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RESEARCH ARTICLE

Metal pollution assessment in surface sediments of Namak Lake, Iran

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Abstract

Desiccation of the Namak Lake (NL) can result in the release of fine-grained dust contaminated with heavy metals, while there is little information available on the propagation of metals in the bed sediments of this lake. In this study, contamination of metals in the surface sediments of the NL was analyzed and the pollution status of sediments was assessed using geo-accumulation index (I_{geo}), enrichment factor (EF), the consensus-based sediment quality guidelines (CBSQGs), and mean probable effect concentration quotient (mPECQ). Results indicated that metal concentrations at the southern part were higher than at the middle and northern parts of the lake. Possible reasons are (i) pollution loads mainly entered the lake through the rivers at the west and northwest, but accumulated at the southern parts, (ii) hard layer of salt covering the bottom of the NL at the northern part suppresses adsorption of metals to the sediment, and (iii) the muddy nature of sediments at the southern part makes it easier for metals to be absorbed. EF results showed that sediments at the southern part of the lake were moderately enriched with lead (Pb). The low I_{geo} values suggested no pollution with the metals, and CBSQG values showed that the sediments of the NL were not toxic, while the mPECQ index suggested a toxicity probability of less than 25%. Cluster analysis classified the metals into two clusters. In general, the results showed that metal pollution in the surface sediments of NL was generally low although the concentration of Pb at the southern part of the lake was worrisome.

Keywords Heavy metal pollution · Enrichment factor · Cluster analysis · Surface sediment · Geo-accumulation index · Namak Lake

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Introduction

Most lakes contain freshwater because they are well flushed and constituents do not accumulate in the lake. However, under some conditions such as excessive evaporation and constituent input, the lake becomes saline (Eugster and Hardie 1978). In specific parts of the globe, saline lakes are common. But they have attracted less attention because they are small in size and number (Eugster and Hardie 1978).

Saline lakes are common in Iran. Similar to other saline lakes in Iran, Namak Lake (NL) is also facing an extensive lack of water resources due to the recent drought, climate change, and damming on its contributing rivers and tributaries. Meanwhile, desertification of this lake can result in extreme environmental crisis in the central parts of Iran as reported by the Technical Director of Iran's Department of Environment. Drying up NL will provide a 200-ha source of fine-grained dust that will adversely affect the cities of Tehran (capital of Iran) and Qom, and the central provinces of Iran, which almost contain more than half of Iran's population. In addition, settled pollutants in the sediments, such as heavy metals (HMs), could further add to

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the problem. HMs have low solubility and mostly (over 90%) tend to deposit into the lake sediments (Calmano et al. 1993; Gaur et al. 2005; Zahran et al. 2015). Accumulated metals in the sediments can re-suspend when the environmental conditions change or the sediments experience external disturbances (Noori et al. 2018; Aradpour et al. 2020). Hence, it is vital to understand pollution status and the origin of metal inputs into NL and investigate the potential ecological risks imposed to the surrounding environment. In a study conducted on Maharlu Lake, Iran, it was concluded that wastewater inputs into the lake are the major cause of lake's water and sediment quality degradation (Moore et al. 2009). Gao and Li (2012) stated that sediment grain size is a key parameter in propagation and fractionation of the HMs in the sediments. Islam et al. (2015) reported severely contaminated water and sediment in the Korotoa River in Bangladesh. Zahran et al. (2015) reported high levels of cadmium (Cd) and lead (Pb) using geo-accumulation index (I_{geo}) in the sediments of Manzala Lake, Egypt. Wang et al. (2018) investigated sediments of Hongfeng Lake and discovered that the environmental protection programs carried out by authorities had resulted in a fall in enrichment factor (EF) trends of the sediments throughout the lake since 1995. Some metals, i.e., copper (Cu), zinc (Zn), and Pb, were reported to be troublesome in water and sediment of the Swarnamukhi River, India (Patel et al. 2017).

Although understanding the metal pollution status in NL sediments provides necessary information for Iran's Department of Environment, there is little information available on the distribution of metals in the lake's sediment. Analysis of metals in the sediments of the NL is crucial to determine the biological impact of the suspended sediments in case of complete drying up of the lake. Therefore, in this study, concentrations of metals in the surface sediments of NL were studied using EF (Pekey 2006), I_{geo} (Muller 1979), and two other indices, i.e., consensus-based sediment quality guidelines (CBSQGs) (MacDonald et al. 2000) and mean probable effect concentration quotients (mPECQs) (MacDonald et al. 2000; Long et al. 2006). Also, correlation and cluster analyses were employed to understand the similarities among the metals in the sediments of NL. A main unresolved issue with the application of cluster analysis is the determination of the optimum number of clusters. In this study, two indices, i.e., the Dunn index (DI) and Davies and Bloudin index (DBI), proposed by Dunn (1974) and Davies and Bloudin (1979), respectively, were used to specify the optimal number of clusters in the application of cluster analysis method.

