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Journal of King Saud University - Science

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

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Khaled Al-Kahtany

Department of Geology and Geophysics, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

ARTICLE INFO	A B S T R A C T
Keywords: Heavy metals Risk assessment Multivariate analysis Agriculture soil Saudi Arabia	Soil acts as a tank for heavy metals through surface complexation, ion exchange and surface precipitation. 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). Enrichment factor (EF), contamination factor (CF), pollution load index (PLI), and potential ecological risk index (RI) were applied. The average values of the HMs (dry weight, mg/kg) had the following order: $Fe > Al > Mn > Zn > Ni > Cr > V > Cu > Pb > Co > As. Results of contamination indices revealed low contamination, low risk and no enrichment for all HMs, except some minor enrichment for Zn and Ni. The considerable positive correlations between all elemental pairings in the correlation matrix and the one extracted principal component suggested that HMs in Al Majmaah soil were formed from weathering of Jurassic to Quaternary sediments in the research area.$

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. 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; Alzahrani et al., 2023). 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; 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).

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., 2019a; Chahouri et al., 2023). The non-essential metals include lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), silver (Ag) and antimony (Sb). 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. 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).

Agriculture is one of the most significant activities because it is the primary source of food security. 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. 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). Furthermore, multivariate techniques such as hierarchical clustering analysis and principal

https://doi.org/10.1016/j.jksus.2023.102993

Received 5 August 2023; Received in revised form 2 October 2023; Accepted 6 November 2023 Available online 8 November 2023

Peer review under responsibility of King Saud University.

E-mail address: kalgatani@KSU.EDU.SA.

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

component analysis can be used to identify probable HM sources (Al-Kahtany et al., 2015; El-Sorogy et al., 2016; Alhabri et al., 2023). 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 back-grounds, 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 $25^{\circ}00'061 - 45^{\circ}19'526$ N and $26^{\circ}03'375 - 45^{\circ}20'116$ E (Fig. 1). 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 et al., 1966; Powers, 1968; Gameil and El-Sorogy, 2015; El-Asmar et al., 2015; Youssef and El-Sorogy, 2015; El-Sorogy et al., 2016; 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). 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.

2.2. Analytical methods

Soil samples were dried at air temperature, then cleaned from large rocks and organic particles. 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). 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. 0.50 g of the < 63 μ m fraction was digested for 45 min on a hot plate with sand at temperatures ranging from 60 to 120 degrees Celsius. The selected HMs are sensitive for environmental and human health risks (Al-Kahtany et al., 2023; Alharbi



Fig. 2. Sampling location and stratigraphic lithology of the study area (Modified after Vaslet et al., 1988).

et al., 2023). The limit of detection (LOD) of the ICP-AES technique was validated. The LOD value was the concentration that corresponded to three times the standard deviation of the measurements for the blank solutions divided by the slope of calibration curves for each element (Papadoyannis and Samanidou, 2004; Christodoulou and Samanidou, 2007). Several QA/QC (Quality Assurance/Quality Control) stages are conducted during the heavy metals analysis to verify the correctness and reliability of the results. Calibration of the instrument is one of these processes. 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. EF, CF, RI, and PLI were used to assess the amounts of HMs contamination in soil samples (Hakanson, 1980; Birch, 2003; El-Sorogy et al., 2018). 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.

3. Results and discussion

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). Fig. 3 presents the distribution of HMs in the study area. In comparison with other HM values from other Saudi, back-ground, 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). 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).

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,

Table 1

Classification of the indices applied in this work.

