Heavy metal pollution in well water and ecological risk assessment for the surrounding soil

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ABSTRACT

The present study aims to evaluate the level of heavy metal contamination of well water and soil in the Al-Quwayiyah governorate, Kingdom of Saudi Arabia (KSA). The samples for the study were selected from 10 different sites and then tested for the presence of chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd), lead (Pb), and iron (Fe). The physicochemical properties of well water and soil samples were investigated. Multivariate analyses including the correlation matrix (CM), principal component analysis and analysis of variance were used to specify the correlation between and the impact of heavy metals contamination of soil on well water. The potential ecological risk was assessed using the sediment quality guidelines (SQGs), enrichment factor (EF), geo-accumulation index (I_{geo}), contamination factor (C_a), and the degree of contamination (C_a) to identify the sources of heavy metals in the soil samples. Two ratios prescribed by the SQG's were used. The first was "effect range low (ERL) to effect range median (ERM) values" and the second was "threshold effect level (TEL) to probable effect level (PEL)". The results revealed that these ratios did not exceed the United States Environmental Protection Agency (USEPA) guidelines. The EF values of the soil samples showed minimal to deficient enrichment with Cr, Ni, Cu, Zn and As, and extremely low enrichment with Cd and Pb. The data obtained demonstrated that all the sites were polluted with very low levels of these heavy metals. The results strongly and positively correlated the metals in well water with these in soil and clarified that all metals were of a lithogenic origin.

Keywords: Heavy metal pollution; Well water; Soil; Multivariate analysis; Risk assessment

1. Introduction

Contamination of groundwater and soil by heavy metals is a common problem at many sites due to leaks or misuse of various hazardous materials which contribute to groundwater pollution and soil contamination [1]. The heavy metals Pb, Cr, Hg, As, Cd and Cu are the most commonly found pollutants [2]. Toxic heavy metals are one of the principal contaminants that have negative effects on the environment [3–5]. The United States Environmental Protection Agency (USEPA) indicates that more than 20 million cubic yards of soil are contaminated with metals [6]. Distinguishing

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the different sources of potentially toxic elements (PTE) in soils is complicated because several sources are involved. Discrimination between anthropogenic and natural sources of PTE comprises element speciation, and profile and spatial distributions [7]. The water quality criteria are strongly affected by the presence of heavy metals in water and soil. Thus, they need to be evaluated before they are used [8]. The USEPA's Sediment Quality Guidelines (SQGs) were used to assess heavy metal toxicity in Turkey's Izmit Bay surface sediment [9]. The health risks on polluted soil and food crops caused by heavy metals were evaluated in Beijing, China, using wastewater within the permitted limits [10]. The source of trace elements and the related risk evaluation in vegetables and soils of the many areas of Hangzhou, China, were identified [11]. The contamination rank of some heavy metals based on the geo-accumulation index (I_{reo}) , enrichment factor (EF), pollution index and integrated pollution index in street dust in Baoji, China, was also assessed [12]. Heavy metals were traced in wetland soil in the reclaimed region of the Pearl River estuary, south China [13]. Moreover, trace heavy metal ions were assessed in road dust in the Delta region using I_{geo} [14]. To the best of our knowledge, no quality guidelines for soil heavy metals exist in the Kingdom of Saudi Arabia (KSA). Therefore, the heavy metal contents were compared with other guidelines, including the widespread range in the earth crust, average shale values, worldwide average soil, and Dutch optimum and Act target values [15]. Also, as far as we know, no previous data exist concerning the levels of concentrations of heavy metals in well water and soils of the Al-Quwayiyah governorate in the KSA. Al-Quwayiyah is considered one of the largest governorates in KSA in terms of area and abundance of groundwater. Many people depend on well water for agriculture. Also, it is characterized by its strategic location and the availability of mineral wealth and the presence of gold, iron, zinc, marble and granite mines. Agriculture and its growth in the governorate are the most prominent features of the next, it will grow along the way with a view of greenery and beauty. Due to its location on the eastern edge of the Arabian Shield rock, the water level in its wells is not stable according to rainfall, so the farms are concentrated on the banks of the valleys and the region is famous for planting the most famous and finest palm species in addition to some other agricultural crops. Nowadays, agriculture in the governorate has evolved until its lands contained Khalidiya farm, one of the largest farms in KSA, which is located in the town of Tebrak of the governorate of Quwayiyah on the highway (Riyadh - Mecca), which has approximately 12,526 palm trees produce 618 tons of dates. Being an agricultural and grazing area, the current work is conducted to quantify the toxic elements concentrations in well water and soils to evaluate the potential ecological risk to the environment and the human body.

This investigation aims to detect the extent of heavy metals in well water and surrounding soil, to determine if the Al-Quwayiyah governorate is affected by environmental pollution and, the physicochemical properties of well water and soil, and to compare the present results with data obtained in future surveys. Eventually, this study will allow the representative authorities to make any technical and policy decisions to protect the governorate from pollution in the future.

2. Study area criteria

The governorate of Al-Quwayiyah is located at 165 km to the west of the capital Riyadh of KSA. A map for the Al-Quwayiyah governorate with the location of the studied sites is shown in Fig. 1. It is one of the widest governorates. Its location is between latitudes 22°–24° and longitudes 44°–46°. The weather in Al-Quwayiyah is usually cold in winters, hot in summers, and the humidity is around 20%. The temperature of the Al-Quwayiyah region ranges from 36°C to 41°C in summer and drops to an average of 8°C in winter.

The population is approximately 126,161 inhabitants. It is considered as a main stopping point on Riyadh-Mecca highway. The governorate consists of about 600 villages and a scattered number of water wells which are usually used for agriculture purposes and for drinking by camels and sheep. The governorate involves several government departments, colleges, and health institutes.

