Mapping of Trace Elements in Topsoil of Arid Areas and Assessment of Ecological and Human Health Risks in Qatar

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Abstract:

Soil is the incubator of human activities. Mapping of soil contaminants needs to be constantly updated. It is fragile in arid regions, especially if it accompanies dramatic and successive industrial and urban activities in addition to the climate change. Contaminants affecting soil are changing due to natural and anthropogenic influences. Sources, transport and impacts of trace elements including toxic heavy metals need continuous investigations. We sampled soil in accessible sites in the State of Qatar. An inductively coupled plasma-optical emission spectrometry (ICP-OES) and an inductively coupled plasma-mass spectrometry (ICP-MS) were used to determine the concentrations of Ag, Al, As, Ba, C, Ca, Ce, Cd, Co, Cr, Cu, Dy, Er, Eu, Fe, Gd, Ho, K, La, Lu, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pr, S, Se, Sm, Sr, Tb, Tm, U, V, Yb and Zn. The study also presents new maps for the spatial distribution of these elements using the World Geodetic System 1984 (projected on UTM Zone 39N) which is based on socio-economic development and land use planning. The study assessed the ecological risks and human health risks of these elements in soil. The calculations showed no ecological risks associated with the tested elements in soil. However, the contamination factor (CF) for Sr (CF>6) in two sampling locations calls for further investigations. More important, human health risks were not detected for population living in Qatar and the results were within the acceptable range of the international standards (hazard quotient HQ<1 and Cancer risk between 10^{-4} and 10^{-6}). Soil remains a critical component with water and food nexus. In Qatar and arid regions, fresh water is absent and soil is very poor. Our findings enhance the establishment of scientific strategies for investigating soil pollution and potential risks to achieve food security.

Keywords: Trace elements; Topsoil; Ecological risks; Human health risks; Arid areas.

1. Introduction

The arid regions, including the Arab World, suffer a rapid environmental deterioration as a result of the depletion of natural resources represented by water scarcity, land desertification and biodiversity challenges (Ayangbenro and Babalola, 2021). Climate change and its serious consequences are also causing severe droughts (IPCC, 2022). In addition, human socio-economic development models remain minimal, coupled with population growth and limited spending and investment on research, development and technologies (Lefèvre et al., 2022). This led to soil erosion and less productivity.

Soil planning in dry areas represents a great challenge, especially where local agricultural activities are limited and soils are quickly eroded (Kumar et al., 2022). Soils of local farms and agricultural fields of Qatar are imported, and they are enriched annually with more soil and fertilizers (Shomar et al., 2013). The presence of various chemical elements in desert soils is critical for land use including agricultural activities, pollutant estimation and remediation technologies (Wang et al., 2022). Chemicals find their way into the soil through various human activities as well as deposition from air or transmission through successive dust storms crossing the country borders (Ahmed et al., 2022). The negative impacts resulting from the presence of toxic chemicals in soils could be direct and indirect. The direct impacts include exposure to these chemicals through dermal (Omeka and Egbueri, 2022), inhalation (Jia et al., 2022) and digestive system (Xiao et al. 2022). The indirect impacts include their transport to the food chain (Yan et al., 2022) or their leakage to water sources (Mallants et al., 2022).

Investigations of chemical elements in general and heavy metals in particular in the soils of arid areas are of great importance (Zhang M et al., 2022). Soil is a reservoir of nutrients and can also be a source of toxic elements that can be a part of the food chain (Hu et al., 2022; Sun L et al., 2022; Zaynab et al., 2022). It is necessary to estimate the concentration of these elements (Yang W et al., 2022), their sources, the mechanism of transmission to plants (Anaman et al., 2022) and humans (Xue et al., 2022), and to calculate the ecological risks (Li Y et al., 2022) and assess the human health risks (Zerizghi et al., 2022).

Many studies appeared in the past few years on the risks of chemicals on ecosystems and human health. There are many studies focused on the risks of a particular element in soil based on high concentrations, sources and effects (Cocârţă et al., 2016; Li et al., 2022). Lead and zinc in the soil and their effect on children and adults have been studied (Paltseva et al., 2022; Yang L et al., 2022). Mercury and its effects have also been studied (Meneses et al., 2022), as well as chromium (Huang et al., 2022), copper (Sereni et al., 2022) and rare earth elements (REE) (Ramos et al., 2016). The carcinogenic risk of Cr, Ni, and As in soils of residential areas was investigated by Yang J et al. (2022).

Several studies used various methods and tools to calculate the ecological and human health risks of heavy metals in soil (Pinedo et al., 2014). The study of Xiang et al. (2022) used self-organizing map for the calculation of ecological risk assessment of heavy metals in soil. The study of Sun J et al. (2022) used the probabilistic non- carcinogenic health risks. The study of Pandey et al. (2016) used enrichment factor, contamination factor, and pollution load index. Moreover, studies used several contamination indices. Examples include geo-accumulation index (Igeo), contamination factor (Cf), pollution load index (PLI), degree of contamination (Cd), potential ecological risk index, Nemerow's pollution index (PIN), and human health risk assessment analysis (carcinogenic and non-carcinogenic risks) to assess heavy metal contamination in soils (Saha et al., 2022a; Ma et al., 2022; Maurya and Kumari, 2021; Qi et al., 2020). Finally, the studies of Latosińska et al. (2021) and Yang L et al. (2022) used multi-factors including geo-accumulation index, environmental risk indicator, risk assessment code, environmental risk factor, and the authors' own environmental risk determinant indicator.

This study should add great significance and scientific values to the existing information and database related to soil quality in Qatar. The last comprehensive study that produced "Soil Atlas of Qatar" was conducted in 2009. The Atlas focused mainly on soil types without addressing the chemical and mineralogical characteristics of the topsoil. The necessity for revised Atlas also stems from the huge changes occurred in Qatar during the past ten years; the construction of new cities, the transportation networks, the establishment of industrial zones, the nature reservations, and the World Cup 2022 infrastructure.

This study has a significant impact on urban planning, land use, and more importantly the use of soil in agriculture to achieve food security. The study highlights the sources of pollution in this geographical area, which represents arid regions, where soil is exposed to anthropogenic impacts, and natural influences including climate change.

Understanding the sources of soil pollution in Qatar can contribute to the formulation of strategies and action plans to monitor, control and reduce pollution. Such strategies may help in understanding potential risks and establishing mitigation plans.

The objectives of this study include: (i) determination of chemical elements in the topsoil of Qatar as an example of arid regions; (ii) establishment of new maps for the spatial distribution of the tested elements to be a reference for further investigations; (iii) assessment of the ecological and human health risks associated with the occurrence of the tested elements in the topsoil.

2. Methodology

2.1. Study area, soil sampling, analysis and quality control

Qatar is a small peninsula located in the Arabian Gulf. It is among the richest countries globally with a GDP growth rate of 3.6% in 2021 (QPSA, 2022). More than 99.3% of the population is concentrated in the major city of Doha and its surrounding, Umm Salal Ali, Al Wakra and Al Khor (FAO, 2021). The other cities are mainly industrial areas such as Ras Laffan, Ad Dahirah, Mesaieed, Dukhan, and Al Ruwais (Fig. 1). Qatar depends on food imports to feed its population of 3 million (QPSA, 2022). Though oil and gas constitute the backbone of Qatar's economy, Qatar imported approximately 90% of its food until 2017 (Miniaoui et al., 2018) when neighboring Arab countries and their allies imposed an air, sea, and land blockade. The blockade raised national concerns regarding food security and led the country to explore alternative supply-side strategies and sources to satisfy the country's food demand. In response, food production in Qatar greatly increased and it was soon appreciated that agricultural production was both economically viable and a much more sustainable solution (Karanisa et al., 2021). Consequently, agriculture in Qatar is now considered to be an emerging industry and research on the quality and risks of soils in Qatar is inevitable.

