

ECOLOGICAL RISK ASSESSMENT PROFILE OF LAKE SURFACE SEDIMENT USING METAL(LOID)S: A CASE STUDY, THE BORABOY LAKE, TÜRKİYE


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ABSTRACT. Anthropogenic activities have increasingly threatened aquatic ecosystems with the gradual increase of metalloids in the lake sediment. The profile of Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, and Zn metal(loid)s that have been investigated in natural Boraboy Lake have been investigated in sediment. Their amounts in the sediment have been found as Mn>Fe>Al>Zn>Cu>Cr>Ni>Co>Pb>As>Mo>Cd. The findings have been analyzed using sediment quality values. The Enrichment Factor, one of the sediment quality values, has indicated that the lake has highly enriched in As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn. In addition to that, it has been detected that As, Ni, and Cu together constituted the 67% of the total toxic effect. While the mean value of Cu has been found to be higher than the reference value of the earth's crust at, 58.1 ± 6.8 ppm, the mean values of As and Ni have been found to be lower than the reference value of the earth's crust (9.4 ± 0.7 ppm) and (18.8 ± 12.8 ppm) respectively. As and Cu have been detected above the Threshold Effect Level. Despite all these results, it has been revealed through sediment quality indexes that there is no threatening accumulation in the lake.

1. INTRODUCTION

Due to their ability to accumulate metal(loid)s (Ms), sediments are generally defined as aquatic cleaners of Ms [1]. Ms are found in the natural composition of the earth crust; however they have been gradually increasing in lake sediments with anthropogenic effects. Increasing Ms level has toxicological effects on both wetland and organisms in wetland when it is over a certain threshold value. Therefore, it is crucial to study the possible ecotoxicological effects of a metal(loid) and to reveal the Ms-Ms interactions of a lake [2]. Ms, which are harmless and naturally found in trace amounts in the earth crust, have been subject to many studies in which they generate ecotoxicological stress in wetlands due to anthropogenic effects such as industry, agriculture, trade, etc. [3-6]. It is very important to determine the distribution of Ms to stations in a sediment and to identify the spatial points where it is concentrated. Therefore, it is shown by these studies that such studies are of great importance in terms of timely intervention.

Keywords. Multivariate statical analysis, sediment quality guidelines, Ms-Ms interactions, ecotoxicity
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The Ms concentrations acquired from the sediment are not meaningful on their own. The results are only meaningful when they are evaluated with background level and sediment quality guides [6]. Thus, in investigation of the sources (natural/anthropogenic) of Ms, background levels such as probable effect level (PEL), threshold effect level (TEL), effects range low (ERL), and effects range median (ERM) and sediment evaluation methods such as Degree of Contamination (C_d), Modified Degree of Contamination (mC_d), Contamination factor (C_f^i) and Enrichment factor (EF), Geoaccumulation index (I_{geo}), Toxic unit (TU), Pollution Load Index (PLI), mean ERM quotients (m-ERM-q) and mean PEL quotients (m-PEL-q) have been frequently used in the literature [3-6]. The separation of the source of an Ms in the sediment provides important information about the contamination degree of that Ms. It also offers advantages in determining and maintaining the health status of the lake water system [2].

Boraboy Lake is 750 m long in general and 100 m wide in the eastern half and 200 m wide in the western half. It has a perimeter of 2 km and an area of 11 ha (0.11 km²). The lake is generally used for irrigation of agricultural areas and recreation [7]. In the study, 13 different Ms in the sediment of Boraboy Lake, which is an important natural lake, have been investigated in terms of both accumulation and ecological hazard. The amounts of these metals have been interpreted using the sediment quality guidelines (SQGs) limit values, and their effects have been evaluated through the sediment assessment indexes. Ms-Ms accumulation relations have also been examined using multivariate statistical analysis. The main objective of this study is to understand the current Ms composition of the lake by determining the distribution of Ms at the stations in the sediment of Lake Boraboy.

2. MATERIALS AND METHODS

A total of 15 samples were taken from the surface sediment at one time in October 2021 (Figure 1, Table 1). The samples collected were sent directly to Bureau Veritas Mineral Laboratories Canada (ACME LAB.) and analyzed according to the AQ270 method. Duplicate, reference material and blank results and detection limits are as in Table 2.

