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[1] Ecological risk assessment of heavy metals contamination in agricultural soil from Al Majma'ah, central Saudi Arabia

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Abstract

Soil acts as a tank for heavy metals through surface complexation, ion exchange and surface precipitation. [2] The purpose of this study was to assess the contamination and ecological risk of heavy metals (HMs) in agricultural soil in the Al Majma'ah area of central Saudi Arabia. Soil samples from 34 farms were collected, and HMs were evaluated using inductively coupled plasma-atomic emission spectrometry (ICP-AES). [7] Enrichment factor (EF), contamination factor (CF), pollution load index (PLI), and potential ecological risk index (RI) were applied. [1] The average values of the HMs (dry weight, mg/kg) had the following order: Fe Al Mn Zn Ni Cr V Cu Pb Co As. Results of contamination indices revealed low contamination, low risk and no enrichment for all HMs, except some minor enrichment for Zn and Ni. [3] The considerable positive correlations between all elemental pairings in the correlation matrix and the one extracted principal component suggested that HMs in Al Majmaah soil were formed from weathering of Jurassic to Quaternary sediments in the research area.

Keywords: Heavy metals, Risk assessment, Multivariate analysis, Agriculture soil, Saudi Arabia.

1. Introduction

Agriculture soils receive metal pollutants through natural and human sources. Most natural sources belong to weathering and erosion of different parent rocks, and volcanic activities.[21] Metal-based pesticides or herbicides, phosphate-based fertilizers, wastewater irrigation, spillage of petroleum distillates, livestock manure, river flooding that brings sewage and contaminated water to the land, and accidental spillage of toxic chemicals from vehicles during transport are the main human sources of heavy metals (HMs) in soils (El-Kady and Abdel-Wahhab 2018; Azizullah et al. 2011; Ullah et al. 2020). The excessive deposition of HMs in soil causes environmental degradation for living organisms and can be enriched through the food chain (Su et al., 2014;[2] Alharbi and El-Sorogy, 2023). Many research studies have found that vegetables grown in urban and suburban areas absorb a higher amount of different chemical pollutants than those grown in rural areas (Christou et al., 2017). In the terrestrial ecosystem, soils are the most important sink for HM contaminants. (Nriagu and Pacyna, 1988; Li et al., 2013).

[16] Cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), and zinc (Zn) are key HMs that are required at low amounts in many biological activities. When these micronutrients or trace metals are present at ideal levels, they increase plant nutrition as well as normal development and yield. However, an excess of these micronutrients has a detrimental effect on plant growth by causing oxidative stress and suppressing enzyme activity, affecting cell structural and functional integrity (Arif et al. 2016; Ali et al. 2019). The non-essential metals include lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), silver (Ag) and antimony (Sb).[9] Although the biological roles of these elements in plant metabolism have yet to be determined, a number of investigations have shown that they are poisonous to both eukaryotic and

prokaryotic organisms.[85] Excess concentrations of these HMs in the environment can cause severe soil and water resource contamination, which is a major global environmental concern (Azizullah et al. 2011; Di Toppi and Gabbrielli 1999, Nour et al., 2022).

[9] Agriculture is one of the most significant activities because it is the primary source of food security.[9] Al Majma'ah governorate has about 6,000 farms producing various crops (wheat, barley, corn), vegetables, and trees, the most important of which are date palm trees. In addition, Al Majma'ah governorate is characterized by animal production of sheep, goats, camels and poultry.[3] Enrichment factor (EF), geo-accumulation index (I-geo), contamination factor (CF), and ecological risk index (RI) can all be used to assess HM contamination in soil (Cheng and Yap, 2015; Al-Kahtany et al., 2023).[25] Furthermore, multivariate techniques such as hierarchical clustering analysis and principal component analysis can be used to identify probable HM sources (Al-Kahtany et al., 2015; El-Sorogy et al., 2016; Alhabri et al., 2023).[29] The purpose of this study was to (i) quantify the levels of HM contamination content in agricultural soils in the Al Majma'ah governorate, (ii) compare HM levels in the research region to other soils and backgrounds, and (iii) assess the ecological concerns associated with HMs in Al Majma'ah's soil.

