SPATIAL AND TEMPORAL ASSESSMENT OF METAL(LOID) CONTAMINATION IN ASARTEPE DAM LAKE (ANKARA, TURKEY) USING POLLUTION INDICES AND MULTIVARIATE STATISTICAL ANALYSIS

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ABSTRACT

This study has investigated metal(loid) contamination in Asartepe Dam Lake, which is used for irrigation in Ankara, Turkey. Contamination Factor and Degree of Contamination were applied to evaluate contamination in the lake sediment. The contamination was shown to be moderate according to a modified Degree of Contamination analysis. Chromium was found to be the highest calculated metal on the Geoaccumulation Index, and the lake was found to be moderate-to-strongly contaminated according to the same method. The Pollution Load Index for the lake sediment varied between 3.11 and 3.5. Enrichment Factors suggest a minor anthropogenic origin for metal(loid) pollution; various statistical techniques were implemented. The greatest correlation among water-borne metal(loid)s was shown by analysis to be between iron and titanium. No strong correlation was observed for sediment samples. The results show that the lake water is relatively free of metal(loid)s. However, this is not the case for the lake sediment.

KEYWORDS:
Environmental contamination assessment, metal pollution, water and sediment pollution indices, Asartepe dam lake (Turkey)

INTRODUCTION

The inordinate impact of human activities on the environment has led to various environmental crises, including the contamination of soils and freshwater sources with heavy metals. While some metals are essential for the regular functioning of both humans and other organisms, both essential and non-essential metals are invariably toxic at higher doses. Aquatic environments are especially sensitive to heavy metal contamination, as the Earth's crust, atmospheric pollution and industrial by-products all contribute to the influx of heavy metals into freshwater. The sediment plays an important role in heavy metal accumulation in these environments, as heavy metals are principally deposited in the sediment. Consequently, the release of heavy metals from the sediment may also contribute to the contamination of the water source itself. The evaluation of heavy metal concentrations in the sediment and in the groundwater is vital for water quality surveys [1-5]. The sediment also yields important information for the determination of environmental and geochemical contributions to water contamination [6] and plays a vital role in the reintroduction of the sequestered heavy metals into aquatic environments [7]. As such, investigations of heavy metal contamination in aquatic environments and organisms often take into consideration the heavy metal presence in the sediment [8-10].

Turkey has been subjected to a large-scale immigration over only a short period of time [11]. For this reason, the potable water demand has been augmented due to use for agricultural activities [12, 13]. This situation restricts freshwater sources and has caused an increase of pollution in existing water sources. These unpredictable circumstances were not considered in the agricultural irrigation planning during the project phase of Asartepe Dam. As the periodical irrigation for agricultural activities is supplied by Asartepe Dam Lake, the sediment-water interactions are crucial for maintaining public health and the ecosystem. Briefly, the present work aims to investigate the spatio-temporal interactions between the sediment and the freshwater source in terms of heavy metal contamination, as well as assess the sediment contamination, which is a determinant of water quality, with the use of statistical techniques such as cluster analysis, correlation analysis and pollution assessment methods.

The sampling site of interest, Asartepe, is a dam lake located at 47 km to the north west of Ankara, the capital of Turkey (44°44'21″ N, 36°44'83″E) (Figure 1). The dam is constructed on *İlhan* stream and is employed for the irrigation of a net area of
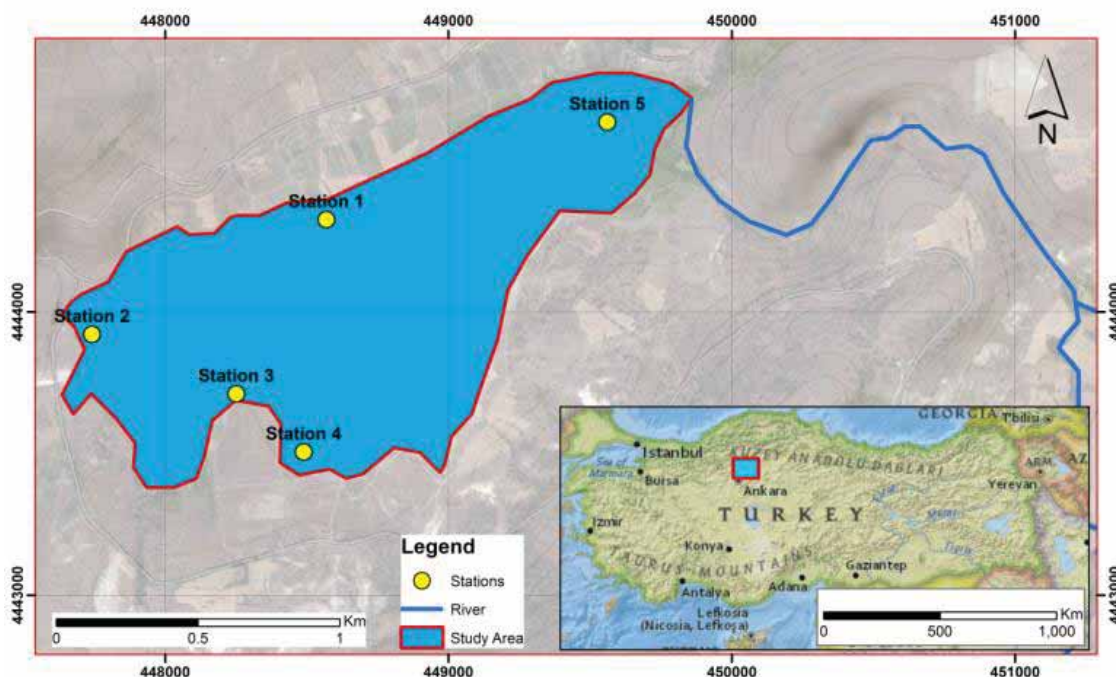
FIGURE 1
Location map of the Asartepe Dam Lake and the sampling stations

