Potentially Toxic Elements Contamination in Sediment, Surface and Pore water of Maharlu Saline Lake, South – West Iran

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Abstract

Maharlu Lake, located in the SW of Iran, has acted as a sink for various wastewater discharges in the last few decades. This study aimed at assessing potentially toxic elements (PTEs) distribution in sediment, surface and pore water samples of Maharlu Lake. To achieve that, the samples were collected from each compartment and the total concentration of PTEs (Al, Fe, Sc, Cr, Co, Ni, Zn, As, Sb, Cu, Pb, Mn, V, Cd, and Mo) analyzed by inductively coupled plasma – optical emission spectrometry (ICP–OES). Based on enrichment factor (EF) analysis the lake sediments were categorized as: minimally enriched with Sb, Co, Zn, V, Cu, Pb, As, Mn, Fe, Al and moderately enriched with Mo, Ni, Cr, and Cd. Analysis of contamination factor (Cf) and potential ecological risk factor (Er) of PTEs in sediment samples showed that there was low to moderate level of contamination. The sediment–water partition coefficients (Kd) for PTEs in both water groups decreased in the order of Fe> Al>Mn>Zn>Pb>Mo>Sb>Cd. The low value of Kd (log Kd <2.9) for Cd, Sb, Mo, Pb, and Zn revealed that there is a potential exchange of these PTEs with the lake's water column if the physicochemical condition of lake changes.

Keywords: *Pore Water; Potentially Toxic Elements; Maharlu Lake; Sediment Contamination; Partition Coefficient.*

Introduction

In recent years the accumulation of contaminants in aquatic systems has been regarded one major quality issue in fast–growing cities due to the fact that, the protection of water quality and sanitation substructures have not improved along with population and urbanization growth (Ideriah *et al.,* 2012; Geo *et al.,* 2015). Each aquatic system is constructed by three compartments (sediment, surface water and pore water) (Carling *et al.,* 2013). Sediments act as a sink and in turn it probably acts as a source of contaminants (Rai, 2009). Indeed, transported contaminants into an aquatic system through surface water are mainly immobilized by binding to humic acids, clay minerals, oxides coated with organic matter and sulfide precipitation (Cheng *et al.,* 2015), and they may acquire toxic features to aquatic organisms when threshold concentrations are reached. Most adsorbed contaminants on the sediments are not bioavailable but some mechanisms may induce their release back to the pore water and then to the water column, including bioturbation, sediment re–suspension, desorption, redox reactions or (bio–)degradation of the adsorptive particles (Khaled *et al.,* 2017). Desorption of contaminants is a long–term problem and may continue even after contamination sources are eliminated (Ramamoorthy & Rust, 1978). Pore water acts as a "transfer bridge" between sediment and surface water, and plays important geochemical and ecological role in contaminants cycling in an aquatic system (Escher & Hermens, 2004). The fraction of contaminants in pore water is considered to be more bioavailable than the sedimentary fraction (Harmsen, 2007) and poses a risk to ecosystem and human health due to uptake by living organisms and its entrance into the food chain (Iqbal & Shah, 2014). Due to many advantages in term of simplicity and costs, direct measurement of the composition of pore water to assess the bioavailability and desorption of contaminants has been progressively applied (Beesley *et al.,* 2010; Moreno–Jimenez *et al.,* 2011; Shaheen *et al.,* 2014). Despite increasing recognition of the importance of pore water, there is no available research to determine the concentration of PTEs on this compartment in Maharlu Lake and previous investigations have been focused on total concentrations of PTEs in sediment and surface water (Forghani *et al.,* 2012; Moore *et al.,* 2009). Therefore, this research was carried out to: 1) investigate the abundance and spatial distribution of the PTEs in the coastal sediments, surface water and pore water of Maharlu Lake, 2) determine the potential sources, the degree of contamination and the potential ecological risk of PTEs in the coastal sediments, and 3) reveal possible relation between PTEs concentrations in sediment, surface water, and pore water.

Materials and Methods

Study area

Maharlu Lake is a saline depression 23 km southeast of Shiraz city between latitudes 29' 17◦ to 29' 33◦ N and longitudes 52' 42◦ to 52' 59◦ E. The mean length and width of the lake is 31 and 11 km, respectively and encompasses an area of about 250 km². Maharlu Lake is an ephemeral lake in the semi–arid catchment area with a mean annual rainfall of 334 mm (Tajabadi *et al.,* 2017). Geological formations surrounding the lake comprise Cenozoic formations (including: shale–marl, carbonate, silty marl, sandstone, silty limestone and limy conglomerate) and recent (alluvium) deposits (Forghani *et al.,* 2009) (Fig. 1). The high salinity of the lake's water is due to the existence of Late Proterozoic salt domes in the lake's catchment area. The bed rock of the lake is underlain by silty limestone and silty marl from the Oligo–Miocene age (Forghani *et al.,* 2012).

No permanent river flows into the Maharlu Lake. There are three seasonal rivers in the catchment area namely, Khoshk, Soltan–Abad, and Nazar–Abad Rivers. Khoshk River, originates from peaks North –West of Shiraz city. This river flows from North–West towards South–East and finally drains into the Maharlu Lake. Soltan–Abad River, originates from heights in the South–West, South, and South– East of Shiraz where tributaries join together and form Soltan–Abad River (Karami & Bahmani, 2008). These two rivers pass inside Shiraz city through which direct urban sewage and industrial wastewater, pours into the lake (Forghani *et al.,* 2009; Moore *et al.,* 2009; Qishlaqi *et al.,* 2008). Nazar–Abad River originates from Meyan Jangal heights South–East of Maharlu Lake. Nazar–Abad River flows from South–East towards the north–west. This river does not receive significant urban contamination load (Karami & Bahmani, 2008) but guides agricultural runoff from Sarvestan plain into the lake. Due to climate changes in recent years, seasonal flows are at rare and wastewater is the dominant input into the Lake.

Sampling

To achieve the research objectives, sediment, surface and pore water samples were collected at seven stations (S1 to S7) encompassing the lake in April (the wet season) 2016 (Fig. 1). Accessibility to some areas was limited due to the marshy condition, so sampling was done in accessible areas. Redox potential is a vital factor to determine the concentration of PTEs in pore water. In the oxidizing process, the concentration of most PTEs in pore water increases by oxidation of insoluble sulfides precipitation (Allen & Deng, 1993). The common procedure for pore water extraction involves centrifugation (Edmunds & Bath, 1976).
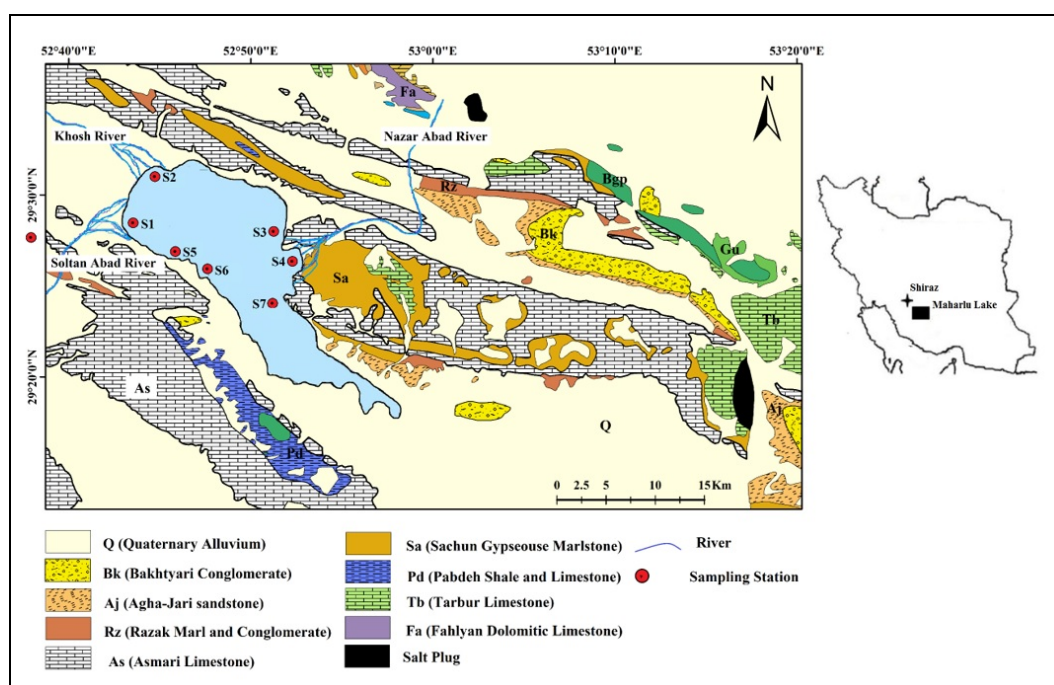

