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Heavy metals in the soils of the Arabian Gulf coast affected by industrial activities: analysis and assessment using enrichment factor and multivariate analysis

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Abstract The concentrations of nine heavy metals (Fe, Mn, Zn, Cu, Ni, Cd, Cr, Co, and Pb) in soil samples of Arabian Gulf coast, Saudi Arabia, were investigated. Sediment Quality Guideline (SQGs), SQG-Quotient (SQG-Q), toxicity degree index (TDI), enrichment factor (EF), and multivariate analysis, including principle component analysis (PCA) and hierarchical cluster analysis (HCA), were used to measure heavy metals of concern in the study area and to identify their possible sources. The results showed that the concentrations of different heavy metals were 530–5,700 mg kg? 1 for Fe; 9–150 mg kg^{-1} for Mn and 8–69 mg kg^{-1} for Zn; 1–21 mg kg^{-1} for Cu and not detectable—17 mg kg^{-1} for Ni; 6.9–130 mg kg^{-1} for Cr and not detectable—5 mg kg^{-1} for Co; and not detectable—24 mg kg^{-1} for Pb. Based on SQGs, only the maximum and mean Cr concentrations of study area were in heavy and moderate rates of pollution, respectively. The values of SQG-Q and TDI revealed that the investigated sampling points showed the lowest potential of adverse biological effects. The considerable number of collected soil samples has relatively higher EF values of 5–20 for Zn, Cu, Cr, and Pb, suggesting that these four metals may be derived from anthropogenic origin. Multivariate analysis also confirmed this finding that the sources of Zn, Cu, and Pb resulted primarily from anthropogenic sources, whereas Co, Ni, Fe, and Mn were mainly attributed to lithogenic sources. It could be generally concluded that it is possible to use multivariate analyses in combination with EF values as useful tools to identify the natural or anthropogenic sources of heavy metals in soils.

Keywords Heavy metals · Sediment Quality Guidelines (SQGs) · Principal component analysis (PCA) · Hierarchical cluster analysis (HCA)

Introduction

Among organic and inorganic pollutants, heavy metals are considered to be one of the main sources responsible for causing a significant negative impact on ecological quality of the costal environments (Jara-Marini et al. 2008; Fernandes et al. 2012; Bodin et al. 2013; Attia et al. 2012). Heavy metals can enter into the coastal environments from different sources including natural weathering processes and anthropogenic activities (Sadiq and Alam 1989; Sadiq et al. 1992; Krishna and Govil 2007; Badr et al. 2009; Venkatramanan et al. 2012; Garali et al. 2010; Madkour 2013; El-Sorogy et al. 2013). Anthropogenic sources not only lead to increasing heavy metals concentrations in the environment, but also it can cause an unnatural enrichment, leading to metal pollution of the surface soils. The soil enriched with heavy metals can significantly cause an adverse impact on the population via inhalation, ingestion and dermal contact. The soil-accumulated heavy metals can also pose potential long-term hazards to plants and to animals as well as humans that consume these plants (Singh and Kumar 2006). Furthermore, the heavy metals increases in

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soils or sediments are considered as a potential secondary source for water pollution, especially with changes in environmental conditions (e.g., pH, redox potential, organic matter content, temperature, etc.; Nayek et al. 2013).

During the past few decades, discharging elevated levels of heavy metals into the coastal and marine ecosystems of the Arabian Gulf are becoming an increasingly serious problem that threatens both the naturally marine ecosystems and humans (Naser 2013). Since the Arabian Gulf is characterized by a shallow and semi-enclosed basin, the impact of pollutants on marine environment as a result of intensive anthropogenic activities may be significant (Pourang et al. 2005; Naser 2013). Industrial and sewage effluents, and wastewater discharges from desalination plants are considered as anthropogenic sources that may significantly contribute to damage the environment of Arabian Gulf (Sheppard et al. 2010; Naser 2013). It has been reported that oil can also be considered as a significant and chronic pollution source in the Gulf environment (Naser 2013). Additionally, chimney emissions of many industrial complexes may contribute to the metal pollution in the Gulf, leading to disturbance to the coastal environment (Sadiq and Alam 1989). In a study conducted on contamination of marine sediment with heavy metals in the Arabian Gulf of Bahrain, Oman, Qatar, and the United Arab Emirates, De Mora et al. (2004) noted that there are elevated concentrations of Cu, Hg, Pb, and Zn in Bahrain, mainly due to the industrial effluents from there finery and other industries located on the eastern coastline in Bahrain. Additionally, they found higher concentrations of Co, Cr, and Ni at Akkah beach on the east coast of the United Arab Emirates, attributing to the metal-rich mineralogy of the region. The concentrations of heavy metals in sediments from sub-tidal areas of the Iranian coastline of the Arabian Gulf were studied by Pourang et al. (2005). They reported that the concentrations of Cd, Pb, and Ni in the sediments were significantly higher than global baseline concentrations.

There is a rapidly industrial development on the coast of the Arabian Gulf in Saudi Arabia, which may be as regional pollution source, causing a concern regarding the environmental quality. Therefore, the proper assessment of heavy metals pollution in the soils and sediments of the Arabian Gulf in Saudi Arabia is a crucial issue to provide a successful management of marine ecosystems. In this context, the enrichment factor (EF) is considered as a convenient measure of geochemical trends and is applied for speculating on lithogenic or anthropogenic origin of heavy metals (Sutherland 2000). The quality guidelines of sediment (SQGs) were also applied to measure heavy metals of concern in the ecosystems of fresh water and coastal areas (MacDonald et al. 2000). The SQGs guidelines can be used as an approach to assess to which degree the sediment-associated contaminants might have adverse impacts on aquatic organisms (MacDonald et al. 2000; Caeiro et al.

2005). The multivariate analysis such as the principal component analysis (PCA) and hierarchical cluster analysis (HCA) have been widely used in environmental studies to investigate the origin of heavy metal in soils (Ratha and Sahu 1993; Abollino et al. 2002; Yongming et al. 2006; Luo et al. 2007; Praveena et al. 2007; Wu and Zhang 2010; Anju and Banerjee 2012; Krami et al. 2013). Therefore, the objectives of this study were (a) to determine the levels of heavy metals (Fe, Mn, Cd, Cr, Cu, Co, Ni, Pb, and Zn) in the coastal soils of industrial petrochemicals area at Arabian Gulf, Saudi Arabia; (b) to measure heavy metals of concern and toxicity degree in the study area using the quality guidelines of sediment (SQGs) and SQG-Quotient (SQG-Q); (c) to evaluate the possible relationships among the investigated heavy metals in soil of study area; and (d) to identify their natural or anthropogenic sources by using enrichment factor and multivariate analysis.

Material and methods

Sampling and analytical methods

This study was conducted on the coast of the Arabian Gulf of Jubail in Saudi Arabia, which is considered one of the largest industrial cities in the Kingdom and the Middle East. This industrial city includes many factories and located on the Arabian Gulf coast at longitude (30–49°) E and latitudes (10–27°) N. Figure 1 presents study area.