1500 ha. An evaluation of heavy metal contamination in this area is therefore essential, as crops could be irrigated by potentially contaminated water sources. As such, these crops may qualify as a health hazard for their consumers [14].

The present study has five principal goals; (a) determining the metal(loid) concentrations of water and sediment samples in Asartepe Dam Lake, (b) evaluating the correlations between the metal(loid) concentrations in the water and sediment, (c) establishing the extent of anthropogenic influence on the lake, (d) evaluating whether the present situation poses a risk to the health of the ecosystem or the public, and (e) creating a background for future studies involving this economically important artificial lake.

MATERIALS AND METHODS

Water and sediment sampling was conducted between March 2012 and November 2013. Five stations were chosen to be representative of the general metal(loid) profile of the lake. A total of 12 samples were taken from each station at 30 day intervals. The region is subject to a harsh continental climate; consequently, the lake is almost entirely frozen during the winter period and as such, no sampling was performed during this period. All samples were taken from the littoral zone, and due to prohibition and other restrictions, sampling could not be performed at the centre of the lake. Water samples were collected in 500 mL plastic bottles at a depth of 0.5 m. Water parameters were measured by a YSI multi-probe system. Samples were acidified with 65% nitric acid to a final concentration of 2%, and filtered through syringe filters with pore sizes of 0.45 µm. Sediment samples were taken in plastic containers at a sediment depth of 20 cm (only surface sediment was used for the elemental analysis, the rest was used for further works). All samples were read in triplicate and were stored at 4°C prior to analysis. All statistical analyses were performed using SPSS 17.0 and 21.0 (IBM, USA).

X-ray fluorescence spectroscopy elemental analysis. Concentrations of elements in the sediment samples were determined using x-ray fluorescence spectroscopy (XRF). Sediment samples were dried on a watch glass in a vacuum oven at 100°C for 1 day, then crushed to homogenize the sample and allow removal of remnants of water. Powders were then poured into aluminium rings while still hot and pressurized to form dry flat pellet discs which were immediately placed into the XRF instrument (ZSX Primus II, Rigaku, Tokyo). The energy span value of the instrument can reach up to 30 KeV. PHA (pulse height analyser) was performed before each analysis. Assay was performed using both types of counters (Scintillation and proportional counters for heavy and light elements respectively) and LiF ((2 0 0) reflection face) crystal for detection of fluorescence. Measurement method and crystal of choice allow detection of all elements from F to U. Prior to analysis, sediment samples were crushed in a FRITSCH tungsten carbide mortar, mixed with connective material (Wachs) at a ratio of 4 g samples to 0.9 g Wachs, and pelleted under 15 N force using a hydraulic press.

Pellets were analysed using a Spectro X-Lab 200 PED-XRF, analysis was conducted with the Tq-7220 method.

Inductively coupled plasma – mass spectrometry elemental analysis. Water samples were analysed using inductively coupled plasma – mass spectrometry (ICP-MS) with high sensitivity and precision. Elemental analyses were performed by XSeries2 ICP-MS (Thermo Scientific, US-MA). To assure full quantification with high sensitivity, series of calibrations for each element were performed (from 0.05 ppb to 10 ppm). Correlation coefficients were at least $R^2 = 0.99$ for each element. Plasma power was adjusted to 600W for 1A and 2A group elements and Fe ions, and to 1400W for other elements. Isotope interference probabilities and abundance parameters were utilized for computation to select optimal isotopes. Internal standard solution (10 ppb Bi) was used in the entire analysis. Measurements were done in triplicates while each measurement was the average of three runs. Calibrations were prepared with the solution QCS-27(high-purity). Expected concentrations of each element in the sediments were considered for the curves. A minimum 0.99 value was obtained for each correlation coefficient.