Figure 1. Geological and location of sampling stations in Maharlu Lake

Nevertheless, this method does not adequately consider the redox condition of the sediment and the oxidation of sulfides during extraction (Doyle *et al.,* 2003). To minimize the effects of this process, 10 sediment subsamples were collected from each station at 20 cm depth using a 63 mm diameter split tube sampler. This split tube sampler was used to avoid surface and pore water mixing. Furthermore, to prevent imbalance between phases, subsamples were stored in sealed, labeled clean zip–mouthed polyvinylchloride packages and kept cool (4°C) until analysis in the laboratory. In the laboratory, pore water was extracted by centrifugation in polyethylene tubes for 30 min at 3000 rpm. The supernatant pore water was re–centrifuged for an excessive 15 min to eliminate excess particulates. Extracted pore waters of subsamples were combined, and were stored in polyethylene containers in the dark at 4°C afterwards.

Instrumental analysis
Sediment subsamples were dried at room temperature, in a controlled ventilated clean setting. Then, were mildly crushed an agate mortar and to pestle break up aggregates. Then, sieves were used to divide the needed sediment fractions (diameter ≤ 2 mm for physicochemical parameters analysis and diameter ≤ 63 μm for chemical analysis). Separated fractions from each subsample were mixed and stored until chemical analysis. Textural characteristics of sediment samples were determined using hydrometer method (Gee & Bauder, 1986). Statistical characterization of textural parameters was carried out using Folk's 1954 formula. PH was measured through balance with a homogeneous suspension of 10 g of sediment sample in 50 ml of distilled water after 5 min shaking and 1–hour pause. The pH of the unfiltered suspension was measured electrochemically utilizing a glass electrode (Singh *et al.,* 2005). The filtered suspension was used to demonstrate electrical conductivity (EC) of the sediment samples by applying a conductivity cell. Organic matters content in the sediment samples was measured using loss on ignition method (Heiri *et al.,* 2001). Cation exchange capacity (CEC) was measured by sodium acetate solution, replacement of the absorbed sodium by ammonium, and designation of replacing sodium by atomic absorption spectrometry. Total element concentrations in sediments were carried out using an acid digestion mixture (HF+HClO4+HNO3) in an open system.

Summarily, 1 g of sediment was treated with 10 ml HF and 2 ml HClO4 and heated on a hot plate up to dryness. The residue was further treated firstly with 5 ml HClO4 and then with 5 ml HNO3 and heated up to dryness. The residue was ultimately dissolved in 1:1 HCl. Resulting solutions were analyzed for selected elements (Al, Fe, Sc, Cr, Co, Ni, Zn, As, Sb, Cu, Pb, Mn, V, Cd and Mo) using ICP–OES. Surface water was sampled at the same time as sediment samples using acid washed polyethylene bottles. Samples were filtered using a vacuum pump with 0.45 μm pore diameter membrane filters immediately after collection. A split of samples was acidified with HNO3 for dissolved PTEs measurement and the second unacidified fraction was used for determination of dissolved ions. All collected samples were kept cool (4°C) to reduce the activity and metabolism of probable microorganisms. PH and EC of surface water samples were measured in–situ, using a waterproof Eutech portable meter (model PCD650). Bicarbonate and carbonate were analyzed by titration with 0.25 N H2SO4 in the presence of methyl orange as an indicator. Chlorine was analyzed by titration with 0.25 N AgNO3 in the presence of potassium bichromate as an indicator. Sulfate concentration was determined by turbidimetry. Na, Mg and K measured by flame atomic absorption spectroscopy and Al, Fe, Sc, Cr, Co, Ni, Zn, As, Sb, Cu, Pb, Mn, V, Cd, and Mo were measured by inductively coupled plasma optical emission spectrometry (ICP–OES). All the steps were repeated on extracted pore water. The ICP–OES method (JY 2000) for element analysis was chosen because of the very high salinity of Maharlu Lake water. High salinity can affect element concentration during analysis by inductively coupled plasma mass spectrometry (ICP–MS) (Batley & Simpson, 2016). Measurements accuracy and precision were controlled using SPEX Certi Prep standards (manufactured under UL ISO 9001 Quality Assurance System). Also, replicate measurements of elements in each sample were carried out and the mean concentrations were reported.

Assessment of PTEs contamination level in sediment
In order to evaluate impacted sediment with PTEs the enrichment factor (EF) was calculated (Ho *et al.,* 2010), using the following equation :

$$EF=(\frac{C_X}{C_{Sc}})_s /(\frac{C_X}{C_{Sc}})_c \qquad (1)$$

where C_X and C_{Sc} refer to the concentration of

element X and Sc in the sediment samples (s) and global standard shale values (c), respectively. Sc was selected because it is a major component of the Earth's crust and shows low variability in concentration. Enrichment factor classes are presented in Table S1.

In addition to EF, the modified degree of contamination (mC_d) as a multi–element pollution index was used to assess the sediment contamination degree with the following equation (Duodu *et al.*, 2016) :

$$mC_d = \frac{1}{n} \sum_{i=1}^{n} C_f^i . \text{ where } C_f^i = \frac{C_x^i}{C_{ref}^i} \quad (2)$$

where C_x^i is the element concentration in sediment; C_{ref}^i the reference value of the element and C_f^i the contamination factor of each element (Brady *et al.*, 2015). The classification of the modified degree of contamination (mC_d) in the sediment is depicted in Table S1.

Potential ecological risk index
The potential ecological risk index (PERI) determines the sensitivity of local ecosystem to the PTEs and represents ecological risk resulting from the overall contamination. The equations to calculate PERI were proposed by Hakanson (Hakanson, 1980) which as:

$$C_f = \frac{C_s}{C_n} \quad (3)$$

$$E_r = T_r \times C_f \quad (4)$$

$$RI = \sum_{i=r}^{m} E_r \quad (5)$$

where RI is the sum of all risk factors for the specific element in sediments, E_r is the ecological risk for individual PTEs or potential risk factor, T_r is toxic response factor which for the analyzed PTEs is taken as $Zn = 1 < Cr = 2 < Cu = Ni = Pb = 5 < As = 10 < Cd = 30$ (Hakanson, 1980), C_f is the contamination coefficient, C_s represents element content in sediment, and C_n is the regional background value for element. Different E_r and RI classifications are presented in Table S1. Sediment quality guidelines (SQGs) such as effects range–low (ERL) and threshold effect level (TEL) refer to the concentrations below which harmful effects upon sediment dwelling fauna are implausible. In contrast, harmful effects are more plausible to occur when metal concentrations are higher than effect range medium (ERM) and probable effect level (PEL) (Long *et al.*, 1995). Table 2 shows standard pollution criteria of the PTE matrix. Furthermore, the mean PEL quotient was used to estimate the potential risk of combined element groups in Maharlu Lake. The formula was applied as follows (Long *et al.*, 2000):

$$\text{mean PEL quotient} = \sum (C_x / PEL_x) / n \quad (6)$$

where C_x refers to the concentration of element X in the sediment samples, PEL_x is probable effect level for element X and n is the number of elements. The PEL values of As, Cd, Cr, Cu, Ni, Pb and Zn are presented in Table 2.

