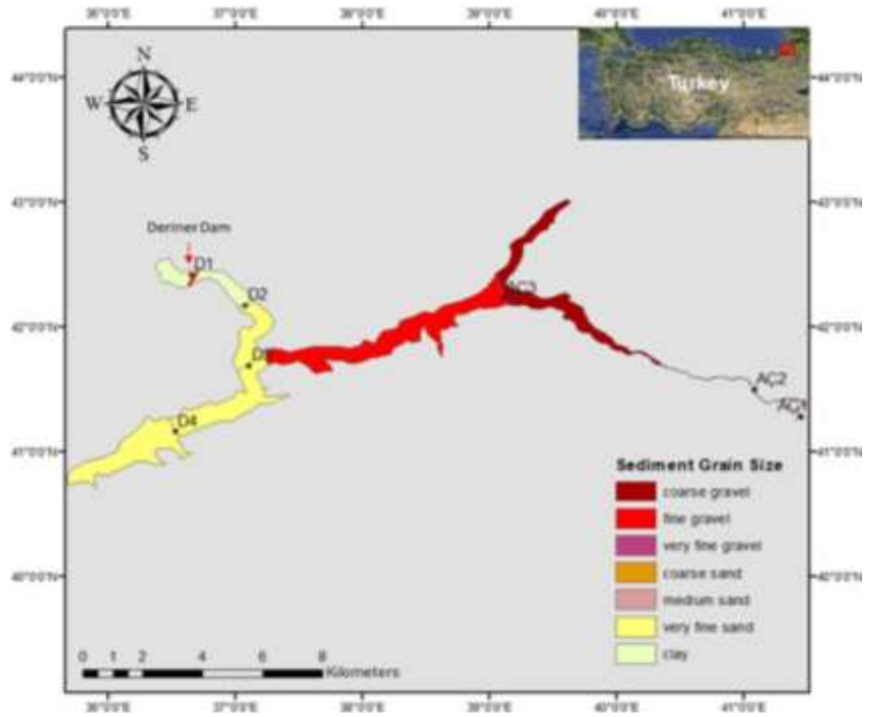

Figure 3. The spatial distribution of material in study area

Metal concentrations in pore water samples collected from the study area were given in Figure 4. Metal concentrations in sediment pore water were varied from 357.6 to 478.1 µg kg^{-1} for Cu, 147.3 to 168.2 µg kg^{-1} for Pb. The highest metal concentrations were determined in A1 and A3 stations (Figure 4). The means of Cu and Pb were founded as 425.70 µg kg^{-1} and 163.52 µg kg^{-1}, respectively.

