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Assessment of Heavy and Trace Metals in Surface Soil Nearby an Oil Refinery, Saudi Arabia, Using Geoaccumulation and Pollution Indices

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Abstract

The present study deals with the measurement of heavy and trace metals in the soils of Ras Tanura city nearby one of the oldest and largest oil refineries located on Arabian Gulf, eastern Saudi Arabia. Metals were analyzed in 34 surface soil samples using plasma atomic emission spectrometer (ICPE-9820). The result showed that the mean values of the metals concentrations were in the order: Cd > Mo > Tb > Ce > Hf > Eu > Yb > U > Sm > Rb > Cr > Ni > Pb > Sc > Cs > Zn > Lu > Co. The mean values of Cd (39.9 mg/kg), Mo (13.2 mg/kg), Eu (4.01 mg/kg), Hf (6.09 mg/kg), Tb (8.23 mg/kg), and Yb (3.88) in soil samples were higher than the background values in soil and the world average. The obtained results indicated to elevated levels of Cd and Mo in most samples, with mean concentrations exceeded the background levels by 113 times for Cd and 5 times for Mo. Pollution index (PI) and Geoaccumulation (I_{geo}) for each metal were calculated to assess the metal contamination level of surface soil in the study area. The assessment results of PI and I_{geo} revealed a significant pollution by Cd, Mo, Eu, Hf, Tb, and Yb in most of sampling sites nearby Ras Tanura refinery.

In an ecosystem, occurrence of heavy metals (Co, Al, Fe, Bi, V, Cu, Zn, Ti, U, Th, etc.) in the environment is generally within the acceptable limits. The natural sources of heavy metals in the ecosystem are geologic sources, such as rock formation, soil, and transported sediments by wind (Al-Dabbas et al. 2015a; Christoforidis and Stamatis 2009; El-Taher 2010a, b; El-Taher and Abdel Halim 2014). However, this optimum ecological equilibrium may be impaired due to the increase of heavy metals in the environment as a result of industrial production processes and human consumption activities (Cai et al. 2015). Thus, anthropogenic inputs become a source of hazard far superior to that of natural concentrations (Ajayi et al. 2009).

Crude oil is one of the sources of trace metals, which include heavy minerals leached during migration and contamination during production (Ajayi et al. 2009). Furthermore, oil refineries produce refined products that are the important source of energy for industry sector, agriculture and essential for daily life. During refining process, a huge amount of toxic elements may contaminate the surrounding environment due to poor management, lack of environmental controls, and faulty equipment (Tiwari et al. 2011). The waste produced from refinery processes is known as oil refinery sludge that has a high content of petroleum-derived hydrocarbons and heavy metal (vanadium, zinc, chromium (total), iron, nickel, copper, etc.) (Reinecke et al. 2016; Marín et al. 2006). The concentrations of heavy metals (such as Zn, Pb, Cd, Ni, Cu, Cr, and Mn) in oily sludge are relatively higher than those in soil (Marín et al. 2006; Venkateswar Reddy et al. 2011; Tiwari et al. 2011). Despite all feasible precautions, some oil refinery and gas operations would upset natural balance of ecosystem.

Heavy metal pollution in the environment has become a worldwide problem. This is attributed to their toxicity, extensive causes, and accumulative characteristics. The accumulation of large amounts of heavy and trace metals in water and soil for long time can be harmful to land, marine animals, and plants, upsetting delicate ecological balances and contaminating food sources, which are potentially harmful to human health (Hardaway et al. 2004; Sarkar et al. 2011). Essential ones, such as copper, nickel, zinc, and manganese,

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are fundamental for soil and have positive effect but in limited concentrations, whereas lead, mercury, and cadmium are nonessential, even at extremely low concentrations are toxic and potential cofactors in cancer. Elevated levels of heavy metals in soil can be easily transferred into human bodies from suspended dust or direct contact (Benhaddya and Hadjel 2014). Generally, the impact of high concentrations of toxic metals on human and animals include reduced growth, development, organ damage, blood forming, cardiovascular, renal and reproductive systems, nervous system damage, and, in extreme cases, death. Moreover, these metals lead to attention deficit and behavioral abnormality and reduced intelligence for adults (Christoforidis and Stamatis 2009; Ogoyi et al. 2011; Rahman et al. 2012; Kim et al. 2015; Alshahri 2017).

Naturally occurring radioactive materials (NORMs) are encountered in oil and gas exploration. NORMs contain radioactive materials, which include long-lived radioactive elements, such as uranium, thorium, and their daughter products (Ajayi et al. 2009). During oil refining operations, NORM may leak into the surrounding environment, which may lead to health risk and potential environmental hazards.

People living in or near the vicinity of an oil refinery are at greater risk of exposure to heavy metals through inhalation and direct contact with contaminated media. Monitoring and estimating of heavy metals in soil surrounding residential area nearby an oil refinery are extremely important to control their pollution in the environment and protect the population from their risk. Therefore, the main objectives of this study are as follows:

- Measure the concentration of heavy and trace metals in the soil surrounding the residential area near the oil refinery area in Ras Tanura city.
- Assess the contamination of heavy and trace metals in the soil.
- The single pollution index (PI_i) and geoaccumulation index (I_{geo}) were calculated to assess the pollution levels of metals.

Materials and Methods

Study Area

The present study was performed in Ras Tanura City, which is the most important city in the eastern province of the Kingdom of Saudi Arabia. Ras Tanura City is situated on the Arabian Gulf (26°38′38″N and 50°9′33″E) and covers approximately 290 km². The city is surrounded by seawater from three sides, east, west, and south. Natural spring waters are located in the west of Ras Tanura City. Summer is the longest season in the Arabian Gulf. The climate is hot, and the absolute maximum of temperature is 45.6 °C with high humidity, which frequently exceeds 85%. Strong northerly wind blows dust and sand, mostly in the summer. One of the largest and oldest oil refineries in Saudi Arabia and the Middle East is located south of Ras Tanura City on the coast of the Arabian Gulf. In addition, there are an oil well, a gas plant, and the largest port to oil ship. The residential area is located along the border of the oil refinery area, with a population of approximately 73,933 inhabitants. West of the city, the soil of the coast is mainly composed of sand, mud, sediments, and sludge, whereas the soil of the eastern coast of the city is composed of sand and marine sediments.

Due to the strong wind, heavy and trace metals may be transported and accumulate in the surrounding environment, which may cause a lot of health concerns regarding both the population and environment.