Collecting topsoil samples from highly eroded arid regions is always challenging because of frequent sand storms, soil instability, desertification, rainfall scarcity, variation of vegetation and farming systems. However, a sampling strategy has been developed. It focused on the protected-limited agricultural areas where soil is available and could be visited and collected regularly. The sampling campaigns considered five major elements: (a) the most stable soils of the agricultural areas for both open farms and greenhouses (b) the soils closed to groundwater wells (c) the modified soils by introducing fertilizers, composts and nutrients (d) the environmentally hotspots and pollution sources, and (e) the transportation network. The approach was limited to achieve the objectives of the study in collecting representative composite samples for this arid area over two years.

Briefly, in 2019 and 2020 composite samples of soil were collected from the depth of 0 and 10 cm in open and grass soils, 20 cm in vegetable soils, and up to 30 cm in ploughed soils. At each location, a circle of 2-5 m in diameter was identified and 10 subsamples were collected within the perimeter and

mixed to form a composite sample. Samples (0.5 kg) were collected and placed into polyethylene cups and stored at 4 °C. The soils were dried in an oven at 45 °C until of a constant weight. Samples were freeze-dried until complete dryness and then sieved through a 2-mm sieve and ground to a powder by using a ring mill. Amounts of 0.5-1.0 g of sample was dissolved in 10.5 mL of conc. HCl (37%) and 3.5 mL of conc. HNO_3 (65%) in 50-mL retorts. The samples were degassed (12 h) and then heated to 160 °C on a heating block until a complete extraction had taken place (3 h). After cooling, the solutions were diluted with distilled water in 50-mL volumetric flasks and kept in 100-mL polyethylene bottles for analysis. Samples were analyzed by an inductively coupled plasma - optical emission spectrometry (ICP/OES) (VISTA-MPX, VARIAN) for Ag, Al, Ca, K, Mg, Na and Sr. While all other elements were analyzed using an inductively coupled plasma-mass spectrometry (ICP-MS) (Bruker aurora M90). The total C and S were determined in dried samples by using a carbon-sulfur analyzer (LECO CS-225). Methodology details of sample collection, preservation, labeling, recording coordinates, soil preparation and laboratory work, analysis protocols and quality control/quality assurance (QC/QA) are well described in Shomar et al. (2005) and Shomar et al. (2013).

Figure (1) shows the locations of collected samples. Sampling was not possible from several restricted areas including military bases, industrial areas, closed areas, seashores and sand dunes.

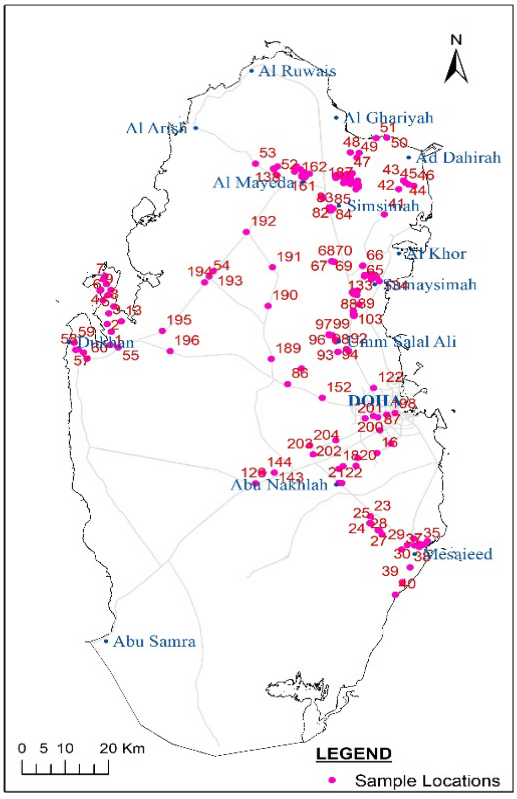

Fig. 1. Soil sampling locations within the State of Qatar.

2.2. Soil mapping

In this study, spatial distribution of certain chemical parameters of geo-referenced soil samples were carried out using a Geographic Information System (GIS) technique. The study collected 204 samples from representative sites (Fig. 1) in Qatar and studied the occurrence and spatial distribution of constituent elements of the samples using ArcGIS software. The preparation and prediction of soil chemical properties were studied from interpolation maps of certain chemical parameters using geochemical data and predicting the data at unknown locations using Geo-statistical Analyst extension available in Arc Map. Briefly, the interpolation method computes grid by considering neighboring locations within a user defined search radius and the method is used widely for soil investigations since it is easy to implement (McGrath et al., 2004; Lee et al., 2006; Ali and Moghanm, 2013). The potential of GIS technique is demonstrated well in several studies to map and study soils (Abdellatif et al., 2021; Barrena-González et al., 2022; Gasmi et al., 2022; Molina-Moral., 2022; Smith et al., 2022). Here, the maps were prepared with the World Geodetic System 1984 (WGS84) coordinate system and projected on UTM Zone 39N and interpreted visually to understand the spatial variation of such chemical parameters.

2.3. Ecological risk assessment

To assess ecological risk, contamination soil indices were adapted from Sharifinia et al. (2022). The key indices calculated for metal contamination in soil include contamination factor (CF) and potential load index (PLI). They are given in equations 1 and 2, respectively.

$$CF = \frac{C_{soil}}{C_0} \quad (1)$$

$$PLI = \sqrt[i]{CF_1 \times CF_2 \times \ldots \times CF_i} \quad (2)$$

Where C_{soil} is the concentration of metal in soil and C_o is the background levels of metals.

According to Sharifinia et al. (2022), CF below unity indicates low contamination, between 1 and 3 moderate contamination, between 3 and 6 considerable contamination and above 6 high contamination for that specific metal or metalloid. PLI above unity (1) means that metal pollution is present. Pollution indices were calculated for the following metals and metalloids: Al, As, Ba, Ce, Cd, Co, Cr, Cu, La, Mn, Mo, Nd, Ni, Pb, Pr, Se, Sm, Sr, U, V, and Zn.

2.4. Human health risk assessment

To assess human health risks of metals and trace elements through soil ingestion and dermal absorption, the US EPA methodology were followed (US EPA, 1989). Equations and parameters used were described in several studies (Rovira et al., 2010a; 2010b; 2011) and summarized in Table 1. Briefly, exposure through soil ingestion (Equation 3) and dermal absorption (Equation 4), hazard quotients (HQ) (Equation 5) and carcinogenic risk (CR) (Equations 6).

$$Soil\ ingestion = \frac{C_{soil} \times EF \times IR_{soil}}{BW} \quad (3)$$

$$Dermal\ absorption = \frac{C_{soil} \times EF \times AF \times ABS \times SA}{BW} \quad (4)$$

$$HQ = \frac{Soil\ ingestion \times ED}{RfDo \times AT_{nc}} \text{ or } HQ = \frac{Dermal\ absorption \times ED}{RfDd \times AT_{nc}} \quad (5)$$

$$CR = Soil\ ingestion \times SF_0 \times \frac{ED}{AT_c} \quad \text{or} \quad CR = Dermal\ absorption \times SF_d \times \frac{ED}{AT_c} \qquad (6)$$

In addition, the relationship between dermal and oral exposure were described in the following equation:

$$RfD_d = RfD_0 \times GIABS \quad \text{or} \quad SF_d = \frac{SF_0}{GIABS} \qquad (7)$$

Table 1. Parameters used in human health risk assessment.