Pollution indicators		Proce	edures of calculatio	n and classifica	tions							
		EF	= (M/Fe) sample / (M/Fe) backgrou	nd							
F)	(M/Fe) sample is the	(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										
(E)	concentrations in the Earth's crust. Birch (2003) determined seven classes of EF in sediments.											
chr	EF < 1	EF<3	EF= 3-5	EF= 5-10	EF= 10-25	EF= 25-50	EF > 50					
tor	no enrichment	minor enrichment	moderate	moderately	severe	very severe	extremely					
E			enrichment	severe	enrichment	enrichment	severe					
				enrichment			enrichment					
			С	$f = C_o/C_b$								
ion (F	Co is the sediment m	etal content in the sample a	and Cb is the normal	background val	ue of the metal.	Hökanson (1980) classified CF					
CI	into four groups:											
or	Cf < 1	$1 \le Cf \le 3$	$3 \le Cf \le 6$	$Cf \ge 6$								
act	low contamination	moderate	considerable	very high								
^B C	factor	contamination factor	contamination	contamination contaminati								
-			factor	on factor								
_			$RI = \Sigma Er^i = \Sigma$	ETr ⁱ × Cf ⁱ								
cologica ex (RI)	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). Eff. and RJ volues were classified into five and four categories respectively (Moudu et al. 2016):											
nd	Er ⁱ <40	$40 \le Er^i \le 80$	$80 \le Er^i \le 160$	$160 \le Er^{i} \le$	$Er^{i} > 320$							
k I	RI<150	$150 \le RL \le 300$	300< RL <	320	RI > 600							
Ris			600									
Po	low risk	moderate risk	considerable	high risk	very high							
			risk	U	risk							
		PLI	$= (CF_1 \times CF_2 \times CF_2)$	$_3 \times CF_4 \dots \times CF_1$) ^{1/n}							
d v (where CF is the curre	ent metal concentration/me	tal background conc	centration and Cl	Fn is the contam	ination factor of	metal n. The					
L] de a	PLI values were inter	preted in two ways (Harik	rishnan et al., 2017)	:								
L L L	PLI < 1	PLI > 1										
_	unpolluted	polluted										

S.N.	Al	As	Со	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	12,400	7.00	7.00	47.00	15.00	40,400	432	34.00	8.00	43.00	34.00	0.38	16.14
S 3	8800	4.00	5.00	28.00	10.00	14,000	192	30.00	5.00	29.00	26.00	0.23	10.29
S 4	12,000	4.00	7.00	40.00	16.00	33,300	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	19,200	242	15.00	2.00	9.00	55.00	0.16	7.03
S 7	16,400	7.00	10.00	44.00	19.00	24,500	362	47.00	8.00	51.00	57.00	0.42	17.60
S 8	14,100	6.00	8.00	42.00	17.00	28,200	381	42.00	8.00	41.00	50.00	0.39	15.97
S 9	14,000	5.00	8.00	36.00	20.00	20,300	332	39.00	8.00	35.00	72.00	0.37	14.99
S 10	20,900	7.00	12.00	53.00	27.00	29,800	471	59.00	11.00	54.00	71.00	0.52	21.10
S 11	18,100	6.00	10.00	45.00	24.00	23,800	400	50.00	13.00	45.00	65.00	0.45	18.99
S 12	20,100	6.00	12.00	51.00	25.00	27,700	410	56.00	11.00	55.00	72.00	0.49	19.64
S 13	16,800	5.00	9.00	45.00	20.00	25,700	358	48.00	11.00	44.00	55.00	0.41	16.90
S 14	20,300	7.00	11.00	52.00	22.00	27,400	412	54.00	13.00	52.00	59.00	0.48	20.21
S 15	10,500	4.00	6.00	29.00	14.00	17,400	232	29.00	6.00	30.00	36.00	0.27	11.22
S 16	14,200	4.00	8.00	37.00	20.00	22,100	341	38.00	8.00	37.00	66.00	0.36	14.19
S 17	11,000	4.00	6.00	30.00	12.00	18,300	264	29.00	7.00	31.00	34.00	0.28	11.36
S 18	19,200	6.00	10.00	47.00	24.00	25,500	427	52.00	11.00	47.00	65.00	0.46	18.84
S 19	16,300	5.00	9.00	41.00	22.00	22,400	362	48.00	10.00	41.00	54.00	0.40	16.66
S 20	4500	4.00	4.00	17.00	6.00	15,500	192	14.00	4.00	18.00	16.00	0.17	7.67
S 21	10,300	5.00	6.00	31.00	13.00	20,800	289	29.00	7.00	29.00	37.00	0.29	12.38
S 22	6700	3.00	4.00	23.00	10.00	15,800	235	23.00	5.00	21.00	37.00	0.22	8.90
S 23	5500	3.00	4.00	18.00	8.00	11,600	167	18.00	4.00	18.00	23.00	0.17	7.43
S 24	7000	3.00	4.00	26.00	11.00	18,000	249	25.00	4.00	21.00	37.00	0.22	9.08
S 25	6500	4.00	4.00	21.00	9.00	12,200	186	23.00	4.00	25.00	43.00	0.21	9.20
S 26	6700	3.00	4.00	22.00	9.00	12,900	189	23.00	4.00	23.00	24.00	0.19	8.24
S 27	6800	3.00	5.00	21.00	9.00	12,400	198	23.00	4.00	21.00	26.00	0.20	8.24
S 28	7300	3.00	4.00	22.00	9.00	12,900	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	12,100	169	17.00	4.00	16.00	22.00	0.16	6.41
S 31	6000	3.00	4.00	24.00	9.00	13,500	180	25.00	4.00	21.00	22.00	0.19	8.40
S 32	7200	3.00	5.00	22.00	11.00	12,400	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	13,500	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
	20,900	7.00	12.00	53.00	27.00	40,400	471	59.00	13.00	55.00	72.00	0.52	21.10
	10,550	4.07	6.08	30.47	13.92	19,108	270	31.11	6.47	29.83	41.25	0.28	11.79