Fifty-six soil samples were collected to represent the investigated area that affected by the industrial petrochemicals. There are two groups of soil samples, first was under the influence of tide (tidal zone), while the second groups was far around 300 m from the tidal zone (out of the tidal zone). Soil samples were collected at sampling depth of 0–30 and 30–60 cm. The disturbed soil samples for physico-chemical analyses as well as the total content of heavy metals were collected from each sampling site by augur. The soil samples were kept in sealed polyethylene bags to avoid contamination and immediately transported to the laboratory and preserved in a refrigerator. All soil samples were air-dried at room temperature (20–22 °C) and ground to pass through a 2-mm sieve. The particle size distribution was determined by the pipet method (Gee and Bauder 1994). Soil chemical properties were measured according to standard methods (Sparks 1996). Soil pH was measured using a glass electrode in a suspension of 1:4 ratio of soil to water. Electrical conductivity (EC) was measured in the soil extracts (1:4). Calcium carbonate content was determined volumetrically by measuring the CO_2 volume evolved from the reaction of HCl with soil carbonate using a calcimeter. The soil organic matter was measured by oxidation using a mixture of sulfuric acid and potassium dichromate, and the excess of dichromate was titrated with ferrous ammonium sulfate (Nelson and Sommers 1996).
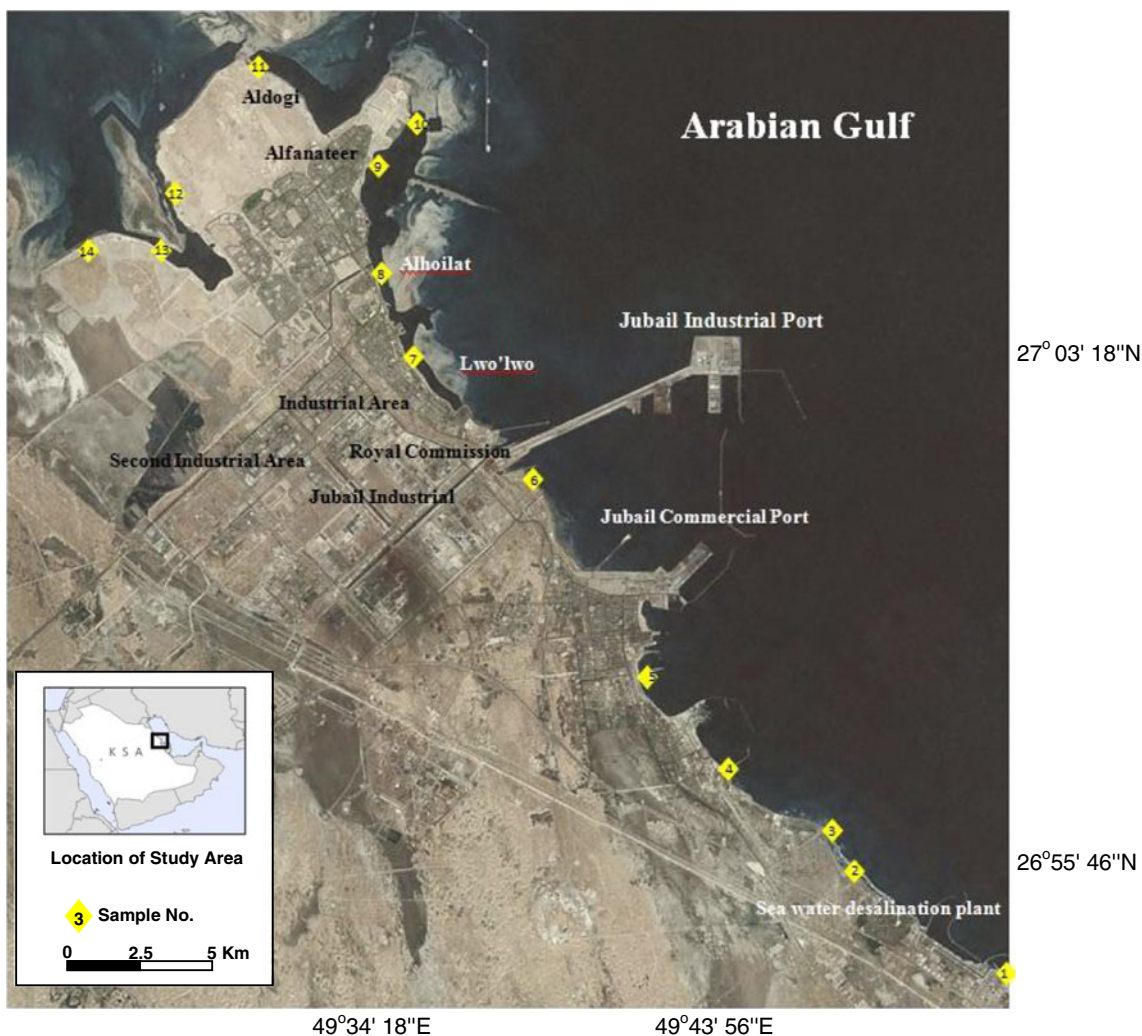
Fig. 1 The location of study area and distribution of sampling points

The total content of heavy metals (Fe, Mn, Zn, Cu, Cr, Co, Ni, Pb, and Cd) in the soil samples was determined after digestion using Hossner method (Hossner 1996). It is well known that heavy metals can be completely digested using Hossner method (total-total method), since this includes the use of HF in addition to H_2SO_4-$HClO_4$. This mixture is appropriate for dissolving silicates completely. Specifically, in the present study, 0.5 g of each soil sample was digested using HF-H_2SO_4-$HClO_4$. After cooling, the digested solutions were filtered using Watman 42, then brought to a total volume of 50 mL with deionized water in a volumetric flask. The concentrations of total metal were analyzed using AAS. For quality control, each collected soil sample was digested and analyzed in four replicates. Q test was applied to exclude abnormal readings at a confidence level of 90 %.

Data calculation and analysis

The multivariate analysis including the PCA and HCA was performed to identify the relationship among investigated metals in study area and their possible sources. The PCA, HCA, and Spearman's correlation coefficient analysis were performed by using Statistica for Windows statistical software (Statsoft 1995). In the PCA, varimax raw was used as the rotation method in the analysis to determine total variance and loading of investigated metals in the soil of the study area. The HCA was obtained by Ward's method (Pearson's r).

In the present study, the quality guidelines of sediment (SQGs) were applied to measure heavy metals of concern in the study area (MacDonald et al. 2000). Moreover, two indices were computed: the toxicity degree index (TDI; Jamshidi-Zanjani and Saeedi 2013) and Sediment Quality Guideline Quotient (SQG-Q; Long and MacDonald 1998). The toxicity degree is a recent index (TDI) suggested based on the results of multivariate statistical analysis of the data from the study area (Jamshidi-Zanjani and Saeedi 2013). The TDI was calculated using the following equation:

$$TDI = \sum w_i(1 + (C_i/SQG-Q_i))^2$$

Where w_i is the variable weight that was computed based on the proportion of eigen values obtained from PCA results. C_i is metal concentration and SQG-Q$_i$ is the effect range median (ERM) values of each metal. The TDI values consist of five categories: low toxic level ($1 < \text{TDI} \leq 1.5$), low-median toxic level ($1.5 < \text{TDI} \leq 2$), median toxic level ($2 < \text{TDI} \leq 3$), median-high toxic level ($3 < \text{TDI} \leq 4$), and high toxicity (TDI > 4).