	Description	Value	Reference
Csoil	Trace element concentration in soil	Present study (mg/kg)	-
EF	Exposure frequency	350 days/year	Rovira et al, 2010a
IRsoil	Soil ingestion rate	114 mg/day	Rovira et al, 2010a
AF	Adherence factor of soil to skin	1 mg/cm^2·day	Rovira et al, 2010a
ABS	Dermal absorption rate	Element specific (unitless)	US EPA, 2022
SA	Exposed skin area (head and hands)	2430 cm^2/day	US EPA, 2011
BW	Body weight	85 kg	Worlddata, 2022
RfD_o	Oral reference dose	Element specific (mg/(kg·day))	US EPA, 2022
SF_o	Oral slope factor	Element specific (kg·day/mg)	US EPA, 2022
GIABS	Gastrointestinal absorption factor	Element specific (unitless)	US EPA, 2022
ED	Exposure duration	30 years	Rovira et al, 2010a
AT_{nc}	Average time non-carcinogenic risk	30 years	Rovira et al, 2010a
AT_c	Average time carcinogenic risk	70 years	Rovira et al, 2010a

3. Results and discussion

3.1. Soil mapping and contaminant distribution

3.1.1. Major and trace elements

The concentrations of major and trace elements in soil were studied for risk assessments by comparing the Global Background standard (Kabata-Pendias and Mukherjee, 2007). Table (1) provides the minimum, maximum, average and standard deviation concentrations (mg/Kg) of major, trace and rare-earth elements (REE) in the 204 soil samples of Qatar and allows us to compare the findings with the global Background.

The results of major elements show presence of high concentration of Ca, Mg, Al and Na in the soils compared to the concentrations of other elements such as Fe, K and Mn (See Table 1S in Supplementary material). The minimum and maximum concentrations of Ca, Mg, Al and Na were 0.246 and 357.732 g/Kg, 3.569 and 71.862 g/Kg, 1.034 and 18.696 g/Kg, and 0.240 and 93.120 g/Kg, respectively (Table 2). The study of such concentrations with the concentration of global background shows that the concentration of Al is relatively low and the Ca and Mg are high (Table 2).

Table 2. Minimum, maximum and average concentrations (mg/Kg) of major, trace and rare-earth elements (REE) in the soils of Qatar (n=204)

Elements	Minimum	Maximum	Average	Standard Deviation	Global Background (mg/Kg) (Kabata-Pendias and Mukherjee, 2007)
Major elements					
Al	1034	18696	6507	2400.44	77400
Fe	549	26895	8092	4655.86	31000
Ca	246	357732	151198	45479.49	29500
Mg	3569	71862	22277	13578.34	13500
Mn	14	589	199	96.5271	527
Na	240	93120	13213	12454.6	25700
K	629	12922	6798	2177.26	28600
Trace elements					
Cu	0.06	472	13	39.75	14.3
Ag	1.43	1.68	1.55	0.18	0.10
Se	0.001	1.86	0.24	0.17	0.7
Co	0.22	15.04	4.26	2.57	11.6
Cr	2	312	29	24.33	35
V	2	67	24	10.02	60
Cd	0.02	0.6	0.14	0.07	0.102
Sr	142	6299	941	828.60	316
Ni	1.88	184.56	29.32	20.88	18.6
Mo	0.06	4.01	0.71	0.47	1.8
Ba	15.06	240.78	65.73	30.27	688
Pb	0.64	32.73	5.00	4.16	17
Zn	2.77	180.93	31.81	22.95	52
As	0.46	7.63	2.57	1.00	2
U	0.34	2.91	0.95	0.43	4
C	1.09	12.4	5.80	1.79	0.32 (%)
S	0.00285	6.9	1.31	1.13	0.95 (%)
Rare-earth elements					
La	0.77	12.33	5.00	1.99	26
Ce	1.53	25.72	9.97	4.28	49
Pr	0.18	3.1	1.22	0.50	8
Nd	0.74	12.43	4.87	2.01	19
Sm	0.17	2.63	1.01	0.43	3.1
Eu	0.03	0.57	0.23	0.10	-
Gd	0.14	2.52	0.92	0.39	-
Tb	0.02	0.36	0.13	0.06	-
Dy	0.12	1.89	0.80	0.33	-
Ho	0.03	0.39	0.16	0.06	-
Er	0.07	1.03	0.42	0.17	-
Tm	0.01	0.13	0.06	0.02	-
Yb	0.06	0.75	0.32	0.13	-
Lu	0.01	0.1	0.05	0.02	-

The concentration of Na exceeds the global background (25700 mg/Kg) in few locations. The Fe, Mn and K are within the limit of the global background. The interpretation of spatial maps drawn for such major elements (Fig. 2) shows a presence of the enrichment of such elements in the soils, which may be due to the occurrence of carbonate formations such as limestone and dolomite formations, and alumino-silicate minerals bearing shale and clay formations in the region (El Behairy et al., 2022; Saha et al., 2022b). The occurrence of low concentrations of Fe, Mn and K suggest the absence of igneous rocks in the region, and such concentrations are due to the presence of alumino-silicate minerals bearing formations (shale and clay formations). The results can be studied with the geology of Qatar. The high concentration of Al in the northern part of the state (Fig. 2c) is due to the occurrence of alluvium silty soil in the region which is being used highly in the agriculture region. In general, K is an essential macronutrient for plants growth. Large quantities of K have been taken up during the plants lifecycle. The actual cultivated land area of Qatar includes green fodder, date palms, fruits, vegetables, and cereals. Understanding the concentration of K in soil is important, especially for green fodder, date palms, fruits, vegetables, and cereals. The potassium distribution map (Fig. 2d) shows the available K in the region. The concentration is significantly higher in the northern part of the state, which may be due to plantation and agricultural activities in the region.

The study of trace elements and metals in the soils show the presence of low concentration of transition metals such as Cu, Co, Cr, V, Ba, Pb, Zn, Ag, Se, Cd, and Mo when study with the concentration of Sr, Ni, and As (Table 2S in Supplementary material). The interpretation of data with the Global background data showed the presence of low concentrations of such elements (Cu, Ag, Se, Co, Cr, V, Cd, Mo, Ba, Pb, Zn and U) except the Sr, Ni and As elements in the soils of State of Qatar (Table 2) (Table 2S in Supplementary material). The concentrations of such trace metals in the soils are due to the occurrence and weathering of shale and clay formations in the region (El Behairy et al., 2022; Fei et al., 2022).

The spatial distribution map of Sr showed slightly high concentrations at the agricultural locations (Fig. 3) which may be due the inputs of phosphate fertilizers (Vengosh et al., 2022). Ni was noticed in the same locations and this could be due to the farming system and fertilizer inputs (Zhang X et al., 2022). Although As was found in the same locations, the sources could be more of a natural origin (Postma et al., 2013).