Material and methods

Study area

Namak Lake, as a part of the Paratethys Sea, is located approximately at an elevation of 790 m above sea level and 100 km east of Qom city and 60 km north of Kashan city (Fig. 1a). From the east, the lake is located near Kavir National Park. The lake has an area of approximately 1806 km^2 and its bed is covered by salt sediments with a depth varying between 5 and 54 m separated by some clay layers. The northern part of the NL is covered with a thick hard layer of salt and the southern part is mostly muddy.

Average annual precipitation in the NL basin is less than 200 mm for the southeast part of the basin and it raises up to 800 mm moving towards the heights at the north (Maghrebi et al. 2020). Average annual temperature was observed to be 18 °C at the eastern part of the basin to − 3 °C at the northern heights (Abtahi et al. 2014). According to Iran's Ministry of Energy, the precipitation rate over NL has reduced about 22.5% during the last 50 years, and the evaporation rate has raised to about five times greater than the global rates. Also, the drought intensity has accelerated inland migration from the surrounding villages of NL to big cities like Tehran, Esfahan, Qom, and Kashan.

Generally, NL is a seasonal lake with a triangular shape nourished by surface runoff (mainly from Qom River) and groundwater resources. Qom River crosses industrial and municipal areas such as Hamedan and Qom. Jajrood and Karaj rivers also flow into NL, which cross extensive industrial and municipal areas as well. However, Amirkabir and Latian dams at the upstream of Karaj and Jajrood rivers have adversely affected the amount of flow discharge into NL. Also, the implementation of 15-Khordad and Saveh dams on Qom and Qara-Chai rivers, respectively, has further reduced the inflow to the lake. Recent droughts have caused a major decline in the water level of NL, and it is almost entirely dried out so that water only covers about 1 km^2 of its area. Therefore, the lake is considered to have a big potential to release suspended dusts in the surrounding atmosphere, which alternatively could have severe consequences for the environment and local habitats.

Surface sediment sampling

The surface sediment samples were taken in January 2019. Eight locations were considered as the sampling sites. It is noteworthy to mention that field studies are both time-consuming and expensive. Also, although more sampling locations can provide further information about the contamination status of sediments, raising the number of samples can cause uncertainties in the results. Because of the triangular shape of the lake, sampling locations were distributed in a specific order to be properly representative of the whole area of the lake. Three sampling locations were chosen at the three vertices of the triangle, and five other sampling locations were chosen in a way that one is located at the middle of the lake and others at the middle of the sides of the triangle (Fig. 1b).

A hard layer of salt covers the lake so that its thickness varies from one point to another. Under the salty layer, there existed a muddy layer. Because the upper layer of the lake's

