

Ecological risk assessment of heavy metals in surface sediments of northern littoral zone of Lake Çıldır, Ardahan, Turkey

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Abstract In this paper, the heavy metal levels (Cu, Pb, Zn, Ni, Mn, Fe, As, Cd, Cr, Hg), organic carbon, and chlorophyll degradation products were studied to prove their ecological effects in Lake Çıldır, where fossil fuels are used as an energy source in the studied area for most of the year, and domestic waste from settlements is discharged directly into the lake. Sediment samples were collected from six sites on the northern shore of Çıldır Lake, Turkey in November 2012. Enrichment (EF) and contamination factor (CF) values were determined, and Pollution Load (PLI) and Potential Ecological Risk (PER) indices were calculated. Average concentrations of heavy metals in the sediments were, in descending order, $Fe > Mn > Zn > Ni > Cr > Cu > Pb > As > Cd > Hg$, respectively. According to mean values, the source of these elements may be considered natural due to lack of enrichment in Cu, Pb, Zn, Ni, and Cr in the sediment samples. Regarding enrichment of As, Cd, Mn, and Hg, the highest

EF belongs to Hg. PLI and PER values indicate there are moderate ecological risk in the lake.

Keywords Lake Çıldır · Sediment · Heavy metal · Ecological assessment

Introduction

Heavy metals are considered to be point or nonpoint pollutant sources of lakes, seas, and rivers. In general, heavy metals originate from terrestrial flows, atmospheric deposition, and waste water discharge in water ecosystems (Guo et al. 2010). Heavy metals tend to accumulate in water, sediment, and biota and do not easily decompose. Because they are not degradable and metabolize easily, heavy metals are stable and therefore accumulate in soft tissues and show toxicity in living organisms (Sures et al. 2012). Furthermore, they do not dissolve easily nor are absorbed by solid suspended matter in the water matrix (Jain et al. 2008). The study of sediments yields important insights regarding the amount of contaminants precipitated as a suspended load from water bodies.

Metals found in sediments as well as soils are either natural or anthropogenic in origin. Even though the level of metals within sediments and soils in rural areas is expected to be quite low, they may exist in higher amounts in some soils (Kahkonen et al. 1997). An increase in heavy metal concentrations due to anthropogenic impacts gives rise to environmental problems in the coastal areas of lakes, seas, and rivers. This can create negative impacts on organisms when the concentrations

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are higher than their tolerance limits (Kannan et al. 2008). One of the major sources of metal pollution in marine and freshwater systems comprises outputs from domestic wastewaters, notably if enriched in As, Cr, Cu, Mn, and Ni. In addition, coal-burning and other power plants are the main agents of effluents such as As, Hg, and Se. Other heavy metals, such as Cd, Ni, Pb, and Se, are released from non-ferrous metal smelteries. Cr, Mo, Sb, and Zn from iron and steel plants, as well as As, Mn, and Pb from dumping of sewage sludge, are among the main contaminants (Nriago and Pacyna 1988). As and Cd can also increase due to agricultural activities (Bai et al. 2011a, 2012). Copper and zinc are the two micronutrients for aquatic life in all natural waters and sediments (Bai et al. 2011b) but both of them are known as toxic compounds at higher concentrations. Generally, Fe has highest value among the metals because it is an important compound of Earth's crust (Mico et al. 2006; Bai et al. 2011c; Kükrcer 2013).

Water reservoirs accumulate vast amounts of heavy metals and organic matter, for different reasons. Large lakes are mostly oligotrophic and have low carbon concentrations since carbon precipitates five times slower than in small lakes (Turcq et al. 2002). Usually the organic materials arise from autochthonous and allochthonous sources. While autochthonous sources are produced by phytoplankton, allochthonous sources originate from terrestrial plants and macrophytes in lakes (Meyers and Teranes 2001). Additionally, discharge waters from settlement areas around a lake are an important source of organic and inorganic enrichment.

The monitoring of organic carbon and chlorophyll level (as a source of organic carbon) in sediment is important. Besides this, the linear relationship between organic carbon and heavy metals provides a convenient insight into heavy metal levels. Hence, studies on lake sediments play a key role in assessment of aquatic environmental pollution. In this paper, the heavy metal levels, organic carbon and chlorophyll degradation products (CDP), together with their ecological effects, were studied in Lake Çıldır, where fossil fuels are used as an energy source in the studied area for most of the year, and domestic waste from settlements is discharged directly into the lake.

Materials and methods

With an area of approximately 115 km² and a depth of 42 m (Atalay 1978), fresh water Lake Çıldır constitutes

the second largest lake in the Eastern Anatolian Region, NE Turkey. The lake basin is delimited to the north by an east–west aligned volcanic ridge at altitudes between 2,000 and 2,150 m. The surface of the lake, which is frozen for about 6 months in harsh winters, lies at an elevation of 1,959 m. It has a triangular shape with a long north–south axis of 18.3 km and a shorter axis of 16.2 km from east to west. Excess waters of the lake are discharged by the Çarçı Stream, a northern tributary of the Arpaçay River to the south.