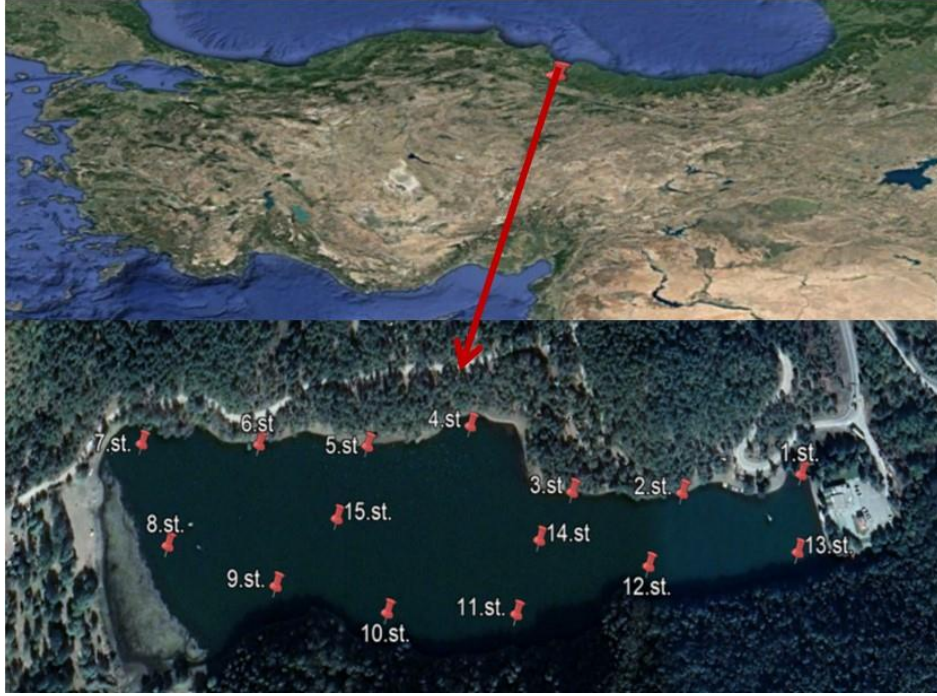


FIGURE 1. Boraboy Lake stations

TABLE 1. Coordinates of work stations

Station No	Latitude	Longitude
1	40°48'15.53"K	36° 9'29.03"D
2	40°48'15.02"K	36° 9'24.10"D
3	40°48'15.04"K	36° 9'19.59"D
4	40°48'16.84"K	36° 9'15.41"D
5	40°48'16.28"K	36° 9'11.15"D
6	40°48'16.31"K	36° 9'60.67"D
7	40°48'16.33"K	36° 9'10.81"D
8	40°48'13.59"K	36° 9'30.11"D
9	40°48'12.54"K	36° 9'70.56"D
10	40°48'11.85"K	36° 9'12.07"D
11	40°48'11.82"K	36° 9'17.26"D
12	40°48'13.08"K	36° 9'22.63"D
13	40°48'13.45"K	36° 9'28.70"D
14	40°48'13.76"K	36° 9'18.22"D
15	40°48'14.32"K	36° 9'90.96"D

TABLE 2. Duplicate samples, reference material, blank solution results and detection limits

	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
	(%)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(%)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Pulp Duplicates-1	3.38	5.8	0.23	24.2	9.7	60.97	4.30	968	0.37	10.8	29.61	240.4
Pulp Duplicates-2	3.47	6.0	0.23	24.0	9.9	61.87	4.37	982	0.39	11.1	29.64	248.4
Reference value BVGEO01	2.46	124.8	6.11	27.7	192.9	4604.86	3.86	788	10.75	179.3	191.33	1858.7
Reference value OREAS262	1.26	34.8	0.60	30.3	45.1	126.94	3.46	570	0.65	64.4	57.02	156.2
Blank	<0.01	<0.1	<0.01	<0.1	<0.5	0.02	<0.01	<1	<0.01	<0.1	<0.01	<0.1
Detection Limit	0.01	0.1	0.01	0.1	0.5	0.01	0.01	1	0.01	0.1	0.01	0.1

Sediment Quality Indexes

Source data from Turekian and Wedepohl [8] have been taken as reference. The scale including the meaning of the sediment quality indexes is as in Table 3.