The SQG-Q index was also calculated to assess the potential for adverse biological effects of study area. The SQG-Q was calculated using the following equations (Long and MacDonald 1998):

$$\text{SQG-Q} = \left(\sum \text{ERM-Q}_i \right)/\text{n}$$

$$\text{ERM-Q}_i = C_i/\text{ERM}$$

Where n and C_i are the number and concentration of heavy metals, respectively. ERM-Q$_i$ is the effect range median concentration suggested by Long et al. (1995) and MacDonald et al. (1996). The SQG-Q values consist of four categories: lowest potential for adverse biological effect (SQG-Q ≤ 0.10), low-median potential for adverse biological effect (0.1 < TDI ≤ 0.5), median-high potential for adverse biological effect (0.5 < SQG-Q ≤ 1.5), and highest potential for adverse biological effect (SQG-Q > 1.5).

To assess the level of metal enrichment and to speculate the metal origin in soil samples of study area, enrichment factor (EF) was computed using the following equation (Sutherland 2000):

$$\text{EF}_m = \left[C_{m(\text{soil})}/C_{\text{Fe(soil)}} \right] / \left[C_{m(\text{earth crust})}/C_{\text{Fe(earth crust)}} \right]$$

Where $C_{m(\text{soil sample})}$ is content of the examined metal in the soil sample; $C_{\text{Fe(soil sample)}}$ is content of the reference metal (Fe) in the soil sample; $C_{m(\text{earth crust})}$ is content of the examined metal in the earth crust; and $C_{\text{Fe(earth crust)}}$ is content of the referenced metal (Fe) in the earth crust. The EF values consist of five categories: deficiency to minimal (EF < 2), moderate (2 < EF < 5), significant (5 < EF < 20), very high (20 < EF < 40), and extremely high enrichment (EF > 40).

In addition to the calculation of EF values, the lithogenic heavy metal content was calculated by the following equation (Hernandez et al. 2003):

$$[\text{M}]_{\text{lithogenic}} = [\text{Fe}]_{\text{sample}} \times ([\text{M}]/[\text{Fe}])_{\text{lithogenic}}$$

Where $[\text{M}]_{\text{lithogenic}}$ is the lithogenic heavy metal content; $[\text{Fe}]_{\text{sample}}$ is the total content of Fe in soil samples; and $([\text{M}]/$

$[\text{Fe}])_{\text{lithogenic}}$ is the ratio in the earth's crust. The anthropogenic heavy metal content was calculated by the following equation:

$$[\text{M}]_{\text{anthropogenic}} = [\text{M}]_{\text{total}} - [\text{M}]_{\text{lithogenic}}$$

Where $[\text{M}]_{\text{anthropogenic}}$ is the anthropogenic heavy metal content and $[\text{M}]_{\text{total}}$ is the total content of heavy metal measured in soil samples.

Results and discussion

Physico-chemical properties of soil samples

Some physico-chemical properties of the studied soil samples are presented in Table 1. The pH values of soil samples ranged between 6.3 and 9.2 with an average value of 7.7, suggesting alkaline conditions for the most soil samples. The EC values ranged between 0.2 and 12.3 dSm^{-1}, indicating that the studied soil samples were significantly affected by salinity of sea water. The texture of studied soil samples is mainly dominated by sand fraction, ranged from 73 % to 92 %. The content of organic matter (OM) and calcium carbonate (CaCO$_3$) varied in the studied soil samples from 0.1 to 2.6 % with an average of 1.4 % and from 0.5 to 69 % with an average of 1.4 %, respectively.

Soil heavy metal concentrations and quality guidelines

Data in Table 2 show the minimum, maximum, mean, standard deviation, coefficients of variation, and skewness of heavy metals (Fe, Zn, Cu, Ni, Cr, Co, Cd, Mn, and Pb) at soil sampling depth of 0–30 and 30–60 cm. Among all heavy metals, the concentrations of Cd were not detectable in all soil samples. The minimum, maximum, and mean concentrations of all investigated heavy metals (except for Cr) are lower than their corresponding values of the common range in soil according to Lindsay (1979). In the case of Cr, its minimum and maximum concentrations are higher than those of common

Table 1 Physico-chemical soil properties

Characteristic	Max	Min	Average	Std	CV
p H	9.2	6.3	7.7	0.6	7.4
EC (dSm^{-1})	12.3	0.2	1.8	2.1	119.3
O.M%	2.6	0.1	1.4	0.6	38.4
CaCO$_3$ %	69	0.5	25	22	88
Clay %	16	6	9	2.6	29
Silt %	14	2	2.5	1.7	69
Sand %	92	73	88.5	3.4	3.8

Table 2 Minimum, maximum and average content of heavy metals in soil samples of study area

Sampling sites		Heavy Metals							
		Fe	Mn	Zn	Cu	Ni mg kg^{-1}	Cr	Co	Pb
Tidal zone									
0–30 cm	Max	4100	120	46	18	6	130	ND	12
	Min	530	9	8	1	ND	7.5	ND	1.1
	Mean	1800	36	21	5	1	34	–	4
	SD	972	29.8	9.83	4.27	2.06	33.5	–	2.61
	CV, %	55	83	47	86	175	98	–	66
	Skewness	1.04	2.12	1.21	2.7	1.48	2.23	–	2.11
30–60 cm	Max	4100	93	44	11	6	110	ND	24
	Min	770	11	8	2	ND	6.9	ND	ND
	Mean	1800	38	22	5	2	42	–	5.2
	SD	854	24.6	9.77	3.13	2.25	30.7	–	6.56
	CV, %	46	65	45	65	112	73	–	125
	Skewness	1.28	1.03	0.98	1.01	0.48	1.00	–	2.35
Out of the tidal zone									
0–30 cm	Max	5400	140	52	21	10	120	5	9.1
	Min	1800	35	11	3	ND	20	ND	1.5
	Mean	3400	78	25	6	6	69	0.9	4.3
	SD	1015	31.9	11.5	4.74	2.67	33.9	1.88	2.11
	CV, %	29	41	46	74	46	49	200	49
	Skewness	0.58	0.66	1.25	2.46	−0.40	0.27	1.62	0.71
30–60 cm	Max	5700	150	69	11	17	93	4	20
	Min	680	12	9	2	ND	8.1	ND	0.42
	Mean	3000	70	23	5	5	55	1	4.5
	SD	1377	39.6	16.0	2.28	4.45	24.3	1.85	4.73
	CV, %	46	56	69	44	81	45	166	105
	Skewness	0.22	0.55	2.10	0.58	1.38	−0.29	1.15	2.75
Common range[a]	Max	55000	3000	300	100	500	1000	40	200
	Min	7000	20	10	2	5	1	1	2
	Av.	38000	600	50	30	40	100	8	10
Background in shale[b]		47200	850	95	45	68	90	19	20
SQG non-polluted[c]		–	–	90	25	20	25	–	40
SQG moderately polluted		–	–	90–200	25–50	20–50	25–75	–	40–60
SQG heavily polluted		–	–	200	50	50	75	–	60
Threshold effect concentration (TEC) SQGs[d]									
TEL		–	–	124	18.7	15.9	52.3	–	30.2
ERL		–	–	150	34	20.9	81	–	46.7
Probable effect concentration (PEC) SQGs[d]									
PEL		–	–	271	108	42.8	160	–	112
ERM		–	–	410	270	51.6	370	–	218