Sediment samples were collected from six selected stations (Fig. 1) in the littoral zone along the northern shores of Çıldır Lake using Van Veen Grab. Some of the samples were stored dry at room temperature, and some were stored wet at −18 °C. Samples which were dried and stored for analyses of organic carbon and heavy metal were powdered in a mortar. Wet sediment samples were used for analysis of the CDP. Organic carbon values were determined according to the Modified Wakley–Black Titration Method (Gaudette et al. 1974). CDP were analyzed through acetone extraction and spectrophotometry (Lorenzen 1971).

Concentrations of Cu, Pb, Zn, Ni, Mn, Fe, As, Cd, Cr, and Hg were determined in the digested phase by inductively coupled plasma mass spectrometer (ICP–MS) analysis (ACME Analytical Labs, Vancouver, BC, Canada). The prepared sample is digested with a modified aqua regia solution of equal parts concentrated HCl, HNO₃, and DI H₂O for 1 h in a heating block. Sample was made up to volume with dilute HCl. Quality control was assessed using duplicates, method blanks, and internal standard reference material (DS 9) obtained from ACME Analytical Labs. The values obtained (mg/kg) for the analyses of this sample were as follows:

Element	Observed	Certified	Detection limits
Cu	104	108	0.01
Pb	118	126	0.01
Zn	319.6	317	0.1
Ni	38.7	40.3	0.1
Mn	575	575	1
Fe	23,000	23,300	100
As	25	25.5	0.1
Cd	2.41	2.40	0.01
Cr	110.7	121	0.5
Hg	0.0203	0.0200	0.005

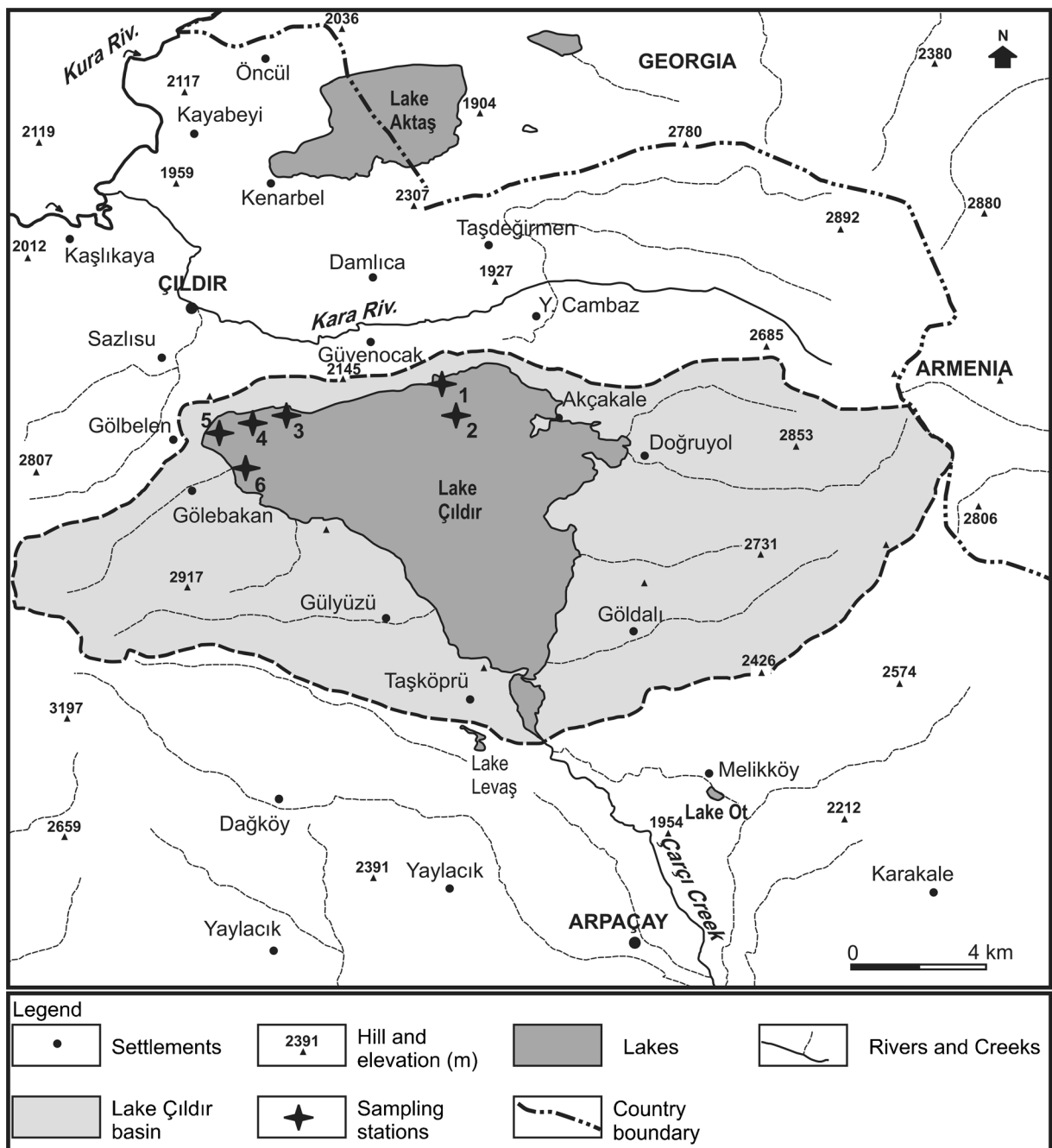


Fig. 1 Location of sampling stations at Lake Çıldır

Two techniques were used to determine contamination. Firstly, the enrichment factor (EF) was used to determine the anthropogenic contribution to the heavy metal concentration in the sediment (Zhang et al. 2007). This factor was obtained by dividing the measured metal/Al (or Fe) rate into the metal/Al (or Fe)