Contamination factor (C_f^i) [9]

$$C_f^i = C^i / C_n^i \quad (1)$$

C^i = Amount of Ms

C_n^i = Reference value

Degree of Contamination (C_d) [9]

$$C_d = \sum_{i=1}^n C_f^i \quad (2)$$

C_f^i = Contamination factor

Modified Degree of Contamination (mC_d) [10]

$$mC_d = \frac{\sum_{i=1}^n C_f^i}{n} \quad (3)$$

C_f^i = Contamination factor

n = Number of Ms studied

Pollution load index (PLI) [11]

$$PLI = (C_{f1} \times C_{f2} \times C_{f3} \dots \times C_{fn})^{1/n} \quad (4)$$

C_{f1} = Contamination factor

n = Number of Ms studied

Enrichment factor (EF) [12]

$$EF = \frac{C_n/C_{ref}}{B_n/B_{ref}} \quad (5)$$

C_n = Amount of Ms

C_{ref} = Amount of Ms in the reference environment

B_n = Amount of reference element in sample

B_{ref} = The value of reference element in reference environment

Al has been preferred as reference element.

Geoaccumulation index (I_{geo}) [13]

$$I_{geo} = \log_2 \frac{C_n}{1.5 \times B_n} \quad (6)$$

C_n = Amount of Ms

B_n = The amount of metal in the reference environment

1.5 = natural oscillation coefficient

Mean effect range median ratio (m-ERM-Q) and average probable effect level ratio (m-PEL-Q) [14]

$$m - ERM - Q = \frac{\sum_{i=1}^n C_i/ERM_i}{n} \quad (7)$$

$$m - PEL - Q = \frac{\sum_{i=1}^n C_i/PEL_i}{n} \quad (8)$$

C_i = Amount of metal

ERM = effect range median of metal

PEL = average probable effect level of metal

n = number of Ms studied

Total toxic unit (Σ TU) and rational toxic unit

$$\Sigma TUs = \sum_{i=1}^n C_i/PEL_{C_i} \quad (9)$$

$$Proportional TU = \frac{C_i/PEL_{C_i}}{\sum TU_s} \times 100$$

(10)

Statistical Analysis

The relationship between Ms-Ms has been revealed through correlation, principal components analysis (PCA) and clustering (CA) analysis. SPSS 21v. has been used for all statistical analysis.

TABLE 3. Meaning scale of sediment quality indexes

Contamination factor [9]	
CF<1	low contamination
1≤CF<3	moderate contamination
3≤CF<6	considerable contamination
CF≥6	high contamination
Degree of contamination (Ca) [9]	
Cd≤8	low degree of contamination
8≤Cd≤16	moderate degree of contamination
16≤Cd≤32	considerable degree of contamination
Cd≥32	very high degree of contaminations
Modified degree of contamination (mCd) [10]	
mCd < 1.5	nil to very low degree of contamination
1.5 ≤ mCd < 2	low degree of contamination
2 ≤ mCd < 4	moderate degree of contamination
4 ≤ mCd < 8	high degree of contamination
8 ≤ mCd < 16	very high degree of contamination
16 ≤ mCd < 32	extremely high degree of contamination
mCd ≥ 32	ultra high degree of contamination
Pollution load index (PLI) [11]	
PLI <1	no pollution
PLI is >1	deterioration

TABLE 3 (continued)