Comparison of metal(loid) accumulation between stations. This analysis was performed to determine whether the differences in metal(loid) concentrations observed in different stations are statistically meaningful, and to assess the usability of the water accumulated in the Asartepe Dam Reservoir for agricultural purposes. This was done by reviewing all observed results under a single pool. Each of the 60 samples collected throughout the duration of the study were considered separately for their water and sediment components. The Shapiro-Wilk test was employed to determine whether the metal(loid) concentration values followed a normal distribution. Averages that did not display a normal distribution were compared using the Mann-Whitney U test (log transform does not work in many cases), while those that were distributed normally were tested for homogeneity of variance using Levene's test. Samples with homogeneous variance were analysed using the Tukey multiple comparison test, while those with heterogeneous variance were analysed using the Tamhane test. Significance criteria were set at 95% for all tests unless noted [15].

Correlation analysis. Correlation analysis was used to determine whether metal(loid) concentrations in the lake water and sediment are dependent on each other. The correlation analysis is only an indicator, and utilized simply to reflect the general state of pollution within the lake without discriminating between station and time differences among the samples. Water and sediment data were considered separately under two groups and analysed with respect to their yearly changes in concentration. Sample distributions were checked using the Shapiro-Wilk test. Samples displaying normal distribution were analysed using Pearson correlation analysis, those that did not were analysed using Spearman correlation analysis. 95% and 99% were chosen as the significance criteria [16].

Cluster analysis. Cluster analysis (CA) is a technique employed to separate huge amounts of data into distance matrices depending on their similarities. The dendrogram prepared from the distance matrix can then be used to visualize these similarities. Water and sediment samples were grouped separately depending on the temporal accumulation trends of metal(loid)s; such that the closer the distance between two metal(loid)s in the relationship matrix, the more similar the accumulation trends between them. The analysis was performed following the Ward method, using Euclidean distances and Z-score correction [17].

Pollution assessment methods. Contamination factor C_f^i is the ratio between the measured amount of a given metal in the sediment and the pre-industrial reference value for that metal [18].

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

where, C^i is metal concentration in the sediment of a specific station and C_n^i is pre-industrial reference value of the metal (Hakanson, 1980).

Contamination factor results are fall into four classes, $C_f^i < 1x$, $1 \leq C_f^i 3$, $3 \leq C_f^i 6$ and $C_f^i \geq 6$, which correspond respectively to low, moderate, considerable, and very high contamination [19].

Degree of contamination (C_d) is the sum of all contamination factors and indicates low, moderate, considerable and very high degrees of contamination at the values of $C_d \leq 8$, $8 \leq C_d \leq 16$, $16 \leq C_d \leq 32$ and $C_d \geq 32$, respectively [19].

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

C_f^i and C_d are general measures of heavy metal contamination for lake ecosystems and have been commonly employed for that purpose [20, 21]. However, as it is a sum of all contamination factors for each individual metal, and the results could change because of the number of the measured metals, a third factor called modified degree of contamination (mC_d) was proposed by Abrahim & Parker [22].

$$mC_d = \frac{\sum_{i=1}^{n} c_f^i}{n} \qquad (3)$$

where n is total number of metals investigated [22].

mC_d is the total contamination factor measured in a particular study, divided by the total number of metals considered in that study. Seven degrees of contamination exist under this system: nil to very low, low, moderate, high, very high, extremely high and ultra-high; respectively for mC_d < 1.5, 1.5 ≤ mC_d

< 2, $2 \leq mC_d < 4$, $4 \leq mC_d < 8$, $8 \leq mC_d < 16$, $16 \leq mC_d < 32$, $mC_d \geq 32$. This alternative metric is also used frequently for water quality assessment [23, 24]. All pre-industrial reference and background content values required for the determination of contamination factor values were taken from [25].

Enrichment factor (EF) is a measure of geochemical trends and has considerable importance for the comparison of chemical profiles for different areas [26].

$$EF = \frac{C_n/C_{ref}}{B_n/B_{ref}} \qquad (4)$$

where C_n is metal concentration in a sample, C_{ref} is metal concentration in the reference environment (*e.g.*, Earth's crust), B_n is the reference element (*e.g.*, Fe or Al) concentration in a sample and B_{ref} is the reference element concentration in a reference environment.

EF can also be used to determine the extent of anthropogenic pollution in an area. A variety of elements can be used for the normalization of EF values, with Fe being one of the more common [27, 9, 28]. This is because Fe is an abundant element, and the anthropogenic effect on its levels in the sediment are negligible [29]. As such, Fe was used as the reference element for EF measurements in this study. Continental Fe values to be used for normalization were taken from [25]. Different classification systems exist for the interpretation of EF results. The scale used by [30] considers values between 0.5 and 1.5 to be natural, while values above 1.5 can be linked to anthropogenic sources. More extensive scales are also presented in the literature, such as those used by [31], which recognizes five different classes with EF values of <2, 2–5, 5–20, 20–40, and >40, which respectively correspond to depletion to minimal, moderate, significant, very high and extremely high enrichment. [24] used a seven-class system for EF values of <1, 1-3, 3-5, 5-10, 10-25, 25-50, >50, which respectively stand for no enrichment, minor, moderate, moderately severe, severe, very severe and extremely severe enrichment.