2. Material and Methods

2.1 Study area and sampling

The Al Majma'ah city is located about 180 km northwest of Riyadh on the path of the Riyadh-Sudair Al-Qassim Highway. It is about 140 km away from Qassim, 300 km away from Hafar Al-Batin, and about 85 km away from the city of Shaqra. The study area has the geographic coordinates of 25°00′061 - 45°19′526 N and 26°03′375 - 45°20′116 E (Fig. 1).[43] The research region is predominantly made up of marine carbonates and siliciclastics from the Oxfordian Hanifa

Formation, the Kimmeridgian Jubaila and Arab formations, the Cenomanian Wasia Formation, and Quaternary gravel sheets and alluvial terraces (Powers, 1968; Gameil and El-Sorogy, 2015; El-Asmer et al., 2015; Youssef and El-Sorogy, 2015; El-Sorogy et al., 2016, 2018; Tawfik et al., 2016; Khalifa et al., 2021). Surface soil samples were taken at a depth of less than 10 cm with a hard-plastic hand trowel from 34 palm and citrus farms in the Al Majmaah district of central Saudi Arabia. From geological point of view, 10 samples were collected from Quaternary, 9 from Jubaila, 6 from Arab, 6 from Wasia, and 3 samples from Hanifa (Fig. 2).[1] At each site, a representative sample was created by combining three subsamples, which were then sealed in plastic bags and stored in an ice box.

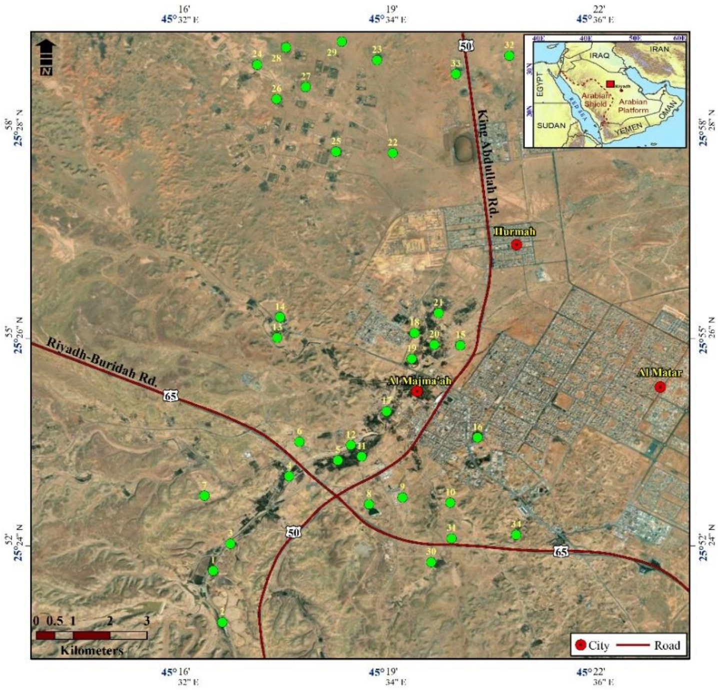


Fig 1.[2] Location map of the study area and sampling sites.