ND not detectable, *SQG* sediment quality guidelines, *TEL* threshold effect level, *ERL* the effect range low, *PEL* probable effect level, *ERM* the effect range median

[a] Lindsay 1979; [b] Turekian and Wedepohl (1961); [c] MacDonald et al. 2000; [d] MacDonald et al. 1996

range in soil. Additionally, the maximum concentrations of Cr are higher than the geochemical background in average shale. It was observed generally that the mean heavy metal concentrations in soil samples of 0–30 cm depth are closed with those of 30–60 cm depth. Moreover, at the sites out of the tidal zone, the minimum, maximum, and mean concentrations

of most heavy metals (especially at 0–30 cm depth) are higher than those of soil samples collected along the tidal zone.

The raw data of studied metals were strongly positively skewed, with skewnesses much higher than 0, indicating some extremely high values (Wu and Zhang 2010). It may also indicate that the investigated heavy metals positively skew toward their lower values. The coefficients of variation for metals were between 29 % and 200 %. These obtained variations in soil total metal content and coefficients of skewnesses suggest that these heavy metals may be related to different sources.

Numerical sediment quality guidelines (SQGs) have been used to determine the ecotoxicological sensibility of contaminants in marine and coastal ecosystem and to identify contaminants of concern in aquatic ecosystems (MacDonald et al. 1996; 2000). Based on the SQGs, sediments can be categorized into three classes: non-polluted, moderately polluted and heavily polluted. The results showed that the soil samples in the study area were in non-polluted for the investigated heavy metals (except Cr; Table 2). The data showed that the maximum Cr concentrations were in heavy rate of pollution, but its mean concentrations were in moderate rate of pollution. To have a better insight on the adverse biological effects of each contaminant, the obtained data should be compared with the following SQGs including: threshold effect levels (TEL), probable effect levels (PEL), the effect range low (ERL), and the effect range median (ERM) for each metal (Long et al. 1995; MacDonald et al. 1996). Our results indicated that only the maximum concentrations of Cr were found to be above threshold effect concentrations (TEL and ERL) as well as above PEL (Table 2). Furthermore, its average concentrations were found to be above the TEL. Therefore, the adverse effect by Cr on dwelling organisms might be expected.

To have a more realistic measure of predicted toxicity, the mean SQG quotients (SQG-Q) were calculated based on the effect range median (ERM; Long and MacDonald 1998; Jamshidi-Zanjani and Saeedi 2013; Usman et al. 2013). In the present study, the SQG-Q was determined as the mean of the ERM-Q_i for Zn, Cu, Cr, Ni, and Pb, which have the reported values of ERM. This quotient was classified as lowest potential of adverse biological effect (SQG-Q $\leq$ 0.1), low-medium potential of adverse biological effect (0.1 < SQG-Q $\leq$ 0.5), medium-high potential of adverse biological effect (0.5 < SQG-Q $\leq$ 1.5), or high (SQG-Q > 1.5) potential of adverse biological effect (Long and MacDonald 1998). Our results revealed that the most investigated sampling points at soil sampling depths of 0–30 and 30–60 cm showed the lowest potential of adverse biological effects (Fig. 2), suggesting no toxic impacts or significant risk to the biota.

In the present study, the recent proposed index of toxicity degree (TDI) was also calculated based on ERM and the results of multivariate statistical analysis (PCA) of the data from the study area (Jamshidi-Zanjani and Saeedi 2013).

Results of TDI are shown in Fig. 2. The values of this index in all investigated sampling points of study area were less than 1, indicating that soil samples of study area have no potential of toxic effect on biota. It was also observed that there is a high positive significant correlation between SQG-Q and TDI at 0–30 cm depth (r^2=0.94) and 30–60 cm depth (r^2=0.92) of study area (data not shown). Similarly, Jamshidi-Zanjani and Saeedi (2013) found high value of r^2 (0.81) between these two indices, suggesting that TDI may be a more realistic measure of predicted toxicity and more capability to differentiate areas with different pollution extents.