Sampling and Sample Preparation

In this study, surface soil samples were randomly collected from 34 sites in Ras Tanura near the oil refinery and surrounding residential area (Table 1; Fig. 1). One kilogram of soil was collected (0–20 cm) from each site in different directions. All soil samples were bulked as a single sample and dried in an oven at 70 °C for 24 h. After drying the samples and removing stones, leaves, and foreign particles, soil samples were crushed and sieved for more homogeneity.

Chemical Analysis

Microwave digestion technique was used to digest the soil samples, where 0.5 g of each dried sample was added to 16 ml of 60% HNO_3 and 4 ml of H_2O_2 in a beaker (As indicated in the manual of microwave technique). After standing for 2 days, the solution was heated at 180 °C for 40 min. After cooling to room temperature, the obtained extract was filtered, and distilled water was added up to 60 ml. The filtered solution was transferred to polyethylene volumetric flask for analysis. The standard solutions used contained metal ions at different concentrations, which were prepared by diluting 1000 mg/L multielement standard solution (PANREAC QUIMICA S.L.U.) immediately before use.

The concentrations of metals were measured by Plasma Atomic Emission Spectrometer (Shimadzu ICPE-9820) (located at Environmental Research Laboratory, Imam Abdulrahman Bin Faisal University). The operating conditions were: frequency ~ 27 MHz, RF power Maximum ~ 1.6 kW (0.2 kW step), Output stability: Within ± 0.3%, efficiency ~ 75%, plasma gas (Ar) flow rate ~ 0.5 L/min step, auxiliary gas (Ar) ~ 0.05 L/min step, Carrier gas ~ 0.01 L/min step and purge gas (Axial view) ~ approximately 0.5 L/min. Spectrometer and CCD (charge coupled device) detector can conduct

Table 1 Heavy metals concentrations (mg/kg) in soil samples collected from Ras Tanura city near refinery

Sample ID	Cd	Ce	Co	Cr	Cs	Eu	Hf	Lu	Mo	Ni	Pb	Rb	Sc	Sm	Tb	U	Yb	Zn
S1	33.1	12.7	0.548	2.68	2.05	5.86	5.44	1.22	10.5	3.54	2.05	4.33	2.92	4.61	12.8	5.46	5.83	0.6
S2	30.5	12.7	0.56	1.84	2.39	5.99	5.20	1.22	10.2	3.66	2.05	4.55	2.98	4.8	13.0	5.53	5.99	0.50
S3	31.8	12.7	0.55	1.76	2.53	6.07	5.42	1.25	10.7	3.65	2.06	4.62	2.99	4.90	13.1	5.52	6.11	1.51
S4	33.1	13.4	0.57	3.90	2.68	6.35	5.69	1.28	12.0	3.92	2.16	4.86	3.10	5.14	13.6	5.72	6.42	0.90
S5	36.5	13.0	0.57	1.90	2.68	6.29	6.01	1.30	12.2	3.78	2.14	4.81	3.10	5.10	13.4	5.66	6.36	0.55
S6	32.8	5.58	0.51	1.61	2.35	3.86	4.90	1.02	10.5	2.52	1.36	3.17	2.22	3.22	7.90	3.60	3.73	0.63
S7	35.2	7.26	0.53	1.64	2.41	4.67	5.38	1.12	11.4	2.94	1.62	3.65	2.54	3.83	10.0	4.30	4.54	0.80
S8	86.2	10.4	0.67	2.30	2.47	5.64	14.6	1.58	33.8	3.50	2.28	4.28	2.89	4.60	12.1	5.14	5.57	1.42
S9	36.2	11.7	0.55	1.75	2.65	6.02	5.90	1.26	12.0	3.62	2.02	4.58	3.00	4.88	12.8	5.42	6.02	3.05
S10	44.6	11.1	0.58	2.11	2.58	5.84	6.91	1.32	14.6	3.6	2.11	4.52	3.00	4.75	12.5	5.30	5.82	2.11
S11	51.2	8.47	0.58	2.33	2.47	5.08	7.55	1.26	16.6	3.23	1.94	3.96	2.71	4.13	10.7	4.66	4.93	1.94
S12	44.8	4.64	0.54	2.14	1.92	3.26	6.10	1.09	13.0	2.15	2.51	2.95	1.93	2.63	6.91	3.16	3.10	3.46
S13	40	6.35	0.52	1.67	2.34	4.18	5.78	1.08	12.4	2.74	1.54	3.40	2.38	3.44	8.71	3.94	4.01	1.46
S14	67.4	6.76	0.61	2.11	1.94	4.34	9.85	1.28	22.3	2.68	2.29	3.38	2.29	3.44	9.58	4.10	4.14	2.09
S15	107	6.96	0.72	3.77	1.94	4.68	21.2	1.74	52.8	2.96	3.26	3.49	2.41	3.71	10.4	4.38	4.45	2.33
S16	44	4.43	0.54	3.58	1.79	3.32	5.93	1.02	13.2	2.36	1.56	2.78	1.98	2.63	7.16	3.28	3.07	1.56
S17	76.4	–	0.61	3.96	–	–	10.3	1.05	21.2	1.48	1.67	–	–	–	0.64	0.86	2.4	1.32
S18	36	–	0.51	4.0	–	–	2.60	0.69	7.27	0.60	1.34	–	–	–	1.01	0.67	3.32	0.80
S19	47.9	1.96	0.55	4.24	–	1.46	5.29	0.91	11.0	0.18	1.55	–	–	1.17	3.65	1.04	1.25	0.62
S20	35.9	0.87	0.50	4.13	–	0.85	4.10	0.84	7.97	0.75	1.26	–	0.04	0.56	3.49	1.36	0.63	0.63
S21	45.4	3.11	0.53	3.95	–	2.39	5.41	0.95	11.5	1.14	1.55	0.62	0.85	1.96	5.36	2.09	2.18	1.07
S22	40.7	2.98	0.51	3.9	–	2.08	5.06	0.92	10.2	1.56	1.33	1.16	1.05	1.58	5.46	2.38	1.81	0.97
S23	33.2	4.10	0.50	3.86	0.37	2.50	4.12	0.90	8.39	1.51	1.46	1.40	0.99	1.93	6.23	2.53	2.26	0.89
S24	49.1	6.95	0.57	4.61	0.90	3.86	6.56	1.13	14.3	2.04	2.03	2.18	1.52	3.12	8.57	3.40	3.78	2.53
S25	35.8	2.84	0.49	3.65	0.97	2.50	4.46	0.86	9.97	1.32	1.18	1.22	1.16	2.06	4.72	2.0	2.33	1.13
S26	29.2	9.6	0.52	4.02	1.40	4.97	4.54	1.08	9.04	2.60	1.72	2.78	2.15	4.01	10.2	4.13	4.90	0.51
S27	39.8	8.81	0.55	4.26	1.66	5.02	6.06	1.17	12.6	2.80	3.17	2.88	2.39	4.06	10.0	4.16	4.91	0.59
S28	34.0	7.86	0.51	3.17	1.36	4.39	4.79	1.02	9.96	2.29	1.60	2.39	2.05	3.48	8.89	3.66	4.18	0.51
S29	43.0	8.05	0.53	1.91	1.68	4.79	6.37	1.14	13.3	2.52	1.75	2.76	2.36	3.83	9.47	3.98	4.57	0.60
S30	23.1	1.96	0.36	0.42	1.66	1.57	0.87	0.52	1.36	1.03	0.18	1.34	1.21	1.34	1.32	0.87	1.46	0.24
S31	1.85	–	0.34	0.38	–	–	–	0.11	–	1.82	0.31	–	–	–	–	0.07	–	0.24
S32	5.56	–	0.32	0.27	–	–	–	0.13	–	1.34	0.19	–	–	–	–	2.06	–	0.23
S33	0.87	–	0.34	0.48	–	–	0.53	0.44	1.72	0.65	0.28	–	–	–	–	1.45	–	0.27
S34	23.9	–	0.43	3.40	–	0.25	1.96	0.61	4.12	0.66	1.01	–	–	0.20	1.37	0.45	0.07	0.70