3. Experimental

3.1. Chemicals and reagents

A 0.1 mol L⁻¹ of standard hydrochloric acid (HCl) was prepared by an appropriate dilution from a stock solution obtained from CDH fine chemicals company (New Delhi, India). This solution was calibrated against 0.1 mol L⁻¹ sodium carbonate solution. A 0.1 mol L⁻¹ sodium hydroxide (NaOH) solution was prepared by dissolving 4.0 g from the substance solid pellets purchased from CDH chemical company. The HCl and NaOH solutions were used to quantify the total alkalinity of the water samples. Ethylenediamine tetra acetic acid (EDTA) was procured from Suvchem Company for laboratory chemicals (Mumbai, India). A standard 0.01 mol L⁻¹ solution was prepared by dissolving 3.72 g from the solid material in double distilled water. It was used in the titrimetric determination of the total hardness (TH) of water samples. Nitrate (NO₃) and nitrite (NO₃) ions were



Fig. 1. Map of Al-Quwayiyah governorate and locations of the studied areas.

measured using the phenol-2,4-disulphonic acid and USEPA diazotization 8507 methods, respectively.

3.2. Instrumentation

The pH measurement was recorded on advanced bench Jenway pH meter model 3510 (Keison International Ltd., Chelmsford, UK). Electrical conductivity (EC) was measured using a Jenway bench electrical conductivity meter model 4510. A Cintra 1010 model UV-Vis spectrophotometer with a double beam produced by GBC scientific equipment (Braeside, Australia) was used to determine the concentration of NO_3^- and NO_2^- in well water. A digestion system model top wave from Analytik Jena AG Company (Jena, Germany), was used for digesting the soil samples. An Ohaus electronic balance (NJ, USA) and a Kumtel electric drying oven (Istanbul, Turkey) were used for the gravimetric measurement of total dissolved solids (TDS).

Inductively coupled plasma-mass spectrometer (ICP-MS) model Elan DRC II PerkinElmer (MA, USA), was employed to determine the studied heavy metals in water and soil samples. Sample preparation and analysis were performed at the central laboratory at the college of science, King Saud University, Riyadh City, KSA.

3.3. Sampling

Well water and soil samples were collected during March and April 2018 from four areas distributed in Al-Quwayiyah governorate namely Tebrak, Al-Fuwayliq Ar-Ruwaidah, and Labkha. Ten sites were selected, at Tebrak T1 and T2, Al-Fuwayliq F1 and F2, Ar-Ruwaidah R1, R2, and R3, and Labkha L1, L2 and L3. In general, well waters are classified either as highly salty or salty type. The studied soil areas are very adherent to the studied wells. The land around wells is categorized as a desert, an agricultural or a residential type.

3.4. Water analysis

Plastic bottles were used to draw the well water samples that were washed first with double distilled water and then washed by the well water. After that, the bottle was entirely filled with water and tightly sealed then stored in ice box at a temperature below 5°C. The collection, preservation, and physicochemical analyses of the samples were treated according to the standard method for water and wastewater [16]. The studied physicochemical parameters included the pH, EC, salinity, TDS, and TH. The TH was determined by the EDTA titrimetric method. Total alkalinity was measured as the soluble carbonate and bicarbonate and determined by titration against standardized HCl and NaOH solutions using methyl orange as indicator. NO₃⁻ and NO₂⁻ were measured by the colorimetric phenol-2,4-disulphonic acid method [17].

3.5. Soil analysis

For physicochemical analyses, the soil samples were air dried and sieved to a mesh size around 2 mm. The

hydrometer method was used to determine the particle size distribution of soil texture (sand, silt, clay) [18]. The organic matter (OM) content in soil was determined following the weight loss by the ignition method. The weight loss in dry soil sample when subjected to high temperatures (360°C) correlates to the oxidizable organic carbon. The pH and EC values of the soil samples were measured in 50% (w/v) soil-water suspension. For determination of the content of heavy metal in soil, the samples were digested using the microwave digestion method. About 0.3 g of soil sample was put into the perfluoroalkoxy alkanes digestion vessel with a capacity of 60 mL. In this sample, a 6.0 mL aliquot from 50% (v/v) solution of concentrated HNO₃ and HCl was added and the blend was carefully shaken [19]. The samples were initially heated in the microwave oven at a programmed temperature of 130°C and a pressure of 30 bar for 35 min. After this, they were subjected to a reduced temperature of 80°C and a pressure of 10 bar for 5 min. The inner walls of the vessels were then washed down with doubled distilled water. The vessels were swirled during the digestion to keep the walls clean and avoid the loss of samples. After that, the digested samples were increased to 50 mL by adding double-distilled water. The final solution was filtered and the concentration of heavy metals was quantified by using the ICP-MS technique. A blank solution without the sample was identically prepared by following the complete procedure. Calibration of the method was carried out by using the multi-element standard of the ultra-scientific analytical solution. Each sample was then analyzed in three replicates. Table 1 shows the operating conditions of the ICP-MS analysis.