Enrichment factor (EF) and heavy metals origin

The EF is a convenient measure of geochemical trends and is applied for speculating on lithogenic or anthropogenic origin of heavy metals (Sutherland 2000; Ye et al. 2011). The maximum, minimum, and mean results of EF values are presented in Fig. 3. From the obtained data, the heavy metals of the tidal zone at soil sampling depth of 0–30 and 30–60 cm have EF values, respectively, (3.5–29) and (2.2–23) for Zn, (1.3–19) and (0.99–14) for Cu, (0.0–1.9) and (0.0–2.7) for Ni, (2.8–12) and (3.4–21) for Cr, (0.75 to 1.9) and (0.73–1.7) for Mn, and (1.9–27) and (0–32) for Pb. Meanwhile, the EF values of the out of the tidal zone at soil sampling depth of 0–30 and 30–60 cm were, respectively, amounted to (2.8–18) and (2.1–19) for Zn, (0.89–7.8) and (0.71–10) for Cu, (0–2.1) and (0.0–2.9) for Ni, (2.8–16) and (4.5–12) for Cr, (0–4.7) and (0.0–5.7) for Co, (0.83–1.8) and (0.87–1.9) for Mn, and (1.3–9.9) and (0.62–23) for Pb. Some researchers suggest that heavy metals with EF values less than 2 were not a major concern contaminant (Han et al. 2006; Ye et al. 2011). In this context, the EF values for Co (in 71–100 % of soil samples), Ni (in 86–100 % of soil samples) and Mn (in all the soil samples) were less than 2 (Fig. 4), suggesting that their contaminations may be not a major concern. However, few number of soil samples (out of the tidal zone) has EF values 2–5 for Co and Ni, indicating moderate enrichment. By contrast, the considerable number of collected soil samples in the surface and subsurface layers has relatively higher EF values 5–20 for Zn, Cu, Cr, and Pb. Additionally, around 10–15 % of samples reached very high enrichment (20<EF<40) for Zn and Pb. This indicates that a severe degree of Zn, Cu, Cr, and Pb contamination may be possible in the study area. The obtained variations in EF values may be as a result of the difference in the magnitude of input for each metal in the soil. Generally, it was observed that the maximum EF values of Zn, Cu, Cr, and Pb in the soil samples at out of the tidal zone were higher than those at the tidal zone. This suggests that the soil samples located farthest away from the coastal and near the activities of petrochemical industries may have high potential to enrich soil with such heavy metals.
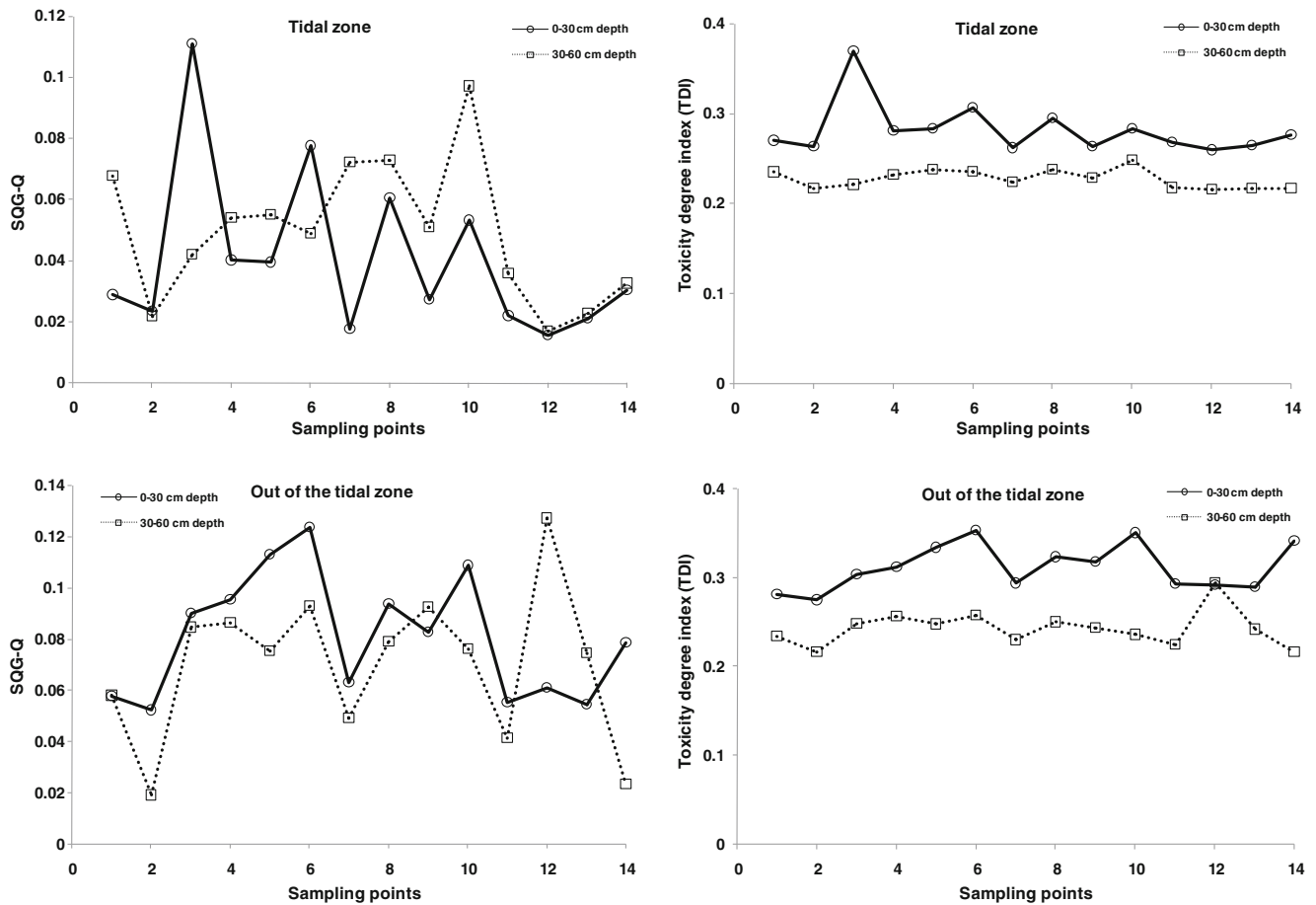
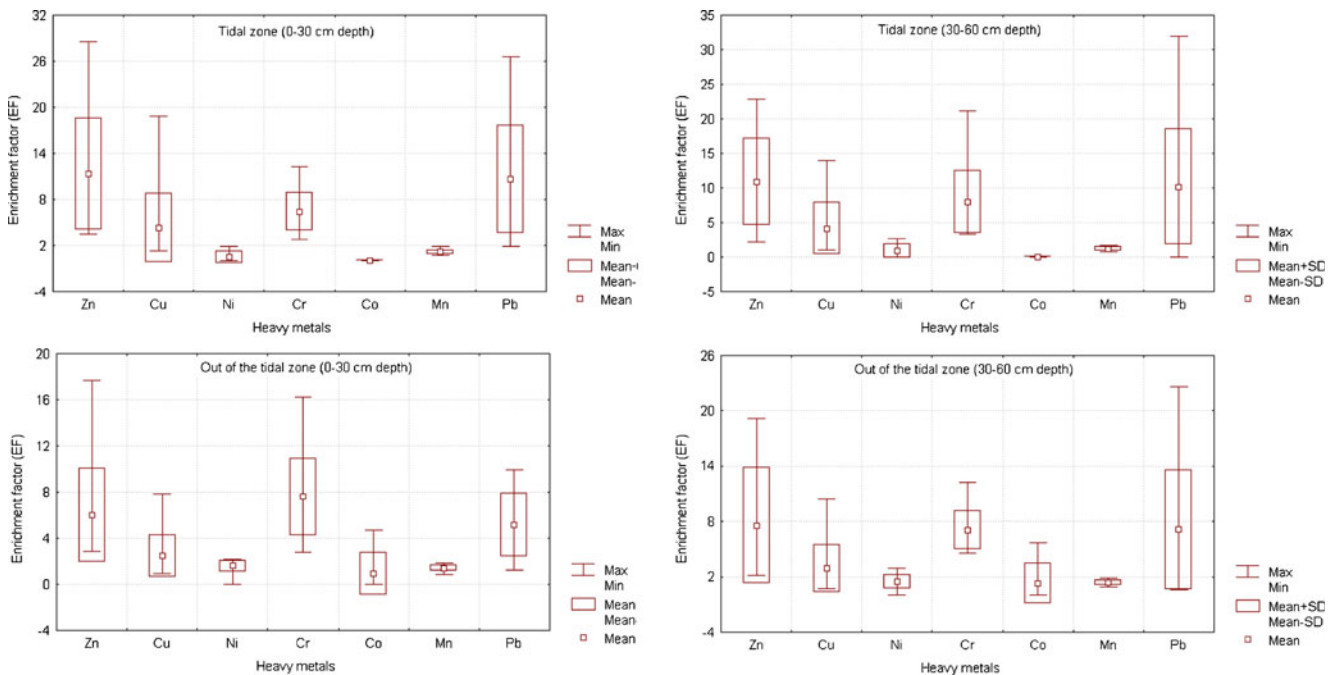**Fig. 2** Sediment quality guideline quotient (SQG-Q) and the toxicity degree index (TDI) of soil samples