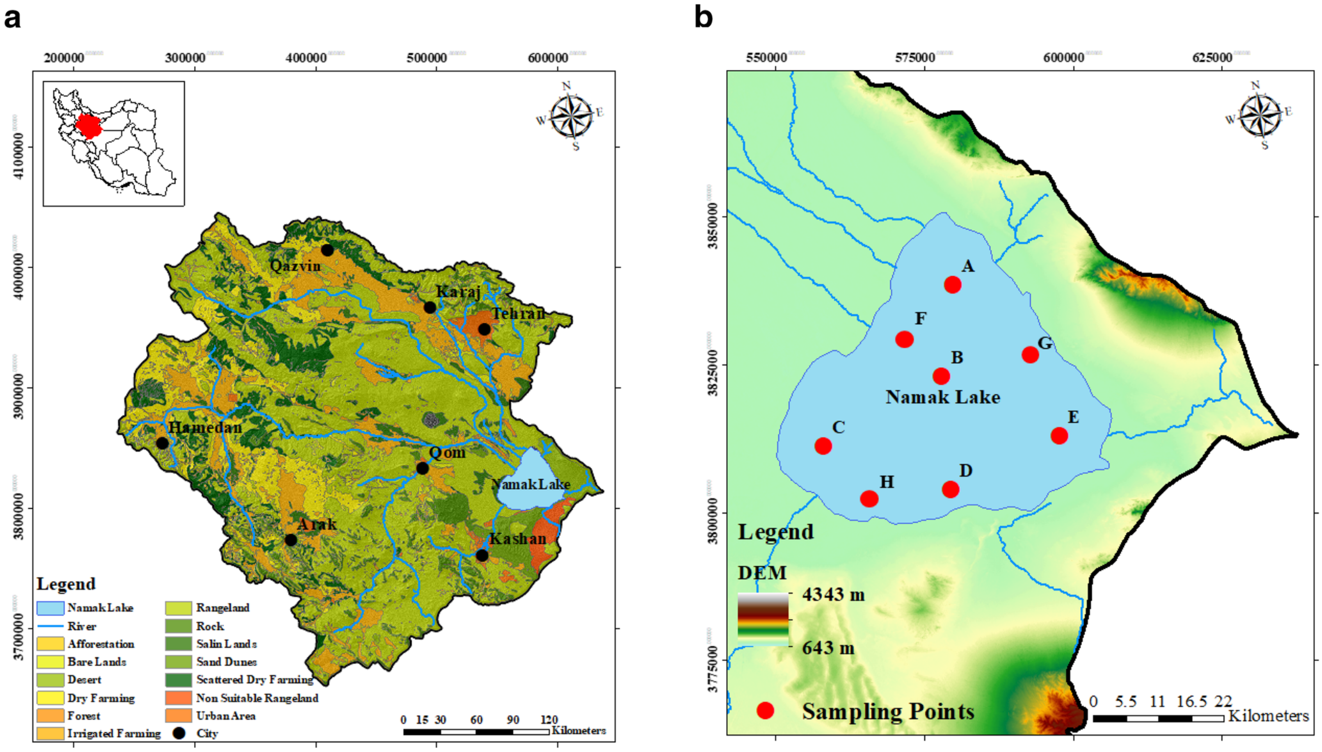

Fig. 1 **a** Basin of Namak Lake, located in the center of Iran. **b** Digital elevation map of NL and sampling locations

sediment was hard, hatchet and shovel were used for sampling. The color of samples varied from point to point. At points A, C, B, and F, the colors of the samples were a combination of green, white (from salt), and brown. The color of the samples was entirely brown at points E and G and mostly red at points D and H. At points A and F, the surface of the lake was covered with water to a depth of nearly 3 cm, and a hard layer of salt covered the lake's bed. At points B and C, the surface of the lake was dry, but the sediments were moist. At points D and H, the surface of the lake had entirely dried out, but the soil had finer grains in comparison to other sampling locations. At points G and E, the surface of the lake was entirely dry, and the sediments were extremely salty (Fig. S1). However, eight samples were taken randomly from sediments within a circular zone with a radius of 2 m at each sampling location. Thereafter, the samples were mixed together and the final mixture was put into pre-cleaned polyethylene bags, sealed and preserved in 4 °C, and transferred to the lab. The sediment samples were sieved and air-dried for 12 h at 80 °C in a laboratory and then, a blend of HNO_3, HCL, $HCLO_4$, and HF was used to digest samples according to the test method guideline suggested by U.S. EPA 3050B (USEPA 1996). Analysis of the sediment samples was performed using inductively coupled plasma optical emission spectroscopy (ICP-OES) and concentrations of the following metals were measured for each sample: aluminum (Al), Cd, Pb, Cu, iron (Fe), Zn, manganese (Mn), vanadium (V), chromium (Cr), nickel (Ni), cadmium (Cd), arsenic (As), cobalt (Co), and mercury (Hg). Also, to check the accuracy of ICP-OES measurements, the liquid reference materials NIST 1643 (trace elements in natural water) and NIST 1640 (trace elements in water) were used. To check the quality of the measurements, blanks and certified reference material NIST 2709a were used. Also, acceptable recovery rate and standard deviation of 92–104% and SRD ≤ 5% were observed as a result of duplicate analysis of samples, blanks, and certified reference materials.

Indexing approach

To clarify natural and anthropogenic sources of the metals from each other, EF was used. In this regard, observed metal concentrations are normalized using a conservative constituent such as Fe, Al, and Mn (Mishra et al. 2004; Yongming et al. 2006; Karbassi et al. 2008; Zahra et al. 2014; Torabi Kachoosangi et al. 2020). Aluminum is very abundant in the clay minerals. Since the NL's bed consisted of dense clay layers and Al was widely used by other researchers as a conservative constituent (Rubio et al. 2000; Pekey 2006; Karbassi et al. 2008), the conservative element was considered to be Al. However, EF was calculated as Eq. (1) and the computed enrichment values for each element were classified using Table 1 (Birch 2003):

$$\mathrm{EF} = \frac{C_{\mathrm{Sample}}/\mathrm{Al}_{\mathrm{Sample}}}{C_{\mathrm{Shale}}/\mathrm{Al}_{\mathrm{Shale}}} \qquad (1)$$

where C_{Sample} is the sample metal concentration, Al_{Sample} is the Al concentration in the sediment, C_{Shale} is the metal shale concentration, and Al concentration in the Earth's crust is Al_{Shale}.

To evaluate the sediment pollution, I_{geo} was also used and calculated as Eq. (2), and the results were evaluated using Table 2 (Muller 1979), as well.

$$I_{geo} = \log_2\left(\frac{C_n}{1.5 \times B_n}\right) \tag{2}$$

where the concentration of metal in the sediment is C_n and the available metal concentration in the Earth's crust is B_n.

To account for the lithogenic differences between the sampling locations and the shale values provided in Table 3 (Taylor and McLennan 2001), factor 1.5 was considered as suggested by Hejabi (2011) and Gao and Li (2012).