Enrichment factor (EF) [12]	
<1	no enrichment
1 to 3	minor enrichment
3 to 5	moderate enrichment
5 to 10	significant enrichment
10 to 25	severe enrichment
25 to 50	very severe enrichment
>50	extremely severe enrichment
Geoaccumulation index (Igeo) [13]	
$I_{geo} \leq 0$	practically uncontaminated
$0 < I_{geo} < 1$	uncontaminated to moderately contaminated
$1 < I_{geo} < 2$	moderately contaminated
$2 < I_{geo} < 3$	moderately to strongly contaminated
$3 < I_{geo} < 4$	strongly contaminated
$4 < I_{geo} < 5$	strongly to extremely contaminated
$I_{geo} \geq 5$	extremely contaminated
Ratio of average effects range median (m-ERM-Q) [50]	
$m-ERM-q < 0.1$	9%
$0.11 < m-ERM-q < 0.5$	21%
$0.51 < m-ERM-q < 1.5$	49%
$m-ERM-q > 1.50$	76% probability of being toxic
Ratio of average probable effect level (m-PEL-Q) [14]	
$m-PEL-Q < 0.1$	unimpacted
$0.1 < m-PEL-Q < 1$	moderately impacted
$m-ERM-Q > 1$	highly impacted

3. RESULTS AND DISCUSSION

As a result of the analysis, Ms accumulation in the sediment has been found as Mn>Fe>Al>Zn>Cu>Cr>Ni>Co>Pb>As>Mo>Cd, respectively (Table 4). Manganese (Mn) is in the form of Mn^{2+} in aquatic ecosystems [15]. The distribution of Mn in lakes may vary depending on the hydrophysical characteristics of the lakes and the redox changes of the lake habitat [16]. The Mn value in the study varied between 991 and 1675 ppm. The mean Mn value has been calculated as 1217.3 ± 172.9 ppm. It is higher than the earth crust reference value. Due to its lower turbulence and higher pH compared to rivers,

the lake sediments act as an efficient sink for the iron element (Fe) [17]. Mn is affected more by redox changes than Fe [18]. The amount of Fe and Mn in a lake sediment does not only depend on redox changes. It also depends on the biogeochemical alteration of the lake water and the diagenesis of the sediment [19]. In the study, while the Fe concentration has varied between 351 and 682 ppm, the mean value has been calculated as 536.1 ± 86.1 ppm. This result is low, compared to the earth crust reference value.

Although its content varies depending on the type of the rock, Aluminum (Al), one of the main elements of the earth crust, has been detected in all rocks. It constitutes approximately 7.91% of the lithosphere. Along with silicium and oxygen, it is one of the main elements of the earth crust and it is mostly in the form of Al^{+3} cation. It shows affinity for oxygen bonds [20]. Al is easily absorbed by sediment as it is in the form of metastable compounds and can activate as the acidity increases in water [21]. In the study, the Al value varied between 247 and 457 ppm. The mean value has been calculated as 368.1 ± 63.6 ppm. It has been found to be lower than the earth crust reference value. On the basis of anthropogenic zinc (Zn) release, there is the production of energy, cement, medicine, cosmetics and rubber etc. as well as processes such as waste incineration [22]. The Zn value in the study varied between 72.1 and 94.1 ppm. The mean value has been calculated as 85.1 ± 6.4 ppm. While some stations of the lake are close to the earth crust reference value, the mean value has been found to be low. Copper (Cu) is a very important trace element for carbohydrate metabolism and the functioning of some enzymes [23]. However, it can also cause the pollution of a lake when it exceeds the threshold value. Vehicle exhausts, pesticides, mining and burning coal are effective Cu resources [24, 25]. Cu values varied between 46.9 and 71.5 ppm, and the mean value has been calculated as 58.1 ± 6.8 ppm. The Cu concentration in each station has been observed to be higher than the earth crust reference value. Cr contamination in lakes is associated with the discharge of wastewater from industrial facilities [26]. In this study, Cr concentration has been observed in the range of 8.1 to 40.1 ppm and the mean value has been calculated to be 24.2 ± 12.1 ppm. The detected Cr concentration has been observed not to exceed the earth crust value at any of the stations.