Table S1. The grades of sediments quality and risk assessment methods

EF[a]		C_i^f		mC_d[c]		E_r[b]		PERI[b]	
EF value	Pollution level	C_i^f value	Pollution level	mC_d value	Pollution level	E_r value	Risk level	PERI value	Risk level
EF<2	Minor	C_i^f <1	Low	mC_d < 1.5	Nil to very low	E_r < 40	Low risk	RI < 150	Low
2≤EF <5	Moderate	1≤ C_i^f <3	Moderate	1.5 ≤ mC_d< 2	Low	40 ≤ E_r <80	Moderate risk	150 ≤ RI < 300	Moderate
5≤EF <20	Severe	3≤ C_i^f <6	Considerable	2 ≤ mC_d < 4	Moderate	80 ≤ E_r <160	Considerable risk	300 ≤ RI < 600	Considerable
20≤EF<40	Very severe	C_i^f ≥ 6	Very high	4 ≤ mC_d < 8	High	160 ≤ E_r <320	High risk	RI ≥ 600	Very high
EF≥40	Extremely severe			8 ≤ mC_d < 16	Very high	E_r ≥ 320	Very high risk		
				16 ≤ mC_d<32	Extremely high				

[a] According to (Sutherland, 2000)
[b] According to (Hakanson, 1980)
[c] According to (Abrahim & Parker., 2008)

Based on the classification of possibilities of acute toxicity in sediments, mean PEL quotients of< 0.1, 0.11–1.5, 1.5–2.3, and > 2.3 have an 8, 21, 49, and 73% incidence of adverse biological effects, respectively (Long *et al.*, 2000).

Partition coefficient (K_d) of PTEs
Desorption is a long–term process and may be posing even after elimination of sources of pollution (Ramamoorthy & Rust, 1978). The calculation of partition coefficient is the most common method of determining the amount of contaminant retardation from sediment to water (Gormley–Gallagher *et al.,* 2015) that is widely used in waste management plans (USEPA, 2012). The K_d was calculated using below formula (Jung *et al.,* 2005):

$$K_d = \log\left(\frac{C_{Sed}}{C_w}\right) \tag{7}$$

where K_d is the coefficient of partition; C_{Sed} and C_w are the element concentrations determined in sediments and water, respectively. A high value of K_d (log $K_d > 2.9$) underlines that the element has low solubility and is preferentially sediment–associated while a low value (log $K_d < 2.9$) means that the element has high solubility and is less sediment–associated (Jung *et al.,* 2005).

Statistical analysis
In this study, Shapiro –Wilk and Kolmogorov–Smirnov tests indicated that PTEs concentrations in sediment samples were non–normally distributed (significance level was considered at P value ≤ 0.05). Therefore, Spearman's correlation coefficient analysis and cluster analysis (CA) were performed to identify the relationships among PTEs in sediments of Maharlu Lake and their possible sources. This was done using SPSS software version 19.0 for Windows. In the statistical analysis, concentrations lower than the detection limit were presumed to be equal to 0.75 of the detection limit.

Results and Discussion
Sediment assessment
Physicochemical characteristics of sediments
The physicochemical characteristics of sediments are summarized in Table 1. Based on the USDA textural classification sediments texture are classified as sand–silt–clay and clayey sand (mean contents: clay 25.32%, silt 31.77%, and sand 49.90%) (Fig. S1). The maximum value of clay content (33.04 %) occurs in S2 station. pH ranged from 8.15 to 8.84, indicating the alkaline nature of the sediments while $CaCO_3$ content in sediments ranged from 10.07 to 22.04 % averaging 17.45 %, which reflects the calcareous nature of the surrounding geological formations and soil. Organic matter content of Maharlu Lake sediments varied between 17.28 and 18.61% with an average of 17.94%. Maximum organic matters content occurred in S7 station due to discharging of urban wastewater and inflow of agricultural runoff from Sarvestan plain (Fig. 2a). CEC ranged from 31.31 to 40.41 meq 100 g^{-1}, and EC varied from 74.03 to 120.90 mS cm^{-1}. The maximum value of EC occurred in S2 station (Fig. 2b).
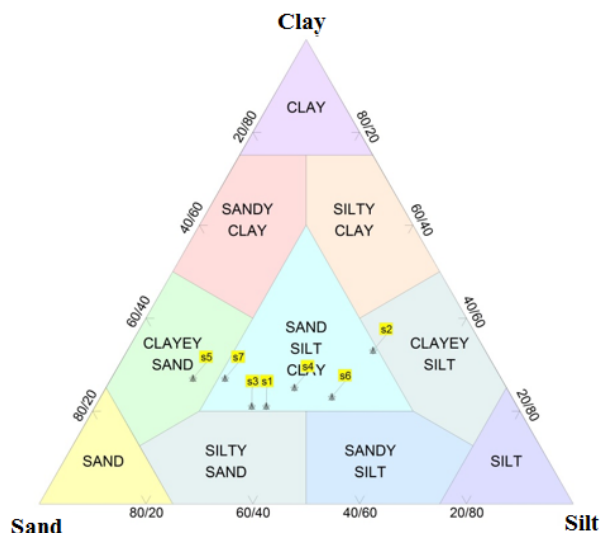

Figure S1. Textural triangle of sediment samples
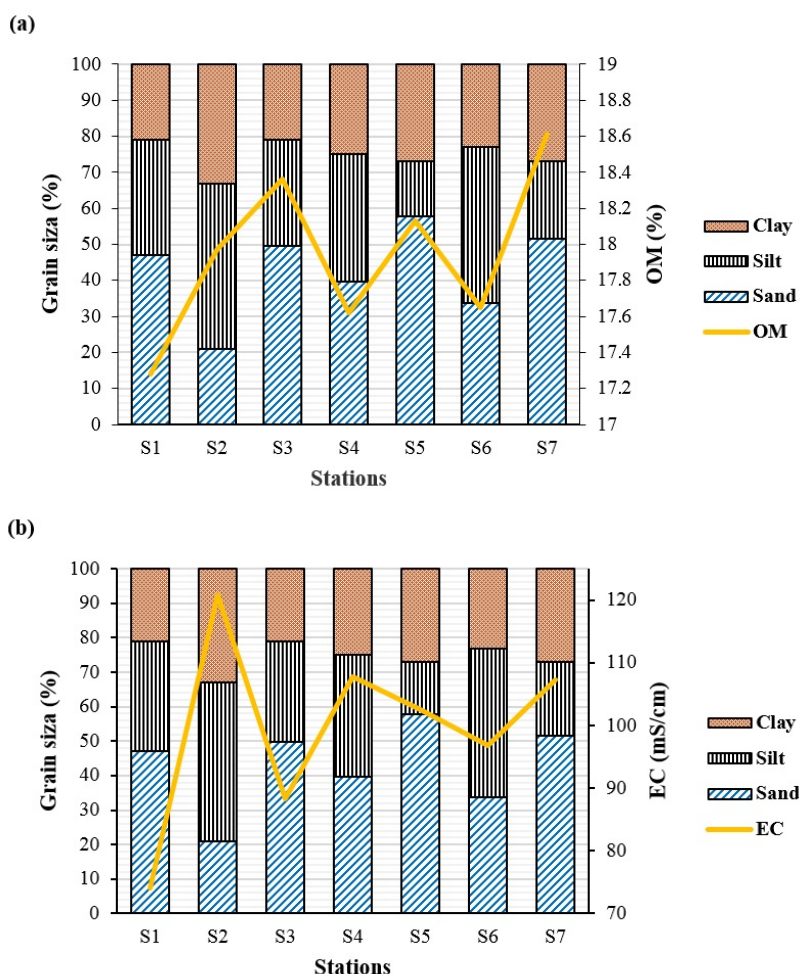
(a)

(b)

Figure 2. Grain size, a) OM and b) EC distributions of Maharlu Lake sediments

PTE contamination and its risk assessment in sediments

Table 1 summarizes PTEs concentrations in Maharlu Lake sediments. Average concentrations of Al and Fe in sediments of the lake are less than continental crust, world shale's and the average of global sediments, most likely due to their leaching during weathering (Delshab *et al.,* 2017) (Table 2). Average concentrations of Sc, Mn, Zn, Pb, and Co were lower than those of upper continental crust and Earth's shale. Also, average concentrations of Ni, Cr, V, and Mo were higher than those of upper continental crust and Earth's shale. The maximum concentration of Ni (156 mg kg $^{-1}$) and Cr (181 mg kg $^{-1}$) occurred in S2 and S3 stations, respectively. S2 station also displayed the highest concentrations of Al, Fe, Sc, As, Ni, Cu, Pb, Co, and Zn (Table 1). This station represents the Khoshk River inflow to the Maharlu lake. Molybdenum exhibited the highest

level in S7 station. Calculated EF values of Maharlu Lake sediments are shown in Fig. 3a. The median values of EF in study area sediments yield the following decreasing trend: Ni > Mo > Cd > Cr > Co > Sb > As > Cu > Zn= V > Mn > Fe > Pb > Al.