Generally, the concentration of Ag is <1 mg/Kg in all the samples. The study of spatial map of the essential trace elements that required for normal growth of vegetation and agriculture, such as Na, Fe, Mn, Zn, Cu, Mo, and possibly Co show the presence of low concentrations of all of these elements except for Na (Fig. 4). However, few agricultural locations showed elevated concentrations of Zn, Cu, Mo and Co in the topsoil. The explanation behind such slight increase is that such sampling locations are close to industrial areas and transportation network.

In addition, the concentration of contaminants metals such as the Ni, Cd and Pb in the soil were studied for their spatial distribution. The interpretation of spatial maps of the metals shows the presence of high concentrations of Ni and Cd elements in few locations close to transportation network and more applications of fertilizers. However, Pb showed low concentrations in most of the collected samples (Fig. 3 and 5). Few locations showed slightly high Pb concentrations and these locations are close to oil and gas industrial areas.

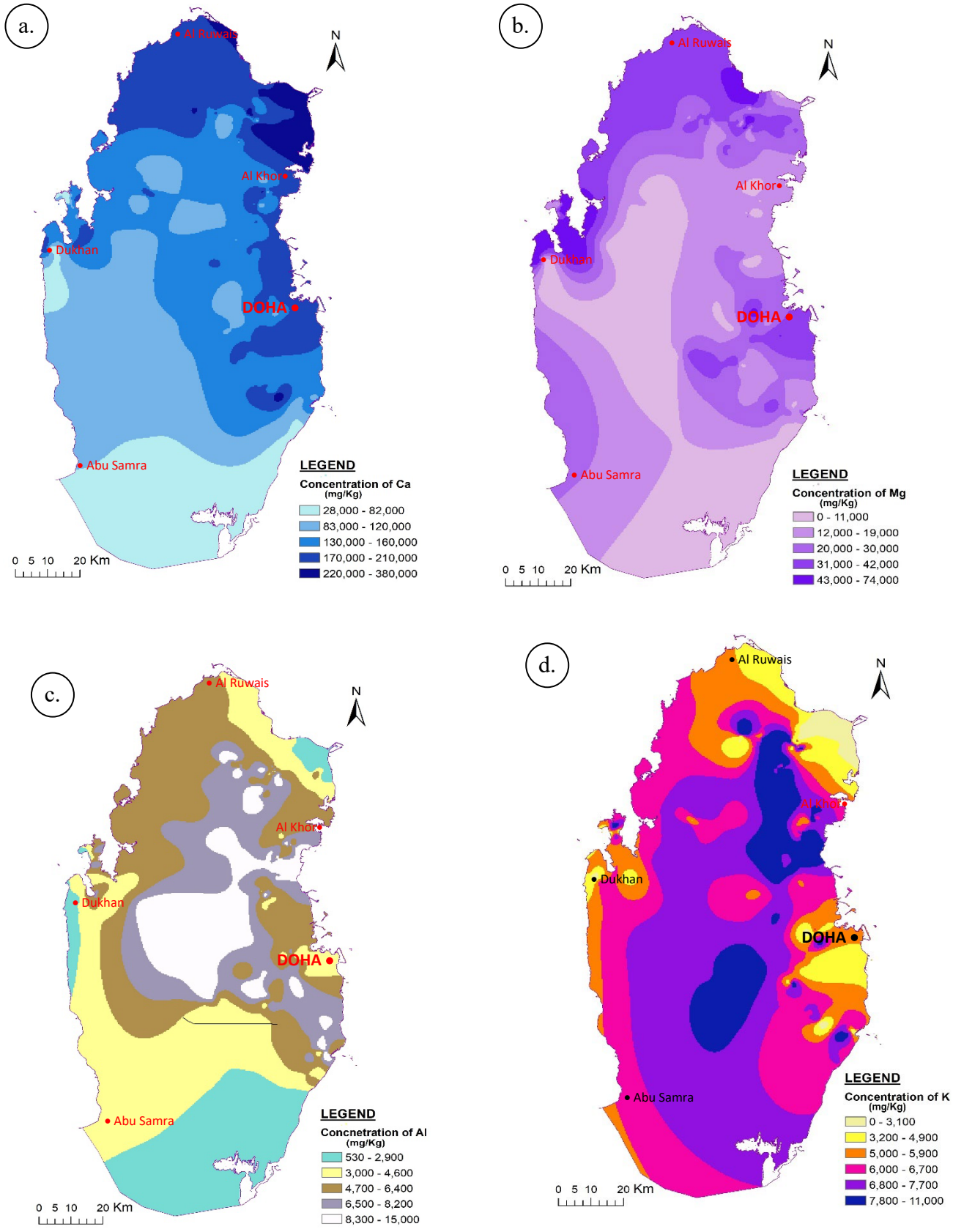

Fig. 2. Spatial maps showing the concentrations of (a) Ca, (b) Mg (c) Al and (d) K in the soils Qatar.