Nickel (Ni) is a commercially important metal that is used in stainless steel, metallurgy and food industry. Therefore, its oscillation into lakes is both natural and anthropogenic and it is a metal commonly found in waters [27]. In the study, its concentration has been found in the range of 8.9 to 43.3 ppm, while the mean value has been calculated as 18.8 ± 12.8 ppm. Its concentration at each station has remained low compared to the earth crust reference data. Cobalt (Co) is one of the trace elements for organisms; however, it has very dangerous effects when it exceeds the threshold value. It is found in the stable cobalt sulfate phase in sediments [28]. In the study, its concentration has been measured between 10.9 and 24.6 ppm. Its mean value has been calculated as 16.2 ± 4.1 ppm. Although it exceeded the earth crust reference value at some stations, its average value has

been found to be lower. Adsorption and desorption speeds of lead (Pb) in the sediment vary due to the structure of the sediment. Pb ranks third in the world in Ms production. This makes Pb potentially dangerous among the lake pollutants [29]. It reaches the lake sediment easily due to its wide use in such as mining, ammunition, pipe construction, paint making and pesticides [30]. The mean value of Pb, which is detected between 7.8 and 24.6 ppm concentrations, has been calculated as 13.1 ± 6.2 ppm. Except for a few stations, it has been observed to be below the earth crust reference value. Although in small amounts, Arsenic (As) is an Ms found in earth crust all over the world. Anthropogenic activities play a role in the distribution of As pollution. It is mostly used in wood preservatives and pesticides [31]. In the study, As concentrations have been found between 8.1 and 10.6 ppm. Its mean value has been calculated as 9.4 ± 0.7 ppm. It has been observed to be lower than the earth crust reference value.

Molybdenum (Mo) is a metal that is naturally found in sediment and rocks, however, it has harmful effects when in high concentrations [32]. Mo can be absorbed by Al, Fe and Mn under acidic conditions and precipitated with cations such as Pb, Mn, Zn, and Cu [33]. While the mean Mo has been found to be 0.48 ± 0.12 ppm in the study, it has been found in the range of 0.28-0.67 ppm throughout the lake. This amount is a lot less than the earth crust reference value. Cadmium (Cd) is a highly toxic and non-essential Ms for organisms [9]. Its toxic effect may increase with other Ms such as Zn [34]. In the study, the Cd concentration range has been found to be between 0.05-0.18 ppm, while the mean concentration has been calculated as 0.09 ppm. It is quite low compared to the earth crust reference data as well.

The result of the Ms has been compared with the limit values (Table 4). All the calculated metal(loid) values have been found to be below the Probable Effect Level (PEL). Only As and Cu values have been observed to exceed the Threshold Effect Level (TEL) value, and Ni, at the TEL limit value. Therefore, no toxic effects of Ms other than As, Cu and Ni are expected in the lake, and the effect of these Ms have been determined to be rare (Table 3) [35].

TABLE 4. Ms values and limit values in sediment

	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
Mean	368.1	9.41	0.091	16.25	24.17	58.08	536.1	1217	0.476	18.83	13.05	85.12
Min	247	8.1	0.05	10.9	8.1	46.87	351	991	0.28	8.9	7.77	72.1
Max.	457	10.6	0.18	24.6	40.1	71.52	682	1675	0.67	43.3	24.64	94.1
Std. Dev.	63.6	0.77	0.05	4.10	12.12	6.79	86.1	172.9	0.12	12.8	6.24	6.41
PEL		17.00	3.53		90.00	197.00				36.00	91.30	315.00
ERM		85.00	9.00		145.00	390.00				50.00	110.00	270.00
TEL	X	5.9	0.60	X	37.30	35.70	X	X	X	18.00	35.00	123.00
ERL		33.00	5.00		80.00	70.00				30.00	35.00	120.00
Earth Crust	80000	13.00	0.30	19.00	90.00	45.00	47200	850.00	2.6	68.00	20.00	95.00

Ms with the potential of toxic effects in the lake are As (26.6%), Ni (25.7%), Cu (14.2%), Zn (13.0%) and Cr (12.9%), respectively. Studies supporting this result are available in the literature [5, 36]. Although the rates seem high, they are not highly risky for the lake and CF supported this result. The CF value is one of the most important indexes to observe the time-dependent increase of an Ms in the sediment and to evaluate the Ms [9,37]. This index has been used by many researchers studying metal(loid) pollution in sediment [5, 25, 38, 39]. The CF values of Al, As, Cd, Co, Cr, Fe, Mo, Ni, Pb, and Zn have been calculated to be less than 1. Therefore, the effect of these Ms on the lake is low contamination. The CF value of Cu and Mn is higher than 1, and its effects have been observed to be moderate contamination (Table 5). Thus, Cu and Mn indicate a moderate pollution, while other Ms's potential to pollute is low.