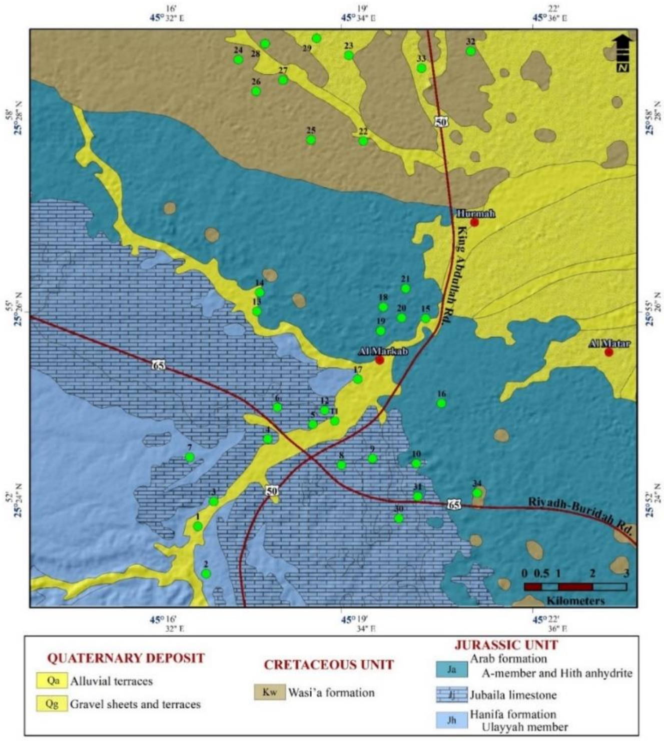


Fig 2.[5] Sampling location and stratigraphic lithology of the study area.

2.2. Analytical methods

Soil samples were dried at air temperature, then cleaned from large rocks and organic particles.[1] Physical breakdown with an agate mortar and pestle was used, followed by size separation with a nest of sieves (500 m, 500-250 m, 250-125 m, 125-63 m, and 63 m).[1] Fe, Al, As, Co, Mn, Ni, V, Zn, Cr, Pb, and Cu were studied using inductively coupled plasma-atomic emission spectrometry (ICP-AES) at the ALS Geochemistry Lab, Jeddah branch, Saudi Arabia. 0.[8]50 g of the 63 µm fraction was digested for 45 minutes on a hot plate with sand at temperatures ranging from 60 to 120 degrees Celsius. Calibration curves were created for each element by graphing the peak area of the optimum emission line against the concentration of the spike solutions for standard addition curves. The linearity of the calibration curves for each element was excellent.[1] The ALS Geochemistry Laboratory employed a standard analytical batch that includes a reagent blank for background assessment and certified reference material (CRM) to ensure data accuracy before release.

[1] The enrichment factor (EF), contamination factor (CF), potential ecological risk index (RI), and pollution load index (PLI) were used to assess the amounts of HM contamination in soil samples.[1] Using SPSS software, multivariate statistical approaches such as hierarchical clustering analysis (HCA), correlation matrix (CM), and principal component analysis (PCA) were used to identify likely sources of HMs in the examined soil. Table 1 categorizes the indices used herein and their classifications.

Table 1. Classification of the indices applied in this work.

Pollution indicators	**Procedures of calculation and classifications**						
Enrichment factor (EF)	EF= (M/Fe) sample / (M/Fe) background						
	(M/Fe) sample is the ratio of metal and Fe concentrations in the sample, and (M/Fe) background is the ratio of metal and Fe concentrations in the Earth's crust. Birch (2003) determined seven classes of EF in sediments.						
	EF < 1 no enrichment	EF<3 minor enrichment	EF= 3–5 moderate enrichment	EF= 5–10 moderately severe enrichment	EF= 10–25 severe enrichment	EF= 25–50 very severe enrichment	EF > 50 extremely severe enrichment
Contamination Factor (CF)	$C_f = C_o/C_b$						
	Co is the sediment metal content in the sample and Cb is the normal background value of the metal. Hökanson (1980) classified CF into four groups:						
	Cf < 1 low contamination factor	1 ≤ Cf <3 moderate contamination factor	3 ≤ Cf < 6 considerable contamination factor	Cf ≥ 6 very high contaminati on factor			
Potential Ecological Risk Index (RI)	$RI = \Sigma Er^i = \Sigma Tr^i \times Cf^i$						
	Where Eri is the potential ecological risk factor of an individual element, Tri is the biological toxic response factor of an individual element and Cf i is contamination factor for each single element (Hakanson, 1980). Er^i and RI values were classified into five and four categories respectively (Duodu et al., 2016):						
	Er^i <40 RI<150 low risk	40 ≤ Er^i < 80 150 ≤ RL < 300 moderate risk	80 ≤ Er^i < 160 300≤ RL < 600 considerable risk	160 ≤ Er^i < 320 high risk	Er^i > 320 RI > 600 very high risk		
Pollution Load Index (PLI)	$PLI = (CF_1 \times CF_2 \times CF_3 \times CF_4 \ldots \times CF_n)^{1/n}$						
	where CF is the current metal concentration/metal background concentration and CF_n is the contamination factor of metal n. The PLI values were interpreted in two ways (Harikrishnan et al., 2017):						
	PLI < 1 unpolluted	PLI > 1 polluted					