Table 1

Operating conditions for inductively coupled plasma-mass spectrometry (ICP-MS) analysis

Parameters	Value/condition
Radio frequency generator	40 MHz
Radio frequency power	1,548.6 W
Pirani pressure	1E + 2 mbar
Penning pressure	9.549E-8 mbar
Detector counting voltage	1,750 V
Detector analog voltage	–1,825 V
Nebulizer gas flow [Ar, 99.997]	0.9 L min ⁻¹
Cool gas flow [Ar, 99.997]	13.84 L min ⁻¹
Auxiliary gas flow [Ar, 99.997]	0.8 L min ⁻¹
Sampler and skimmer cone	Nickel
Scan mode	Standard mode
Sample uptake	30 s
Peristaltic pump rate	40 rpm
Nebulizer	Glass concentric
Spray chamber	Quartz
Spray chamber temperature	-20°C
Dwell time	0.01 s
Number of replicates	3
Rinse time	30 s

4. Statistical analysis

The multivariate statistical analyses, including principal component analysis (PCA), the correlation matrix (CM), and one-way analysis of variance (ANOVA) techniques were conducted to get the heavy metals determination results using SPSS 15.0 software. The PCA is commonly utilized to reduce the data set and try to preserve the relationships that exist in the original data [20]. While, the CM tests the correlation between the variables to investigate whether the relationship between the data points is positive or negative, the strength of this correlation is based on the value of the coefficient of correlation (r). Its numerical value ranges from +1.0 to -1.0 and the relationship is said to be positive or negative when r > 0 or r < 0, respectively. At r = 0, no relationship exists or the variables are independent. But, when r equals +1.0 or -1.0 it corresponds to perfect positive or perfect negative correlation, respectively. As r is close to +1 or -1, the greater is the strength of the relationship between the variables. Multivariate statistics provides several useful tools for distinguishing between sources of metals concentrations. These methods can analyze the whole data sets instead of individual metal concentration and take into accounts several factors [7]. Moreover, multivariate statistical analyses and factor analysis give information about the distribution and source identification of metal pollution based on eigenvalues (eigenvalue > 1) [21-23]. For comparison of the heavy metal content in water and soils, statistical significance was calculated by the ANOVA. Differences are considered being significant if *p* < 0.05 [24,25].

In order to look for a possible linear dependence between the different heavy metal homologs in samples, the obtained heavy metals in water and soil, and the physical and chemical properties of water samples were tested for correlations using the Pearson correlation coefficient derived from the assumption of normal distribution of the data.

5. Results and discussion

5.1. Physicochemical properties

5.1.1. Water

The physicochemical properties of the studied samples are given in Table 2. The pH values of all samples ranged from 8.1 at Tebrak T2 to 8.9 at T1. This finding indicated a moderately alkaline pH in all well waters in Al-Quwayiyah governorate. EC is defined as the capacity of water to carry an electric current and depends on the quantity of TDS present in the water [26]. EC varied from a minimum of 421 dS cm⁻¹ at R3 to a maximum of 26,119 dS cm⁻¹ at Labkha L1. The TDS and EC values present a correlation, in which 1.0 mg L⁻¹ of TDS corresponded to an EC of 2.0 µS cm⁻¹ [27]. The TDS varied from 282 mg L⁻¹ at Ar-Ruwaidah R3 to 17,500 mg L⁻¹at Labkha L1. As is well known, salinity is considered a measure of all dissolved salts in water. If salty water is used as irrigation water, the salt may pass from the plant root back into the soil leading to plant dehydration and death. The data indicate that high salinity was detected at L1 followed by T2 at which the concentrations were 16,200 and 5,000 mg L⁻¹, respectively. The TH was evaluated based on Ca and Mg concentrations, which are usually high in well

Properties					Sit	es ^a					Guidel	ines of drinking	water
	T1	T2	F1	F2	R1	R2	R3	L1	L2	L3	WHO [48]	GSO [49]	SASO [50]
Hq	8.9	8.1	8.6	8.6	8.6	8.6	8.6	8.2	8.2	8.6			6.5-8.5
EC, dS cm ⁻¹	8469	13313	642	2239	642	2239	421	26119	7388	7925	I	I	800-2300
TDS, $mg L^{-1}$	5674	8920	430	1500	430	1500	282	17500	4950	5310	1000	I	1000
Salinity, mg L ⁻¹	1700	5000	400	400	400	400	400	16200	800	2000	I	I	I
TH, mg L^{-1}	240	2100	180	150	180	150	150	2700	210	1200	500	I	500
Alkalinity, mg L ⁻¹	95	120	100	140	100	140	100	120	140	110	I	I	I
NO_{3}^{-} , mg L ⁻¹	0.39	0.51	0.91	1.30	0.91	1.30	0.8	3.3	2.6	2.9	50	50	45
NO_{2}^{-} , mg L ⁻¹	0.03	0.07	0.08	0.07	0.08	0.06	0.11	0.11	0.11	0.11	I	I	I

water samples. The TH varied from 150 mg L⁻¹ at R2, R3 and F2 to 2,700 mg L⁻¹ at L1. Alkalinity determines the capability of water to compensate for acidity. The test of alkalinity usually measures the bicarbonate (HCO₃⁻), carbonate (CO₃²⁻), and hydroxide (OH⁻) in water. In general, the data are represented by mg L⁻¹ of CaCO₃. The adequate irrigation water range is considered to be 0 to 100 mg L⁻¹ CaCO₃. Alkalinity levels at Fuwayliq F2, Ar-Ruwaidah R2 and Labkha L2 sites were maximum (140 mg L⁻¹), and the lowest value of 95 mg L⁻¹ was recorded at Tebrak T1. The higher the alkalinity, the higher the ion exchange between Ca and Na ions, which later contributes to levels of alkalinity [28]. In natural water, HCO₃⁻ is the predominant ion contributing to alkalinity levels. CO₃²⁻ containing minerals in rocks and the partitioning of carbon dioxide are considered the natural sources of HCO₃⁻ [29].

 NO_3^- can originate from the run-off of the nitrogen fertilizers used for agricultural practices and from the decomposition of organic compounds. The higher inflow of water and consequent land drainage will cause an increase in NO_3^- content [30]. Results indicated the highest $NO_3^$ concentration of 3.30 mg L⁻¹ at Labkha L1 and the lowest concentration of 0.39 mg L⁻¹ at Tebrak T1. NO_2^- showed a maximum concentration of 0.11 mg L⁻¹ at R3, L1, L2 and L3, and a minimum concentration of 0.03 mg L⁻¹ at T1.