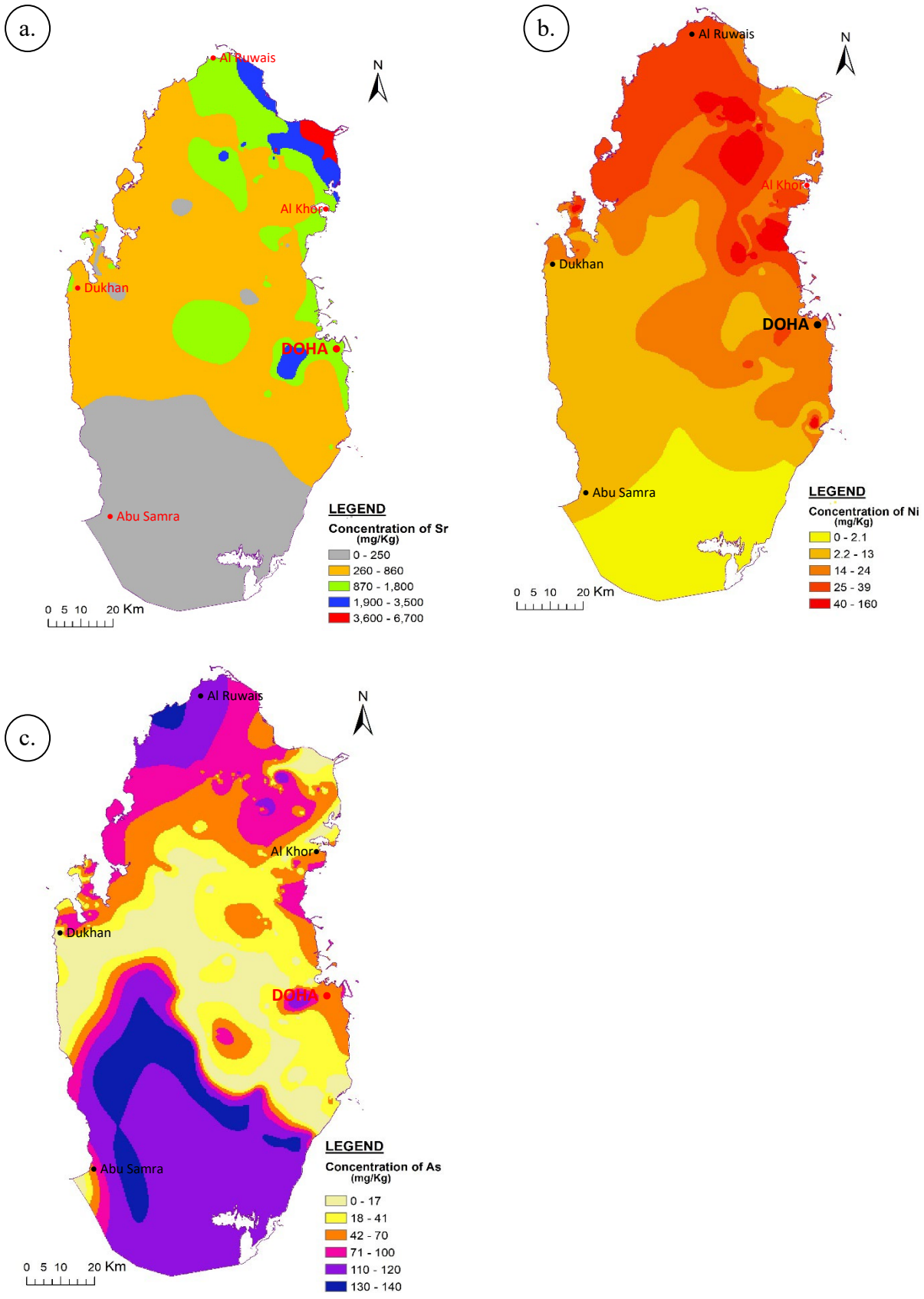

Fig. 3. Spatial maps showing the concentrations of (a) Sr, (b) Ni, and (c) As in the soils of Qatar.

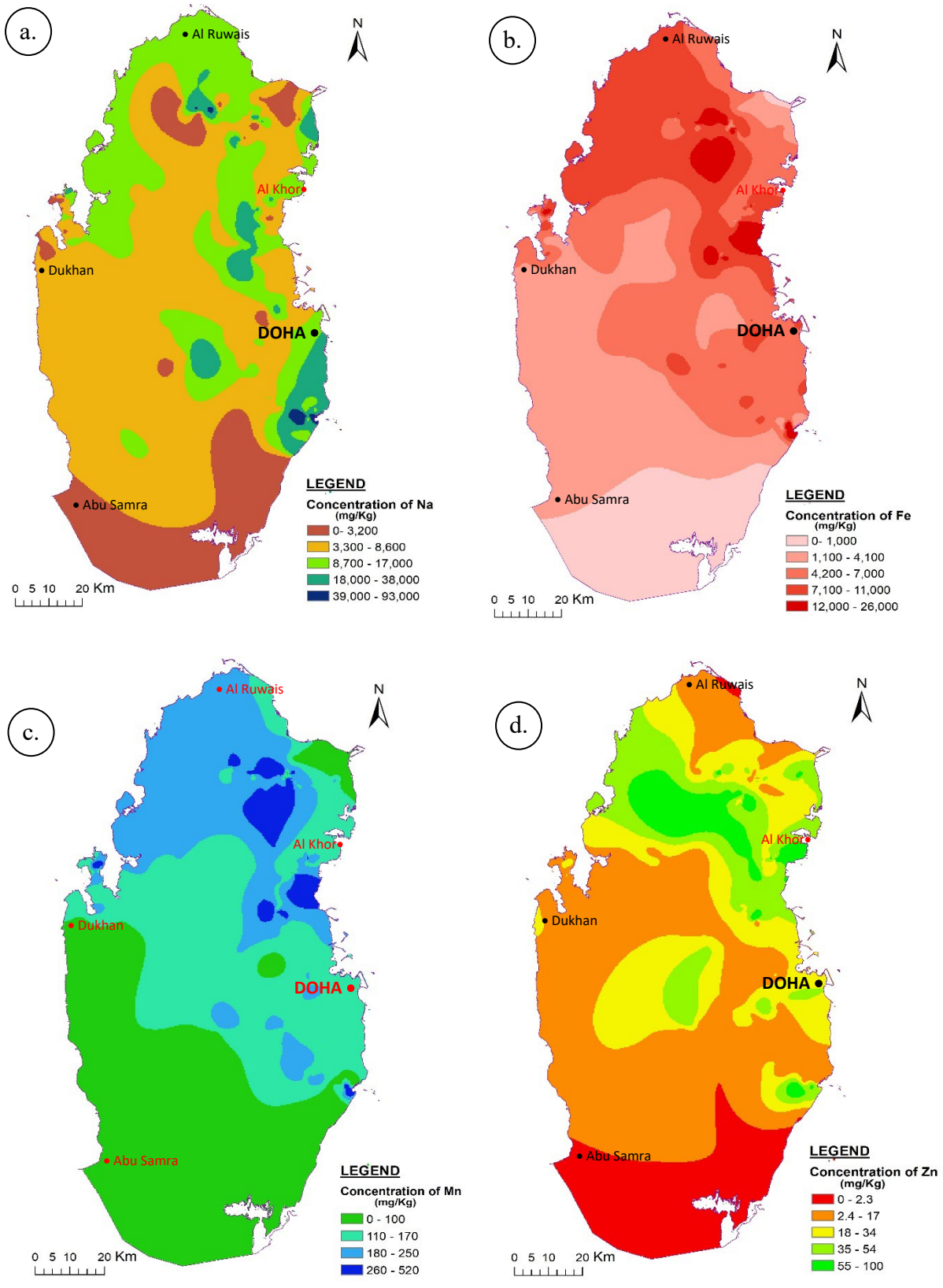

Fig. 4. Spatial maps showing the concentrations of (a) Na, (b) Fe, (c) Mn, (d) Zn, (e) Cu, (f) Mo and (g) Co in the soils of Qatar