3. Results and discussion

[97] 3.1. Concentration and distribution of heavy metals

The average HM levels (dry weight, mg/kg) in the examined soil were as follows (Table 2): Fe (19108), Al (10550), Mn (270), Zn (41.25), Ni (31.11), Cr (30.47), V (29.83), Cu (13.92), Pb (6.47), Co (6.08), and As (4.07).[1] Figure 3 presents the distribution of HMs in the study area. In comparison with other HM values from other Saudi, background, and world soils (Table 3), our average Al, Fe, Ni, Mn, Cu, As, Pb, Cr, Co, and V were higher than those recorded from Al Majma'ah and Al-Ahsa soils, Saudi Arabia (Alarifi et al., 2022; Alharbi and El-Sorogy, 2023).[35] Our Fe, Zn, Mn, Cu, As, V, Pb, and Cr readings, on the other hand, were lower than the Wadi Jazan and background values, as well as the global average (Al-Boghdady and Hassanein, 2019; Turekian and Wedepohl, 1961; Kabata-Pendias, 2011).

Table 2.[1] Concentration of HMs (mg/kg), and the results of PLI and RI in Al Majma'ah soil.

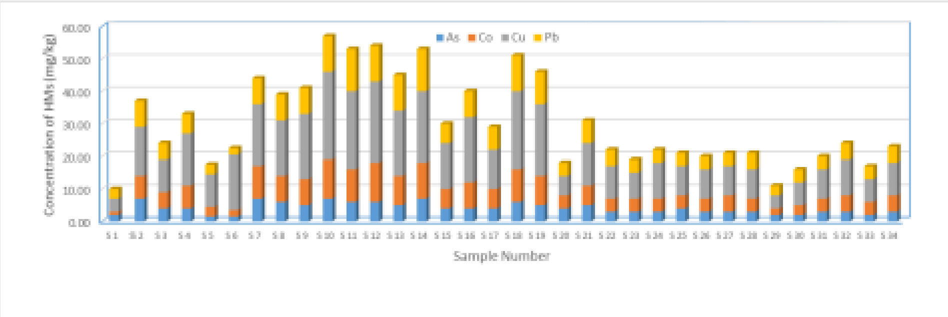
S.N.	Al	As	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn	PLI	RI
S 1	3900	2.00	1.00	12.00	4.00	8800	98	10.00	3.00	11.00	17.00	0.10	4.67
S 2	12400	7.00	7.00	47.00	15.00	40400	432	34.00	8.00	43.00	34.00	0.38	16.14
S 3	8800	4.00	5.00	28.00	10.00	14000	192	30.00	5.00	29.00	26.00	0.23	10.29
S 4	12000	4.00	7.00	40.00	16.00	33300	409	33.00	6.00	33.00	42.00	0.34	12.93
S 5	4800	1.50	3.00	13.00	10.00	9600	165	14.00	3.00	10.00	52.00	0.15	5.90
S 6	4700	1.50	2.00	19.00	17.00	19200	242	15.00	2.00	9.00	55.00	0.16	7.03
S 7	16400	7.00	10.00	44.00	19.00	24500	362	47.00	8.00	51.00	57.00	0.42	17.60
S 8	14100	6.00	8.00	42.00	17.00	28200	381	42.00	8.00	41.00	50.00	0.39	15.97
S 9	14000	5.00	8.00	36.00	20.00	20300	332	39.00	8.00	35.00	72.00	0.37	14.99
S 10	20900	7.00	12.00	53.00	27.00	29800	471	59.00	11.00	54.00	71.00	0.52	21.10
S 11	18100	6.00	10.00	45.00	24.00	23800	400	50.00	13.00	45.00	65.00	0.45	18.99