The geoaccumulation index (I_{geo}) is a seven-class scheme proposed by [32] for the determination of metal enrichment in geological samples. These classes are $I_{geo} \leq 0$, $0 < I_{geo} < 1$, $1 < I_{geo} < 2$, $2 < I_{geo} < 3$, $3 < I_{geo} < 4$, $4 < I_{geo} < 5$, $I_{geo} \geq 5$, and they correspond to samples that are practically uncontaminated, uncontaminated to moderately contaminated, moderately contaminated, moderately to strongly contaminated, strongly contaminated, strong to extremely contaminated and extremely contaminated. This index is also used frequently as a standard of sediment quality measurement [33, 34].

$$I_{geo} = log_2 \frac{C_n}{1.5 \times B_n} \qquad (5)$$

where B_n is background content of the metal analyzed, and *1.5* is constant, used to account for natural fluctuation [32].

The pollution load index (PLI) is another type of pollution measurement developed by [35] and serves as a commonly used technique for contamination analysis [36, 37]. In PLI, zero is the desired value as it indicates an unpolluted case, a value of one is the baseline level of heavy metals, results above one are considered deterioration, which becomes more pronounced as the PLI value increases.

$$PLI = (C_{f1} \times C_{f2} \times C_{f3} \dots \times C_{fn})^{1/n} \qquad (6)$$

where C_{fn} is contamination factor and *n* is total number of metals studied [33].

RESULTS

Lake water parameters. The measured ranges of pH, specific conductivity (SPC), total dissolved solid (TDS), salinity (SAL) and ammonium ($NH_4^+ - N$) are listed in Table 1. SPC values were consistent across the lake profile and generally stayed under 400 µS/cm throughout the year, with the exception of Station 5. The onset of the dry season triggered a deviation in SPC values of this station, as it is located in a shallow area and used for agriculture when water levels are low.

TDS values were in line with SPC values. Low TDS concentrations were observed throughout the lake area. However, Station 5 experienced an increase in TDS with the onset of the dry season. $NH_4^+ - N$ and SAL values displayed similar trends. Station 5 also differed from the rest of the lake area with respect to pH. During the rainfall season, pH values of this station were similar to the rest of the lake, but in dry season, an increase at Station 5 was measured, whereas other stations experienced a decrease.

Spatial and temporal analyses. Comparison of metal(loid) accumulation between stations. With respect to the stations, metal(loid) contamination occurred to the greatest extent at Station 5, followed by Station 1 (Table 2). The difference between Station 5 and the other stations was not as pronounced as the differences between the remaining four stations; in fact, no significant differences were observed between Stations 3 and 4. No significant fluctuations were noted during the observation period and barium had the highest concentration in the lake water throughout the year.

Sediment samples are generally more consistent than those of the lake water, with less pronounced seasonal peaks and a relatively flat profile. Fe is the element with the highest concentration across all sediment samples. Non-essential elements such as Cd and Pb, which occasionally appeared in the water measurements, were not present in the sediment (Table 2).

TABLE 1
Various lake water parameters

Sampling Stations	1	2	3	4	5
SPC (µs/cm)	349-425	381-415	320-409	339-412	392-947
TDS (mg/l)	224-276	247-270	208-265	220-268	254-604
SAL (ppt)	0.16-0.2	0.18-0.2	0.15-0.2	0.15-0.2	0.19-0.47
pH	8.22-9.72	8.09-9.41	8.14-9.98	8.24-9.57	7.52-8.36
$NH_4^+ - N$ (mg/l)	0.07-0.54	0.07-0.21	0.07-0.11	0.07-0.13	0.08-1.72

TABLE 2
Comparison of metal(loid) accumulation in the water and sediments between stations