simultaneous measurement of all elements at all wavelengths (167–800 nm) even when there are many target elements and samples with resolution of ≤ 0.005 nm at 200 nm.

Analytical quality control (QC) was performed to assess the precision and accuracy of the laboratory determinations. The methods of element measurement were validated and controlled by preparation of standard solutions, calibration of instrument according to the manufacturer's recommendations, and daily run of blank samples and duplicates with each analytical cycle. As internal standard elements, Indium and yttrium, which are few concentrations in soil, as a recovery standard and showed 98 and 104%, respectively. The limits of detection for examined metals ranged from 0.007 ppm for Cd to 0.2 ppm for Sc. The analytical results showed that the accuracy of method was within the acceptable limits.

Data Analysis

Descriptive statistics (minimum, maximum, mean, standard deviation, and standard error) of the analytical data were calculated using Microsoft Excel. The mean values of all metals were compared with the Background values and world average. However, the data of surface soil in the area surrounding an oil refinery in Ras Tanura City were compared with the mean values of other studies. Furthermore, the pollution indices for each metal in different sites were computed.
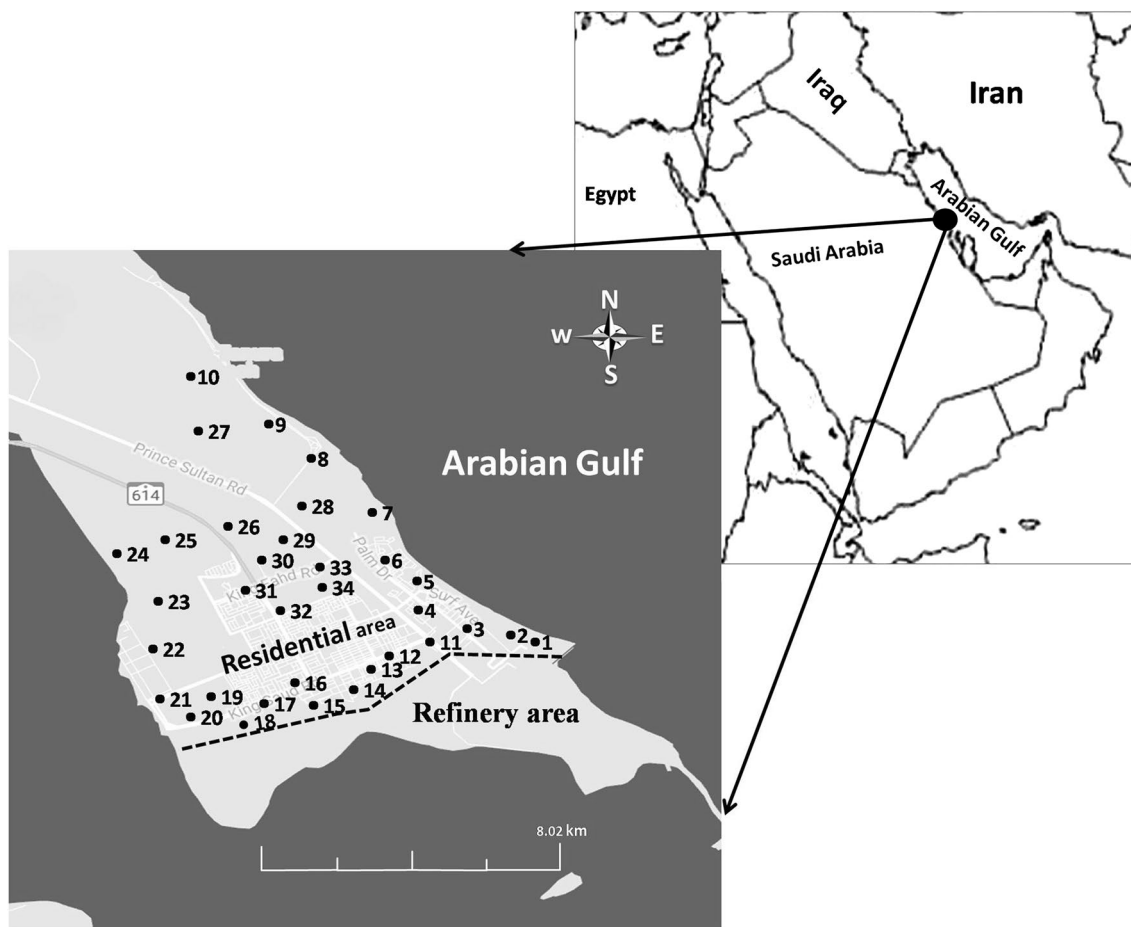
Fig. 1 Location map of sampling sites in Ras Tanura City, Saudi Arabia

Pollution Indices

The pollution index (PI) and geoaccumulation index (I_{geo}) for each heavy and trace metal were evaluated. These indices were applied in assessing the metal contamination of soil. The formulas of PI and I_{geo} are defined as the following (Khalilova and Mammadov 2016; Benhaddya and Hadjel 2014):

$$PI_i = C_i/S_i \qquad (1)$$

$$I_{geo} = \text{Log}_2\left[C/\left(1.5 B_n\right)\right] \qquad (2)$$

C_i is the metal concentration in sample, S_i is the background value, B_n is the geochemical background concentration of metal n, and the constant 1.5 is introduced to minimize the effects of possible variations in the background values that may be attributed to lithologic variations in soils.