The CBSQGs were employed to determine the toxicity of the sediments (MacDonald et al. 2000). The CBSQGs were derived from sediment quality guidelines (SQGs). Two threshold values were calculated in CBSQGs: (i) threshold effect concentration (TEC) and (ii) the probable effect concentration (PEC). Thereafter, sediment toxicity was evaluated using Table 4 (MacDonald et al. 2000). According to MacDonald et al. (2000), sediment samples were considered to be nontoxic if the observed concentration of the metals was below the TEC value. On the other hand, sediments were estimated to be toxic for concentrations higher than the PEC value. Note that the concentrations between PEC and TEC values were classified to be neither nontoxic nor toxic (MacDonald et al. 2000).

To further evaluate the toxicity of sediments considering the combined effect of toxic metals, mean mPECQ was also used and calculated by Eq. (3) (MacDonald et al. 2000; Ingersoll et al. 2001; Long et al. 2006).

$$\text{mPECQ} = \sum_{i=1}^{n} (C_i/\text{PEC}_i)/n \tag{3}$$

where C_i is the calculated concentration of the ith metal, PEC is the probable effect concentration of the ith metal, and the number of metals is n.

Table 1 EF classification (Birch 2003)

Enrichment factor	Status
EF < 1	No Enrichment
1 < EF < 3	Minor enrichment
3 < EF < 5	Moderate enrichment
5 < EF < 10	Moderately severe enrichment
10 < EF < 25	Severe enrichment
25 < EF < 50	Very severe enrichment
EF > 50	Extremely severe enrichment

Table 2 I_{geo} classification (Muller 1979)

I_{geo}	Status
< 0	Unpolluted
0–1	Unpolluted to moderately polluted
1–2	Moderately polluted
2–3	Moderately to strongly polluted
3–4	Strongly polluted
4–5	Strongly to very strongly polluted
> 5	Very strongly polluted

Values of mPECQ are classified in three categories: (i) mPECQ < 0.1 at which the incidence of toxicity is considered to be relatively low (< 25%) and sediment is regarded to be nontoxic; (ii) 1 < mPECQ < 5 at which sediment is predicted to be toxic with the toxicity incident of 70–75%; and (iii) mPECQ > 5 at which sediment is toxic with the probability of more than 75% (Liu et al. 2017; Farkas et al. 2007; Ingersoll et al. 2001).

Statistical analysis

To evaluate the relationship among metals in the sediments of NL, correlation analysis was employed. Correlation analysis is a means to differentiate the sources of constituents from each other (Niu et al. 2015; Noori et al. 2019). Ward's hierarchical cluster method was used to classify the sampling locations and metal concentrations based on their similarities (Bostanmaneshrad et al. 2018).

Table 3 Metal shale values in the earth's crust (Taylor and McLennan 2001)

Metals	Shale values* (μg/g)	ICP-OES Wave length	Detection limit** (μg/L)
Al	80,400	328.068	5.04
As	1.5	188.980	6.87
Cd	0.098	228.802	0.05
Co	17	228.615	2.20
Cr	85	267.716	1.10
Cu	25	324.754	1.10
Fe	35,000	259.940	1.10
Hg	0.40	435.834	22.08
Mn	600	260.568	0.06
Ni	50	231.604	1.10
Pb	16	220.353	6.12
V	110	292.401	1.1
Zn	71	334.502	1.1

*Taylor and McLennan (2001)

**Provided by the Lab

Table 4 Consensus-based sediment quality guideline values (MacDonald et al. 2000)

Metals	PEC (μg/g)	TEC (μg/g)
As	33	9.79
Cd	4.98	0.99
Cr	111	43.4
Cu	149	31.6
Pb	128	35.8
Hg	1.06	0.18
Ni	48.6	22.7
Zn	459	121

DI and DBI methods were employed to specify the optimal number of clusters. DI is an internal evaluation method in which the result is based on the clustered data. In DI, clusters are ascertained in a way that they are compact, scattered well, and have little variance between cluster members, and the means of different clusters are satisfactorily far apart in comparison to the variance within cluster. DI is calculated as follows (Dunn 1974):

$$DI = \frac{\min\limits_{1 \le i \le j \le q} d(C_i.C_j)}{\max\limits_{1 \le k \le q} \mathrm{diam}(C_k)} \tag{4}$$

where $d(C_i.\ C_j)$ is the similarity function between C_i and C_j; $\mathrm{diam}(C_k)$ is the cluster diameter which can be used as a metric to determine the diffusion and dispersion of the cluster members.

The DBI is an internal assessment method where validation takes place using features and quantities inherent to the dataset. The DBI can be calculated as follows (Davies and Bloudin 1979):

$$\mathrm{DBI} = {}^{1}/_{q} \sum_{k=1}^{q} \max_{k \neq 1} \left(\frac{\delta_k + \delta_l}{d_{kl}} \right) \tag{5}$$

where d_{kl} is the distance between the center of masses of C_k and C_l clusters and δ_k and δ_l are the compact factor of the C_k and C_l clusters.

Results and discussion

Sediment analysis

Concentrations of metals in the NL sediment are shown in Fig. 2. Point E metal concentrations preceded the order, as follows: Al > Fe > Mn > V > Cr > Pb > Cu = Zn > Ni. This order is also accurate at most of the sampling locations. The As, Cd, Co, and Hg concentrations were below the detection limit. Thus, in further analyses, they were omitted.