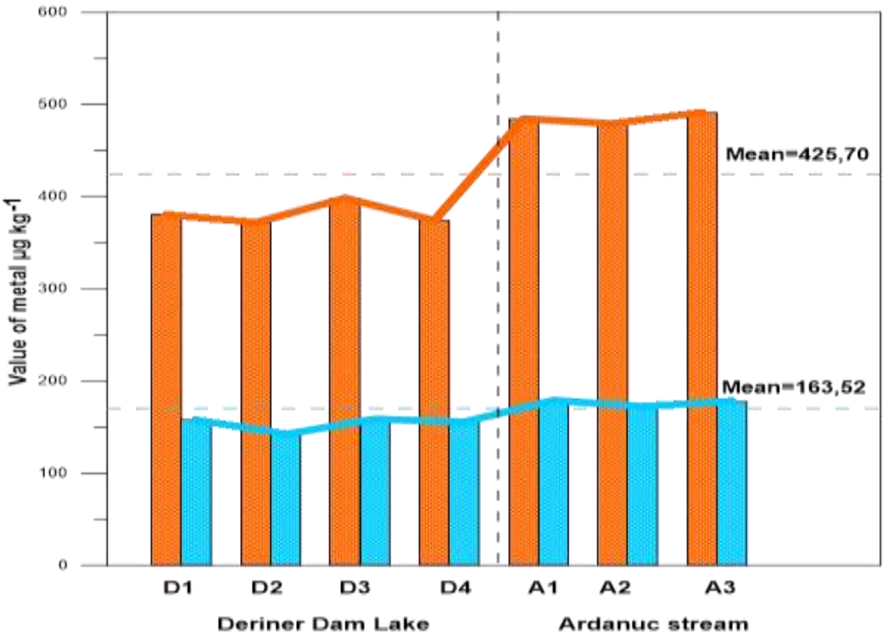

Figure 4. Change of metal values according to stations in sediment pore water

Sediment pore water chemistry used to the comparison of chemical pollution levels of pore water in the literature, copper and lead values were reported as 9 and 2.5 µg kg^{-1}. When we compare the metal values the present results were very high. According to the sediment pore water guidance values for freshwater provided by the United States Environmental Protection Agency (US EPA, 1997) sediment pore waters were classified into three classes: low risk, moderately contaminated, and highly contaminated (Table 4).

Table 4. Classification of metal concentration according to pollution limits

Metal	Mean value µg kg^{-1}	WQC µg kg^{-1}	SGV for fresh water		
			Class A low risk	Class B moderately contaminated	Class C highly contaminated
Cu	425.70	9	<32	32-150	>150
Pb	163.52	2.5	<36	36-130	>130

SGVs: Sediment pore water guidance values for fresh water sediment (US EPA, 2002);
WQC: Pore water chemistry(Heredia and Cirelli, 2009)

Accordingly, sediments were classified as highly contaminated in Deriner Dam Lake and Ardanuç Stream with regard to Cu and Pb levels. Metal concentrations in sampling area decrease in the order A1 > A3 > A2 > D3 > D1 > D2 > D4.

One way ANOVA test was performed to test whether there is a significant difference between the averages of two or more groups. The results revealed significant differences in Cu values according to region (F 817.304; $p<0.05$), Pb values showed no significant difference according to region (F 0.541; $p>0.05$).

DISCUSSION

According to the results, the highest metal concentrations and environmental risks in Deriner Dam Lake and Ardanuç Stream, which is a branch of the Coruh river that feeds this lake, were observed in October for Cu and Pb. Toxic metal concentration can vary depending on many factors, such as pH, dissolved oxygen, temperature,and redox conditions. These factors are also related to activity of meteorology. At the region, in October, the changes in meteorological conditions were fast and strong (Table 3) (Anonymous, 2016). This confirms the role of rain in removing metal-contaminated airborne dust (Melaku et al., 2008). In this study, the highest metal concentration was determined in A1 station.

When the metal values were analyzed according to the stations, it has been determined that high results were generally in the order of the Ardanuç Stream feeding the lake. Ardnuç stream is the main factor that feeds the reservoir due to erosion in the region. The selected A1 station on the stream is a important station that intensively discharges of domestic and industrial waste and their results can be observed directly. In the present study, it was expected that the highest metal values would be observed at this station. Furthermore, when considering the four stations that the Deriner dam has in its own context, it was observed that the high metal concentrations were at the D3 and D1 stations, which are denoted by the clay material intensively, for metals exhibits usually a higher affinity to small grains (Morillo et al., 2004). The high pollution levels around Deriner Dam Lake reveal the high natural mineralogical structure of the lake and its surroundings, indicating that the anthropogenic impact on the region should be considered.

Today, the quality of the aquatic environment is being threatened by different types of pollutants from natural and anthropogenic sources; however, human activity is the main reason for the pollution (Ozseker and Eruz, 2017). Considering the environmental impact of mines, it is known that wastewater that flows to the waterways from mining operations changes the natural characteristics of surface water and forms layers of different sediments in the aquatic environment, which adversely affects the aquatic ecosystem (Altınbas et al., 2014). Depending on the anthropogenic effects, wastewaters from mining operations and Cu waste cause high levels of environmental pollution resulting from environmental conditions, such as rain, and erosion causes high levels of metal concentration in the region.

Metal concentrations in other research areas are believed to be related to the natural mineralogical structure of the region (e.g., wastewater, mineral sources, meteorological conditions, and river runoff). In the land areas surrounding the lakes, the General Directorate of the Mineral Research & Exploration has investigated toxic metal concentrations in detail (Altınbas et al., 2014). In addition, construction activities, which is an important anthropogenic effect, greatly increase the concentration of metals in the aquatic environment. Road construction, dam construction and stone crushing facilities are intensively active in the continental part surrounding the lake. Based upon the results from this study Cu and Pb can be considered as contributor to toxicity around the Deriner Dam Lake.

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