Results and Discussion

Heavy and Trace Metals in Soil Samples

In the present study, 29 heavy and trace metals were measured in soil samples collected from Ras Tanura City nearby the most important oil refinery in Saudi Arabia. Eighteen elements were determined, whereas 11 elements not detectable, such as As, Ir, La, Sb, Se, Sn, Ta, Te, Th, W, and Zr. Table 1 shows the detectable metals (Cd, Ce, Co, Cr, Cs, Eu, Hf, Lu, Mo, Ni, Pb, Rb, Sc, Sm, Tb, U, Yb, and Zn). Descriptive statistics of heavy and trace metals concentrations in Ras Tanura soils, world average, and background are summarized in Table 2. Widely variations can be shown in the concentrations of Cd (0.87–107 mg/kg), Ce (0.87–13.4 mg/kg), Co (0.32–0.72 mg/kg), Cr (0.27–4.61 mg/kg), Cs (0.37–2.68 mg/kg), Eu (0.25–6.35 mg/kg),

Table 2 Descriptive statistics of heavy and trace metals concentrations (mg/kg) in Ras Tanura soils

	Cd	Ce	Co	Cr	Cs	Eu	Hf	Lu	Mo	Ni	Pb	Rb	Sc	Sm	Tb	U	Yb	Zn
Min	0.87	0.87	0.32	0.27	0.37	0.25	0.53	0.11	1.36	0.18	0.18	0.62	0.04	0.20	0.64	0.07	0.07	0.23
Sample ID	S33	S20	S31	S32	S23	S34	S33	S31	S30	S19	S30	S21	S20	S34	S17	S31	S34	S32
Max	107	13.4	0.72	4.61	2.68	6.35	21.2	1.74	52.8	3.92	3.26	4.86	3.10	5.14	13.6	5.72	6.42	3.46
Sample ID	S15	S4	S15	S24	S4, S5	S4	S15	S15	S15	S4	S15	S4	S4, S5	S4	S4	S4	S4	S12
Mean	39.9	7.40	0.52	2.70	1.97	4.01	6.09	1.02	13.2	2.67	2.27	3.16	2.16	3.28	8.23	3.30	3.88	1.14
SD	20.9	3.82	0.09	1.29	0.63	1.75	3.78	0.35	9.31	1.09	0.72	1.27	0.82	1.42	4.02	1.75	1.78	0.82
SE	3.58	0.72	0.02	0.22	0.03	0.32	5.66	0.06	1.65	0.19	0.12	0.25	0.16	0.26	0.72	0.30	0.32	0.14
Count	34	28	34	34	25	29	32	34	32	34	34	26	27	29	31	34	31	34
Background value[a]	0.3	59	19	90	5	1	1.8	2.8	2.6	68	20	140	13	6.4	1	3.7	2.6	95
World average[b]	0.3	55	10	67	5	1	6.4	–	1.1	24	29	68	9	4.5	0.7	4	–	67

[a]Turekian and Wedepohl (1961)

[b]Bowen (1979) and Kabata-Pendias (2010)

Hf (0.53–21.2 mg/kg), Lu (0.11–1.74 mg/kg), Mo (1.36–52.8 mg/kg), Ni (0.18–3.92 mg/kg), Pb (0.18–3.26 mg/kg), Rb (0.62–4.86 mg/kg), Sc (0.04–3.10 mg/kg), Sm (0.20–5.14 mg/kg), Tb (0.64–13.6 mg/kg), U (0.07–5.72 mg/kg), Yb (0.07–6.42 mg/kg), and Zn (0.23–3.46 mg/kg). The mean values of Cd (39.9 mg/kg) and Mo (13.2 mg/kg) were 133 and 5 times, respectively, higher than the background. Also, the mean values of Cd and Mo in soil samples were higher than the world average of metals in soil. The mean concentrations of Eu (4.01 mg/kg), Hf (6.09 mg/kg), Tb (8.23 mg/kg), and Yb (3.88) were slightly higher than the background values and the world average values. The mean concentrations of the other heavy and trace metals, such as Ce, Co, Cr, Cs, Lu, Ni, Pb, Rb, Sc, Sm, U, and Zn, were lower than the background and world average of elements in soil. The mean of metals concentrations in the soil samples showed in the following order: Cd > Mo > Tb > Ce > Hf > Eu > Yb > U > Sm > Rb > Cr > Ni > Pb > Sc > Cs > Zn > Lu > Co. Table 1 shows that all cadmium values in soil are higher than the background in all sites while the values of the rest metals range from lower to higher than the background.

The elevated levels of Cd and Mo in soil samples collected from the region near oil refinery and gas plant suggest that the environment in this region was contaminated with Cd and Mo. The concentrations of Cd in all samples collected from roadside in the city exceeded the limit for public and residential area. This contamination may be related to the leakage of heavy metals from oil and oily sludge, where the emitted Cd is carried away by the wind to other sites. The presence of heavy metals in oil (such as cadmium, chromium, cobalt, molybdenum, nickel, zinc, lead, etc.) has been well documented by several studies (Tiwari et al. 2011; Atagana 2011; Bettmer et al. 2012; Jasmine and Mukherji 2015).

The maximum values of Cd (107 mg/kg) and Mo (52.8 mg/kg) were found in soil sample S15, which was collected from the location at the border of oil refinery area (Table 2). These values for Cd and Mo are 356 and 20 times higher than the background, respectively. The presence of these samples in an area close to oil refinery indicates to the potential contribution of oil refinery as a source of cadmium and molybdenum contamination. According to cadmium effect in environment, it is categorized as a super dangerous metal (Khalilova 2015). Furthermore, cadmium is carcinogenic or toxic element and affecting the kidney, liver, skin or teeth (Zevenhoven and Kilpinen 2001; Nwaichi et al. 2014; Alshahri 2017). Similarly, the maximum value of Hf (21.2 mg/kg) was found in the same sample S15, where the maximum value of Hf is 11 times higher than the background value and 3 times higher than the world average value, which may indicate to the metal contamination in this site. In contrast, the maximum values of Eu (6.35 mg/kg), Tb (13.6 mg/kg), and Yb (6.42 mg/kg) were found in soil sample S4, which are higher than the background and the world average values. However, the maximum values for the other metals (Ce, Co, Cr, Cs, Lu, Ni, Pb, Rb, Sc, Sm, U, and Zn) were relatively lower than the background values. In the other hand, elevated levels of Cd, Mo, and Eu may be accompanied by high concentrations of radioisotopes of ^{109}Cd, ^{99}Mo, ^{155}Eu, ^{154}Eu, and ^{152}Eu. The exposure to gamma rays emitted from these radioisotopes for long-term may have serious health implications if living organisms are exposed to them.