rate from the period before contamination. In these calculations, either Al or Fe was preferred as it was conservative and free from anthropogenic effects. We used Fe to calculate the EF (and also contamination factor (CF)), which is commonly used to normalize metal concentrations in order to reduce the influence

of particle grain size (Zhang et al. 2007). Several authors have successfully used iron to normalize heavy metal contaminants (Zhang et al. 2007; Esen et al. 2010; Kükürer 2013). Background values for trace metals calculated from Lake Çıldır sediments were used in this study as background levels. Evaluations were made according to Sutherland (2000), where as follows:

- EF<2, deficiency to minimal enrichment
- EF=2–5, moderate enrichment
- EF=5–20, significant enrichment
- EF=20–40, very high enrichment
- EF>40, extremely high enrichment

The second method utilized was the CF, calculated as the ratio between metal content of the present sediment and normal concentration levels, thereby reflecting metal enrichment of the sediment. CF was classified into four groups, as per Hakanson (1980), as below:

- CF<1, low contamination
- 1≤CF<3, moderately contaminated
- 3≤CF<6, considerably contaminated
- CF>6, very high contamination

In order to calculate background levels of Lake Çıldır, a total of six core sediments collected from six different stations along east–west and north–south directions were analyzed. Heavy metal data were normalized using Al values. The obtained values were standardized to fit normal distribution. After normal probability graph was plotted for each heavy metal, cluster of lowest values was selected, mean of which with a confidence interval of 95 % was determined as a background level.

To determine environmental quality of the sediment, an integrated Pollution Load Index (PLI) was used, according to Suresh et al. (2011). The PLI gave an assessment of the overall toxicity status of the sample as a result of the contribution of the ten metals. The formula used for PLI was as follows:

$$PLI = (CF_1 \times CF_2 \times \dots \times CF_n)^{1/n}$$

The Potential Ecological Risk Index (PER) was used to evaluate the toxicity of metals in the sediment

(Hakanson 1980). The formula for the PER of a single heavy metal was

$$E_f^i = C_f^i \times T_f^i$$

where T_f^i is the response coefficient for the toxicity of a single heavy metal, as formulated by Hakanson (1980). C_f^i was calculated as the ratio between sediment metal content at a given station and background concentration levels. The corresponding coefficients, based on their toxicity, were the following: Hg=40, Cd=30, As=10, Cu=Pb=Ni=5, Cr=2, and Zn=1 (Guo et al. 2010).

The PER for various heavy metals in the sediments was calculated; thus.

$$PER = \sum E_f^i$$

The relationship between PER, E_f^i , and pollution levels is given in Table 1.

Analysis of relationships between variables was carried out using Pearson's correlation test on data sets. Cluster analyzes were applied for determination of the distance between variables. Principal component analysis (PCA) was also utilized in order to learn which parameters were the main sources of variations between the studied parts of the lake.

Results and discussion

Heavy metal content

Heavy metal content, organic carbon, and the CDP of the sediment samples are shown in Table 2. A comparison between heavy metals and toxicological references (Threshold Effect Level (TEL) and Probable Effect Level (PEL)) is given in Table 3.

Average concentrations of heavy metals were, in descending order, Fe>Mn>Zn>Ni>Cr>Cu>Pb>As>Cd>Hg, respectively. According to the distribution of the stations, minimum levels were detected for all heavy metals at St6 except As. This station has a sandy soil structure, unlike the other sampling sites, and had the lowest organic level. Maximum levels varied according to the station. While maximum levels of Cu, Ni, Mn, Cr, and Hg were detected at St2; maximum levels of Pb, Zn, and Cd were detected at St3. Samples from these stations contained more than 2 % of the organic carbon levels. At variance with the others, As reached its highest value at St5. Background

Table 1 Relationship between PER, E_f^i and pollution levels (from Guo et al. 2010)

Scope of potential ecological risk index (E_f^i)	Ecological risk level of single factor pollution	Scope of PER	General level of potential ecological risk
$E_f^i < 40$	Low	PER < 150	Low grade
$40 \leq E_f^i < 80$	Moderate	$150 \leq \text{PER} < 300$	Moderate
$80 \leq E_f^i < 160$	Higher	$300 \leq \text{PER} < 600$	Severe
$160 \leq E_f^i < 320$	High	$600 \leq \text{PER}$	Serious
$320 \leq E_f^i$	Serious		

values were determined from sediment of Lake Çıldır for comparison of heavy metal levels. As and Hg had the higher value at all stations, while concentrations of Cu, Ni, and Fe were detected below the background levels. The content of Mn, Pb, and Zn were higher than the background values at St1, St2, and St3. Cr value was less than the background level at all stations except St2. The concentration of Cd showed a lower value than the background at St5 and St6. The two values were considered as resulting from the toxic effects of heavy metals. It was assumed that while some negative influences might occur rarely under TEL, most of expected influences would occur frequently above PEL. The concentration of Pb, Zn, As, Cd, Cr, and Hg were below TEL at all stations of Lake Çıldır. Cu concentrations were detected higher than TEL and lower than PEL at all stations except St5 and St6. The concentrations of Ni were in between TEL and PEL, except at St6, where it was under TEL.