Following Sutherland classification (Sutherland, 2000), samples of Maharlu Lake sediment can be categorized as: minor enriched with Sb, Co, Zn, V, Cu, Pb, As, Mn, Fe, and Al and moderately enriched with Mo, Ni, Cr and Cd. Severe contamination level occurs for Mo in S5 (8.12) and S7 (6.78) stations and Cd in S5 (5.17). The results of C_f and mC_d calculations (Table S2) indicated that C_f values of elements in all stations were mostly within the range of low to moderate contamination (C_f <1 and 1< C_f <3, respectively) (Fig. 3b) and demonstrated nil to very low degree of contamination (mC_d<1.5). The highest contaminations occurred at station S2 (Table S2), which are the site for wastewater discharges.

Table 1. Physicochemical characteristics and PTEs concentrations of Maharlu Lake sediments

Parameters	DL[a]	Min	Max	Mean	SD[b]	UCC[c]	WS[d]	Shale[e]
Sand (%)	–	20.96	57.68	42.90	12.48	–	–	–
Silt (%)	–	15.00	46.00	31.77	11.07	–	–	–
Clay (%)	–	21.04	33.04	25.32	4.23	–	–	–
OM (%)	–	17.28	18.61	17.94	3.08	–	–	–
CaCO$_3$ (%)	–	10.07	22.04	17.45	0.45	–	–	–
CEC(meq 100g^{-1})	–	31.31	40.41	33.89	4.03	–	–	–
EC(mS cm^{-1})	–	74.03	120.90	99.68	15.15	–	–	–
pH	–	8.15	8.84	8.41	0.26	–	–	–
Al (mg kg^{-1})	100	12269	35662	21541	7715	77400	72000	88000
Fe (mg kg^{-1})	100	8084	23994	14521	5297	30900	41000	48000
Sc (mg kg^{-1})	0.5	3.000	8.700	5.271	1.984	7.000	10.000	13.000
Mn (mg kg^{-1})	5	131.000	487.000	302.714	146.700	527.000	770.000	870.000
Ni (mg kg^{-1})	1	52.000	156.000	98.857	41.715	18.600	52.000	68.000
Cr (mg kg^{-1})	0.05	49.000	181.000	97.714	49.503	35.000	72.000	90.000
V (mg kg^{-1})	1	28.000	66.000	45.142	12.361	53.000	105.000	130.000
Zn (mg kg^{-1})	1	17.000	64.000	40.142	15.920	52.000	95.000	95.000
Cu (mg kg^{-1})	1	10.00	25.000	16.000	4.472	14.300	33.000	39.000
Pb (mg kg^{-1})	1	6.000	11.000	7.428	1.618	17.000	19.000	23.000
Co (mg kg^{-1})	1	5.000	15.000	10.142	4.099	11.600	14.000	19.000
As (mg kg^{-1})	0.5	3.200	7.800	4.900	1.488	2.000	7.700	13.000
Mo (mg kg^{-1})	0.5	2.040	7.730	3.865	1.923	1.400	2.000	2.600
Cd (mg kg^{-1})	0.1	0.270	0.360	0.295	0.031	0.102	0.170	0.300
Sb (mg kg^{-1})	0.5	0.660	0.740	0.704	0.026	0.3100	1.200	1.500

[a]Detection limit.
[b]S.D = Standard deviation.
[c]Average contents in the upper continental crust (Wedepohl, 1995).
[d]Average contents in the global sediment (Bowen, 1979).
[e]Average contents in the Earth's shale (Turekian and Wedepohl, 1961).

Table 2. Effect range low (ERL), effect range median (ERM), threshold effect level (TEL) and probable effect level (PEL) values of PTEs in sediment (Long et al. 1995)

	As	Cd	Cr	Cu	Ni	Pb	Zn
Average concentration (This study)	4.900	0.295	97.714	16.000	98.857	7.428	40.142
ERL	8.2	1.2	81	34	20.9	46.7	150
ERM	70	9.6	370	270	51.6	218	410
TEL	7.24	124	52.3	18.7	15.9	30.2	124
PEL	41.6	4.21	160	108	42.8	112	271

Table S2. Contamination C$_f$ and modified degree of contamination (mC$_d$) of Maharlu Lake sediments

Station	C$_f$							mC$_d$	
	As	Cd	Cr	Cu	Ni	Pb	Zn		
S1	0.32	0.90	0.60	0.41	0.78	0.30	0.61	0.56	Low
S2	0.60	0.97	1.46	0.64	2.29	0.48	0.67	1.02	Low
S3	0.33	0.97	2.01	0.38	1.99	0.30	0.38	0.91	Low
S4	0.33	0.93	1.36	0.41	1.85	0.30	0.40	0.80	Low
S5	0.25	1.03	0.54	0.26	0.76	0.30	0.18	0.47	Low
S6	0.38	1.20	0.62	0.38	1.03	0.30	0.36	0.61	Low
S7	0.44	0.90	1.01	0.38	1.47	0.26	0.36	0.69	Low

Table 2 compares our findings to the reference values established in different SQGs. Average concentrations of As, Cu, Pb, Cd, and Zn were below the sediments quality guidelines but average concentration of Ni was above that. The highest value of Ni occurred in S2 station. The results showed that at all stations Cr concentration was above the TEL guideline (expect S5). As shown in Fig. 4, mean PEL quotients varied from 0.26–0.75 with a mean of 0.1–1.5. This underlines that a combination of the seven studied PTEs had a 21% incidence of adverse biological effects. The results of ecological risk assessment of toxic PTEs in Maharlu Lake sediments are outlined in Table S1. The average risk indices (E$_r$) of PTEs were ranked in the order of Cd>Ni>Cr>As>Cu>Pb>Zn. PERI