Elevated levels of heavy and trace metals are released in tiny particulates as dust, which will rise in the wind to be inhaled or transported in topsoil or edible plants through precipitation of their compound or by ion exchange into soils or mud (Nwaichi et al. 2014). Accumulation of heavy metals may cause localized pollution, which can have multiple effects on the environments (Nwaichi et al. 2014). Generally, there are clear variations in the values of heavy and trace metals in soil from site to site (Table 1).

In addition to the effects of the anthropogenic sources on the concentrations of heavy metals and trace elements in soil, the variations of their levels in soil samples also may be associated with the local geological, geographical properties, their abundance in earth's crust, and the different depositional processes in soil. Depositional processes may be affected by sand processes, such as dissolution, sorption, migration, precipitation, binding by organic matter, absorption, and volatilization. Additionally, the accumulation metals in soil depend on different physicochemical factors, such as type of pH, organic matter contents, and grain size. These parameters are thought to play an important role in controlling the concentration of metals in soil (Al-Abdali et al. 1996; Alshahri 2017).

In the current study, the mean value of Cd (39.9 mg/kg) was compared with those found in various soils from Saudi Arabia, Azerbaijan, Australia, China, Greece, Iraq, Turkey, Nepal, Poland, and Italy (Table 3) (Hasayen et al. 2017; Al-Wabel et al. 2017; Khalilova and Mammadov 2016; Birch et al. 2011; Lv et al. 2015; Christoforidis and Stamatis 2009; Al-Dabbas et al. 2015a; Guler et al. 2010; Tripathee et al. 2016; Jarzyńska and Falandysz 2012; Guagliardi et al. 2012). The Cd concentration was generally high compared with those recorded values ranging from 0.080 mg/kg (Poland) to 13.3 mg/kg (Iraq).

The mean value of Mo (13.2 mg/kg) in soil was greater than the reported by El-Taher et al. (2016) (4.71 mg/kg in soil, southern Saudi Arabia), Guler et al. (2010) (4.78 mg/kg in agriculture soil located around various industrial facilities, Turkey), and Guagliardi et al. (2012) (1.9 mg/kg in urban soil, Italy). However, the mean concentrations of Co, Cr, Cs, Hf, Ni, Pb, Rb, Sc, U, and Zn in the analyzed soils were lower than the reported values in soil from Saudi Arabia and other countries (Almasoud et al. 2015; El-Taher et al. 2016; Hasayen et al. 2017; Al-Wabel et al. 2017; Abdel Halim and El-Taher 2014; Khalilova and Mammadov 2016; Birch et al. 2011; Lv et al. 2015; Christoforidis and Stamatis 2009; Tiwari et al. 2011; Al-Dabbas et al. 2015a; Guler et al. 2010; Tripathee et al. 2016; Jarzyńska and Falandysz 2012; Guagliardi et al. 2012). The comparison of Ce, Eu, Lu, Sm, Tb, and Yb with other studies was difficult due to the lack of the data in literatures.

Pollution Assessment in Soil

In the current study, pollution and geoaccumulation indices were calculated for each metal to confirm and justify the pollution in soil. The degree of metal pollution was assessed based on the classification of pollution levels as shown in Table 4 (Benhaddya and Hadjel 2014; Khalilova and Mammadov 2016).

Pollution Index

To assess the contamination level for each metal in soil, the pollution index (PI) was calculated according to the natural background value of metal in soil.

Table 5 shows the calculation values of the PI for each metal in all soil samples. The PI values for Ce, Co, Cr, Cs, Lu, Ni, Pb, Sc, Sm, and Zn ranged between 0.015 and 0.227 (mean value 0.13), 0.02–0.40 (mean value 0.05), 0.003–0.40 (mean value 0.04), 0.07-0.54 (mean value 0.40), 0.04–0.62 (mean value 0.36), 0.003–0.06 (mean value 0.03), 0.01–0.16 (with a mean value of 0.08), 0.004–0.03 (mean value 0.02), 0.003–0.24 (mean value 0.17), 0.03–0.80 (mean value 0.51), and 0.002–0.04 (mean value 0.013), respectively. Based on the classification of pollution in Table 4, the study area can be categorized as unpolluted by Ce, Co, Cr, Cs, Lu, Ni, Pb, Rb, Sc, Sm, and Zn. The PI value ranged between 0.03 and 2.47 (with a mean value of 1.49) for Yb, which is categorized as unpolluted to moderately polluted. Similarly, the soil in the study area was classified as being at an unpolluted to very strongly polluted level by Eu, Hf, Mo, Tb, and U; the PI values for these metals ranged between 0.25 and 6.35 (mean value 4.07) for Eu, 0.29–11.8 (with a mean value of 3.38) for Hf, 0.52–20.3 (mean value 5.07) for Mo, 0.64–13.6 (mean value 8.23) for Tb, and 0.07–4.16 for U (mean value 1.61). The PI value for Cd ranged from 2.90 to 357, which mean the classification of pollution level in soil by cadmium was moderately polluted to very strongly polluted, and the highest mean value of PI was for Cd (130).

Figure 2 shows the variations of PI values in soil samples from different sites of the study area. Eleven metals (Ce, Co, Cr, Cs, Lu, Ni, Pb, Rb, Sc, Sm, and Zn) were unpolluted in all sites, whereas the values of PI for Yb, U, and Eu ranged from unpolluted to very strong polluted. The highest values of PI for Yb, U, and Eu were found in site 4 due to the elevated levels of these metals. Similarly, the values of PI for Mo, Hf, and Tb ranged from unpolluted to very strong polluted in all sites, with the exception of Cd, which is classified very strong polluted in all soil samples. The highest values of PI for Mo, Hf, Tb, and Cd were found in soil sample collected from site 15. This result confirms the presence of pollution source close to the area of site 15. The high values of PI for Mo, Hf, Tb, Yb, U, Eu and Cd in different sites indicate to the elevated levels of these metals. The increased levels of Mo, Hf, Tb, Yb, U, Eu, and Cd in different sites in the study area are due the deposition of the atmospheric emissions from transport and oil refinery waste, which could be carried over long distance.