The levels of heavy metals found in some large lakes of Turkey and around the world are compared in Table 4. From this, we can see that the concentration

of Cu in Lake Çıldır was higher than Ulubat, Beyşehir, and Kapulukaya while lower than Lake Hazar. The concentration of Pb and Zn in Lake Çıldır was lower or equal to all other lakes except Ulubat. Despite the Ni measured at Lake Çıldır being close to that of Chapala, it was higher than Sapanca, and all other lakes listed in Table 4 have higher Ni. Although the value of Cr was lower than all other lakes, it was higher than Sapanca and Ulubat. The level of Hg was higher than the Yangtze (China) while it was lower than Kapulukaya.

Enrichment factor

Enrichment factor is an important tool for determining possible sources of heavy metals. Thanks to this method, it is possible to detect whether the sources of heavy metals are natural or anthropogenic. The values of EF in Lake Çıldır are shown in Table 5.

The EF values are, from highest to lowest concentration, $\text{Hg} > \text{As} > \text{Cd} > \text{Mn} > \text{Pb} > \text{Zn} > \text{Cr} > \text{Cu} > \text{Ni}$, respectively. Whereas EF was not detected higher than 2, it is assumed that the source of these elements is natural.

Table 2 Concentration of heavy metal, chlorophyll degradation products (CDP) (mg/kg dry weight) and organic carbon (%) in sediments from Lake Çıldır

Station number (St)	1	2	3	4	5	6
Cu	25.8	29.1	26.4	19.9	14.0	6.92
Pb	14.3	14.9	15.9	11.4	6.35	4.03
Zn	56.6	60.3	60.8	46.6	37.6	33.2
Ni	38.5	43.8	39.6	28.6	19.8	10.9
Mn	617	966	571	404	193	121
Fe	18,300	18,800	19,000	13,800	12,700	12,000
As	2.6	3.6	3.2	2.5	4.5	4.3
Cd	0.3	0.31	0.33	0.23	0.11	0.01
Cr	34.6	36.7	35.5	24.6	18.3	16
Hg	0.06	0.08	0.07	0.07	0.04	0.04
CDP	8.84	39.04	47.65	6.52	24.69	7.61
Organic carbon	2.00	2.41	2.01	1.33	2.55	0.15

Table 3 Descriptive statistics of heavy metal values, background levels (mg/kg), and TEL and PEL values

	Cu	Pb	Zn	Ni	Mn	Fe	As	Cd	Cr	Hg
Mean	20.34	11.14	49.18	30.20	478.67	15,767	3.45	0.22	27.62	0.06
Min	6.92	4.03	33.20	10.90	121	12,000	2.50	0.01	16.00	0.04
Max	29.06	15.92	60.80	43.80	966	19,000	4.50	0.33	36.70	0.08
Standard error	3.48	2.00	4.86	5.25	126.53	1,336	0.34	0.05	3.76	0.01
Background	29.92	11.42	53.83	48.5	409.75	19,225	1.77	0.15	36.44	0.02
TEL ^a	18.7	30.2	124	15.9	–	–	7.24	0.68	52.3	0.13
PEL ^a	108	112	271	42.8	–	–	41.6	4.21	160	0.70

^aMacDonald (1994)

The highest enrichment found was for Hg, which was present at a “moderate” level at all stations except St4 where EF value indicates “significant” level. The highest As enrichment was detected at St5 and St6. Minimal contamination was determined for Zn, Ni, Pb, and Cr at all stations. Although there was moderate enrichment at St2, anthropogenic effects were not detected at other stations for Mn. Moderate contamination was detected at St1, St2, St3, and St4 for Cd. Bai et al. (2012) explained that higher As and Cd values could be originated from agrochemicals and fertilizers. Artificial fertilizers and pesticides contain large amounts of toxic heavy metals, especially Cd,

Pb, Ni, As, and Cu (Sönmez et al. 2008). Levels of Pb, Cd, and As in artificial fertilizers have been proven to exceed maximum limits in Turkey (Köleli and Kantar 2005). It is probable that the enrichment of As and Cd originated from agricultural activities around Lake Çıldır.

Contamination factor

Calculated CF values are shown in Table 6. The mean values of heavy metals with the highest CF are Hg>As>Cd>Mn>Pb>Zn>Fe>Cr>Cu>Ni, respectively.

Table 4 Comparison of concentration of heavy metals found in sediment of lakes in Turkey and various other countries

Lake	Cu	Pb	Zn	Ni	Mn	Fe	As	Cd	Cr	Hg
Ulubat, Turkey ^a	0.75	1.42	3.89	–	–	–	–	0.078	2.95	–
Beyşehir, Turkey ^b	5.44–10.47	–	10.3–58.05	–	57.665–1,029	3,466–15,136	–	–	–	–
Kapulukaya, Turkey ^c	16.25	22.58	66.15	68.06	713.27	2,430	31.23	0.83	559.2	1.19
Sapanca, Turkey ^d	26.68	15.20	62	26.72	337.81	–	–	0.29	19.09	–
Veeranam, India ^e	94.12	30.06	180.08	63.61	–	–	–	0.81	88.20	–
Hazar, Turkey ^f	10–64	ND	46–210	38–130	85–625	3,650–30,000	–	–	17–79	–
Yangtze, China ^g	343	57.78	296.78	40.44	–	–	16.03	0.57	119.2	0.32
Chapala ^h , Mexico	29.26	81.74	102.75	32.24	–	3.97 %	–	–	66.12	–
Çıldır, Turkey	20.34	11.14	49.18	30.20	478.67	1,5767	3.45	0.22	27.62	0.66