5.1.2. Soil

In soil samples, the pH values varied from 8.61 at T1 to 9.51 at R1 indicating moderately alkaline condition in all soil samples. Analytical results for physicochemical properties of selected soils are summarized in Table 3. The moderate alkalinity may be attributed to the presence of some metal oxides and may be mainly because of the neutralization of the soil acidity via a high content of CaCO₃ [15]. The highest EC values were at F2 and at L3 at which, they were 20.30 and 17.55 ds m⁻¹, respectively. The inconsistency of EC results in water and soil samples at T2 and L1 sites may be due to the high sand content of soil which allows high water permeability. Consequently, the proportion of dissolved salts in water exceeds the soil. The OM ranged from 0.22% to 0.68% (w/w), indicating the soils are of poor quality and lack enough nutrients and moisture. The texture of all soil samples was dominated by a high level of sand more than clay and silt and the percentage ranged from 91% at Labkha L3 to 63% at Tebrak T1.

5.2. Heavy metal content in water and soil

The concentration levels of the investigated toxic heavy metals in well water samples are compiled in Table 4. The highest concentration of Cr in well water was 0.14 mg L⁻¹ at T1 and minimum or non-detected (N.D) concentration at F2 and L1. For Ni, Zn, As and Cd ions, the maximum concentrations were 0.30, 0.09, 0.61, 0.18, 0.02 mg L⁻¹, respectively observed at T1. For Cu, the maximum concentration was 0.09 mg L⁻¹ at L2. The minimum concentrations were N.D. for Ni at F2 and N.D. for Cu at T1, F1, F2, R1 and R2, respectively. Pb and Cd were not observed at all investigated sites. The concentration levels of Fe varied from 1.45 mg L⁻¹ at L2 to 0.62 mg L-1 at T1. Comparing the obtained data with the guidelines for drinking water, it was noticed that all well water under the permissible limits except for Cr and As at T1 where the concentrations were 0.14 and 0.18 mg L^{-1} , respectively.

Moreover, the level of Fe exceeded the guidelines in all sites especially at L2 and L3 where the concentrations were 1.45 and 1.23 mg L⁻¹, respectively. Also, the data cleared that well water of T1 is the most contaminated site by the investigated metals. With the exception of Zn and As, the concentrations of the remaining elements were 0.60 and 0.14 mg kg⁻¹ at Tebrak T2 and Labkha L2, respectively.

For soil analysis, the heavy metal contents are shown in Table 5. The concentration of these heavy metals in soil can vary greatly according to the strength and direction of the wind, type of soil and pH. Usually, the heavy metal mobility and distribution in soil have been affected by pH. Also, it was proved that pH is the major controlling factor for the stabilization of heavy metals [31].

The highest concentrations observed in the examined soil corresponded to Cr of 5.60, 2.61 and 2.47 mg kg⁻¹ at T1, F2 and L3, respectively. Cr present in soil, water and air can cause a risk to the natural environment [32]. Next highest levels were found for Zn in F2, T1 and F1 with a concentration of 0.98, 0.70 and 0.69 mg kg⁻¹, respectively. By contrast, concentration levels of Cr and Zn were low in R3 with a concentration of 0.27 and 0.22 mg kg⁻¹, respectively. Zn directly takes part

Table 3 Physical properties and particle size of soil samples of the studied areas of Al-Quwayiyah Governorate

Properties						Sites ^a				
	T1	T2	F1	F2	R1	R2	R3	L1	L2	L3
pН	8.61	8.72	8.84	8.12	9.51	9.0	9.21	8.74	8.62	9.04
EC dS cm ⁻¹	0.73	0.79	0.56	20.3	1.07	1.08	1.08	1.24	3.72	17.55
OM (%)	0.5	0.43	0.41	0.35	0.68	0.68	0.68	0.22	0.28	0.32
Clay (%)	6.0	5.0	4.0	5.0	14.9	12.5	13.5	4.0	5.0	4.0
Silt (%)	6.0	7.0	7.0	4.0	12.2	11.1	10.9	8.0	6.0	5.0
Sand (%)	63	72	69	91	72.7	75.1	74.3	88	89	91
Texture	Sandy	Sandy	Sandy	Sandy	Sandy-loam	Sandy-loam	Sandy-loam	Sandy	Sandy	Sandy

^aTebrak (T1 and T2), Al-Fuwayliq (F1 and F2), Ar-Ruwaidah (R1, R2, and R3) and Labkha (L1, L2 and L3). OM, Organic matter.

Table 4	
Elemental concentrations (mg L-1) of well water samples of the studied areas of Al-Quwayiyah Governo	orate

Heavy					Si	tes ^a					Guideline o	f drinking w	vater (mg L ⁻¹)
metals	T1	T2	F1	F2	R1	R2	R3	L1	L2	L3	WHO [48]	GSO [49]	SASO (701/2000) [50]
Cr	0.14	0.05	0.01	N.D	0.01	0.09	0.03	N.D	0.03	N.D	0.05	0.05	0.05
Ni	0.30	0.09	0.01	N.D	0.05	0.06	0.07	0.06	0.04	0.10	0.07	0.07	0.02
Cu	N.D	0.05	N.D	N.D	N.D.	N.D.	0.03	0.04	0.09	N.D	2.0	0.07	1.2
Zn	0.61	0.60	0.02	0.07	0.12	0.04	0.10	0.11	0.07	0.05	3.0	1.0	0.02
As	0.18	0.12	0.01	0.01	0.04	0.02	0.05	0.04	0.14	0.02	0.01	0.01	0.01
Cd	0.02	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.003	0.003	0.003
Pb	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.01	0.01	0.01
Fe	0.62	0.69	0.91	0.91	0.78	0.80	0.81	0.88	1.45	1.23	0.3	-	1.0

^aTebrak (T1 and T2), Al-Fuwayliq (F1 and F2), Ar-Ruwaidah (R1, R2, and R3) and Labkha (L1, L2 and L3).