Figure 3 shows the pollution characteristics of metals in soil samples of the study area. The result show that 100% of soil samples are classified as unpolluted for 11 metals (Ce, Co, Cr, Cs, Lu, Ni, Pb, Rb, Sc, Sm, and Zn). In contrast, 100% of soil samples collected from the study area were

Table 3 Comparison of heavy and trace metals concentrations (mg/kg) in soil of the present study with other studies around the world

Country	Cd	Ce	Co	Cr	Cs	Eu	Hf	Lu	Mo	Ni	Pb	Rb	Sc	Sm	Tb	U	Yb	Zn	References
Ras Tanura, Saudi AG (East)	39.9	7.40	0.52	2.70	1.97	4.01	6.09	1.02	13.2	2.67	2.27	3.16	2.16	3.28	8.23	3.30	3.88	1.14	Present study
Jubail, Saudi Arabia, AG (East)	–	–	ND-5	6.9-130	–	–	–	–	–	ND-17	ND-24	–	–	–	–	–	–	8-69	Almasoud et al. (2015)
Saudi Arabia (North)	–	–	13.5	103.62	2.34	–	7.03	–	4.71	–	–	44	6.53	–	–	1.85	–	73.33	El-Taher et al. (2016)
Riyadh, Saudi Arabia (Middle)	0.11	–	–	14.88	–	–	–	–	–	15.97	6.5	–	–	–	–	–	–	20.38	Hasayen et al. (2017)
Al-Qassim, Saudi Arabia	1.65	–	1.34	17.4	–	–	–	–	–	2.61	26.9	–	–	–	–	–	–	21.1	Al-Wabel et al. (2017)
Egypt	–	120	13	167	–	2	62	–	–	35.78	130.97	37	16	10	–	–	6	98	Abdel Halim and El-Taher (2014)
Azerbaijan	0.18	–	–	19.9	–	–	–	–	–	–	29.2	–	–	–	–	–	–	47.9	Khalilova and Mammadov (2016)
Australia	0.4	–	6	19	–	–	–	–	–	13	194	–	–	–	–	–	–	187	Birch et al. (2011)
China	0.13	–	13.26	68.28	–	–	–	–	–	29.36	28.40	–	–	–	–	–	–	65.81	Lv et al. (2015)
Greece	0.2	–	–	193.2	–	–	–	–	–	58.2	359.4	–	–	–	–	–	–	137.8	Christoforidis and Stamatis (2009)
India	–	–	4.84	8.29	–	–	–	–	–	18.78	12.52	–	–	–	–	–	–	–	Tiwari et al. (2011)
Iraq	13.3	–	–	71.2	–	–	–	–	–	52.5	9.0	–	–	–	–	–	–	–	Al-Dabbas et al. (2015b)
Turkey	1.34	–	16.62	51.21	–	–	–	–	4.78	209.22	17.68	–	–	–	–	–	–	56.62	Guler et al. (2010)
Nepal	0.12	–	7.92	38.83	–	–	–	–	–	17.31	21.2	–	–	–	–	–	–	66.86	Tripathee et al. (2016)
Poland	0.080	–	–	3.0	–	–	–	–	–	1.1	11	2.1	–	–	–	–	–	4.9	Jarzyńska and Falandysz (2012)
Italy	0.4	72.66	17.05	90.54	–	–	–	–	1.9	34.67	63.67	104.66	–	–	–	–	–	166.73	Guagliardi et al. (2012)

Table 4 Classification of heavy metal pollution levels in soils based on IP and I_{geo}

PI value	Level of pollution	I_{geo} class	I_{geo} value	Level of pollution
PI ≤ 1	Unpolluted	0	$I_{geo} \leq 0$	Unpolluted
1 < PI ≤ 2	Slightly polluted	1	$0 < I_{geo} < 1$	Unpolluted/moderately polluted
2 < PI ≤ 3	Moderately polluted	2	$1 < I_{geo} < 2$	Moderately polluted
3 < PI ≤ 5	Strongly polluted	3	$2 < I_{geo} < 3$	Moderately/strongly polluted
PI > 5	Very strongly polluted	4	$3 < I_{geo} < 5$	Strongly polluted
		5	$4 < I_{geo} < 5$	Strongly/extremely polluted
		6	$5 < I_{geo}$	Extremely polluted

Table 5 Mean and range of pollution index (PI) in soil samples from Ras Tanura City

Metal	Mean of PI	Range of PI	Classification range of pollution level
Cd	130	2.90–357	Moderately polluted—very strongly polluted
Ce	0.13	0.015–0.227	Unpolluted
Co	0.05	0.02–0.40	Unpolluted
Cr	0.04	0.003–0.4	Unpolluted
Cs	0.40	0.07–0.54	Unpolluted
Eu	4.07	0.25–6.35	Unpolluted—very strongly polluted
Hf	3.38	0.29–11.8	Unpolluted—very strongly polluted
Lu	0.36	0.04–0.62	Unpolluted
Mo	5.07	0.52–20.3	Unpolluted—very strongly polluted
Ni	0.03	0.003–0.06	Unpolluted
Pb	0.08	0.01–0.16	Unpolluted
Rb	0.02	0.004–0.03	Unpolluted
Sc	0.17	0.003–0.24	Unpolluted
Sm	0.51	0.03–0.80	Unpolluted
Tb	8.23	0.64–13.6	Unpolluted—very strongly polluted
U	1.61	0.07–4.16	Unpolluted—strongly polluted
Yb	1.49	0.03–2.47	Unpolluted—moderately polluted
Zn	0.013	0.002–0.04	Unpolluted

contaminated with cadmium, which classified as strongly to very strongly polluted. For the other metals, such as Eu, Hf, Mo, Tb, U, and Yb, 3.33–87% soil samples were classified as unpolluted to very strongly polluted.

The percentage of the mean values classification of PI indicates to 61% of the mean values of PI for each metal were unpolluted in soil samples; 11% was slightly polluted and 0% was moderately polluted, whereas 11% and 17% of the mean values of PI were classified as being strongly polluted and very strongly polluted, respectively, due to the elevated levels of Cd, Mo, Hf, Eu, and Tb (Fig. 4).

Geoaccumulation index (I_{geo})

Another commonly index was used to evaluate the contamination of heavy and trace metals in soil is the geoaccumulation index (I_{geo}). The I_{geo} was calculated for each metal in all soil samples. The ranges of I_{geo} for each metal were recorded in Table 6.