values for all PTEs in sampling stations were below 40, indicating that the analyzed PTEs bear low ecological risk in the study area. The maximum potential ecological risk (PERI=59.67) occurred in S2 station.
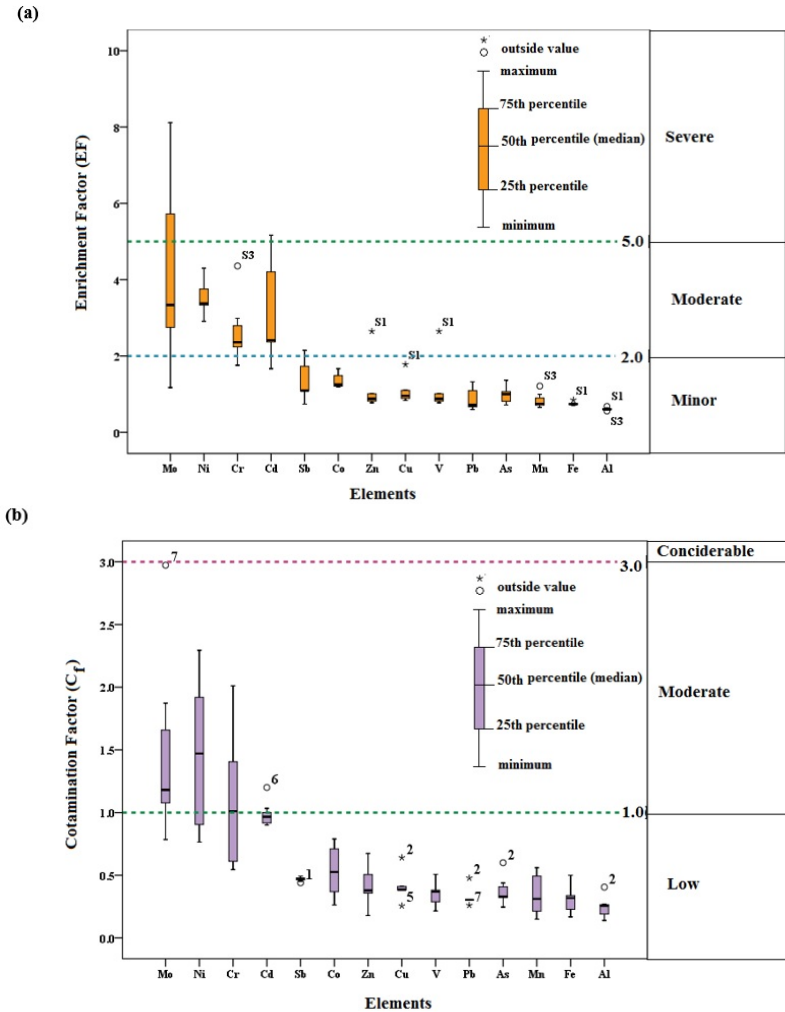

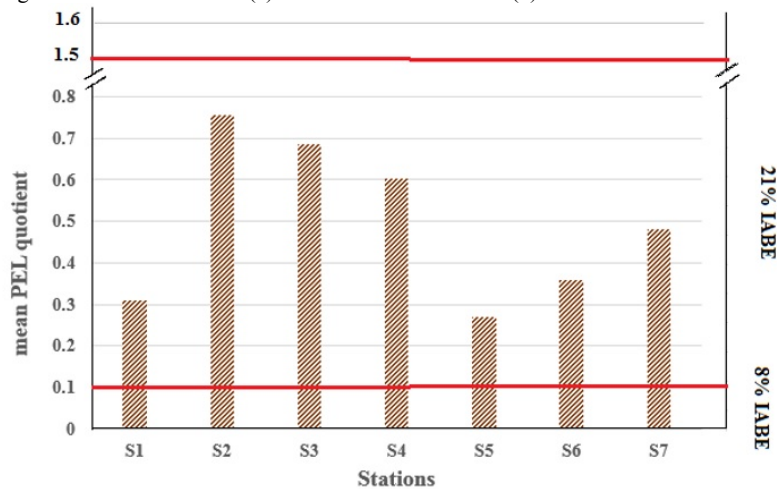Figure 3. PTEs enrichment (a) and contamination factor (b) in Maharlu Lake sediments

Figure 4. Spatial distribution of mean PEL quotient values in sediments of Maharlu Lake, Incidence of adverse

Spearman correlation for PTEs in sediment

The Spearman correlation coefficients of PTEs in sediment are summarized in Table 3. It was done between PTE concentrations to assess possible similar sources. A strong positive correlation was found between a group of elements comprising Al, As, Co, Cr, Fe, Mn, Ni, V, Ni, and Sc. Common lithogenic elements such as Al, Fe, and Sc were observed in this group and confirmed that these elements probably originated from the same geogenic sources (Omwene *et al.,* 2018; Delshab *et al.,* 2017). Also, Salati & Moore (2010) reported that high concentration of Ni, Mn and Sc in Khoshk River sediment samples as one of the main inputs of Maharlu Lake, reflected the geochemical composition of parent rocks. On the other hand, Forghani *et al.,* (2012) confirmed that the high concentration of Cr and Fe in sediment samples of Maharlu lake originated from natural sources.

Similarly, the strong positive inter–relationship was observed among Cu and Zn (r>0.9, P<0.01), and also between Cd and Sb (r>0.8, P<0.05). These strong correlation coefficients indicate the common input sources of these PTEs (Mishra *et al.,* 2015). Furthermore, Mo showed a significant negative correlation (r<–0.8) with Pb, Zn, and Cu. It presumably illustrates that the geochemical behavior of Mo is different from them. Forghani *et al.,* (2012) reported anthropogenic pollution source for Cd and Pb in the study area.

Cluster analysis

Cluster analysis (CA) was performed to identify similar groups of stations in Maharlu Lake sediments based on PTEs concentration. For this, data were classified using Ward linkage (between groups) method. The distance measure used in CA was squared Euclidean distance. The result of CA is illustrated in the hierarchical dendrogram (Fig. 5), which classified the 7 stations into three major groups (distance 25). The first group included S3, S4, and S7 stations, second group S5, S1 and S6 stations and the third group S2 station. These three groups were related to three main inputs discharging anthropogenic contaminants into the lake including Nazar–Abad, Soltan–Abad and Khoshk Rivers, respectively, which were different in terms of the total concentration of PTEs. The mean total concentration of PTEs for Nazar–Abad, Soltan–Abad and Khoshk Rivers were equal to 39790.180, 25618.330 and 60600.840 mg kg $^{-1}$, respectively. Thus, similar to previous findings (Forghani *et al.,* 2009, 2012; Moore *et al.,* 2006), Khoshk River which flows through Shiraz city and enters the lake on the northwestern end of the lake is a major source of pollution because transports a large amount of industrial and municipal effluents from surrounding areas.

Geochemical characterization of surface and pore water samples

Analytical results of the geochemical characterization of surface and pore water of Maharlu Lake samples are given in Table 4.

Table 3. Spearman's correlation coefficients among PTEs concentrations in Maharlu Lake sediments

	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sb	Sc	V	Zn
Al	1														
As	.793*	1													
Cd	−.255	−.046	1												
Co	.883**	.691	−.009	1											
Cr	.786*	.577	−.091	.955**	1										
Cu	.674	.444	−.410	.500	.430	1									
Fe	.964**	.703	−.145	.955**	.893**	.674	1								
Mn	.786*	.577	−.091	.955**	1**	.430	.893**	1							
Mo	−.432	−.209	.028	−.355	−.270	−.887**	−.505	−.270	1						
Ni	.893**	.703	−.091	.991**	.964**	.580	.964**	.964**	−.414	1					
Pb	.267	.135	.408	.405	.267	.560	.401	.267	−.809*	.401	1				
Sb	.037	.150	.849*	.318	.334	−.291	.185	.334	.019	.259	.277	1			
Sc	.883**	.691	−.009	1**	.955**	.500	.955**	.955**	−.355	.991**	.405	.318	1		
V	.964**	.883**	−.309	.847*	.750	.580	.893**	.750	−.270	.857*	.134	−.037	.847*	1	
Zn	.577	.327	−.413	.509	.487	.963**	.631	.487	−.873*	.595	.607	−.280	.509	.487	1

*. Correlation is significant at the 0.05 level (2–tailed).
**. Correlation is significant at the 0.01 level (2–tailed).