Table 5 Elemental concentrations (mg kg⁻¹) of soil samples of the studied areas of Al-Quwayiyah Governorate

Heavy	Sites ^a								EBC ^b		SQG ^c			
metals												Non- polluted	Moderately polluted	Heavily polluted
	T1	T2	F1	F2	R1	R2	R3	L1	L2	L3				
Cr	5.60	0.59	0.38	2.61	0.45	0.27	0.27	0.35	0.49	2.47	90	<25	25–27	>75
Ni	0.47	0.49	0.15	0.37	0.26	0.19	0.20	0.21	0.30	0.03	68	<20	20-50	>50
Cu	0.46	0.34	0.21	0.27	0.17	0.12	0.16	0.15	0.23	1.36	45	<25	25–50	>50
Zn	0.70	0.58	0.69	0.98	0.66	0.32	0.22	0.26	0.34	0.30	95	<90	90–200	>200
As	0.39	0.27	0.13	0.20	0.13	0.16	0.16	0.20	0.32	1.10	13	<3	3–8	>8
Cd	0.003	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.3	-	_	-
Pb	0.09	0.07	0.09	0.11	0.07	0.06	0.09	0.01	0.93	0.05	20	<40	40-60	>60
Fe	2,512	2,500	2,788	2,788	2,680	2,682	2,600	3,980	3,550	3,990	47,200	-	-	-

^aTebrak (T1 and T2), Al-Fuwayliq (F1 and F2), Ar-Ruwaidah (R1, R2, and R3) and Labkha (L1, L2 and L3). ^bElemental background concentration [41].

'Sediment quality guideline USEPA.

in the human physical growth and development, the functioning of the immune systems, and growth of animals and plants [33]. The sources of Zn particles can be from industrial activities or motor vehicle and car tires [29]. Being a lithogenic source, Cr and Zn can form several soluble or insoluble salts [34]. Also, the data cleared that Tebrak T1 was highly contaminated by Ni, Cu and As, where the concentrations were 0.47, 0.46 and 0.39 mg kg⁻¹, respectively. The presence of Ni in soil samples might be highly related soil-forming processes and pollution like fuel combustion [34]. In addition, it was noticed that the site L3 is highly contaminated by Cu and As, where the concentrations were 1.36 and 1.10 mg kg⁻¹, respectively.

Cu is vital trace element for the support of good health for human. The allowable limit of Cu in soil is 63 mg kg⁻¹ [35]. Arsenic (As) occurs in igneous rocks and the greater concentration is found in sedimentary rocks such as shales and mudstones. In agriculture, pesticides and fertilizer compounds containing arsenic have led to the accumulation of it in topsoil [32]. Topographically, the studied are mainly desert-like therefore the possible explanation based on industrial or agricultural activity should be excluded. In addition, the population in the current area is very low which conveys low human contamination sources. But, the plausible explanation can be due to natural soil-forming or movement by sand storming which is common in this area especially during April where an annual dusting wind covers all the studied area by about 1 km height.

Cd can be emitted from roasting, smelting and refining of ores, production of batteries, combustion of fossil fuel and cement manufacturing [36,29]. The studied area is free from all possible industrial sources of Cd expecting low level. Results obtained showed that Cd slightly contaminates all studied areas. The concentration ranged from 0.001 to 0.003 mg kg⁻¹ at all sites.

Pb is a highly accumulated element in the soil and usually attached with clay minerals [32]. Most Pb concentrations are observed in soils rich with organic matters where it can behave as an adsorbent [37]. The highest concentration of Pb was 0.11, 0.09 and 0.09 mg kg⁻¹ at F2, L2 and T1,

respectively. Generally, the concentration levels of heavy metals in well water are very low as compared with soil samples.

By comparing the mean concentrations of the investigated heavy metals in some soils studied in KSA (Table 6), it was found that the concentration levels of all heavy metals in the investigated soils of Al-Quwayiyah governorate are lower than those reported for the ones from different sites in KSA. The comparison indicated that Al Qassim is considered as a dense agricultural area; it had a high concentration of Cr, Zn and Pb where the concentrations were 17.4, 1.10 and 26.9 mg kg⁻¹ while in the present study the concentrations were 5.6, 0.98 and 0.93 mg kg⁻¹, respectively.

5.3. Multivariate statistical analyses

In the current study, the correlation matrix (CM) and principle correlation analysis (PCA) were employed to the total contents of the analyzed heavy metals to predict and distinguish their sources whether in well water or in soil or in both. The CM analysis data are shown in Table 7. Results revealed significant positive correlations among the heavy metals in soil and water samples. The Cr showed significant positive correlations with Ni (r = 0.71), Zn (r = 0.63), Cu (*r* = 0.61), As (*r* = 0.59), Cd (*r* = 0.47) and Pb (*r* = 0.61). Ni is also significantly and positively correlated with Zn (r = 0.85), Cu (r = 0.64), As (r = 0.66), Cd (r = 0.47) and Pb (r = 0.89). Correlations were also found among Zn, Cu, As, Cd and Pb. Cu is highly and significantly correlated with As at the 0.05 level (r = 0.99), while As is correlated with Pb (r = 0.52). The results of the ANOVA showed a significant difference in metals between sites for all soil and water samples which confirm their probable common natural, anthropogenic origin or similar contamination sources [12,13].