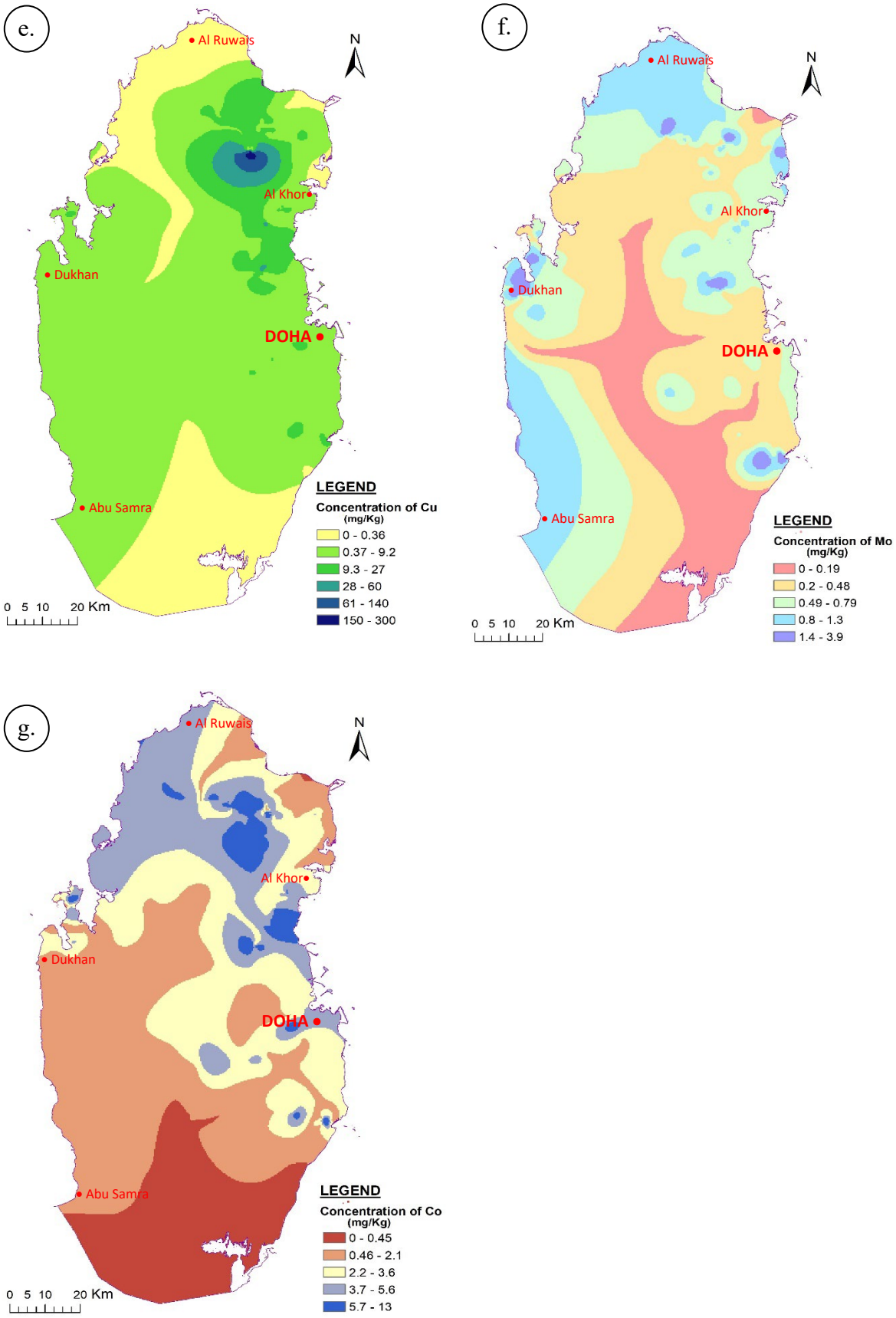

Fig. 4. Continued

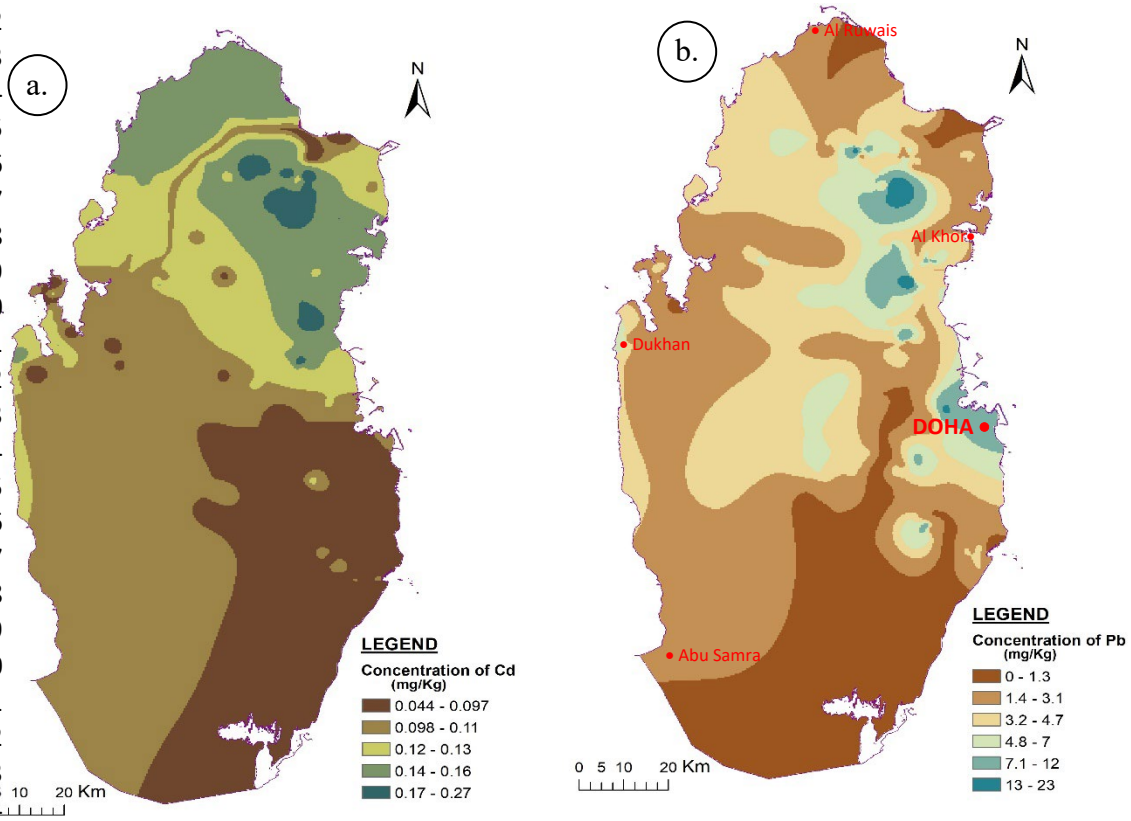

Fig. 5. Spatial maps showing the concentrations of (a) Cd and (b) Pb in the soils of Qatar.

The concentrations of these elements in the topsoil of Qatar can be compared to their concentrations in the soils of similar arid regions. For examples, El Behairy et al. (2022) assessed the soil heavy metals of north Nile Delta in Egypt by the combination of GIS and multivariate analysis. They stated that the contaminant factors (CFs) of As, Co, Cu, Ni, V, and Zn were in the decreasing order of As, Ni, Zn, V, Cu, and Co. They stated that most of the research study area (71.9%) consisted of a class of moderately to heavily polluted areas and a large portion of the study area (49.17%) has a very high risk of contamination. Similarly, Al-Taani et al. (2021) investigated the pollution levels of heavy metals (Mn, Zn, Cr, Ni, Cu, Pb, Cd, Co, and As) in agricultural soils in the Liwa area (UAE). They stated that the presence of variation in the bulk metal contents in the soil samples were related to multiple sources including agrochemicals, atmospheric dust containing heavy metals, and traffic-related metals, and the highly enriched Cd, Ni, Zn, and Cr in the soils were related to non-crustal sources. As well as, Nazzal et al. (2021) assessed heavy metals in the soils of Abu Dhabi Emirate using pollution indices and multivariate statistics. They described that the indices show the highest contamination of Cu, Pb, Zn, and Ni in the soils due to the pollutants from neighboring zones such as highways, roads with high traffic, emissions from fossil fuel, or industrial zones. Their study of enrichment factor analysis showed that the Cd, Ni, Zn, and Cr were highly enriched in soils and these could have originated from non-crustal sources. The interpretation of Cu, Co, Cr, V, Ba, Pb, Zn, Ag, Se, Cd, and Mo elements in the soils of Qatar showed a presence of very low concentrations and are within the acceptable limits. Although Cu, Cr, Zn and Cd exceed slightly the global background limits at a few locations (Table 2S in

Supplementary material). This calls for further investigation and may require long term monitoring programs. However, most of the samples represent the presence of high concentrations of Sr, Ni and As (Fig. 3) and suggest the occurrence of pollution in the soil. The slight enrichments of Cu, Cr, Zn and Cd and high concentrations of Sr, Ni and As are comparable with the above studies conducted in Egypt and the UAE (El Behairy et al., 2022; Al-Taani et al., 2021; Nazzal et al., 2021). The elevations of these elements in the topsoil of Qatar for these specific locations could be due to the practicing of fertilizers, occurrence of atmospheric dust containing heavy metals and traffic-related metals, the non-crustal sources as studied above. Such conclusions need further scientific investigation at the national level.