Since the distribution of metals in sediments is spatially auto-correlated (Kishnéet al. 2003; Hu et al. 2006), interpolation techniques such as inverse distance weighting (IDW) could help the researchers to clearly study the pollution maps regarding each element (Amini et al. 2005; Lee et al. 2006; Xie et al. 2011). In this study, the pollution distribution map for some metals in the sediments of NL was established using IDW as well (Fig. 3). The observed concentrations of metals at point A, the northern part of the NL, were at the lowest level, and at points D and C (mostly D) were at the highest level. These variations are due to a hard salt layer covering the bed of NL in the northern part so that this layer suppresses adsorption of constituents such as metals to the sediment in the lake. Meanwhile, the southern parts of NL are mostly muddy, making it easier for the constituents to get absorbed. Besides, the elevation of the northern part is higher than that of the southern part making the inlet water to flow southward carrying constituents to the muddy area of the lake (Fig. 1b). In general, the northern part of NL shows lower metal concentrations compared to the southern part.

Table S1 shows metal concentrations in the surface sediments for different lakes and reservoirs around the world. This table indicates that the concentrations of all analyzed metals in

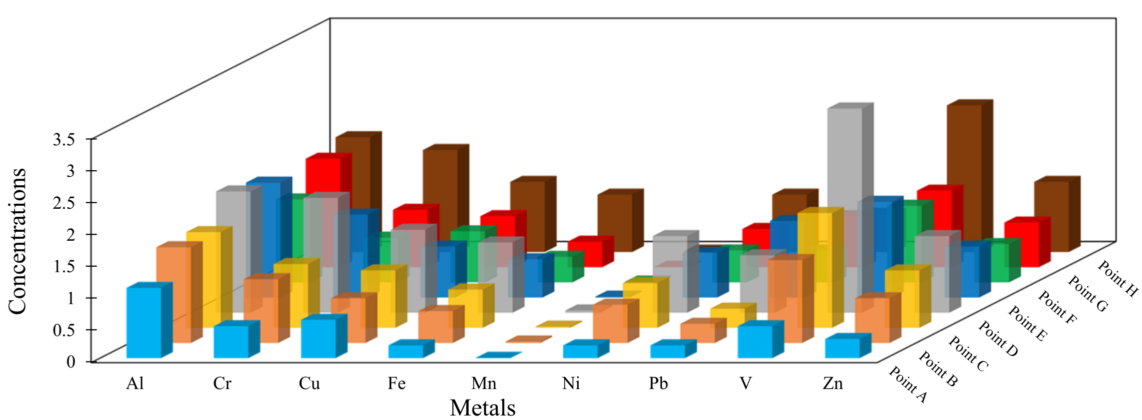

Fig. 2 Observed metal concentrations in the sediments of Namak Lake (concentrations in μg/g except for Al, Fe, and Mn in mg/g)