The results of the PCA are presented in Table 8. Data showed that five principal factors were extracted which amounted to 99.24% of the total variance. Factor 1 was strongly and positively loaded with Cr (0.82), Ni (0.94), Cu (0.79), Zn (0.84), As (0.79) and Pb (0.88) which accounted for the 65.60% of a total of variance. Factor 3 was predominated by Cd (0.72) which accounted for the 10.17% of a total of variance. The factor loadings obtained for various metals having a greater number than 0.7 are marked bold. The rotation of PCA was performed by the varimax method. The 3D rotation plot of the PCA suggests that the studied heavy metals originated from different sources (Fig. 2). Also, it showed high loadings of most studied heavy metals including Cr,

Ni, Cu, Zn, As and Pb. The presence of these metals in the same component and their strongly positive correlations with each other indicates their low concentrations in the soil and water. The PCA loadings indicate also there was loading between Cu and As. The significant correlations among all metals indicate that these metals had a common origin, which is consistent with the results of data of PCA. The 3D plot of PCA showed that Cd stands alone with a significant positive correlation with Pb, suggesting another different source for both. Cd and Pb might be put into the soil through phosphate fertilizers. Moreover, Cu may be introduced into the soil and consequently to water with agrochemicals containing Cu, for example, pesticides and Cu sulfates, which are used in agriculture. Also, more tillage increased the levels of heavy metals such as Cd, Cr, Cu, Ni, Pb and Zn, which were related to anthropogenic entries from domestic sewage and agrochemicals [13]. Additionally, the atmospheric deposition resulted from traffics is a main pollution source for Pb and Cd in soils adjacent to the roadside. This suggested that because of the rapid urbanization and development in KSA, it may increase the deposition of contaminants emitted from traffic and industries which are considered the main sources of soil pollution [15]. It could be concluded that the PCA together with CM may be used as a good mathematical tool for identifying heavy metal sources in soils and water. The elements Cr, Ni, Cu, Zn, As and Pb were found to be grouped into the first component of PCA as can be seen in Fig. 2. This suggested they might be originated from agrochemicals, fertilizers, oil and lithogenic sources. Also, it was

Table 7

Correlation matrix (CM) analysis indicating the values of correlation coefficients (*r*) between analyzed heavy metals in surface soils of Al-Quwayiyah

Cr	Cr	Ni	Zn	Cu	As	Cd	Pb
Ni	0.71**						
Zn	0.63**	0.85**					
Cu	0.61**	0.64**	0.42**				
As	0.59**	0.66**	0.40**	0.99**			
Cd	0.47**	0.47**	0.48**	0.29*	0.26*		
Pb	0.61**	0.89**	0.94**	0.50**	0.52**	0.41**	

*Correlation is significant at the 0.05 level (two-tailed). **Correlation is significant at the 0.01 level (two-tailed).

Table 6 Comparison of the heavy metals content in soil at different sites in Saudi Arabia

City				Mean conc	entrations (n	ng kg ⁻¹)			Reference
	Cr	Ni	Cu	Zn	As	Cd	Pb	Fe	
Al Qassim	17.4	2.6	5.84	21.1	-	1.65	26.9	5,529	[17]
Arabian gulf coast	69	1.0	5.0	25	-	-	4.3	3,400	[23]
Red sea gulf	1.2	58.4	17.2	123.7	-	0.27	21.9	-	[51]
Red sea gulf	9.6	8.8	112	57.5	-	1.23	45.2	-	[52]
Trout Island coast	27.3	-	6.05	18.12	150.3	0.70	67.7	3,612	[53]
Al-Quwayiyah	5.6	0.49	0.46	0.98	1.10	0.003	0.11	3,990	This work

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Cr	0.82*	-0.01	0.16	-0.55	0.01
Ni	0.94*	0.12	-0.15	0.05	-0.28
Cu	0.79*	-0.60	0.06	0.10	0.08
Zn	0.84*	0.43	-0.23	0.04	0.18
As	0.79*	-0.60	0.02	0.12	0.00
Cd	0.56	0.37	0.72*	0.18	0.00
Pb	0.88*	0.31	-0.3	0.11	0.03
Eigen value	4.59	1.15	0.71	0.37	0.12
Total of variance (%)	65.60	16.46	10.17	5.33	1.69
Cumulative (%)	65.60	82.05	92.23	97.55	99.24

Table 8 Principal component analysis (PCA) of surface soil samples of the study area using varimax raw rotation (five components extracted)



Fig. 2. Principal component analysis (PCA) loading three dimensional for the analyzed heavy metals in soil samples.

found that Pb and Zn were significantly correlated with soil phosphorus and nitrogen, indicating that these two metals are from the similar source [12].

5.4. Ecological assessment of heavy metals in soil samples

To assess and evaluate the polluted soils by heavy metals in the studied samples, many indices have been proposed. The present study will employ indices such as SQGs, EF, $I_{geo'}$ C_f and C_d to determine the level of heavy metals contamination in studied soil samples.

5.4.1. SQGs as an assessing tool of heavy metals

The SQGs have been used for identifying contaminants of interest in sediments [37]. Because of sampling and analytical methods may alter the sediment chemistry, SQGs sometimes not reflect the original condition [9]. Burton [38] cleared that SQG should be used only as a screening approach or in a weight of evidence method for polyaromatic hydrocarbon and chlorinated hydrocarbon. In addition, trace heavy metals have been studied by SQGs, which provided the elemental background concentrations [39,40]. They were commonly provided by using the average shale values [41] and average crustal abundance [42]. The SQG developed by USEPA classifies the soil into non-polluted, moderately polluted and heavily polluted. Moreover it reveals the degree of pollution by comparing the concentration means to the guidelines. Accordingly, all studied sites did not exceed the guidelines and are non-polluted. To evaluate the ecotoxicological effect of heavy metals for marine sediments, two sets of SQGs were employed. The first was ratio of effect range low to effect range median (ERL/ERM), while the second was threshold effect level to probable effect levels (TEL/PEL) [43]. These two sets were employed to determine different levels of contaminant toxicity in soil and determine probable contaminant levels having toxic effects in fresh water sediments [44]. ERMs and PELs represent chemical concentrations above the expected adverse effects. In contrast, low range values (i.e., ERLs or TELs) are concentrations below which would be expected to have adverse effects on sediment resident fauna [43].