^aBarlas et al. 2005

^bÖzan 2008

^cKankılıç et al. 2013

^dDuman et al. 2007

^eSuresh et al. 2012

^fÖzmen et al. 2004

^gYang et al. 2009

^hRozales-Hoz et al. 2000

Table 5 EF values of measured heavy metals in Lake Çıldır

Station number	1	2	3	4	5	6	Mean
Cu	0.91	0.99	0.89	0.93	0.71	0.37	0.80
Pb	1.31	1.34	1.41	1.39	0.84	0.57	1.14
Zn	1.10	1.15	1.14	1.21	1.06	0.99	1.11
Ni	0.83	0.92	0.83	0.82	0.62	0.36	0.73
Mn	1.58	2.41	1.41	1.37	0.71	0.47	1.33
As	1.54	2.08	1.83	1.97	3.85	3.89	2.53
Cd	2.10	2.11	2.23	2.14	1.11	0.11	1.63
Cr	1.00	1.03	0.99	0.94	0.76	0.70	0.90
Hg	3.26	3.94	3.39	5.02	3.03	2.88	3.58

According to the mean values (Table 6), moderate enrichment was determined for Hg, As, Mn, and Cd while a low CF was found for other elements. Low contamination was detected for Cu, Ni, and Fe, at all stations. Mn, Zn, and Pb had moderate CF at St1, St2, and St3, whereas Cr had only found at St2. Sediments were moderately contaminated for As at all sampling sites. Moderate contamination was detected for Cd at all stations except St5 and St6. The lake was considerably contaminated for Hg at stations 1, 2, 3, and 4 while moderate contamination was calculated for the other two stations.

Pollution Load Index

Pollution Load Index values are illustrated in Table 6. PLI values were found to be between 0.44 and 1.47. The mean PLI value was calculated as 1.05. The minimum

Table 6 CF and PLI values of calculated heavy metals

Station number	1	2	3	4	5	6	Mean
Cu	0.86	0.97	0.88	0.66	0.47	0.23	0.68
Pb	1.25	1.31	1.39	0.99	0.56	0.35	0.98
Zn	1.05	1.12	1.13	0.87	0.70	0.62	0.91
Ni	0.79	0.90	0.82	0.59	0.41	0.22	0.62
Mn	1.51	2.36	1.39	0.99	0.47	0.30	1.17
Fe	0.95	0.98	0.99	0.72	0.66	0.62	0.82
As	1.47	2.03	1.81	1.41	2.54	2.43	1.95
Cd	2.00	2.07	2.20	1.53	0.73	0.07	1.43
Cr	0.95	1.01	0.97	0.68	0.50	0.44	0.76
Hg	3.10	3.85	3.35	3.60	2.00	1.80	2.95
PLI	1.27	1.47	1.35	1.02	0.73	0.44	1.05

PLI was detected at St6 while the maximum was at St2. According to Suresh et al. (2011), the ideal PLI is 0 (zero), showing no pollution. A finding of 1 point reflects the baseline level of the sediment. Values above 1 indicate progressive deterioration. Detected values for St1, St2, St3, and St4 in this study slightly exceed 1, indicating that there is a problem at minimal level regarding the environmental quality of the sediment.

Potential Ecological Risk

Potential Ecological Risk values are shown both individually and totally in Table 7. According to this analysis, the risk indices of the metals are Hg>Cd>As>Pb>Cu>Ni>Cr>Zn, respectively. PER was calculated as higher for Hg at all stations except St6 where moderate risk was detected. PER indices were <40 for all metals except Hg and Cd. These point to a low ecological risk in the lake. Cd shows low risk at stations 5 and 6, but suggests a moderate risk at stations 1, 2, 3, and 4. PER varied between 103.83 and 255.37 for all metals, and the general average was calculated as 194.31. The lowest and highest values were detected at St6 and St2, respectively. The maximum level resulted from maximum levels of Cu, Ni, Cr, and Hg at St2. Similarly, the lowest PER, at St6, could have resulted from the minimum recorded values of the metals, excluding As.

Pearson’s correlation analysis

Observed correlation coefficients are presented as a linear correlation matrix in Table 8. No relationship was found between any of the metals and As. Although Hg and Fe were not related to each other, there was a strong correlation between all other metals. According to Wang et al. (2012), correlation between heavy metals provides clues about their origin and migration. In other words, a high correlation between two metals indicates the same source of pollution and similar transformation and migration processes.