The I_{geo} for each metal are 0.95 to 35.2 for Cd, -6.67 to -2.72 for Ce, -6.48 to -5.31 for Co, -8.97 to -4.87 for Cr, -4.34 to -1.48 for Cs, -2.58 to 2.08 for Eu, -2.35 to 2.97 for Hf, -5.25 to -1.27 for Lu, -1.52 to 3.76 for Mo, -9.15 to -4.7 for Ni, -7.38 to -3.2 for Pb, -8.4 to -5.43 for Rb, -8.93 to -2.65 for Sc, -5.58 to -0.9 for Sm, -1.23 to 3.18 for Tb, -6.31 to 0.04 for U, -5.8 to 0.72 for Yb, and -9.28 to -5.36 for Zn. The value of I_{geo} for each metal indicates unpolluted to extremely polluted of metals in soil of the study area. Based on the classification of I_{geo} in Table 4, the average value of I_{geo} is 7.0 for Cd that indicates to extremely polluted (Fig. 5). Cadmium is one of the most toxic metals, which is significantly accumulated in soil samples. The average value of I_{geo} for Eu, Mo, and Tb are 1.2, 1.5, and 2.1, respectively, which indicate moderately polluted in soil of study area, whereas the average values of I_{geo} for the rest metals suggest that the area is unpolluted by these metals as shown in Fig. 5.

The results of PI and I_{geo} for investigated metals confirm that the soil of the study area is affected by the oil refinery
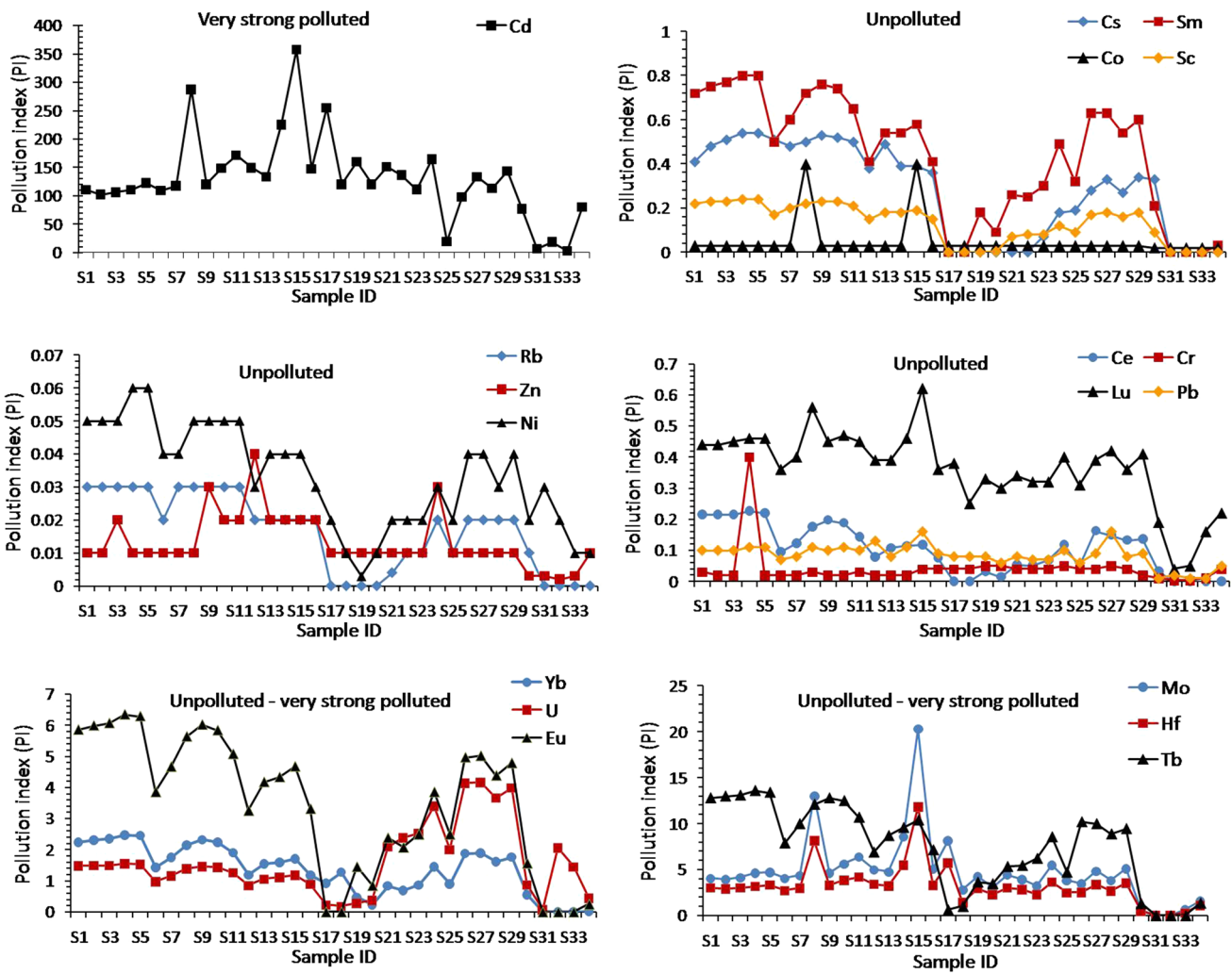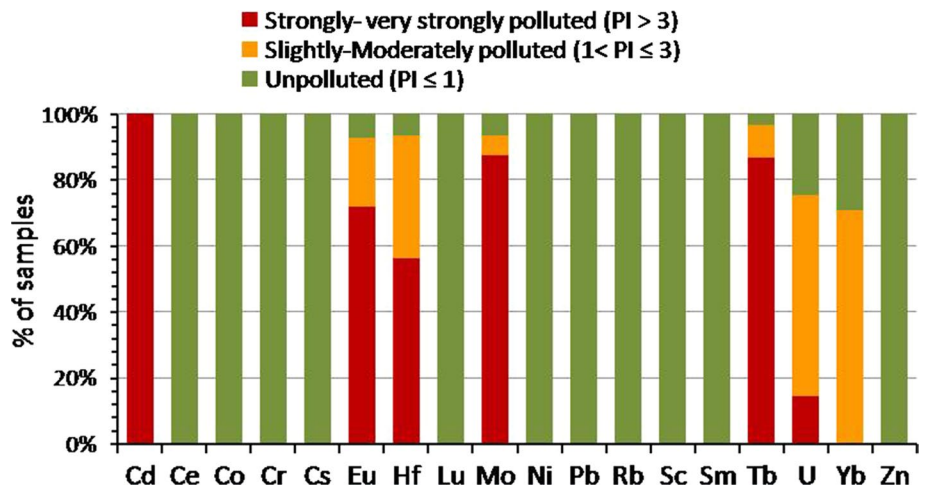
Fig. 2 Variations of PI values in soil samples from different sites of the study area