To assess the expected ability of ERL/ERM, the decrease of toxicity was detected between samples in which none or either one or increasing numbers of the substances equaled and exceeded the ERL concentrations, respectively. But none exceed any ERM and there are samples exceeded ERM concentrations. The same approach was used to assess TELs/ PELs' predictive capacity. Fig. 3 presents the ERL - ERM as well as TEL - PEL values for the studied heavy metals. Results showed that the total content of heavy metals in the studied area in comparison with mentioned SQGs has lower concentrations than the two sets indicating that all heavy metals have a lithogenic origin and the studied area is still non-polluted. Due to the absence of industrial and agricultural wastes in the region and the distance of the studied sites from the capital Riyadh, the study places are, therefore, less polluted at present. Moreover, the divergence of villages and populated places has led to a decrease in pollution in general.

5.4.2. Assessment of heavy metals by enrichment factor (EF)

To estimate the metal origin and the concentration levels of metal enrichment in the studied soil samples, the EF was calculated according to the following equation:



Fig. 3. Concentration of the studied metal ions at the investigated sites showing the ERL (Effect range-low), ERM (Effect range median), TEL (Threshold effect level) and PEL (Probable effect level) limits. Sites: Tebrak (T1 and T2), Al-Fuwayliq (F1 and F2), Ar-Ruwaidah (R1, R2, and R3) and Labkha (L1, L2 and L3).



where $C_{m(\text{soil})}$ is the content of the tested heavy metal in the studied soil sample; $C_{\text{Fe(soil)}}$ is the Fe content as a reference metal in soil sample; $C_{m(\text{earth crust})}$ is the content of the investigated heavy metal in the earth's crust; and $C_{\text{Fe(earth crust})}$ is the content of Fe as a reference in the earth crust.

The EF can be categorized as follows: (EF < 2) deficiency to minimal, (2 < EF > 5) moderate, (5 < EF > 20) significant, (20 < EF > 40) very high, and (EF > 40) extremely high enrichment. The EF is usually used as a good tool for measuring the origin of heavy metals and a geochemical trend for speculating the natural and anthropogenic origin of them in soil samples. If EF values are less than 2, it indicates that the heavy metals are mainly controlled by the soil parent materials and weathering process. While, if EF values are more than 2, the heavy metals could be affected by human activity [45]. The maximum, minimum and mean values of EF data are shown in Fig. 4. The EF values for soil samples are 0.65, 0.06, 0.12, 0.10, 0.37, 0.0 and 0.16 for Cr, Ni, Cu, Zn, As, Cd and Pb, respectively. The heavy metals with EF values less than 2 were not a major contaminant. Accordingly, the studied sites of Al-Quwayiyah governorate are not contaminated

by the examined heavy metals (Fig. 5). The low contamination of heavy metals might be due to the kind of human activities that are restricted to grazing camels and goats and planting dates. restricted to grazing camels and goats and planting dates next to a few factories of date. Consequently, the concentrations of heavy metals were not affected by the human activities as reflected by the data obtained.

5.4.3. Geoaccumulation index (I_{oeo})

The I_{geo} introduced by Muller [46] was used to assess the contamination levels of trace metals in urban, road dust and agriculture soils. This index has been widely used in European heavy metal studies since the late 1960s. The I_{geo} is evaluated using the following equation:

$$I_{\text{geo}} = \log_2 \left[\frac{C_n}{1.5B_n} \right]$$
⁽²⁾

where C_n is the metal content in the tested soil sample, B_n is a geochemical value of trace element in average shale. The constant 1.5 is incorporated to minimize the possible change in values which may be referred to lithologic changes in soils [12]. This permits to analyze natural inconstancy in the composition of a given substance in the environment and to notice very small anthropogenic influences. Geoaccumulation index was classified as follows: $I_{geo} < 0$ practically unpolluted, $0 < I_{geo} > 1$ unpolluted to moderately polluted, $1 < I_{geo} > 2$



Fig. 4. Minimum, maximum, mean and standard deviation (SD) values of the enrichment factor (EF) of the tested heavy metals in the studied soils of Al-Quwayiyah governorate.

moderately polluted, $2 < I_{geo} > 3$ moderately to strongly polluted, $3 < I_{geo} > 4$ strongly polluted, $4 < I_{geo} > 5$ strongly to extremely polluted and $I_{geo} > 5$ extremely polluted. The distribution of I_{geo} values was depicted in Fig. 6. The negative I_{geo} values of Cr, Ni, Cu, Zn, As, Cd and Pb indicated that there was no pollution in all studied sites, which were fell in category –1, and this revealed the lithogenic sources of heavy metals. The I_{geo} ranged from –1.2 to –7.9, –6.5 to –10.5, –4.5 to –7.5, –6.4 to –6.7, –3.0 to –6.1, –6.1 to –7.4 and –3.8 to –8.1 for Ni, Cu, Zn, As, Cd and Pb, respectively. Also, the mean values were –6.9, –7.7, –7.7, –6.7, –5.4 and –7.4, respectively. These data indicate that the concentrations of heavy metals are related to neither urbanization nor agricultural activities and may be referred to lithologic changes.