Table 4. Geochemical characterization and PTEs concentration of of Maharlu Lake surface and pore water (ND = Non–Detection)

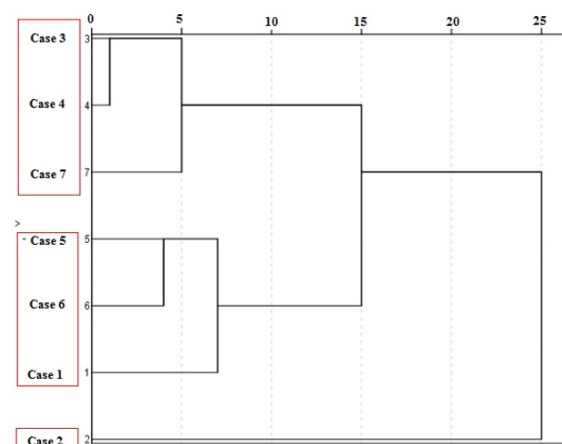| Parameter	DL[a]	Surface water				Pore water			
		Min	Max	Mean	S.D[b]	Min	Max	Mean	S.D[b]
Ca^{2+} (mg l^{-1})		832	1753	1435	344	1503	2805	1993	451
Mg^{2+} (mg l^{-1})		7778	86435	23629	28354	5165	20805	11138	6574
Na^{+} (mg l^{-1})		147351	161480	154912	5802	104962	177628	144754	24960
K^{+} (mg l^{-1})		972	2268	1339	534	942	1418	1156	144
HCO_3^{-} (mg l^{-1})		244	671	397	175	244	763	423	189
SO_4^{2-} (mg l^{-1})		7205	14410	10752	2617	7205	13449	11699	2191
Cl^{-} (mg l^{-1})		194990	222466	204623	8459	177263	194990	188026	6192
pH		6.94	7.35	7.18	0.13	7.14	7.71	7.56	0.19
TDS (g l^{-1})		371.03	406.52	386.27	15.26	326.34	359.46	359.35	25.76
EC (mS cm^{-1})		468.62	497.168	476.17	10.83	381.34	482.99	454.01	36.31
Al (mg kg^{-1})	0.1	ND	0.44	0.18	0.14	0.14	2.79	0.92	1.15
Fe (mg kg^{-1})	0.1	ND	0.18	0.09	0.03	ND	0.82	0.28	0.34
Mn (mg kg^{-1})	0.1	ND	0.61	0.17	0.19	0.1	0.84	0.39	0.26
Zn (mg kg^{-1})	0.05	ND	0.11	0.06	0.027	0.12	0.22	0.15	0.35
Pb (mg kg^{-1})	0.05	ND	0.62	0.06	0.019	ND	0.08	0.05	0.016
Mo (mg kg^{-1})	0.05	ND	ND	ND	–	ND	0.6	0.22	0.182
Cd (mg kg^{-1})	0.05	ND	0.08	0.05	0.016	0.05	0.12	0.08	0.03
Sb (mg kg^{-1})	0.05	ND	0.06	0.04	0.008	ND	0.08	0.05	0.017

[a]Detection limit.
[b]S.D = Standard deviation.

Figure 5. Hierarchical dendrogram for PTEs sampling stations

The average pH values of surface and pore water were 7.18 and 7.56 respectively. The pH values of water samples were less than sediment samples (8.41). Total dissolved solids (TDS) of surface water samples ranged from 371.03 g l^{-1} to 406.52 g l^{-1}, averaging 386.27 g l^{-1}. TDS of pore water samples ranged from 326.34 g l^{-1} to 356.46 g l^{-1}, and averaging 359.35 g l^{-1}. High TDS values reflect drought, high evaporation rate and evaporative formation and salt domes in the studied area.

Average EC for surface and pore water were 476.17 and 454.01 mS cm^{-1}, respectively. Maximum values of EC in both sample groups occurred in S2 station. The relative concentrations of the cations and anions in the surface and pore water displayed the following decreasing trend: $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ and $Cl^- > SO_4^{2-} > HCO^{3-}$. The overall major element chemistry of surface and pore water samples is depicted in the Durov diagram of Fig. S2. In terms of descriptive hydrochemical faces, surface and pore water samples are Na–Cl type. The concentration of PTEs in surface and pore water are outlined in Table 4. Generally, the concentration of PTEs in surface and pore water due to some processes such as adsorption and precipitation were lower than sediments (Liu *et al.,* 1999). In this study, high pH along with the presence of organic matter and clay, promotes adsorption and precipitation of PTEs by sediments (Guven & Akinci, 2013). The concentration of Sc, Ni, Cr, V, Cu, Co, and As in two sample groups of water and concentrations of Fe, Sb, and Mo in surface water samples were below the detection limit. Average concentrations of Pb and Sb in both sample groups were roughly equal (0.05 mg l^{-1}). It must be notified that the concentration of these two PTEs in

half of the stations were below detection limit. The presence of PTEs in pore water can be due to the high proportion of the exchangeable (sediment solution, carbonates, and exchangeable PTEs) fractions of them in the sediments (Li *et al.,* 2013). Furthermore, the oxidation of sulfides _ a chemical process _along with the shaking of samples _ a physical process _ during centrifuge extraction possibly has released the PTEs into the pore water.

Partition Coefficient of PTEs
The partition coefficient (log K_d) values of eight PTEs in the seven stations of Maharlu Lake are shown in Table S4. K_d values are higher in surface water than in those of pore water. In sediments of Maharlu Lake, low partition coefficient (log K_d <2.9) values for Cd, Sb, Mo, Pb, and Zn in most stations suggested high solubility of the elements, indicating that their ecological risks are very high (Jung *et al.,* 2005). In contrast, the relatively higher K_d values (log K_d>2.9) observed for Al, Fe and Mn indicated their preferential association and enrichment in sediments and suggested that they are characterized by a low geochemical mobility in water (Jung *et al.,* 2005).
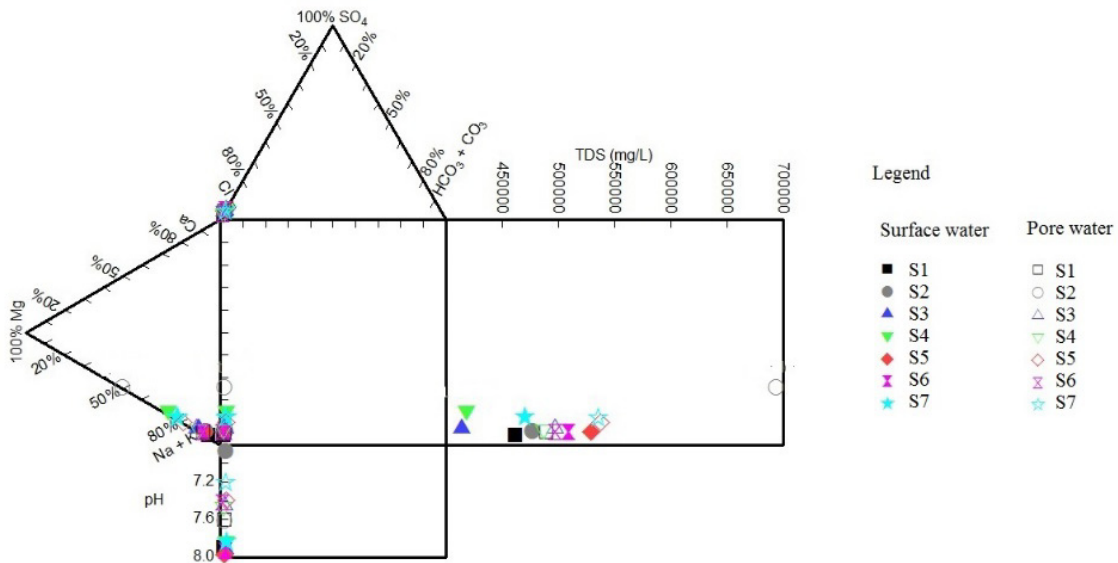