3.1.2. Rare-earth elements

The results of rare-earth elements (La to Lu) show low concentration of light REE (LREE, from La to Gd) when compared to the Global Background data (Table 2) (See Table 3S in Supplementary materiel). The concentration of heavy REE (HREE, from Tb to Lu) is relatively low when compared to the LREE. The spatial correlation of the chemical elements of the soils attributes the different degrees of heterogeneity of field management factors such as land-use pattern, irrigation, fertilization or intrinsic factors such as erosion, relief and drainage. The REE results of this research in terms of concentration and potential sources agree with the study of Ramos et al. (2016).

We studied the distribution of REE in Qatari soils with the summary of qualitative and semi-quantitative observations of Vinogradov (1959), Robinson et al. (1958) and Haskin and Frey (1996). We compared our findings with REE composition of the upper continental sedimentary crust (Rudnick and Gao, 2003; Taylor and McLennan, 1985) (Fig. 5). The interpretation of values of the REE of soils shows the presence of high concentration of LREEs in the soils when compared to the values of HREEs (Table 4S in Supplementary materiel). The REEs plot shows all the samples in similar trend and the REEs of the soils of Qatar show a relative depletion in the overall concentration. The low concentration in the soils may be characteristics to the soils that derived from the carbonate sedimentary formations of arid region. However, the comparative study depends on the use of continental crust and soils data which were analyzed by different methods including atomic absorption, spectrochemical analysis and radiochemical neutron activation analysis (RNAA), and the samples used. Taylor and McLennan (1985) used samples of shale from sedimentary formations, and Vinogradov (1959) and Robinson et al. (1958) used soils from Russia and the USA.

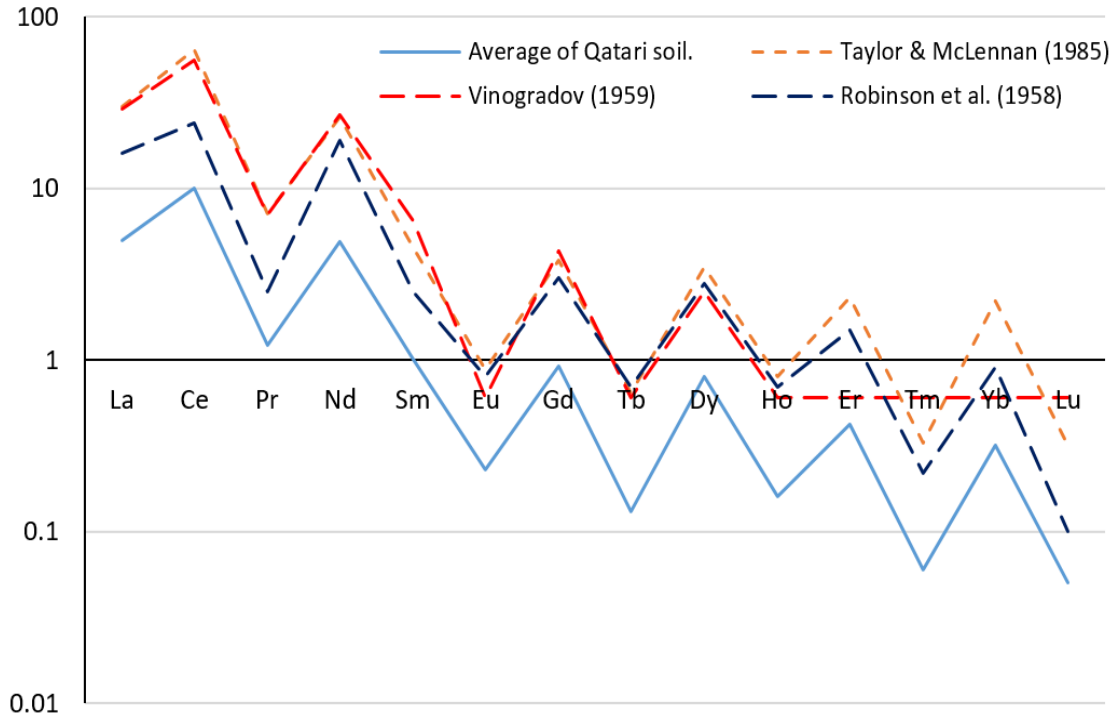

Fig. 5. REE plot compares the concentration in Qatari soil (average in µg/Kg), continental crust (Taylor and McLennan, 1985) and soils of crust (Vinogradov, 1959; Robinson et al., 1958).

3.2. Ecological risks

Table (3) summarizes CF and PLI results. All soil samples have PLI values below 1 (no metal pollution). Maximum PLI values, but still below 1, were around 0.8 in two points (samples #73 and #80) located at the Northern parts of Doha in the region of Al Khour due to high CF for As, Cd, Co, Cr, Cu, Ni, Sr and Zn. These areas are agricultural fields with limited population density.

Strontium (Sr) results show high CF values, ranging from 5 to 19, in the Northern areas of Qatar around Ad Dahirah area where samples of 42 to 52 were collected. Around 80% of samples presented CF between 1 to 3 (low contamination) for As, Cd, Ni and Sr. Sr is naturally occurred in soil and although the CF value is high, it is still in the acceptable range with minimal risks.

Table 3. Contaminant factor (CF) and pollution load index (PLI) summary for Qatar soils (n=204)

	CF>1	CF>3	CF>6	P50	P75	P95	Maximum
Al	0	0	0	0.08	0.10	0.13	0.24
As	140	2	0	1.26	1.58	2.09	3.81
Ba	0	0	0	0.09	0.12	0.18	0.36
Ce	0	0	0	0.18	0.25	0.38	0.52
Cd	135	4	0	1.24	1.63	2.27	5.88
Co	4	0	0	0.30	0.47	0.79	1.30
Cr	48	1	1	0.70	0.99	1.56	8.90
Cu	34	2	2	0.55	0.83	1.51	33.02
La	0	0	0	0.17	0.23	0.35	0.47
Mn	3	0	0	0.34	0.46	0.74	1.12
Mo	9	0	0	0.34	0.45	0.80	2.23
Nd	0	0	0	0.23	0.31	0.48	0.65
Ni	130	19	1	1.23	1.93	3.49	9.92
Pb	7	0	0	0.23	0.33	0.59	1.93
Pr	0	0	0	0.14	0.19	0.28	0.39
Se	3	0	0	0.30	0.42	0.67	2.65
Sm	0	0	0	0.29	0.40	0.60	0.85
Sr	192	46	23	2.02	2.90	8.54	19.93
U	0	0	0	0.21	0.27	0.46	0.73
V	2	0	0	0.39	0.52	0.69	1.11
Zn	29	1	0	0.47	0.75	1.47	3.48
PLI	**0**	-	-	**0.36**	**0.46**	**0.59**	**0.84**

3.3. Human health risks

Table 4 summarizes mean values of exposure, HQ and cancer risks through soil ingestion and dermal contact and toxicological values used in risk assessment. Coarse elements in soil, such as Al, Ca, Fe, K Mg and Na presented the highest exposures.

Regarding non-carcinogenic risk, HQ's were quite below 0.1 for all elements analyzed in all sampling points. In consequence, exposure through soil ingestion and dermal contact to all elements analyzed were in safety zone set at HQ<1.