5.4.4. Contamination factor (C_p) and degree of contamination (C_p) as assessing tools for soil contamination

Hakanson [47] employed the contamination factor (C_j) to describe the contamination of a given heavy metals in soil samples. It was calculated as follows:

$$C_f = \frac{C_n}{B_n} \tag{3}$$

where C_n is the toxic metal in the studied soil sample and B_n is the elemental background concentration of that metal.

The following terminologies are used to describe the contamination factor:

 $C_f < 1$ low contamination factor; $1 \le C_f < 3$ moderate contamination factors; $3 \le C_f < 6$ considerable contamination factors; $C_f \ge 6$ very high contamination factor.

Moreover, the degree of contamination C_d defined as the total of all contamination factors for a given heavy metal. It was calculated as follows:

$$C_d = \sum_{i=1}^7 C_f \tag{4}$$



Fig. 5. Enrichment factor (EF) values of heavy metals in soil samples of the studied area and the pollution limit.



Fig. 6. Boxplot diagram for the distribution of I_{geo} values for the examined heavy metals in the studied soil samples.

The C_d can be described as follows: $C_d < 7$ low degree of contamination, $7 \le C_d < 14$ moderate degree of contamination, $14 \le C_d < 28$ considerable degree of contamination and $C_d \ge 28$ very high degree of contamination. Classification of the contamination factor C_f and degree of contamination C_d values is provided in Table 9. Both of them were very low for all investigated heavy metals suggesting that the lithogenic origin.

6. Conclusion

With the purpose of obtaining safeguard for human health and to protect the environment, the investigation of well water and soil quality is of extreme importance. This enables to access the overall quality of water and soil in order to recognize the source of pollutants and to diminish their levels. The physicochemical studies showed moderate levels of pH, EC, TDS, TH, and total alkalinity. Also, the heavy metal content in well water is very low compared to that in soil. Although, soil presented high levels of heavy metals but

20	21
20	21

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			C_{f}				C_d
Cr	Ni	Cu	Zn	As	Cd	Pb	
0.056	0.006	0.008	0.010	0.217	0.015	0.031	0.343
0.006	0.006	0.006	0.008	0.150	0.01	0.005	0.191
0.004	0.002	0.004	0.008	0.072	0.005	0.007	0.102
0.261	0.005	0.005	0.008	0.011	0.005	0.009	0.309
0.005	0.003	0.003	0.008	0.072	0.005	0.006	0.102
0.003	0.003	0.002	0.008	0.089	0.005	0.004	0.117
0.003	0.003	0.003	0.008	0.089	0.005	0.007	0.118
0.004	0.003	0.003	0.008	0.111	0.005	0.001	0.135
0.005	0.004	0.004	0.008	0.178	0.005	0.007	0.211
0.025	0.000	0.025	0.008	0.611	0.005	0.004	0.678
1.00	1.00	1.00	1.00	1.00	1.00	1.00	7.00
	Cr 0.056 0.006 0.004 0.261 0.005 0.003 0.003 0.003 0.004 0.005 0.025 1.00	Cr Ni 0.056 0.006 0.004 0.002 0.261 0.005 0.003 0.003 0.003 0.003 0.005 0.003 0.005 0.003 0.003 0.003 0.005 0.003 0.005 0.003 0.005 0.003 0.005 0.004 0.005 0.004 0.025 0.000 1.00 1.00	Cr Ni Cu 0.056 0.006 0.008 0.006 0.006 0.006 0.004 0.002 0.004 0.261 0.005 0.003 0.005 0.003 0.003 0.003 0.003 0.003 0.004 0.003 0.003 0.003 0.003 0.003 0.004 0.003 0.003 0.005 0.004 0.004 0.025 0.000 0.025 1.00 1.00 1.00	$\begin{tabular}{ c c c c c c c c } \hline C_f & Ni & Cu & Zn \\ \hline Cr & Ni & Cu & Zn \\ \hline 0.056 & 0.006 & 0.008 & 0.010 \\ 0.006 & 0.006 & 0.008 & 0.008 \\ 0.004 & 0.002 & 0.004 & 0.008 \\ \hline 0.004 & 0.005 & 0.005 & 0.008 \\ \hline 0.005 & 0.003 & 0.003 & 0.008 \\ \hline 0.003 & 0.003 & 0.003 & 0.008 \\ \hline 0.003 & 0.003 & 0.003 & 0.008 \\ \hline 0.004 & 0.003 & 0.003 & 0.008 \\ \hline 0.005 & 0.004 & 0.003 & 0.008 \\ \hline 0.005 & 0.004 & 0.004 & 0.008 \\ \hline 0.005 & 0.004 & 0.004 & 0.008 \\ \hline 0.025 & 0.000 & 0.025 & 0.008 \\ \hline 1.00 & 1.00 & 1.00 & 1.00 \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Contamination factors (C) and degree of contamination (C) of the studied soil samples of Al-Quwayiyah governorate

^aTebrak (T1 and T2), Al-Fuwayliq (F1 and F2), Ar-Ruwaidah (R1, R2, and R3) and Labkha (L1, L2 and L3).

remained below than the national and international guidelines. Factor analysis was performed by using CM and PCA and proved an effective method to identify the correlation among the investigated heavy metals in water and soil samples. Ecological risk assessment for heavy metal content in soil was carried out using SQG, EF, $I_{geo'}$, C_f and C_d . Application of all approaches subsequently represents the actual status of water and soil and further helps in preparing a management plan to reduce the pollution level. It could be concluded from the current results that the heavy metals in the soil samples have a low impact on the metal levels in well water. To close, it appeared that the geological background is mainly responsible for soil pollution which would affect the water in this area.

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Table 9

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