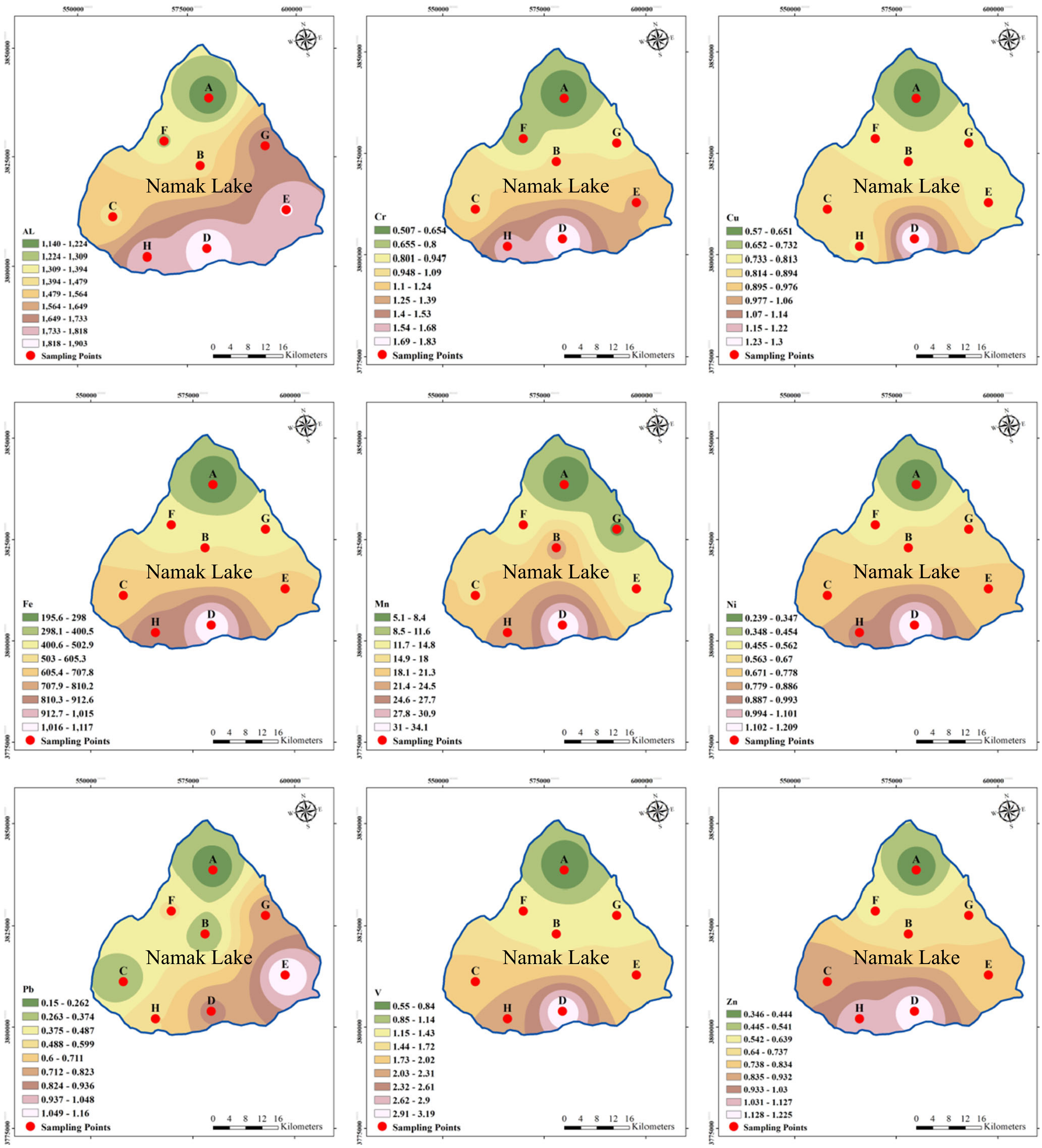

Fig. 3 Spatial distribution of some of the metals in the surface sediments of Namak Lake (concentrations in μg/g)

the NL were lower than those in the mean earth's crust provided by Taylor and McLennan (2001). Therefore, it may be concluded that metal concentrations in the surface sediments of NL are not affected by anthropogenic activities. Table S1 reveals that metal concentrations in NL are far below those values of the Rogoznica lake, Croatia (Mihelcic et al. 1996), Wadi El Natrun lake, Egypt (Taher and Soliman 1999), and Maharlu lake, Iran (Moore et al. 2009). Also, freshwater lakes and reservoirs such as Wisconsin lake, USA (Iskandar and Keeney 1974), Lake Constance, Switzerland (Muller 1977), Great Slave Lake, Canada (Allan 1979), Lake Balaton, Hungary (Nguyen et al. 2005), Bangalore urban lakes, India (Jumbe and Nandini 2009), Avsar reservoir, Turkey (Ozturk et al. 2009), Shadegan (Alhashemi et al. 2011) and Anzali,