Regarding carcinogenic risk, all risk were in the acceptable risk, between 10^{-5} and 10^{-6}. The average total carcinogenic risk through soil ingestion and dermal contact was $1.1 \cdot 10^{-5}$ and $5.7 \cdot 10^{-6}$ for As and Cr, respectively. It should be highlighted that SFo were stablished for inorganic As and Cr(VI), however total As and Cr were analyzed. In present study, we assume that all As are in inorganic form and 1/6 of total Cr are hexavalent Cr (Rovira et al., 2018). It is important to mention that in arid countries such as Qatar, skin surface exposed to soil are usually lower than other countries or regions in the world. Generally, head and hands are exposed to soil with a skin surface of 2430 cm^2 (US EPA, 2011), rather than 4050 cm^2 as the default parameter considered by US EPA. In addition, default body weight used, 70 kg, is lower than body weight reported in online database (Worlddata, 2022), established 85 kg weight for adult men, respectively. In present study, 85 kg is used.

For several elements such as rare earth (Dy, Er, Eu, Gd, Ho, La, Lu Nd, Pr, Tb, Tm) there are still a lack of toxicological values to assess the risk.

Table 4. Mean values of exposure, HQ and Cancer risks (CR) through soil ingestion and dermal contact and toxicological parameters used.

	Soil ingestion mg/kg/day		**Dermal contact** mg/kg/day		**RfDo**	**SFo**	**HQ ingestion**	**HQ dermal**	**CR ingestion**	**CR Dermal**
	Mean	SD	Mean	SD	mg/kg/day	kg·day/mg				
Al	8.24E-03	3.05E-03	1.78E-04	6.42E-05	1		0.00824	0.00018		
As	3.29E-06	1.32E-06	2.12E-06	8.40E-07	0.0003	1.5	0.01100	0.00704	2.1E-06	8.9E-06
Ba	8.24E-05	3.87E-05	1.83E-06	8.40E-07	0.2		0.00043	0.00013		
Ca	1.89E-01	2.31E-06	4.10E-03	4.89E-08						
Ce	1.24E-05	5.85E-02	2.72E-07	1.24E-03						
Cd	1.73E-07	5.52E-06	3.66E-09	1.19E-07	0.0001		0.00173	0.00147		
Co	5.44E-06	8.24E-08	1.14E-07	1.83E-09	0.0003		0.01803	0.00039		
Cr	3.71E-05	3.29E-06	7.91E-07	6.92E-08	1.5	0.5	0.00002	0.00004	3.1E-06	2.6E-06
Cu	1.65E-05	3.13E-05	3.56E-07	6.42E-07	0.04		0.00042	0.00001		
Dy	9.88E-07	5.11E-05	2.17E-08	1.09E-06						
Er	5.35E-07	4.28E-07	1.14E-08	8.89E-09						
Eu	2.88E-07	2.14E-07	6.42E-09	4.55E-09						
Fe	9.88E-03	1.24E-07	2.17E-04	2.62E-09	0.7		0.01462	0.00031		
Gd	1.15E-06	6.01E-03	2.52E-08	1.28E-04						
Ho	1.98E-07	5.02E-07	4.25E-09	1.09E-08						
K	9.06E-03	7.99E-08	1.83E-04	1.73E-09						
La	6.42E-06	2.80E-03	1.38E-07	5.93E-05						
Lu	5.85E-08	2.55E-06	1.24E-09	5.44E-08						
Mg	3.05E-02	2.31E-08	6.42E-04	4.89E-10						
Mn	2.55E-04	1.73E-02	5.44E-06	3.71E-04	0.024		0.01055	0.00562		
Mo	9.06E-07	1.24E-04	1.93E-08	2.67E-06	0.005		0.00018	0.00000		
Na	1.65E-02	6.01E-07	3.51E-04	1.28E-08						
Nd	6.18E-06	1.56E-02	1.33E-07	3.41E-04						
Ni	3.71E-05	2.55E-06	7.91E-07	5.44E-08	0.011		0.00337	0.00179		
Pb	6.18E-06	2.72E-05	1.33E-07	5.93E-07	0.0035		0.00176	0.00004		
Pr	1.56E-06	5.35E-06	3.31E-08	1.14E-07						
Se	3.05E-07	6.42E-07	6.42E-09	1.38E-08	0.005					
Sm	1.32E-06	-	2.77E-08							
Sr	1.15E-03	2.14E-07	2.52E-05	4.55E-09	0.6		0.00196	0.00004		
Tb	1.73E-07	5.52E-07	3.66E-09	1.19E-08						
Tm	7.16E-08	1.07E-03	1.53E-09	2.27E-05						
U	1.24E-06	7.33E-08	2.62E-08	1.58E-09	0.0002		0.00613	0.00013		
V	3.21E-05	2.80E-08	6.92E-07	5.93E-10	0.005		0.00641	0.00525		
Yb	4.12E-07	5.52E-07	8.89E-09	1.19E-08						
Zn	3.87E-05	1.32E-05	8.40E-07	2.77E-07	0.3		0.00013	0.00000		

SD: Standard deviation. HQ: Hazard quotient; CR: Cancer risk.

4. Conclusion

We determined the total concentration of a broad variety of chemicals in the topsoil of Qatar, which is an arid country with huge and accelerated levels of urbanization and industrialization. We built maps for the spatial distribution of Ag, Al, As, Ba, C, Ca, Ce, Cd, Co, Cr, Cu, Dy, Er, Eu, Fe, Gd, Ho, K, La, Lu, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pr, S, Se, Sm, Sr, Tb, Tm, U, V, Yb and Zn in the accessible locations. These maps are important for land use and planning. The mapping should be dynamic and created in a regular base due to the anthropogenic and natural influences. The study found the concentrations of all tested elements within the acceptable global range.

The data were used in the assessment of human health risks associated with the exposure to these elements in soil. Fortunately, no human health risks were observed in all locations including the highly populated areas of Qatar. Additionally, another approach to calculations was employed to assess the ecological risks of the presence of the same elements in soil. Two factors were used to calculate the ecological risks; the contamination factor (CF) and potential load index (PLI). The good news confirm

that there are no ecological risks associated with all elements. However, the contribution of Sr, which is naturally present in the soil and has the concentration still within the acceptable range, needs further measurement/analysis in the two selected areas.

Acknowledgments

This paper was made possible by the lab support of Maria Victoria Navarro and Stefan Rheinberger. Joaquim Rovira received postdoctoral fellowship from "Juan de la Cierva-incorporación" program of the Spanish "Ministerio de Ciencia, Innovación y Universidades" (IJC 2018-035126-I). Special thanks to Dr. Jalal Hawari and Dr. Sergey Rashkeev for their efforts to improve the quality of the paper.

Supplementary material

Table. 1S. Concentration of major chemical elements in the soils of Qatar
Table. 2S. Concentration of trace elements in the soils of Qatar
Table. 3S. Concentration of rare-earth elements in the soils of Qatar
Table 4S. REE of Qatari soil (average), continental crust

Ethical approval

This article does not contain any studies with human or animals performed by any of the authors.

Funding

No funding support has been received for this article.

Data availability

The dataset produced for this study is available within this article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authorship Contribution

Basem Shomar is leading the research project, he coordinated with the relevant farms and sampling locations, collected and analyzed the samples with the support of the labs, drafted the manuscript and he is the corresponding author.
Rajendran Sankaran built the maps of trace elements distribution, and wrote the relevant sections in the manuscript.
Joaquim Rovira Solano made the risk calculations, wrote the relevant sections, and reviewed the manuscript.

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