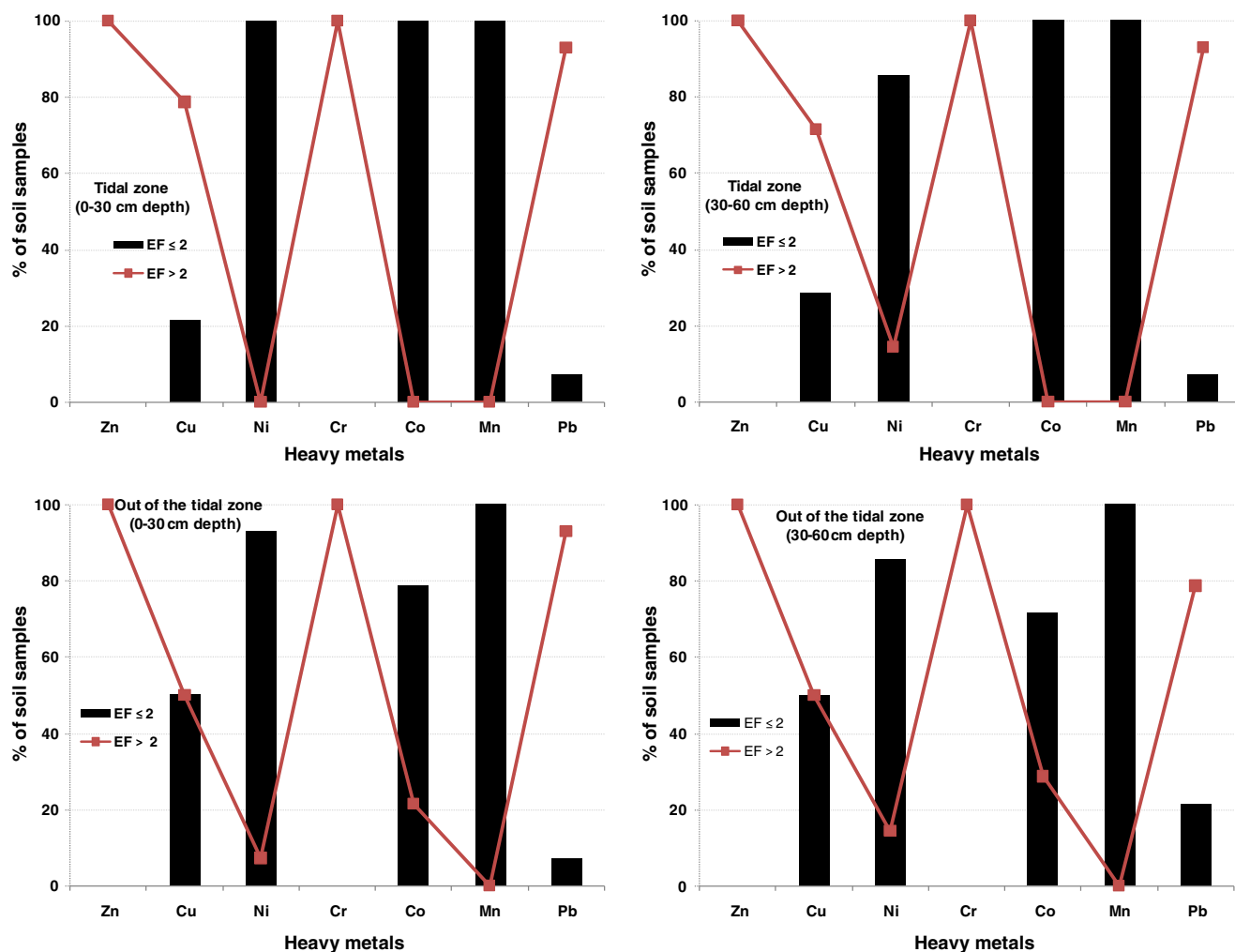**Fig. 3** EF values for heavy metals at tidal and out of the tidal zone

Fig. 4 % of soil samples having EF values less or greater than 2

It has been speculated that a value of EF≤2 indicates that heavy metal may be as a result of crustal materials or natural weathering processes. Meanwhile, soil samples having EF values greater than 2 suggest that a significant portion of the
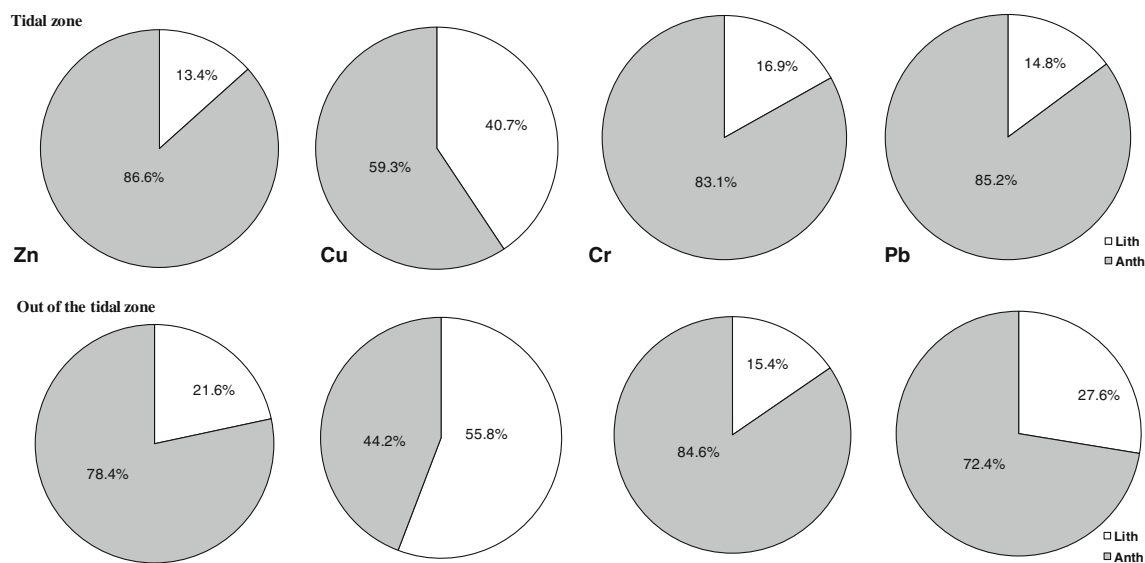

Fig. 5 Lithogenic (Lith) and anthropogenic (Anth) proportion of the tidal and out of the tidal zone regardless soil sampling depth

Table 3 The Spearman correlation coefficients (r) among various metals at soil sampling depth of 0–30 cm and 30–60 cm