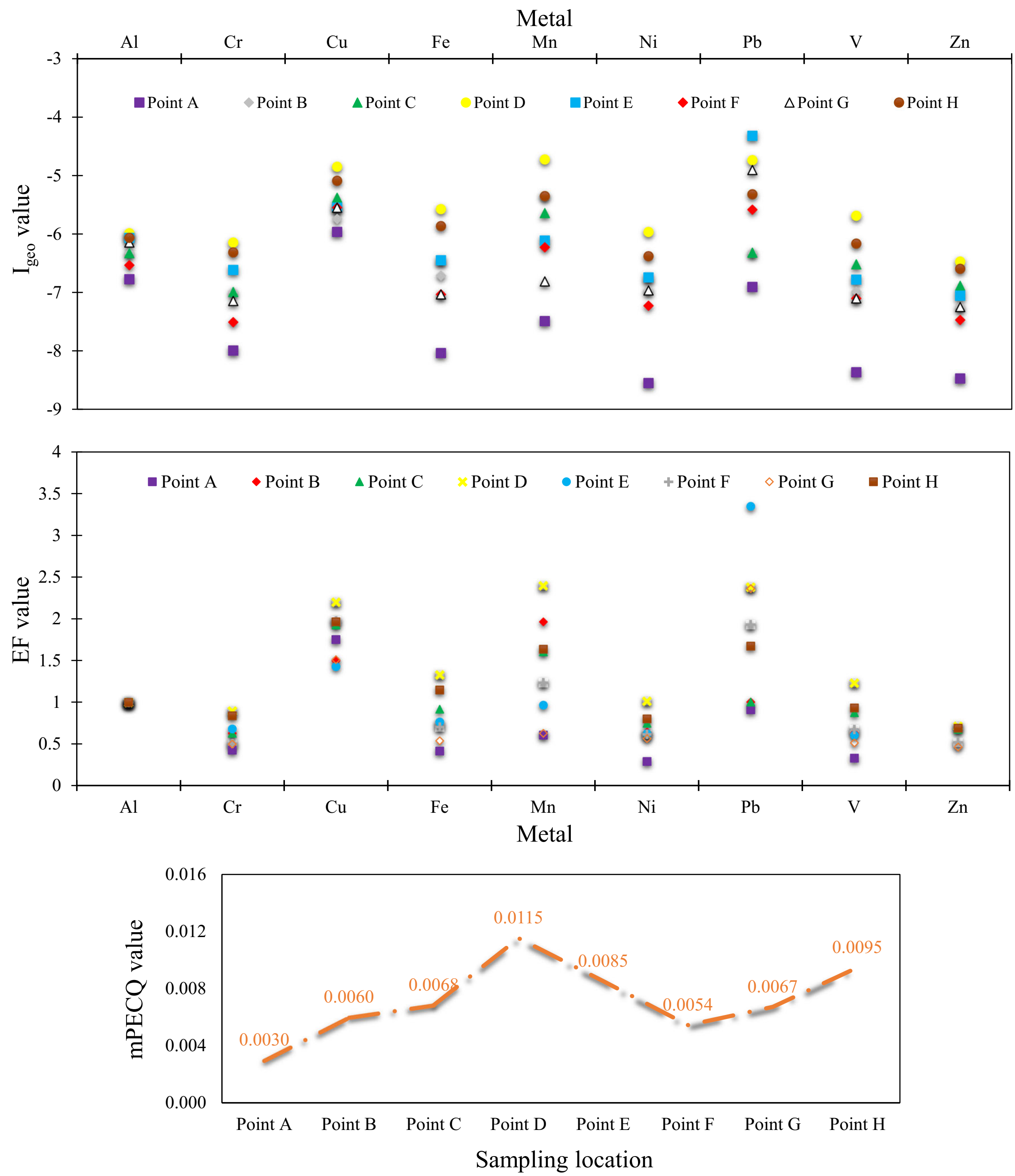

Fig. 4 The EF, I_{geo}, and mPECQ values calculated for each sampling location in Namak Lake

Iran (Jamshidi-Zanjani and Saeedi 2013), Dongting lake, China (Li et al. 2013), and Three Gorges Dam's reservoir, China (Tang et al. 2014) showed much lower metal concentrations than those of NL.

Indexing approach results

The calculated EF values are illustrated in the middle panel of Fig. 4. The As, Co, Cd, and Hg concentrations were below the limit of detection so they were omitted from the analysis. All EF values were compared with the classification suggested by Birch (2003) (Table 1). For most metals, the calculated EF values were higher at point D. The EF values for Cr, Fe, Ni, V, and Zn were almost below 1 indicating no anthropogenic enrichment for these metals in the sediments of the NL. A minor enrichment of Cu was observed at all sampling locations. For Pb, point E was at moderate enrichment status, while at other sampling locations, sediments were observed to have minor enrichment and no enrichment was observed at point A.

The calculated I_{geo} values for each metal are shown in the top panel of Fig. 4. Note that As, Cd, Co, and Hg were omitted

Table 5 Correlation analysis among metals in the bed sediment of Namak Lake

	Al	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
Al	1.00								
Cr	0.96**	1.00							
Cu	0.77	0.90*	1.00						
Fe	0.89*	0.97**	0.97**	1.00					
Mn	0.74	0.85	0.86	0.92*	1.00				
Ni	0.91*	0.98**	0.95*	0.99**	0.92*	1.00			
Pb	0.84	0.75	0.49	0.59	0.31	0.60	1.00		
V	0.84	0.94*	0.99**	0.99**	0.92*	0.99**	0.51	1.00	
Zn	0.89*	0.93*	0.92*	0.97**	0.89*	0.98**	0.55	0.97**	1.00

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

from the analysis because their concentrations were below the detection limit. Evaluation of the sediments using I_{geo} revealed that the NL was not polluted with metals.

The CBSQG values are only available for As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn (Table 4). Concentrations of As, Cd, and Hg were below the detection limit of the methodology used for the analysis. Concentrations of all the considered metals were below the TEC limit. This indicates that the concentrations of metals in the sediments of NL are not hazardous to sediment-dwelling organisms.

The mPECQ values are depicted in the bottom panel of Fig. 4. Comparing the estimated mPECQ values with the classification proposed by Ingersoll et al. (2001), it can be concluded that sediments of NL are nontoxic and the incidence of toxicity is lower than 25%. It should be noted that this conclusion is only valid for the eight metals as described before, and mPECQ does not take into account the effect of other metals in the sediment.