40400, 471, 59.00, 13.00, 55.00, and 72.00 mg/kg, respectively). Samples of the firest cluster were located on Jubaila Formation, Quaternary deposits, Arab Formation, and Hanifa Formation (Fig. 2). 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). Samples of the second cluster were located mostly on Cretaceous Wasia Formation and the Quaternary deposits, while a few ones were located on Jubaila and Arab formations (Fig. 2).

Contamination and risk assessment







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

Table 3

Comparison between average HM concentration in the study area and other local and world backgrounds.

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



Dendrogram using Average Linkage (Between Groups)

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

Table 4

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
Со	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

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 (Duodu et al., 2016; Alharbi and El-Sorogy, 2023). 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). In the study area, PLI ranged from 0.10 to 0.52, with an average of 0.28 indicating unpolluted soil (Alzahrani et al., 2023). The risk index (RI) can be used to understand and control HM pollution at a specific site (Hossain et al., 2021). The RI results varied from 4.67 to 21.10, with an average of 11.79, indicating a minimal risk of HM presence in the current soil (Al-Hashim et al., 2021).

3.2. 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 = 0.819, 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. The contamination indices

Table 5	
Correlation matrix for HN	As of soil samples.

showed that there was no enrichment, low contamination, and low risk for HMs in Al Majma'ah soil 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 (Reimann and de Caritat, 2000; Alharbi and El-Sorogy, 2021; Alarifi et al., 2022).

4. 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. 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. 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.

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.

Table 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

Conciau	Arcadon matrix for this of some samples.												
	Al	As	Со	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn		
Al	1												
As	0.888^{**}	1											
Со	0.984**	0.899**	1										
Cr	0.969**	0.922^{**}	0.957**	1									
Cu	0.941**	0.776**	0.917**	0.910^{**}	1								
Fe	0.782^{**}	0.824^{**}	0.766**	0.894**	0.772^{**}	1							
Mn	0.921^{**}	0.878^{**}	0.907**	0.965**	0.920^{**}	0.942**	1						
Ni	0.988**	0.884**	0.981^{**}	0.966**	0.930**	0.758^{**}	0.906**	1					
Pb	0.966**	0.868^{**}	0.945**	0.928^{**}	0.882^{**}	0.729^{**}	0.871^{**}	0.949**	1				
V	0.972^{**}	0.945**	0.976**	0.975**	0.872^{**}	0.809**	0.908**	0.973**	0.933**	1			
Zn	0.819^{**}	0.625^{**}	0.794**	0.757**	0.926**	0.618^{**}	0.797**	0.803**	0.746**	0.729**	1		

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

Acknowledgments

The authors extend their appreciation to the Deputyship for Research & Innovation, Ministry of Education in Saudi Arabia for funding this research work through the project no (IFKSUOR3– 406-3). Also, the authors would like to thank the anonymous reviewers for their valuable suggestions and constructive comments.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi. org/10.1016/j.jksus.2023.102993.

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