	Zn	Cu	Ni	Cr	Co	Mn	Pb
0–30 cm depth							
Zn	1						
Cu	0.59*	1					
Ni	0.17	0.41*	1				
Cr	0.24	0.35	0.61*	1			
Co	0.22	0.26	0.53*	0.42*	1		
Mn	0.25	0.39*	0.78*	0.85*	0.52*	1	
Pb	−0.39*	−0.15	−0.02	0.13	−0.11	0.04	1
Fe	0.26	0.45*	0.81*	0.88*	0.52*	0.97*	0.04
30–60 cm depth							
Zn	1						
Cu	0.33	1					
Ni	0.16	0.37	1				
Cr	−0.14	−0.18	0.60*	1			
Co	0.19	0.21	0.54*	0.25	1		
Mn	0.01	−0.08	0.79*	0.82*	0.46*	1	
Pb	−0.44*	−0.01	0.15	0.07	−0.04	−0.03	1
Fe	−0.01	0.06	0.84*	0.85*	0.53*	0.96*	0.04

heavy metal is delivered from non-crustal materials and the enrichment is mainly due to anthropogenic inputs (Hernandez et al. 2003). Therefore, the percentage of investigated samples having EF values greater than 2 in the study area calculated and represented in Fig. 4, which indicates that the heavy metals of Ni, Co, and Mn in all soil samples may be as a result of crustal materials or natural weathering processes. On the other hand, the heavy metals of Zn, Cu, Cr, and Pb having EF values greater than 2 in the most soil samples, indicating that these heavy metals may be enriched as a result of

anthropogenic inputs. In addition, the calculated lithogenic and anthropogenic proportion of these four metals in the study area confirms this finding (Fig. 5). The mean values of anthropogenic proportion of these metals in the investigated areas regardless soil sampling depth were amounted to 78.4–86.6 % for Zn, 44.2–59.3 % for Cu, 83.1–84.6 % for Cr, and 72.4–85.2 % for Pb. The value of 50 % can be considered as a minimum value for anthropogenic contribution. In this context, our results indicate that the soil samples showed a higher significant anthropogenic contribution for Zn, Cr, and Pb than for Cu. Generally, it can be speculated that these four metals of the studied area are originated from anthropogenic sources, revealing that the environmental metal contamination of industrial activities might be occurred. The emissions from industrial chimneys of petrochemicals in the study area may be a possible source for heavy metals. Chemical and petrochemical industries have been identified as large emitters for heavy metals. Previously, it has been reported that heavy metals such as Cd, Pb, Cr, and As are the most abundant metals found in soils around chemical and petrochemical sites (Kabir et al. 2012), mainly due to refining operations and burning of residual oils. Overall, it is possible that the marine environment can be polluted with heavy metals, attributing to the industrial and human activities (Badr et al. 2009; Zhang et al. 2012; Usman et al. 2013). Several other researchers have evaluated heavy metal contamination in sediments from some Red Sea coastal areas, Kingdom of Saudi Arabia (Badr et al. 2009; Usman et al. 2013). They found that the sediment samples were enriched with some heavy metals such as Cd, Cu, Zn, Pb, Ni, and Mn, mainly due to discharging uncontrolled industrial and sewage wastes. In other reports, it has been suggested that accumulation of heavy metals (Cu, Zn, Cr, and Pb) in sediments might be attributed to the aquaculture activities (Zhang et al. 2012). The contamination of marine environment with heavy metals such as Zn, Cu, Cr, and Pb can

Table 4 Rotated component matrix of soil samples using varimax raw rotation

Metals	0–30 cm depth				30–60 cm depth			
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3	Factor 4
Zn	0.11	0.90*	−0.20	0.09	0.04	0.83*	−0.42	0.13
Cu	0.21	0.92*	−0.04	0.04	0.13	0.84*	0.16	−0.35
Ni	0.36	0.11	0.13	0.83*	0.91*	0.14	0.09	0.23
Cr	0.96*	0.12	0.02	0.19	0.36	−0.17	0.14	0.85*
Co	0.30	−0.06	−0.21	0.81*	0.88*	0.10	−0.16	−0.16
Mn	0.75*	0.23	0.03	0.57	0.80*	−0.02	0.06	0.53
Pb	0.06	−0.16	0.97*	−0.01	0.04	−0.09	0.94*	0.12
Fe	0.74*	0.24	0.11	0.59	0.86*	0.00	0.14	0.47
Eigenval	4.13	1.68	0.95	0.49	3.76	1.87	0.95	0.63
% total of variance	51.57	20.98	11.90	6.15	46.98	23.42	11.90	7.90
Cumul. %	51.57	72.54	84.45	90.60	46.98	70.40	82.31	90.21

generally be attributed to boat exhaust emissions, antifouling chemicals used in boat paints, sewage effluents, chemical and oil leakage, and discharges of reject water and effluents from a desalination plant (Badr et al. 2009; Zhang et al. 2012; Usman et al. 2013; Naser 2013).

## Multivariate statistical analysis and correlation study

The correlation study showed that significant positive correlations among various metals in soil samples of study area (Table 3). According to Spearman's coefficient, Ni, Co, Cr, and Cu are significantly correlated with Fe and Mn at soil sampling depth of 0–30 and 30–60 cm (0.39<r<0.88), except for Cu at 30–60 cm depth. Ni, Cr, and Co are

also significantly correlated with each other. Additionally, Zn showed significant positive correlation with the Cu at 0–30 cm depth (r=0.59). By contrast, Zn showed significant negative correlation with the Pb at 0–30 cm depth (r=−0.39) and 30–60 cm depth (r=−0.44).

The results of PCA showed that four factors are extracted, which account for 90.60 % and 90.21 % of the total variance at soil sampling depth of 0–30 and 30–60 cm, respectively (Table 4). Factor 1 is dominated by Cr, Fe, and Mn at 0–30 cm depth or Ni, Co, Fe, and Mn at 30–60 cm depth, which amounted to 51.57 % and 46.98 % of the total variance, respectively. Factor 2 is dominated by Zn and Cu accounts for 20.98 % and 23.42 % of the total variance at soil sampling depth of 0–30 and 30–60 cm, respectively. Factor 3 is domi-