Statistical analysis results

Pearson correlation analysis was performed among the metals in the sediments of NL (Table 5). Metals with concentrations below the detection limit were eliminated from the analysis. The analysis showed that Al was highly correlated with Cr, indicating that their source of origin may be similar. Furthermore, Cu, Fe, Ni, and V were highly correlated with each other stating a possible common source. Since V is mostly a result of anthropogenic

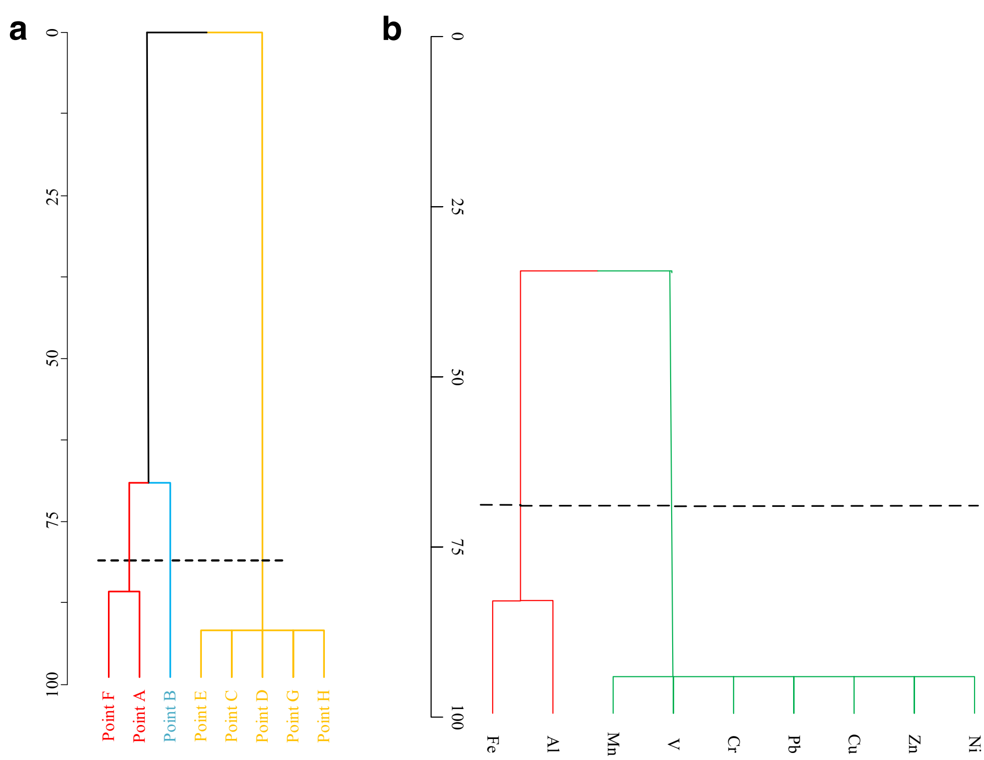

Fig. 5 Hierarchical cluster analysis results using Ward's method on sediments of the Namak Lake for **a** sampling locations and **b** metals

activities (Karbassi et al. 2009), it suggests that the source of Cu, Fe, and Ni is likely from human activities.

Ward's hierarchical cluster method was performed to analyze the similarities among metals at sampling locations in NL (Fig. 5a). The optimum number of clusters was determined according to the DI and DBI methods. The results indicated three clusters for the sampling locations as (i) A, (ii) B, and (iii) E, C, and D. It seems that the elevation variation of the lake plays an important role in the collection of metals in the sediments of NL since the sampling locations with higher elevation were classified in same clusters while lower sampling locations, i.e., points C, D, and E, appear to show similar behavior. Cluster analysis using Ward's method was also performed to classify metals in the sediments of NL and two clusters were recognized based on the DI and DBI methods (Fig. 5b). The first cluster included Al and Fe. The second cluster contained Cr, Cu, Ni, Zn, Pb, V, and Mn. It is probable that Fe was derived from lithogenic sources since it has been classified with Al in the same cluster (Karbassi et al. 2005). Since the second cluster joined the first one at a high level of correlation, the source of metals in the second cluster was probably anthropogenic activities.

Conclusions

Due to recent droughts and poor water management strategies, saline lakes such as NL are desiccating. The desiccation of saline lakes can have severe consequences for the surrounding environment since the contaminated sediments with heavy metals can spread out in the atmosphere as fine-grained dusts. An increasing concern has emerged that the desertification of NL may have severe impacts on the air quality of the surrounding cities such as Tehran, Qom, and Kashan. Nevertheless, there is little information available on the heavy metal distribution in the sediments of this lake. In this study, metal concentrations of some 13 elements were evaluated in the surface sediments of NL using inductively coupled plasma optical emission spectroscopy (ICP-OES). The pollution degree of the sediments was assessed using sediment quality guidelines and pollution indices like the EF, I_{geo}, CBSQGs, and mPECQ. Considering EF, sediments of NL were moderately enriched with Pb at the southern part of the lake. The values of I_{geo} were generally low, suggesting that the NL was not polluted with metals. The concentrations of the metals were not toxic to biota, according to the CBSQGs. The mPECQ results also suggested that the sediments were not toxic with a low probability of toxicity (less than 25%). The statistical analysis using correlation and cluster analyses shows that the northern part of the lake was different from the southern part regarding the metal concentration distributions. The lake's bathymetry at the southern part is lower than at the northern part. It seems that the pollution loads carried by the rivers tend to accumulate in the deep-water sediments in NL.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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