However, according to EF data, it has been observed that there is extremely severe enrichment in terms of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn (>50) in the lake. The enrichment of all these Ms indicates that the anthropogenic release in the lake is high. In the study Withanachchi et al. [40] conducted in Mashavera River (Georgia), they reported that the EF value of Cd metal was similarly extremely severe enrichment at some stations. Seifi et al. [41] determined the EF value of Pb, Cd and Zn metals as significant enrichment in sediment samples they collected from places close to the urban and industrial areas of the Persian Gulf. EF, which is an important contamination index, provides powerful data in determining the raw information of the studied wetland and conveying this information to the necessary authorities [42]. Therefore, it has been determined that if the Boraboy Lake's exposure to the anthropogenic effect is not dealt with, these Ms may create a high potential ecotoxicological risk for the lake in the future. Ms do not disappear in nature and tend to accumulate increasingly. Therefore, preventing continuous input to the lake is very important for the lake ecosystem. Cd, mCd and PLI are indexes used to evaluate the quality of a lake sediment and provide very important information about the quality of the lake [43]. When the Cd, mCd and PLI levels of all Ms are evaluated, it cannot be mentioned that the lake is polluted by the detected Ms (Table 5).

The toxic profile of the lake has been revealed through m-ERM-Q and m-PEL-Q data. According to the result of the m-ERM-Q index, the lake is at level 1, which is 9% of rate. This indicates that the toxicity level of Ms, which have accumulated up to today in the lake, for the organisms in the lake is 9%. According to the m-PEL-Q index, it has been concluded that the lake is moderately impacted. According to the Igeo index result, it has been concluded that the lake is practically uncontaminated. The indexes used, have indicated consistent results in evaluating the presence and accumulation of Ms in the sediment (Table 5).

When similar studies conducted recently in our country are examined, Cd accumulation has been observed to be a common and general problem just as in our study, most of which has been conducted in wetland. Şimşek et al. [3]

investigated the pollution caused by the metals they detected in the sediment of the creeks on the Samsun-Tekkeköy border in the north of Türkiye, through indexes such as EF, CF, PERI and Igeo. They determined that Cd metal, which is common in all creeks, is risky. Yüksel et al. [44] examined the pollution in the sediment of Çavuşlu creek in Giresun through indexes such as EF, Igeo, CF, and PLI. They also stated that the Cd metal was the greatest danger. Cüce et al. [4] examined the metal accumulation profile of the Ömerli Dam Lake sediment in İstanbul through the sediment quality indexes and pointed out that the Cd and Pb moderately enriched. Algül and Beyhan [45] studied metals in the Bafa Lake sediment using EF, CF and Igeo indexes. As a result, they revealed that the lake is contaminated by Ni and Cd metals, while Cu, Mn and Zn metals are included from natural resources. Of course, our wetlands, which are not only under Cd stress but also under other Ms stresses, have been revealed through many studies. In their study in Çubuk-2, Asartepe and Kesikköprü dam lakes, Fikirdeşici-Ergen et al. [5] drew attention to the accumulation of As and Ni Ms in all the three lakes. Metal determination study in a surface sediment made in the Tigris river, Igeo, CF, EF, and PLI indices were used. The results indicated that river sediment moderately polluted because of Co, Cu, Zn and Pb according Igeo [46]. In a study in which heavy metals were detected on the surface of 77 protected lakes in Poland, the amounts of Cr, Ni, Cd, Pb, Zn, and Cu and their ecological effects were examined. They determined that the lake sediment surfaces were contaminated with metals, and that Pb and Cd metals were higher than the background reference data. They reported that the lake surface sediments were also highly contaminated in terms of Pb and Cu, according to the EF and Igeo indexes [47]. Similar indices were used in a similar study on the surface sediment of Lake Manzala (Egypt) (Igeo, PLI etc.). As a result of the study, the researchers reported that the metals that cause the most stress in the sediment are Cd and Cu [48].