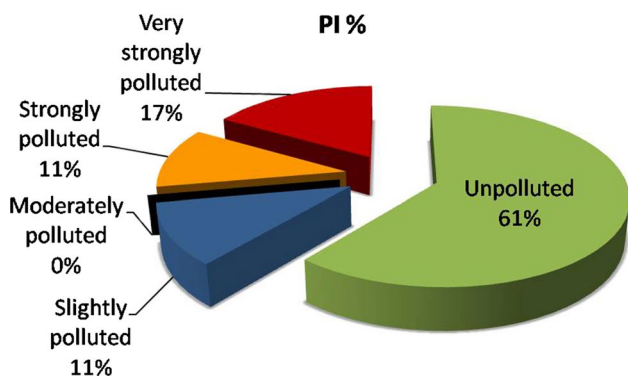**Fig. 3** Pollution characteristics of metals in soil samples

Fig. 4 The percentage of the mean values classification of PI for each metal

and petroleum processes due to the accumulation of some heavy and trace metals, such as Cd, Mo, Eu, and Tb, whereas most of the investigated metals recorded low and moderate accumulation in soil of the study area.

Conclusions

The concentrations of 18 heavy and trace metals (Cd, Ce, Co, Cr, Cs, Eu, Hf, Lu, Mo, Ni, Pb, Rb, Sc, Sm, Tb, U, Yb, and Zn) were investigated in surface soil of Ras Tanura city, Saudi Arabia. The metals were determined by Plasma Atomic Emission Spectrometer (ICPE-9820). The results

Table 6 Range of I_{geo} in soil samples from Ras Tanura City

Heavy metals	Range of I_{geo}	Range of pollution level
Cd	0.95–35.2	Moderately polluted—extremely polluted
Ce	− 6.67 to (− 2.72)	Unpolluted
Co	− 6.48 to (− 5.31)	Unpolluted
Cr	− 8.97 to (− 4.87)	Unpolluted
Cs	− 4.34 to (− 1.48)	Unpolluted
Eu	− 2.58 to 2.08	Unpolluted—moderately polluted
Hf	− 2.35 to 2.97	Unpolluted—moderately/strongly polluted
Lu	− 5.25 to (− 1.27)	Unpolluted
Mo	− 1.52 to 3.76	Unpolluted—strongly polluted
Ni	− 9.15 to (− 4.7)	Unpolluted
Pb	− 7.38 to (− 3.2)	Unpolluted
Rb	− 8.4 to (− 5.43)	Unpolluted
Sc	− 8.93 to (− 2.65)	Unpolluted
Sm	− 5.58 to (− 0.9)	Unpolluted
Tb	− 1.23 to 3.18	Unpolluted—strongly polluted
U	− 6.31 to 0.04	Unpolluted—moderately polluted
Yb	− 5.8 to 0.72	Unpolluted—moderately polluted
Zn	− 9.28 to (− 5.36)	Unpolluted

Fig. 5 The average value of I_{geo} for each metal in soil samples
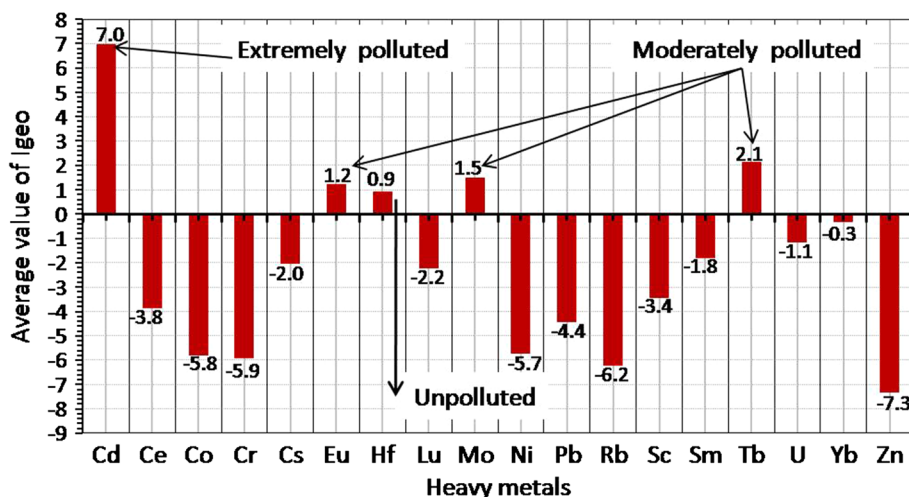
indicate to significant levels of Cd, Mo, Eu, Hf, Tb, and Yb in soil samples. The mean values of these four metals were higher than the world average and background values. Generally, the obtained result suggested that the mean values of the investigated metals in soil were similar or lower compared with the other studies, with the exception of Cd and Mo, which were higher than those in various soils from other countries.

The calculated values of pollution index (PI) and geoaccumulation index (I_{geo}) indicated high levels of Cd in soils from all sites of the study area. In addition, these soils are also strongly polluted by Mo, Eu, Hf, Yb, and Tb in most of sampling sites, while slightly to moderately polluted in some points of study area. The other metals (Ce, Co, Cr, Cs, Lu, Ni, Pb, Rb, Sc, Sm, and Zn) were found to be in the reasonable levels. However, elevated levels of Cd, Mo, Eu, Hf, Yb, and Tb have been detected in the study area indicate to a localized pollution due to the influence of oil refinery in the surrounding region.

Based on the obtained results, it can be concluded that the populations living in the near of Ras Tanura oil refinery may be at great risk of potential exposure to Cd, Mo, Eu, Hf, Tb, and Yb through inhalation and direct contact with contaminated environment. Monitoring heavy and trace metals in soil surrounding Ras Tanura refinery are extremely important to avoid any potential health risk due to increased heavy metals in the long term. In addition, identifying heavy metals, especially cadmium, and assessing pollution is important in terms of managing potential risks and controlling pollution around residential area near oil refinery.

Overall, available information on heavy and trace metals is still limited and does not provide a comprehensive picture of metals levels and their distribution around oil refineries in the Arabian Gulf region. Therefore, the available data of this study indicates to the need of more studies to monitor the accumulation of heavy metals, and a management plan to control and reduce the high levels of heavy metals in the environment, especially around residential areas.

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