		Ti	Cr	Mn	Fe	Co	Ni	Cu
Water (µg/l)	(a) 1	(b,d) 0.66 - 5.86	(d) 1.88 - 6.19	(b,c,d,e) ND - 26.98	(b,c,d,e) ND - 18.7	(b,c,d,e) 0.08 - 4.33	(b,c,d) 0.74 - 6.8	(b,c,d,e) ND - 4.92
	(b) 2	(a,c) 0.97 - 4.25	(c,d) 1.36 - 3.01	(a,c,d,e) 0.04 - 9.49	(a,c,d,e) ND - 39.9	(a,c,d,e) 0.11 - 0.33	(a,c,d,e) 0.89 - 3.98	(a,c,d,e) 0.15 - 7.52
	(c) 3	(b,d) 0.56 - 1.78	(b,d) 1.7 - 3.33	(a,b,d,e) ND - 8.81	(a,b,d,e) ND - 73.79	(a,b,d,e) 0.1 - 0.24	(a,b,d,e) 0.88 - 3.52	(a,b,d,e) 0.11 - 4.01
	(d) 4	(a,c) 0.81 - 1.25	(a,b,c) 1.45 - 3.2	(a,b,c,e) 0.01 - 12.06	(a,b,c,e) ND - 52.49	(a,b,c,e) 0.09 - 0.17	(a,b,c,e) 0.89 - 2.87	(a,b,c,e) ND - 2.38
	(e) 5	( ) 0.6 - 6.2	( ) 1.49 - 6.66	(a,b,c,d) 0.02 - 21.59	(a,b,c,d) ND - 83.39	(a,b,c,d) 0.09 - 0.25	(b,c,d) 0.9 - 3.52	(a,b,c,d) 0.22 - 1.56
Sediment (µg/g)	(a) 1	(b,c,d,e) 11133 - 18248	(b,c,d) ND - 402	(b,c,d,e) 1141 - 3558	(b,c,e) 61802 - 115080	ND	(b,c,d,) ND - 322	ND
	(b) 2	(a,c,d,e) 11803 - 20851	(a,c,d,e) ND - 734	(a,c,d,e) 1061 - 4688	(a,c,e) 89722 - 126060	ND	(a,c,d) ND - 325	ND
	(c) 3	(a,b,d,e) 12522 - 16002	(a,b,d,e) ND - 431	(a,b,d,e) 1528 - 4161	(a,b,e) 72332 - 117910	ND	(a,b,d) 226 - 333	ND
	(d) 4	(a,b,c,e) 12193 - 16636	(a,b,c) ND - 397	(a,b,d,e) 1479 - 3385	( ) 78494 - 110480	ND	(a,b,c) 170 - 386	ND
	(e) 5	(a,b,c,d) 13557 - 15788	(b,c) ND - 505	(a,b,c,d) 1892 - 3854	(a,b,c) 92496 - 110730	ND	( ) 261 - 384	ND

		Zn	As	Mo	Cd	Ba	Pb
Water (µg/l)	(a) 1	(b,c,d,e) ND - 12.91	(b,c,d) 12.08 - 33.8	(b,c,d,e) 1.21 - 14.64	(b) ND - 4.51	(b,c,d) 40.31 - 127.5	(b,c,e) ND - 10.25
	(b) 2	(a,c,d,e) ND - 10.48	(a,c,d) 15.05 - 25.66	(a,e) 1.41 - 3.44	(a) ND - 0.18	(a,c,d) 83.35 - 183.7	(a,c,e) ND - 0.52
	(c) 3	(a,b,d,e) ND -	(a,b,d) 8.48 -	(a,d,e) 1.12 -	(d,e) ND -	(a,b,d) 47.68 -	(a,b,e) ND -

		17.13	26.87	2.1	0.04	118.3	0.29
		(a,b,c)	(a,b,c)	(a,c)	(c,e)	(a,b,c)	
(d)		ND	19.58	1.29	ND	67.92	ND
4		-	-	-	-	-	
		24.9	29.63	1.63	0.07	133.4	
		(a,b,c)	( )	(a,b,c)	(c,d)	( )	(a,b,c)
(e)		ND	18.9	1.26	ND	90.19	ND
5		-	-	-	-	-	-
		14.68	53.42	2.37	0.02	305	0.14

Sediment (µg/g)							
		(b,c,d,e)				(b,d,e)	
(a)		ND	ND	ND	ND	1685	ND
1		-				-	
		751				4261	
		(a,c,d)				(a,d,e)	
(b)		192	ND	ND	ND	2225	ND
2		-				-	
		312				3586	
		(a,b,d,e)				(d,e)	
(c)		201	ND	ND	ND	ND	ND
3		-				-	
		318				2847	
		(a,b,c,e)				(a,b,c,e)	
(d)		188	ND	ND	ND	1610	ND
4		-				-	
		350				3452	
		(a,c,d)				(a,b,c,d)	
(e)		216	ND	ND	ND	1841	ND
5		-				-	
		375				3311	

ND: not detected
Superscript letter means no statistical difference (p>0.05)

TABLE 3
The results of correlation analysis for all water and sediment samples (handled from each station)