As Suresh et al. (2011) points out, correlation may indicate mutual dependency in addition to migration and other sources. If no correlation is found between elements, it means that the metals are not controlled by a single factor. In this study, a strong correlation was found between all metals except As and PLI, PER. Thus, elements present in the Lake Çıldır sediments possess the potential to create ecological risk. However, it was confirmed that there was no correlation

Table 7 Potential ecological risk (PER) indices for single metal (E^i) and PER for heavy metals

Station number	Potential ecological risk indices for single heavy metal (E^i)								
	Cu	Pb	Zn	Ni	As	Cd	Cr	Hg	PER
1	4.32	6.25	1.05	3.97	14.69	60.00	1.90	124.00	216.17
2	4.86	6.53	1.12	4.52	20.34	62.00	2.01	154.00	255.37
3	4.41	6.97	1.13	4.08	18.08	66.00	1.95	134.00	236.62
4	3.32	4.97	0.87	2.95	14.12	46.00	1.35	144.00	217.59
5	2.33	2.78	0.70	2.04	25.42	22.00	1.00	80.00	136.28
6	1.16	1.76	0.62	1.12	24.29	2.00	0.88	72.00	103.83
Mean	3.40	4.88	0.91	3.11	19.49	43.00	1.52	118.00	194.31

between organic carbon and CDP, which represent biological processes and heavy metals. Although it is well known that importance of organic carbon in determining the fate of heavy metals in sediments because of organic carbon has strong complexing capacity for metallic contaminants (Bai et al. 2011a), there was no correlation between organic carbon and heavy metals.

Cluster analysis

Two cluster analyzes were performed, both for determination of the relationship between variables and for differentiation between stations. Fourteen parameters were clustered in the first dendrogram (Fig. 2).

According to the variables analysis shown in Fig. 2, Cu–Ni, Pb–Cd, and Zn–Cr–Fe were clustered, while Mn and Hg were placed far from other clusters. As shows no relationship with other metals, and independency was observed. Cu, Ni, Pb, and Cd were responsible for the PLI, and Hg was responsible for the PER. No relationship was determined between organic carbon, CDP, and measured heavy metals. However, it can be said that organic carbon exhibits a close relationship to the heavy metals, apart from CDP. This indicates that algal biomass plays no important role in the absorption and migration of heavy metals in the water column. The relationship between organic carbon and CDP was weak. Overall, these results show that the organic

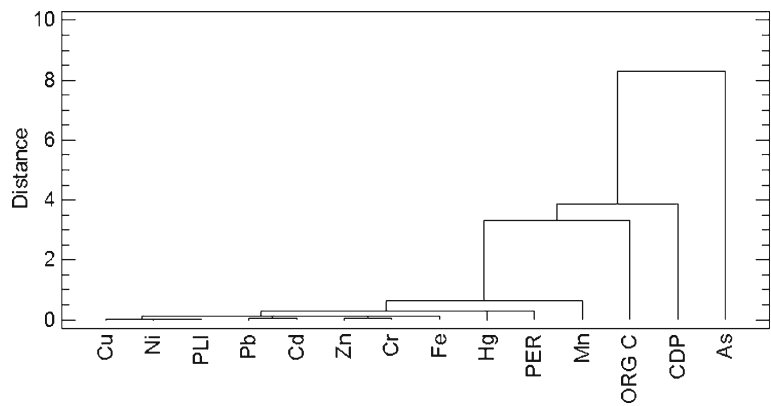
Table 8 Pearson's correlation coefficients between variables for all heavy metals

	Cu	Pb	Zn	Ni	Mn	Fe	As	Cd	Cr	Hg	CDP	ORGC	PER	PLI
Cu	1													
Pb	0.979**	1												
Zn	0.979**	0.989**	1											
Ni	0.998**	0.980**	0.986**	1										
Mn	0.925**	0.869*	0.906*	0.936**	1									
Fe	0.938**	0.945**	0.979**	0.953**	0.887*	1								
As	-0.629	-0.706	-0.616	-0.614	-0.461	-0.513	1							
Cd	0.985**	0.994**	0.976**	0.980**	0.857*	0.922**	-0.713	1						
Cr	0.972**	0.975**	0.994**	0.983**	0.922**	0.989**	-0.603	0.958**	1					
Hg	0.887*	0.891*	0.855*	0.881*	0.855*	0.743	-0.749	0.892*	0.830*	1				
CDP	0.547	0.532	0.595	0.560	0.523	0.612	0.169	0.516	0.555	0.364	1			
ORGC	0.667	0.549	0.560	0.644	0.549	0.542	-0.080	0.616	0.543	0.407	0.588	1		
PER	0.968**	0.967**	0.946**	0.963**	0.900*	0.864*	-0.712	0.970**	0.925**	0.972**	0.492	0.544	1	
PLI	0.998**	0.981**	0.985**	0.999**	0.933**	0.944**	-0.613	0.983**	0.976**	0.895*	0.577	0.647	0.972**	1

** Correlation is significant at the 0.01 level

* Correlation is significant at the 0.05 level

Fig. 2 Dendrogram of all variables



carbon mostly originated from anthropogenic and/or terrestrial effects, not from algal blooms.

St2 was separate from other stations according to cluster analysis (Fig. 3). This result was caused by the high values of PER and PLI, and this station shows strongest ecological risk. The lowest PLI and PER were observed at St5 and St6, which exhibited weak ecological risk. St1, St3, and St4 were clustered between themselves.