S 12	20100	6.00	12.00	51.00	25.00	27700	410	56.00	11.00	55.00	72.00	0.49	19.64
S 13	16800	5.00	9.00	45.00	20.00	25700	358	48.00	11.00	44.00	55.00	0.41	16.90
S 14	20300	7.00	11.00	52.00	22.00	27400	412	54.00	13.00	52.00	59.00	0.48	20.21
S 15	10500	4.00	6.00	29.00	14.00	17400	232	29.00	6.00	30.00	36.00	0.27	11.22
S 16	14200	4.00	8.00	37.00	20.00	22100	341	38.00	8.00	37.00	66.00	0.36	14.19
S 17	11000	4.00	6.00	30.00	12.00	18300	264	29.00	7.00	31.00	34.00	0.28	11.36
S 18	19200	6.00	10.00	47.00	24.00	25500	427	52.00	11.00	47.00	65.00	0.46	18.84
S 19	16300	5.00	9.00	41.00	22.00	22400	362	48.00	10.00	41.00	54.00	0.40	16.66
S 20	4500	4.00	4.00	17.00	6.00	15500	192	14.00	4.00	18.00	16.00	0.17	7.67
S 21	10300	5.00	6.00	31.00	13.00	20800	289	29.00	7.00	29.00	37.00	0.29	12.38
S 22	6700	3.00	4.00	23.00	10.00	15800	235	23.00	5.00	21.00	37.00	0.22	8.90
S 23	5500	3.00	4.00	18.00	8.00	11600	167	18.00	4.00	18.00	23.00	0.17	7.43
S 24	7000	3.00	4.00	26.00	11.00	18000	249	25.00	4.00	21.00	37.00	0.22	9.08

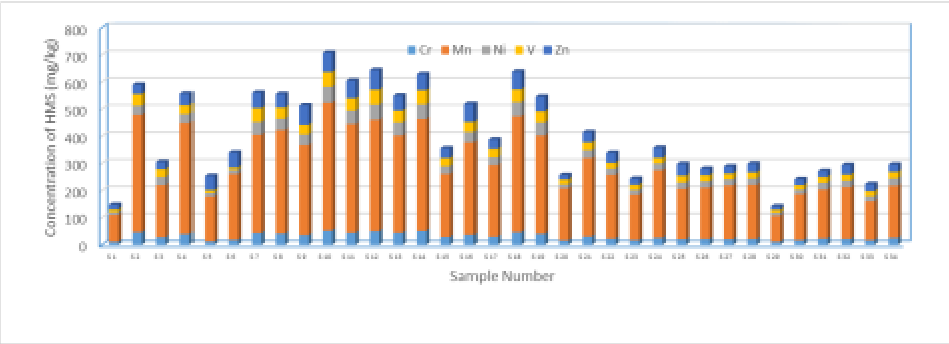
S 25	6500	4.00	4.00	21.00	9.00	12200	186	23.00	4.00	25.00	43.00	0.21	9.20
S 26	6700	3.00	4.00	22.00	9.00	12900	189	23.00	4.00	23.00	24.00	0.19	8.24
S 27	6800	3.00	5.00	21.00	9.00	12400	198	23.00	4.00	21.00	26.00	0.20	8.24
S 28	7300	3.00	4.00	22.00	9.00	12900	199	24.00	5.00	22.00	32.00	0.21	8.67
S 29	3500	2.00	2.00	12.00	4.00	7800	95	11.00	3.00	12.00	12.00	0.11	4.71
S 30	5200	2.00	3.00	18.00	7.00	12100	169	17.00	4.00	16.00	22.00	0.16	6.41
S 31	6000	3.00	4.00	24.00	9.00	13500	180	25.00	4.00	21.00	22.00	0.19	8.40
S 32	7200	3.00	5.00	22.00	11.00	12400	191	24.00	5.00	22.00	35.00	0.21	8.92
S 33	5500	2.00	4.00	18.00	7.00	9900	143	18.00	4.00	19.00	26.00	0.16	6.51
S 34	8200	3.00	5.00	26.00	10.00	13500	192	27.00	5.00	24.00	27.00	0.22	9.13
	3500	1.50	1.00	12.00	4.00	7800	95	10.00	2.00	9.00	12.00	0.10	4.67
	20900	7.00	12.00	53.00	27.00	40400	471	59.00	13.00	55.00	72.00	0.52	21.10
	10550	4.07	6.08	30.47	13.92	19108	270	31.11	6.47	29.83	41.25	0.28	11.79