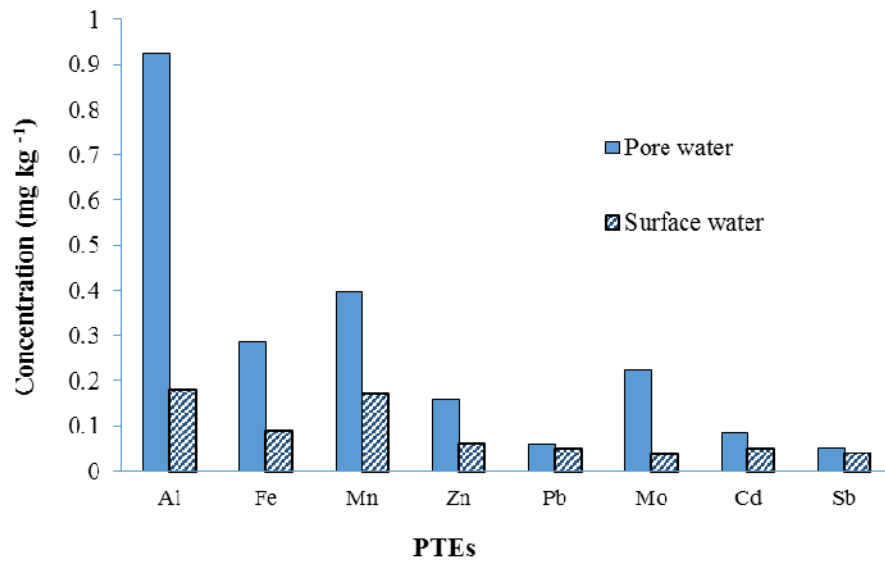Figure S2. Durov diagram for the surface and pore water of the Maharlu saline lake

Figure S3. Heavy metals concentration in surface and pore water samples of Maharlu saline lake

Table S3. Ecological risk of individual metal (Er) and potential ecological risk index (PERI) of Maharlu Lake sediments.

Station	Er							PERI	
	As	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**		
S1	3.15	27.00	3.00	2.05	3.90	1.30	0.61	41.01	Low
S2	6.00	29.00	7.28	3.21	11.47	2.04	0.67	59.67	Low
S3	3.31	29.00	10.06	1.92	9.93	1.30	0.38	55.90	Low
S4	3.31	28.00	6.78	2.05	9.26	1.30	0.40	51.10	Low
S5	2.46	31.00	2.72	1.28	3.82	1.30	0.18	42.76	Low
S6	3.77	36.00	3.11	1.92	5.15	1.30	0.36	51.61	Low
S7	4.38	27.00	5.06	1.92	7.35	1.11	0.01	46.83	Low
mean	3.77	29.57	5.43	2.05	7.27	1.38	0.37	49.84	Low

Table S4. Log K_d variability of heavy metals in Maharlu Lake.

Partition coefficient (Sediment / Surface water)							
Station	Al	Fe	Mn	Zn	Pb	Mo	Cd	Sb
S1	4.66	5.10	3.03	2.72	2.07	1.30	0.53	1.24
S2	4.91	5.12	2.88	2.85	2.47	0.93	0.68	1.27
S3	5.03	5.32	3.48	2.98	1.94	0.80	0.89	1.07
S4	5.50	5.35	3.72	3.01	2.07	1.05	0.75	1.27
S5	5.21	5.03	3.24	2.53	2.00	2.11	0.92	1.27
S6	5.29	5.22	3.34	2.69	1.89	1.16	0.78	1.29
S7	5.49	5.31	3.56	2.83	2.20	1.89	0.86	1.25
mean	5.16	5.21	3.32	2.80	2.09	1.32	0.77	1.24
Partition coefficient (Sediment / Pore water)							
S1	4.88	5.10	2.52	2.59	2.27	1.87	0.73	1.25
S2	4.17	4.47	2.74	2.53	2.26	1.74	0.76	1.15
S3	5.21	5.32	3.21	2.48	2.27	2.00	0.46	0.95
S4	4.81	5.18	2.83	2.38	2.27	1.87	0.45	1.01
S5	3.64	4.02	3.12	1.89	2.07	2.11	0.41	1.28
S6	5.06	5.22	2.76	2.42	2.27	1.91	0.78	1.17
S7	4.75	5.31	3.43	2.39	1.88	2.31	0.35	1.26
mean	4.64	4.94	2.94	2.38	2.18	1.97	0.56	1.15

Among these PTEs, Cd exhibited the lowest log K_d, both for surface water (0.77) and pore water (0.56). The results of previous studies have demonstrated an increase in Cd mobility with increase in water salinity. The reason is that chloro–complexation decreased the activity of free Cd^{2+} in the pore water and increased its desorption (Paalman *et al.,* 1994; Hatje *et al.,* 2003). Therefore, another reason for presence of Cd in pore water is seemingly high concentration of Cl in water samples.

Conclusion
In the present study, distribution of PTEs in sediment, surface and pore water samples of Maharlu Lake was investigated. The results of contamination level assessments revealed that Mo, Ni, Cr, and Cd were moderately enriched in sediment samples. However, PTEs in all sediments samples were mostly within the range of low to moderate contamination degree. The maximum PERI (59.67) occurred in S2 station, which was affected by Khoshk River inflows. Therefore, to reduce the contaminant, a load of the input of untreated wastewater into the rivers should be re–considered. Due to the lake's alkaline condition and adsorption, approximately the concentrations of half of analyzed PTEs in surface and pore water were below detection limit. Among detected PTEs, low values of K_d for Cd, Sb, Mo, Pb, and Zn in most stations showed that the mentioned PTEs bear a potential for fluxing surface water in response to change in the physicochemical condition of the lake's sediment. To obtain accurate result regarding the presence of PTEs in pore water, it is necessary to apply sequential extraction technique.

Furthermore, using Fick's first law is an appropriate method to evaluate flux in dissolved contaminants from pore water to the lake's water column.

References

Allen, H. E., Fu, G., Deng, B., 1993. Analysis of acid–volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments. Environmental Toxicology and Chemistry, 12 (8): 1441–1453.

Batley, G., Simpson, S., 2016. Sediment Quality Assessment: A Practical Guide. 2nd ed. Csiro Publishing.

Beesley, L., Moreno–Jimenez, E., Clemente, R., Lepp, N., Dickinson, N., 2010. Mobility of arsenic, cadmium and zinc in a multi–element contaminated soil profile assessed by in–situ soil pore water sampling, column leaching and sequential extraction. Environmental Pollution, 158 (1): 155–160.

Bowen, H. J. M., 1979. Environmental Chemistry of the Elements. New York: Academic Press.

Brady, J. P., Ayoko, G. A., Martens, W. N., Goonetilleke, A., 2015. Development of a hybrid pollution index for heavy metals in marine and estuarine sediments. Environmental Monitoring and Assessment, 187 (5): 306.

Carling, G. T., Richards, D. C., Hoven, H., Miller, T., Fernandez, D. P., Rudd, A., Pazmino, E., Johnson, W. P., 2013. Relationships of surface water, pore water, and sediment chemistry in wetlands adjacent to Great Salt Lake, Utah, and potential impacts on plant community health. Science of the Total Environment, 443: 798–811.

Cheng, Q., Wang, R., Huang, W., Wang, W., Li, X., 2015. Assessment of heavy metal contamination in the sediments from the Yellow River Wetland National Nature Reserve (the Sanmenxia section), China. Environmental Science and Pollution Research, 22 (11): 8586–8593.

Delshab, H., Farshchi, P., Keshavarzi, B., 2017. Geochemical distribution, fractionation and contamination assessment of heavy metals in marine sediments of the Asaluyeh port, Persian Gulf. Marine Pollution Bulletin, 115 (1–2): 401–411.

Doyle, C. J., Pablo, F., Lim, R. P., Hyne, R. V., 2003. Assessment of metal toxicity in sediment pore water from Lake Macquarie, Australia. Archives of Environmental Contamination and Toxicology, 44 (3): 343–350.

Duodu, G. O., Goonetilleke, A., Ayoko, G. A., 2016 .Comparison of pollution indices for the assessment of heavy metal in Brisbane River sediment. Environmental Pollution, 219: 1077–1091.

Edmunds, W. M., Bath, A. H., 1976. Centrifuge extraction and chemical analysis of interstitial waters. Environmental Science & Technology, 10 (5): 467–472.

Forghani, G., Moore, F., Qishlaqi, A., 2012. The Concentration and Partitioning of Heavy Metals in Surface Sediments of the Maharlu Lake, SW Iran. Soil and Sediment Contamination: An International Journal, 21 (7): 872–888.