Water													
	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Ba	Pb
Ti	1												
Cr	0.590**	1											
Mn	0.446**	0.124	1										
Fe	0.486**	0.318*	0.469**	1									
Co	**0.705****	0.277*	0.684**	0.512**	1								
Ni	0.542**	0.443**	0.331**	0.495**	0.618**	1							
Cu	0.501**	0.314*	0.365**	0.445**	0.582**	**0.836****	1						
Zn	-0.017	-0.098	0.163	0.139	0.051	0.166	0.293*	1					
As	0.542**	0.588**	0.352**	0.352**	0.523**	0.611**	0.401**	-0.016	1				
Mo	0.654**	0.338**	0.254	0.385**	**0.704****	0.667**	0.594**	-0.061	0.607**	1			
Cd	0.344**	-0.025	0.248	0.362**	0.467**	0.285*	0.340**	0.273*	-0.007	0.462**	1		
Ba	0.516**	0.585**	0.032	0.227	0.320**	**0.708****	0.476**	-0.134	**0.706****	0.597**	-0.030	1	
Pb	0.311*	-0.046	0.403**	0.359**	0.491**	0.292*	0.443**	0.272*	-0.068	0.237	0.578**	-0.036	1

Sediment						
	Fe	Ti	Ba	Mn	Cr	Ni	Zn
Fe	1						
Ti	0.393**	1					
Ba	-0.006	0.106	1				
Mn	-0.043	-0.375*	-0.268*	1			
Cr	0.138	0.022	0.000	0.218	1		
Ni	0.377**	0.066	-0.246	0.370**	0.126	1	
Zn	0.177	0.027	-0.372**	0.360**	0.040	0.454**	1

* Correlation is significant at the 00.05 level (2-tailed)
** Correlation is significant at the 00.01 level (2-tailed)

Correlation analysis. Strong correlations were observed for metal(loid)s in the water, suggesting that the contaminating metal(loid)s may have a common source [38]. These correlations did not appear in the sediment samples, which are instead notable for the fact that negative correlations are present between certain metal(loid) pairs. Lake water samples

displayed no negative correlations according to correlation analysis. The maximum correlation observed was Fe - Ti at 0.863. Ni - Cu (0.836), Mo - Cd (0.787), Ba - Ni (0.708), Ca - As (0.706), Co - Ti (0.705) and Mo - Co (0.704) were other strong correlations observed in the water. The strongest correlation in sediment was Ni - Zn at 0.454.

However, the negative correlations of Ba - Zn and Mn - Ti are of note (Table 3).

On the other hand, the spatial variation of contamination (between sites) is greater than the seasonal variation due to the origin of the pollution. The differences in metal(loid) amounts which have geochemical origin, such as Ti, Ca, Fe, and anthropogenic origin, such as Cd, Cu, Zn variates spatially and temporally. The negative correlation between Zn and Ba could be explained by this spatio-temporal variation.
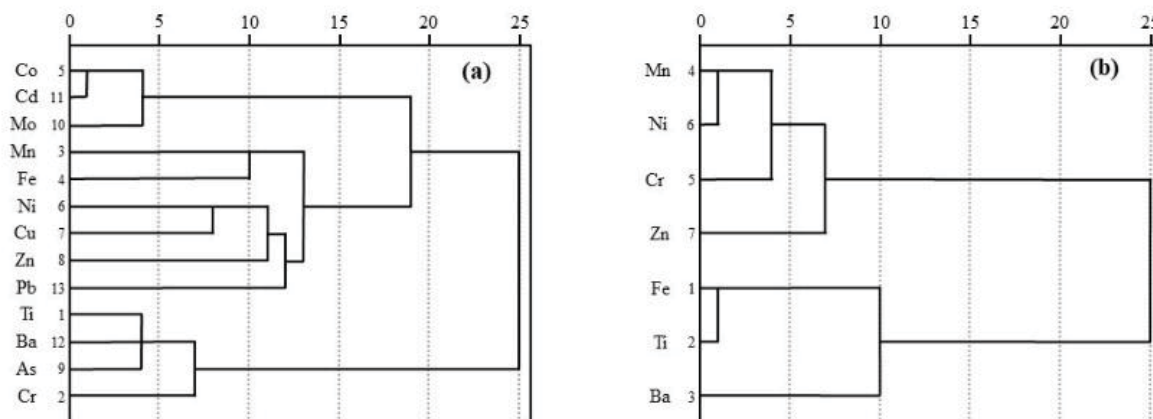
Cluster analysis. Results of the cluster analysis for water and sediment are given in Table 4 and Figure 2. For lake water samples, the metal(loid)s displaying the closest distance by cluster analysis are Co - Cd, with a Euclidean distance of 0.619. The metal(loid)s least related to each other are Zn - Ba, with a Euclidean distance of 11.906. Zn - Pb together formed the group least related to other metal(loid) clusters, suggesting that the profiles of these metal(loid)s in the lake water were substantially different from other metal(loid)s. Metal(loid)-metal(loid) distances were generally further for sediment samples when compared to water samples, suggesting that metal(loid) profiles were all relatively distinct in the sediment. The closest Euclidean distance for sediment samples was Mn - Ni.