TABLE 5. The results of sediment quality indexes

	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
CF	0.005	0.72	0.30	0.86	0.27	1.29	0.01	1.43	0.18	0.28	0.65	0.90
Cd	6.90											
MCd	0.57											
EF	1.00	157.27	65.69	185.85	58.38	280.51	2.47	311.28	39.85	60.20	141.87	194.75
Igeo	-8.35	-1.05	-2.31	-0.81	-2.48	-0.22	-7.05	-0.07	-3.03	-2.44	-1.20	-0.74
PLI	0.354											
m-ERM-Q	0.18											
m-PEL-Q	0.30											
TTU	2.08											
TU		26.62	1.24		12.92	14.18				25.17	6.88	13.00

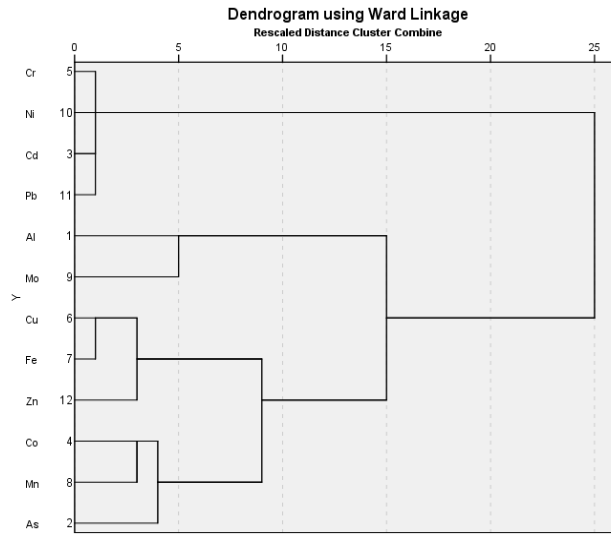


FIGURE 2. PCA analysis of Ms in the lake sediment

TABLE 8. PCA Rotated Component Matrix

	1	2	3
Al	.534	.039	.806
As	.521	.651	-.028
Cd	.969	-.024	.039
Co	.300	.569	-.704
Cr	.966	.074	-.221
Cu	-.463	.812	.095
Fe	-.736	.671	.042
Mn	.152	.800	-.242
Mo	-.414	.064	.836
Ni	.976	.066	-.188
Pb	.994	-.040	-.006
Zn	-.053	.945	.065

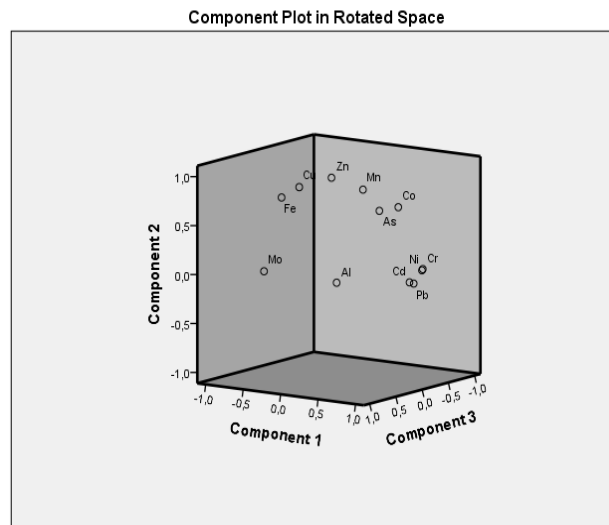


FIGURE 3. Cluster analysis of Ms in the lake sediment

4. CONCLUSIONS

The accumulation profile of metalloids in the sediment of Boraboy Lake has been investigated. The results have shown that there is a very high enrichment in the lake in terms of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn. Additionally, As, Ni and Cu have been determined to be the ones with the highest potential to have a possible toxic effect for the lake. Despite all these results, it would not be correct to speak of any accumulation in the lake. Therefore, it is very important to control the lake regularly in order to prevent the accumulation that this enrichment will create.

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Declaration of Competing Interests The authors declare no conflict of interest.

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