Forghani, G., Moore, F., Lee, S., Qishlaqi, A., 2009. Geochemistry and speciation of metals in sediments of the Maharlu Saline Lake, Shiraz, SW Iran. Environmental Earth Sciences, 59 (1), 173.

Escher, B. I., Hermens, J. L., 2004. Peer reviewed: internal exposure: linking bioavailability to effects.

Gao, B., Zhou, H., Yu, Y., Wang, Y., 2015. Occurrence, distribution, and risk assessment of the metals in sediments and fish from the largest reservoir in China. Royal Society of Chemistry Advances 5 (74): 60322–60329.

Gee, G. W., Bauder, J. W., 1986. Particle–Size Analysis. In A. Klute (Ed.), Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods. Agronomy Monograph No. 9 (2nd Ed., Pp. 383–411). Madison: American Society of Agronomy/ Soil Science Society of America.

Gormley–Gallagher, A. M., Douglas, R. W., Rippey, B., 2015. The applicability of the distribution coefficient, KD, based on non–aggregated particulate samples from lakes with low suspended solids concentrations. Public Library of Science One, 10 (7).

Guven, D. E., Akinci, G., 2013. Effect of sediment size on bioleaching of heavy metals from contaminated sediments of Izmir Inner Bay. Journal of Environmental Sciences (China), 25 (9): 1784–1794.

Hakanson, L., 1980. An ecological risk index for aquatic pollution control. A sedimentological approach. Water Research, 14 (8): 975–1001.

Harmsen, J., 2007. Measuring bioavailability: from a scientific approach to standard methods. Journal of Environmental Quality, 36 (5): 1420–1428.

Hatje, V., Payne,. T E., Hill, D. M., McOrist, G., Birch, G. F., Szymczak, R., 2003. Kinetics of trace element uptake and release by particles in estuarine waters: Effects of pH, salinity, and particle loading. Environment International, 29 (5): 619–629.

Heiri, O., Lotter, A. F., Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. Journal of Paleolimnology, 25 (1): 101–110.

Ho, H. H., Swennen, R., Van Damme, A., 2010. Distribution and contamination status of heavy metals in estuarine sediments near cua ong harbor, Ha Long Bay Vietnam. Geologica Belgica, 13 (1–2): 37–47.

Ideriah,. T. J. K., David–Omiema, S., Ogbonna, D. N., 2012. Distribution of Heavy Metals in Water and Sediment along Abonnema Shoreline, Nigeria. Resources and Environment, 2 (1): 33–40.

Iqbal, J., Shah, M. H., 2014. Occurrence, risk assessment, and source apportionment of heavy metals in surface sediments

from Khanpur Lake, Pakistan. Journal of Analytical Science and Technology, 5 (1): 28.

Jung, H. B., Yun, S. T., Mayer, B., Kim, S. O., Park, S. S., Lee, P. K., 2005. Transport and sediment–water partitioning of trace metals in acid mine drainage: An example from the abandoned Kwangyang Au–Ag mine area, South Korea. Environmental Geology, 48 (4–5): 437–449.

Karami, G. H., Bahmani, M., 2008. Assessing the heavy matal pollution in rivers entering to Maharlu Lake, Iran. In: The 12th World Lake Conference, 283–285.

Khaled, A., Abdel–Halim, A., El–Sherif, Z., Mohamed, L. A., 2017. Health Risk Assessment of Some Heavy Metals in Water and Sediment at Marsa–Matrouh, Mediterranean Sea, Egypt. Journal of Environmental Protection, 8 (1): 74–97.

Li, S. S., Shan, B. Q., Zhang, H., 2013. Characteristics and ecological risk assessment of heavy metal pollution in surface sediments of Fuyang River. Acta Scientiae Circumstantiae, 33: 2277–2284 (In Chinese).

Liu, W., Wang, Z., Wen, X., Tang, H., 1999. The application of preliminary sediment quality criteria to metal contamination in the Le An River. Environmental Pollution, 105 (3): 355–366.

Long, E. R., Macdonald, D. D., Smith, S. L., Calder, F. D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environmental Management, 19 (1): 81–97.

Long, E. R., Mac Donald, D. D., Severn, C. G., Hong, C. B., 2000. Classifying probabilities of acute toxicity in marine sediments with empirically derived sediment quality guidelines. Environmental Toxicology and Chemistry, 19 (10): 2598–2601.

Mishra, S., Kumar, A., Shukla, P., 2015. Study of water quality in Hindon River using pollution index and environmetrics, India. Desal Water Treat, 56: 1–10.

Moore, F., Forghani, G., Qishlaqi, A., 2009. Assessment of heavy metal comtamination in water and surface sediments of the Maharlu saline lake, SW Iran. Iranian Journal of Science and Technology, Transactions A: Science, 33: 43–55.

Moore, F., Tehrani, G. F., Qishlaqi, A., Rastmanesh, F., 2006. Heavy metal concentrations in water and surface sediments of Maharlou Lake, SE of Shiraz, Iran. Chinese Journal of Geochemistry, 25, 168–168.

Moreno–Jimenez, E., Beesley, L., Lepp, N. W., Dickinson, N. M., Hartley, W., Clemente, R., 2011. Field sampling of soil pore water to evaluate trace element mobility and associated environmental risk. Environmental Pollution, 159 (10): 3078–3085.

Omwene, P. I., Öncel, M. S., Çelen, M., Kobya, M., 2018. Heavy metal pollution and spatial distribution in surface sediments of Mustafakemalpaşa stream located in the world's largest borate basin (Turkey). Chemosphere, 208: 782–792.

Paalman, M. A. A., Van Der Weijden, C. H., Loch,. J. P. G., 1994. Sorption of cadmium on suspended matter under estuarine conditions; competition and complexation with major sea–water ions. Water, Air, and Soil Pollution, 73 (1): 49–60.

Qishlaqi,. A, Moore, F., Forghani, G., 2008. Impact of untreated wastewater irrigation on soils and crops in Shiraz suburban area, SW Iran. Environmental Monitoring and Assessment, 141 (1–3): 257–273.

Rai, P. K., 2009. Heavy metal phytoremediation from aquatic ecosystems with special reference to macrophytes. Critical Reviews in Environmental Science and Technology, 39 (9): 697–753.

Ramamoorthy, S., Rust, B. R., 1978. Heavy metal exchange processes in sediment – water systems. Environmental Geology, 2 (3): 165–172

Salati, S., Moore, F., 2010. Assessment of heavy metal concentration in the Khoshk River water and sediment, Shiraz, Southwest Iran. Environmental Monitoring and Assessment, 164 (1): 677–689.

Shaheen, S. M., Rinklebe,. J, Rupp, H., Meissner, R., 2014. Temporal dynamics of pore water concentrations of Cd, Co, Cu, Ni, and Zn and their controlling factors in a contaminated floodplain soil assessed by undisturbed groundwater lysimeters. Environmental Pollution, 191: 223–231.

Singh, K. P., Mohan, D., Singh, V. K., Malik, A., 2005. Studies on distribution and fractionation of heavy metals in Gomti river sediments – A tributary of the Ganges, India. Journal of Hydrology, 312 (1–4): 14–27.

Sutherland, R. A., 2000. Bed sediment–associated trace metals in an urban stream, Oahu, Hawaii. Environmental Geology, 39 (6): 611–627.

Tajabadi, M., Zare, M., Alijani, F., 2017. Unstable convection flow as a controlling process of increasing salinity in the saline lake coastal aquifers: case of Maharlu Lake coastal aquifer. Environmental Earth Sciences, 76 (7), 267.

Turekian, K. K., Wedepohl, K. H., 1961. Distribution of the Elements in some major units of the Earth's crust. Geological Society of America, Bulletin 72: 175–192.

USEPA., 2012. Understanding Variation in Partition Coefficient Kd Values. Vol I.doi:402–R–99–0044A.

Wedepohl, H., 1995. The composition of the continental crust. Geochimica et Cosmochimica Acta, 59 (7): 1217–1232.