TABLE 4
CA results matrices for metal (loid)s in water and sediment samples

								Water					
	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Ba	Pb
Ti	.000	5.334	9.070	8.928	8.799	7.084	9.598	11.178	4.195	8.751	9.135	3.500	10.843
Cr	5.334	.000	8.654	8.486	8.627	7.724	10.313	10.962	5.698	8.834	8.863	6.076	11.230
Mn	9.070	8.654	.000	8.792	10.500	10.936	10.018	10.395	9.784	10.659	10.697	9.778	10.374
Fe	8.928	8.486	8.792	.000	10.317	9.147	9.895	10.721	9.569	10.420	10.501	9.424	10.280
Co	8.799	8.627	10.500	10.317	.000	6.175	8.013	9.462	10.039	2.610	.619	10.743	10.011
Ni	7.084	7.724	10.936	9.147	6.175	.000	7.622	9.647	8.183	6.190	6.388	8.222	10.156
Cu	9.598	10.313	10.018	9.895	8.013	7.622	.000	9.454	10.867	8.389	8.100	10.677	9.951
Zn	11.178	10.962	10.395	10.721	9.462	9.647	9.454	.000	11.391	9.757	9.419	11.906	10.275
As	4.195	5.698	9.784	9.569	10.039	8.183	10.867	11.391	.000	10.019	10.291	3.548	11.559
Mo	8.751	8.834	10.659	10.420	**2.610**	6.190	8.389	9.757	10.019	.000	2.690	10.621	8.568
Cd	9.135	8.863	10.697	10.501	**.619**	6.388	8.100	9.419	10.291	**2.690**	.000	11.005	10.015
Ba	**3.500**	6.076	9.778	9.424	10.743	8.222	10.677	11.906	**3.548**	10.621	11.005	.000	11.412
Pb	10.843	11.230	10.374	10.280	10.011	10.156	9.951	10.275	11.559	8.568	10.015	11.412	.000

				Sediment			
	Fe	Ti	Ba	Mn	Cr	Ni	Zn
Fe	.000	9.181	10.787	11.979	10.847	10.482	11.110
Ti	9.181	.000	10.374	12.739	10.944	10.930	10.224
Ba	10.787	10.374	.000	11.769	10.961	11.594	12.154
Mn	11.979	12.739	11.769	.000	9.450	9.083	10.390
Cr	10.847	10.944	10.961	9.450	.000	9.848	10.206
Ni	10.482	10.930	11.594	9.083	9.848	.000	10.230
Zn	11.110	10.224	12.154	10.390	10.206	10.230	.000

FIGURE 2
Cluster analysis dendograms. a for water samples; b for sediment samples

TABLE 5
The results of pollution assessment analyses for the sediment samples

	Fe	Ti	Ba	Mn	Cr	Ni	Zn			
Stations				C_f^i				C_d	mC_d	PLI
1	2.09	3.44	**4.82**	2.45	3.93	3.77	3.34	23.83	3.40	3.29
2	2.23	3.20	4.67	2.67	**5.56**	3.70	2.67	24.71	3.53	3.37
3	2.08	3.10	4.08	3.50	**4.10**	4.02	2.98	23.86	3.41	3.33
4	1.90	2.98	**4.34**	2.78	3.95	3.78	2.76	22.49	3.21	3.11
5	2.22	3.26	4.46	3.20	4.34	**4.70**	3.05	**25.23**	**3.60**	**3.50**
					I_{geo}					
1	1.64	2.37	**2.85**	1.88	2.56	2.5	2.32			
2	1.74	2.26	2.81	2	**3.06**	2.47	2.01			
3	1.64	2.21	**2.61**	2.39	2.62	2.59	2.16			
4	1.51	2.16	**2.7**	2.06	2.57	2.5	2.05			
5	1.73	2.29	**2.74**	2.26	2.7	2.82	2.2			
					EF					
1		1.64	**2.29**	1.17	1.87	1.79	1.59			
2		1.52	2.22	1.27	**2.65**	1.76	1.27			
3	X	1.47	1.94	1.67	**1.95**	1.91	1.42			
4		1.42	**2.06**	1.32	1.88	1.80	1.31			
5		1.55	2.12	1.52	2.06	**2.23**	1.45			

Fe as normalizing element for EF

Pollution assessment. For every station and every metal(loid) tested, C_f^i values were calculated and found to be considerable, with the exception of Mn - Zn contamination, which were moderate at certain locations. In addition, the results proved that Station 5 has the highest C_d value. However, that value was similar to the rest of the lake, the contamination of which qualified as considerable. mC_d varied between 3.21 and 3.60 through all stations, corresponding to a moderate degree of contamination (Table 5).

When interpreted under all three classification systems, the EF values suggested that the anthropogenic influence of metal(loid) concentrations in the lake is extremely limited. The main source is of mostly geochemical origin. EF values for Ni, Cr and Ba were higher than those of Ti, Mn and Zn (Table 5).