Table 3.[2] Comparison between average HM concentration in the study area and other local and world backgrounds.[2]

Location and references	Al	Fe	Ni	Mn	Zn	Cu	As	Pb	Cr	Co	V
Al Majmaah, central Saudi Arabia (present study)	10550	19108	31.11	270	41.25	13.92	4.07	6.47	30.47	6.08	29.83
Al-Ahsa, Saudi Arabia (Alharbi and El-Sorogy, 2023)	4610	11790	14.53	176	54.43	10.83	2.27	5.23	28.67	3.59	12.33
Al Uyaynah, Saudi Arabia (Alharbi and El-Sorogy 2021)	35667	65200	19.25	-	64.33	10.56	13.8	28.48	30.18	2.45	-
Jazan, Saudi Arabia (Al-Boghdady and Hassanein 2019)	8865	23811	48.66	584	75.80	72.85	14.13	19.41	77.22	7721	122.0
Al-Ammariah, Saudi Arabia (Alarifi et al. 2022)	6331	11581	26.94	179	52.16	11.36	3.78	5.08	19.97	3.89	18.94
World average (Kabata-Pendias 2011)	-	35000	29.0	488	70.0	38.9	6.83	27.0	59.5	19.0	129.0
Background value (Turekian and Wedepohl 1961)	80000	47200	68.0	850	95.0	45.0	13.0	20.0	90.0	-	130.0

Q-mode HCA classified the 34 samples into two groups (Fig. 4). S2, S4, S7-S14, S16, S18, and S19 have the greatest concentrations of Al, As, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn (20900, 7.00, 12.00, 53.00, 27.00, 40400, 471, 59.00, 13.00, 55.00, and 72.[1]00 mg/kg, respectively).[1] The second group accounts S1, S3, S5, S6, S15, S17, and S20-S34, which reported the lowest values of the last mentioned HMs (3500, 1.50, 1.00, 12.00, 4.00, 7800, 95, 10.00, 2.00, 9.00, and 12.00 mg/kg, respectively).