Principal component analysis

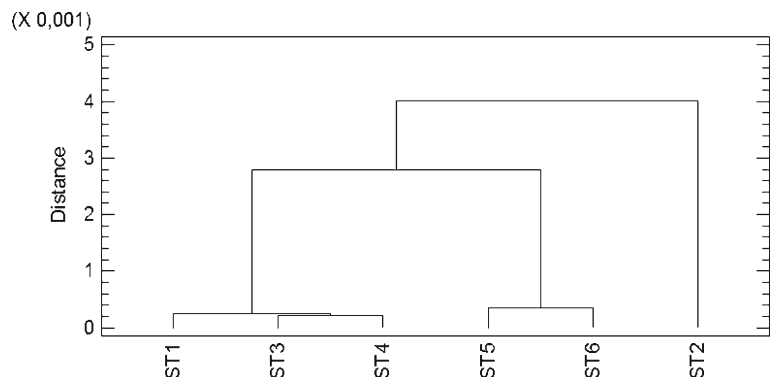
The purpose of PCA was to obtain a small number of linear combinations for the 11 variables that account for most of the variability in the data. In this case, two components were extracted, since these two components had eigenvalues greater than or equal to 1.0. Together they account for 92.64 % of variability in the original data. The first component, including Cu, Pb, Zn, Ni, Mn, Fe, Cd, Cr, Hg, PER, and PLI, accounted for 82.17 % of total variability. The migration and sources of the mentioned metals could be the same,

and they were important for PER and PLI. The 10.48 % of total variability was related to As, CDP, and organic carbon. This component reveals the relocation of As through organic carbon.

Conclusions

The heavy metal content (Cu, Pb, Zn, Ni, Mn, Fe, As, Cd, Cr, Hg) of sediment samples collected from the northern littoral zone of Lake Çıldır was studied. The measurements carried out to determine contamination level and quality of the samples indicated the existence of contamination of Hg, As, Cd, and Mn at moderate levels. Given the presence of heavy metal contamination, PLI and PER values were found to be above the limit of threshold values. Results of statistical analysis revealed that the Cu, Pb, Zn, Ni, Mn, Fe, Cd, Cr, and Hg had similar sources and mutual processes of deposition, in contrast to As, which might have been transported by organic agents. With regard to the potential of pollution, Station 2, with a greater risk, is statistically different

Fig. 3 Dendrogram of CA for all stations



from the other stations studied. Stations 5 and 6 are, however, of the least significance in respect of ecological risk.

Albeit the absence of urbanization and industry in the studied area, our results revealed the presence of anthropogenically induced heavy metal contamination in surface sediments of Lake Çıldır due to the utilization of fossil fuels and agricultural activities. It is very likely that there is a potential risk for the ecosystem of Lake Çıldır in next future.

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References

- Atalay, İ. (1978). Geomorphology of Çıldır Lake and around. *Journal of Geomorphology*, 7, 23–34.
- Bai, J., Huang, L., Yan, D., Wang, Q., Gao, H., Xiao, R., et al. (2011a). Contamination characteristics of heavy metals in wetland soils along a tidal ditch of the Yellow River Estuary, China. *Stochastic Environmental Research and Risk Assessment*, 25, 671–676.
- Bai, J., Cui, B., Chen, B., Zhang, K., Deng, W., Gao, H., et al. (2011b). Spatial distribution and ecological risk assessment of heavy metals in surface sediments from a typical plateau lake wetland, China. *Ecological Modelling*, 222, 301–306.
- Bai, J., Xiao, R., Cui, B., Zhang, K., Wang, Q., Liu, X., et al. (2011c). Assessment of heavy metal pollution in wetland soils from the young and old reclaimed regions in the Pearl River Estuary, South China. *Environmental Pollution*, 159, 817–824.
- Bai, J., Xiao, R., Zhang, K., & Gao, H. (2012). Arsenic and heavy metal pollution in wetland soils from tidal freshwater and salt marshes before and after the flow-sediment regulation regime in the Yellow River Delta, China. *Journal of Hydrology*, 450–451, 244–253.
- Barlas, N., Akbulut, N., & Aydoğan, M. (2005). Assessment of heavy metal residues in the sediment and water samples of Ulubat Lake, Turkey. *Bulletin of Environmental Contamination and Toxicology*, 74, 286–293.
- Duman, F., Aksoy, A., & Demirezen, D. (2007). Seasonal variability of heavy metals in surface sediment of Lake Sapanca, Turkey. *Environmental Monitoring and Assessment*, 133, 277–283.
- Esen, E., Küçüksezgin, F., & Uluturhan, E. (2010). Assessment of trace metal pollution in surface sediments of Nemrut Bay, Aegean Sea. *Environmental Monitoring and Assessment*, 160, 257–266.
- Gaudette, H. E., Flight, W. R., Toner, L., & Folger, W. (1974). An inexpensive titration method for the determination of organic carbon in recent sediments. *Journal of Sedimentary Petrology*, 44, 249–253.
- Gue, W., Liu, X., Liu, Z., & Li, G. (2010). Pollution and potential ecological risk evaluation of heavy metals in the sediments around Dongjiang Harbor, Tianjin. *Procedia Environmental Sciences*, 2, 729–736.
- Hakanson, L. (1980). Ecological risk index for aquatic pollution control, a sedimentological approach. *Water Research*, 14, 975–1001.
- Jain, C. K., Gupta, H., & Chakrapani, G. J. (2008). Enrichment and fractionation of heavy metals in bed sediments of river Narmada, India. *Environmental Monitoring and Assessment*, 141, 35–47.
- Kahkönen, M. A., Kallio, M. P., & Manninen, P. K. P. (1997). Analysing heavy metal concentrations in the different parts of *Elodea canadensis* and surface sediment with PCA in two boreal lakes in Southern Finland. *Chemosphere*, 35(11), 2645–2656.
- Kankılıç, G. B., Tüzün, İ., & Kadioğlu, Y. K. (2013). Assessment of heavy metal levels in sediment samples of Kapulukaya Dam Lake (Kirikkale) and lower catchment area. *Environmental Monitoring and Assessment*. doi:10.1007/s10661-013-3061-2.
- Kannan, S. K., Batvari, B. P. D., Lee, K. L., Kannan, N., Krishnamoorthy, R., & Jayaprakash, M. (2008). Assessment of heavy metals (Cd, Cr and Pb) in water, sediment and seaweed (*Ulva lactuca*) in the Pulicat Lake, South East India. *Chemosphere*, 71, 1233–1240.
- Köleli, N., & Kantar, Ç. (2005). Toxic heavy metal (Cd, Pb, Ni and As) concentration in phosphate rock, phosphoric acid and phosphorous fertilizers (In Turkish). *Ecology*, 14(55), 1–5.
- Kürker, S. (2013). Assessment of heavy metal (Zn, Pb, Fe) contamination in surface sediments of creeks flowing to inner part of Izmir Bay (Eastern Aegean Sea). *Journal of Black Sea and Mediterranean Environment*, 19(1), 82–94.
- Lorenzen, C. J. (1971). Chlorophyll-degradation products in sediments of Black Sea. *Woods Hole Oceanographic Institution Contribution*, 28, 426–428.
- MacDonald, D. D. (1994). Approach to the assessment of sediment quality in Florida coastal waters. Volume 1—development and evaluation of sediment quality assessment guidelines. Florida Department of Environmental Protection Office of Water Policy. Retrieved from http://www.floridadep.org/waste/quick_topics/publications/documents/sediment/volumel.pdf.
- Meyers, P. A., & Teranes, J. L. (2001). Sediment organic matter. In W. M. Last & J. P. Smol (Eds.), *Tracking environmental change using lake sediments* (Vol. 2, pp. 239–269). Dordrecht: Kluwer Academic Publishers.
- Mico, C., Recatala, L., Peris, M., & Sanchez, J. (2006). Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. *Chemosphere*, 65, 863–872.
- Nriago, J. O., & Pacyna, J. M. (1988). Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature*, 333, 134–140.