I_{geo} results displayed a level of contamination greater than the EF results, with the lake being classified as moderately to strongly contaminated. According to I_{geo}; Ba, Cr and Ni were the elements causing particularly strong contamination. PLI values among all sampling stations were found to be between 3.11 and 3.5 (Table 5).

DISCUSSION

The location of Asartepe Dam Lake makes it an important freshwater reserve. Ankara, the capital of Turkey, derives a substantial portion of its agricultural produce from the area irrigated by the lake. As such, quantification of the lake's metal(loid) concentrations is important for public. Various analysis and interpretation techniques were applied to determine the extent of metal(loid) pollution in the lake. The

results obtained suggest that the lake water is relatively free of metal(loid)s. However, this is not the case for the lake sediment.

Values of SPC, TDS, SAL, pH and ammonium were stable and similar with each other for all measurement stations except the station 5. During wet season, measured values at Stn. 5 were also similar with others. Stn. 5 differed from other stations in dry season. Water at Stn. 5 was more acidic and SPC, TDS, SAL and ammonium values were higher. Also, Stn. 5 had accumulated greater amount of metal(loid)s in water than the rest of the lake due to the agricultural activities nearby the station. Furthermore, any distinctive station was detected for sediments.

Cd and Co which were closest and had strong relations according to the cluster analysis of the water samples, couldn't be found as related in correlation matrix as in the cluster analysis. Cu and Ni were the most related elements in correlation analysis. Despite these two elements were situated in the same cluster in cluster analysis, they were related mediocre. When the most powerful correlations of correlation analysis Co-Ti, Mo-Co, Ba-Ni, Ba-As were assessed in the cluster analysis, Mo-Co and Ba-As were also closely related in the cluster analysis. However, the other 2 correlations were related mediocre in the cluster analysis.

The lake sediment contamination was classified as *considerable* by C_f^i and C_d while it was found moderately contaminated by mC_d. Considering EF and I_{geo}, Ni, Cr and Ba were the metals with relatively high contamination. EF results indicated relatively minor anthropogenic origin for metal(loid) entry into the lake. Also, the lake sediment was classified as *moderately to strongly* contaminated and *deteriorating* by I_{geo} and PLI, respectively. The most

TABLE 6
Lake water and sediment samples quality classifications

	Asartepe Lake Water Samples (µg/L)	WHO Guidelines for Drinking-Water Quality(µg/L)	Turkish Inland Water Quality Classes (µg/L)				Asartepe Lake Sediment Samples (µg/g)	Sediment Quality Guidelines (SQG) (µg/g)		
			I	II	III	IV		Non-polluted	Moderately polluted	Heavily polluted
Ti	0.56 - 6.2	-	-	-	-	-	11113-20351	-	-	-
Cr	1.36 - 6.66	50	20	50	200	> 200	ND-242	<25	25-75	>75
Mn	ND- 26.98	400	100	500	3000	> 3000	1061-4688	<300	300-500	>500
Fe	ND - 83.39	-	300	1000	5000	> 5000	61802-126060	<17000	17000-25000	>25000
Co	0.08 - 4.33	-	10	20	200	> 200	ND	-	-	-
Ni	0.74 - 6.8	70	20	50	200	> 200	ND-386	<20	20-50	>50
Cu	ND - 7.52	2000	20	50	200	> 200	ND	<25	25-50	>50
Zn	ND - 24.9	100	200	500	2000	> 2000	188-751	<90	90-200	>200
As	8.48 - 53.42	10	20	50	100	> 100	ND	<3	3-8	>8
Mo	1.12 - 14.64	70	-	-	-	-	ND	-	-	-
Cd	ND - 4.51	3	3	5	10	> 10	ND	-	-	-
Ba	40.31 - 305	700	1000	2000	2000	> 2000	ND-4261	-	-	-
Pb	ND - 10.25	10	10	20	50	> 50	ND	<40	40-60	>60

ND: not detected

contaminated station was found to be Stn. 5 in respect to C_d, mC_d and PLI. In general, *moderate* contamination can be found for the lake sediment.

Station 5 is located on the flowline of a spring which flows in all seasons. The reason that the water and sediment at Station 5 had lower quality values might be due to the presence of the feeding stream in this area, it would have transported water through the agricultural zone. For this reason, contaminants are also possibly moved through Station 5 due to water flow in the dry season.

Comparison with Sediment Quality Guidelines (SQG) revealed *heavy pollution* in the lake (Table 6). In accordance with Turkish Inland Water Quality Classes, the lake water fell under Class I for all contaminants studied except As and Cd, which were in Class III and Class II during their peak periods (Table 6). According to WHOs Guidelines for Drinking-Water Quality, all elements except As and Cd conformed to standard.

The results suggest that, while not major enough to pose a health hazard, there is an anthropogenic influence in the metal(loid) contamination of Asartepe Dam Lake. As a major water source for irrigation, the continuity of these influences may lead to substantial health risks for local people in the future.

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