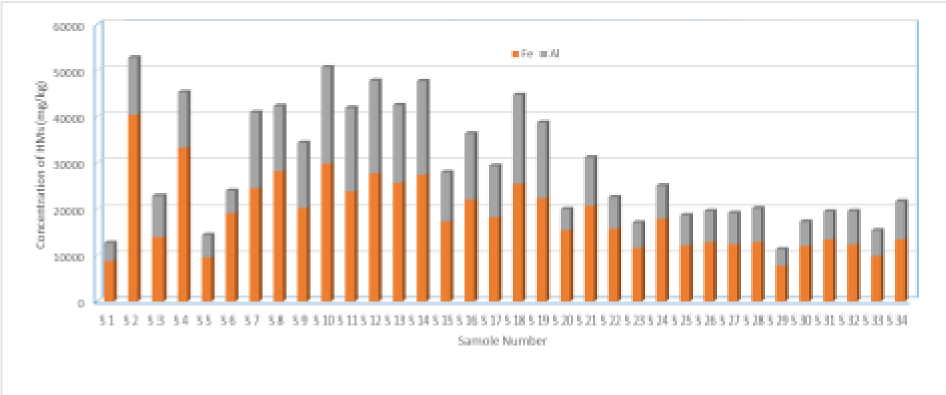


Fig. 3. Distribution of the HMs in Al Majma'ah soil.

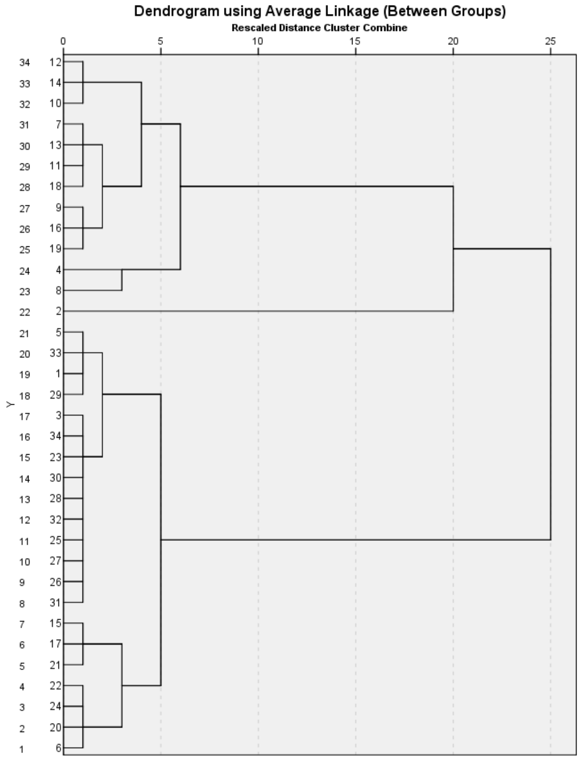


Fig. 4. Q-mode HCA of soil samples.

Contamination and risk assessment

The enrichment factor is used to separate components provided by humans from those of geological origin (Reimann and de Caritat 2005). Average values of EF herein indicated minor enrichment for Zn and Ni (Average EF = 1.15 and 1.14, respectively), while the remaining HMs showed no enrichment (EF < 1) (Table 4). However, some individual samples implying minor enrichment for Pb (S11, S13, S14, S18, and S19), Cr (S3, S14, and S34), Cu (S5, S9, S11, and S19), As (S3, S7, and S25), and Co (S7, S10, S11, S14, S19, S27, S32, and S33). Based on EF categories all HMs were of geogenic source in Al Majma'ah soil, except few anthropogenic factors which lead to minor enrichment in some samples. Contamination factor indicated that all HMs in the investigated soil had a low contamination factor (average values of CF   1). To assess HM contamination in a specific soil location, the pollutant load index (PLI) is utilized (Hossain et al., 2021). It ranged from 0.10 to 0.[4]52 in the study area, with an average of 0.28 suggesting unpolluted soil (Alzahrani et al., 2023).[35] Risk index (RI) can serve as a tool for understanding and controlling pollution of HMs on a particular site (Hossain et al. 2021). Results of RI ranged from 4.67 to 21.[8]10, with an average of 11.[8]79, implying low risk for the presence of HMs in the present soil (Al-Hashim et al., 2021).

Table 4.[2] Minimum, maximum, and average values of the contamination indices.