- Özmen, H., Külahaçı, F., Çukurovalı, A., & Doğru, M. (2004). Concentrations of heavy metal and radioactivity in surface water and sediment of Hazar Lake (Elazığ, Turkey). *Chemosphere*, *55*, 401–408.
- Rosales-Hoz, L., Carranza-Edwards, A., & Lopez-Hernandez, M. (2000). Heavy metals in sediments of a large, turbid tropical lake affected by anthropogenic discharges. *Environmental Geology*, *39*(3–4), 378–383.
- Sönmez, İ., Kaplan, M., & Sönmez, S. (2008). Effect of chemical fertilizers on environmental pollution and its prevention methods (In Turkish). *Journal of Batı Akdeniz Agricultural Research Institute*, *25*(2), 24–34.
- Suresh, G., Ramasamy, V., Meenakshisundaram, V., Venkatachalapathy, R., & Ponnu-samy, V. (2011). Influence of mineralogical and heavy metal composition on natural radionuclide contents in the river sediments. *Applied Radiation and Isotopes*, *69*, 1466–1474.
- Suresh, G., Sutharsan, P., Ramasamy, V., & Venkatachalapathy, R. (2012). Assessment of spatial distribution and potential ecological risk of the heavy metals in relation to granulometric contents of Veeranam lake sediments, India. *Ecotoxicology and Environmental Safety*, *84*, 117–124.
- Sutherland, R. A. (2000). Bed sediment associated trace metals in an urban stream, Oahu, Hawaii. *Environmental Geology*, *39*, 611–627.
- Tekin-Özan, S. (2008). Determination of heavy metal levels in water, sediment and tissues of tench (*Tinca tinca* L., 1758) from Beyşehir Lake (Turkey). *Environmental Monitoring and Assessment*, *145*, 295–302.
- Turg, B., Albuquerque, A. L. S., Cordeiro, R. C., Sifeddine, A., Simoes Filho, F. F. L., Souza, A. G., et al. (2002). Accumulation of organic carbon in five Brazilian lakes during the Holocene. *Sedimentary Geology*, *148*, 319–342.
- Wang, Y., Hu, J., Xiong, K., Huang, X., & Duan, S. (2012). Distribution of heavy metals in core sediments from Baihua Lake. *Procedia Environmental Sciences*, *16*, 51–58.
- Yang, Z., Wang, Y., Shen, Z., Niu, J., & Tang, Z. (2009). Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China. *Journal of Hazardous Materials*, *166*, 1186–1194.
- Zhang, L., Ye, X., Feng, H., Jing, Y., Ouyang, T., Yu, X., et al. (2007). Heavy metal contamination in western Xiamen Bay sediments and its vicinity, China. *Marine Pollution Bulletin*, *54*, 974–982.