Fig. 6 PCA loading 3D plot (PC1 vs. PC2 vs. PC3) for heavy metals at soil sampling depth of 0–30 cm and 30–60 cm
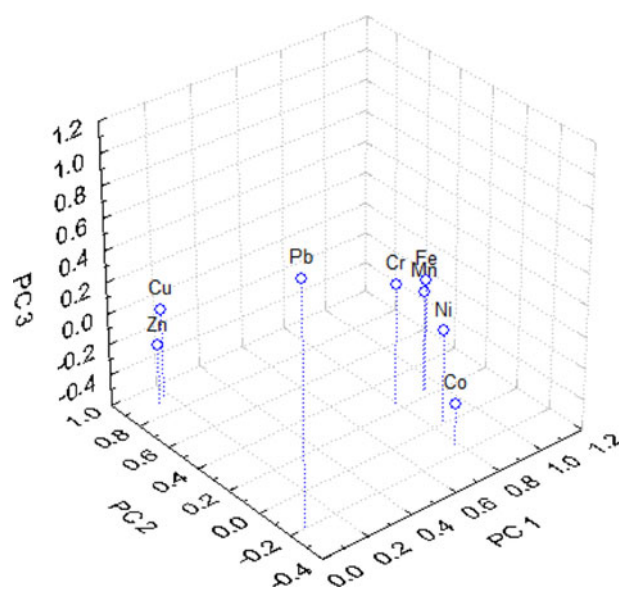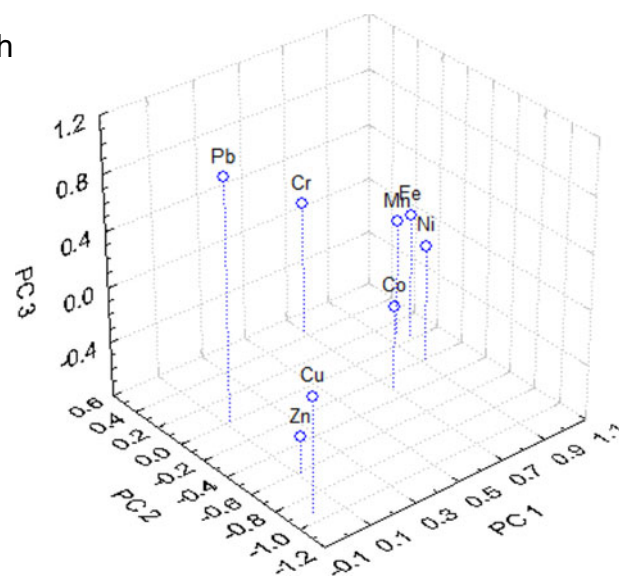
nated only by Pb accounting for 11.90 % of the total variances. However, Factor 4 is dominated only by Ni at 0–30 cm depth or only by Cr at 30–60 cm depth accounting for less than 8 % of the total variance. The 3D plot of the PCA showed that the investigated heavy metals come from different sources (Fig. 6). These data indicate that there is high loading of some metals such as Fe, Mn, Ni, Co, and Cr at 0–30 cm depth and Fe, Mn, Ni, and Co at 30–60 cm depth. Based on the HCA, the investigated heavy metals are grouped into different clusters (Fig. 7). It was observed that there is a cluster containing Fe and Mn, which may be associated with some heavy metals such as Ni, Co, or Cr. Moreover, the correlation coefficients between them are also found to be significant. This finding may reveal that these heavy metals are from the same sources. In this context, Fe, Mn, Ni, and Co originated from lithogenic source, as indicated by EF values (EF≤2). The high obtained loading of these metals and their significant positive correlations with Fe and Mn suggests that Mn and Fe oxides/hydroxides in soil might play a major role in soil metal distribution. Similarly, Chen et al. (2008)

found that Co, Cr, Ni, and Mn had significantly positive correlations with Al_2O_3, Fe_2O_3, and SiO_2 of the soils, indicating that the source of these heavy metals was mainly controlled by soil-forming factors. This could further confirm their natural sources.

An obtained correlation between Cu and Zn in PCA and correlation analyses is an indicator for another common source of the two metals. It was also observed that Pb stands alone (component 3) in PCA analysis and did not show significant positive correlation with other metals, suggesting probably another different source. Similarly, the HCA indicates that these three metals of Zn, Cu, and Pb were also grouped into two clusters: (a) Zn and Cu, and (b) Pb, which have EF values greater than 2, indicating that these heavy metals may be originated from anthropogenic sources. Though the EF values of Cr are greater than 2 and its possible origin is anthropogenic; the concentrations of Cr are significantly correlated with Fe and Mn that is of lithogenic origin. Therefore, this finding speculates that Cr in soil may be controlled by both natural and anthropogenic sources. Our results generally suggest that Zn, Cu, Cr, and Pb can be

Fig. 7 Cluster dendogram for heavy metals by Ward's method (Pearson's r) at soil sampling depth of 0–30 cm and 30–60 cm
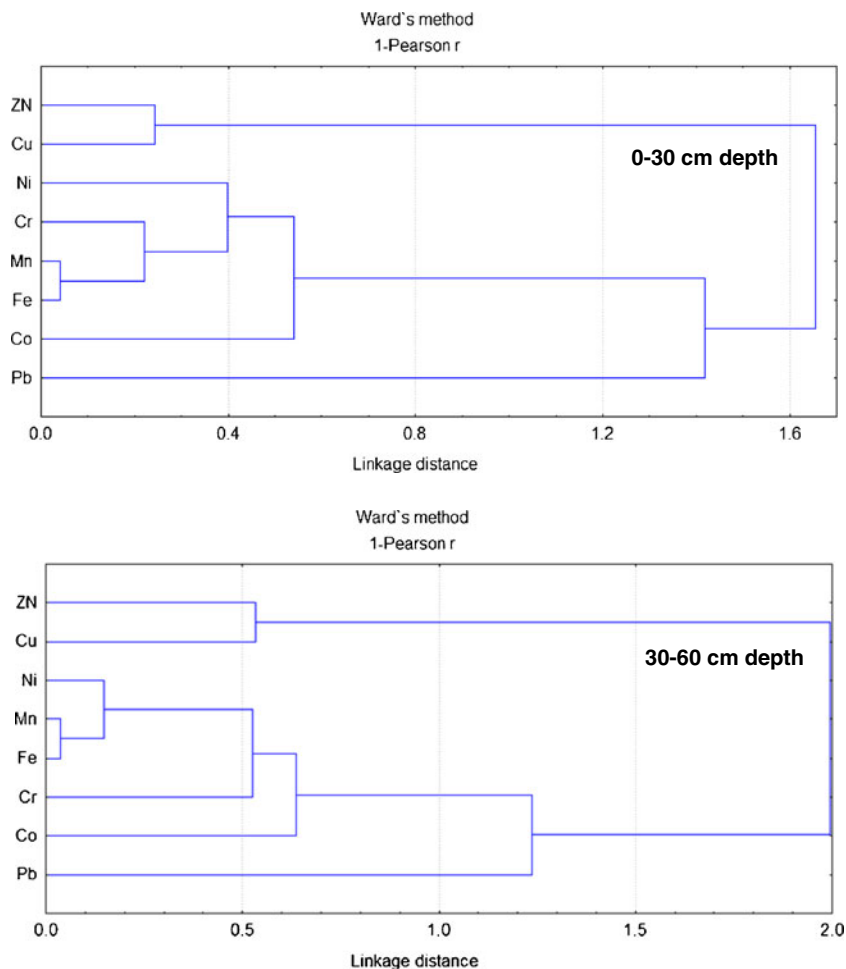
affected by anthropogenic activities, whereas Fe, Mn, Co, and Ni can be controlled by original materials and therefore interpreted as natural sources.

Conclusions

The results of the study showed that only Cr concentrations are higher than those of the soil common range as well as the geochemical background in average shale. Based on the obtained data of EF values, PCA, HCA, and correlation analysis, the soil samples of study area may be enriched with some heavy metals such as Zn, Cu, Cr, and Pb, which are defined as anthropogenic sources. By contrast, Ni, Co, Mn, and Fe may be originated from the soil parent materials and natural process. It should be mentioned that it is possible to use multivariate analyses in combination with EF values as useful tool to investigate the origin of heavy metal in soils. Future studies should focus on investigation of speciation, leachibility, and bioavailability of heavy metals in such soils of the Arabian Gulf coast affected by industrial activities.

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