HMs	Indices	Min.	Max.	Aver.
Pb	EF	0.25	1.29	0.81
	CF	0.10	0.65	0.32
Zn	EF	0.42	2.69	1.15
	CF	0.13	0.76	0.43
Cr	EF	0.52	1.05	0.85
	CF	0.13	0.59	0.34
Ni	EF	0.54	1.49	1.14
	CF	0.15	0.87	0.46
Cu	EF	0.39	1.09	0.77
	CF	0.09	0.60	0.31
Fe	CF	0.17	0.86	0.40
Al	EF	0.14	0.45	0.32
	CF	0.04	0.26	0.13
As	EF	0.28	1.19	0.80
	CF	0.12	0.54	0.31
Mn	EF	0.59	0.95	0.80
	CF	0.11	0.55	0.33
Co	EF	0.26	1.08	0.79
	CF	0.02	0.27	0.14
V	EF	0.17	0.76	0.57
	CF	0.07	0.42	0.23

Statistical analysis

The correlation matrix (CM) presenting in Table 5 showed significant positive correlations between all elemental pairs, e.g. Zn-Al, Zn-As, Zn-Co, Zn-Cr, Zn-Cu, Zn-Fe, Zn-Mn, Zn-Ni, Zn-Pb, and Zn-V (r =.819, 0.625, 0.794, 0.757, 0.926, 0.618, 0.797, 0.803, 0.746, and 0.729), indicating similar source for these HMs.[27] The contamination indices showed that there was no enrichment, low contamination, and low risk for HMs in Al Majma'ah soil;[2] additionally, the presence of Fe, Al, and Mn in such significant correlations with all investigated HMs indicated a natural source for these HMs, which was primarily derived from weathering of Jurassic to Quaternary sediments in the study area (El-Sorogy and Al-Kahtany, 2015; El-Sorogy et al., 2014, 2017; Farouk et al., 2018). Principal component analysis (PCA) extremely support the results of contamination indices and correlation analysis, where one PC accounting 89.13 of the total variance was extracted (Table 6). It showed high loading of Al, As, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn (0.987, 0.918, 0.978, 0.988, 0.948, 0.856, 0.964, 0.979, 0.948, 0.975, and 0.828). HMs of the such PC might be derived from geogenic source.

Table 5. Correlation matrix for HMs of soil samples.

	Al	As	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
Al	1										
As	.888**	1									
Co	.984**	.899**	1								
Cr	.969**	.922**	.957**	1							
Cu	.941**	.776**	.917**	.910**	1						
Fe	.782**	.824**	.766**	.894**	.772**	1					
Mn	.921**	.878**	.907**	.965**	.920**	.942**	1				
Ni	.988**	.884**	.981**	.966**	.930**	.758**	.906**	1			
Pb	.966**	.868**	.945**	.928**	.882**	.729**	.871**	.949**	1		
V	.972**	.945**	.976**	.975**	.872**	.809**	.908**	.973**	.933**	1	
Zn	.819**	.625**	.794**	.757**	.926**	.618**	.797**	.803**	.746**	.729**	1

**.[1] Correlation is significant at the 0.01 level (2-tailed).

Table 6.[6] Loading matrix of the PC and the total variance explained.

	PC1
Al	0.987
As	0.918
Co	0.978
Cr	0.988
Cu	0.948
Fe	0.856
Mn	0.964
Ni	0.979
Pb	0.948
V	0.975
Zn	0.828
% of Variance	89.13
Cumulative %	89.13

4.[1] Conclusions

The current study used contamination indices to emphasize the HM contamination and associated ecological hazards in agricultural soil from Al Majma'ah, central Saudi Arabia.[2] The contamination indices used in this investigation resulted in minimal contamination, low risk, and no enrichment for all HMs, with the exception of relatively slight enrichment for Zn and Ni.[2] The single extracted PC and the significant positive correlations between all elemental pairings in the CM revealed a single, mostly natural source of HMs in Al Majmaah soil, generated from weathering of Jurassic to Quaternary strata.

[28]

Declaration of Competing Interest

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

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