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Risk assessment through evaluation of potentially toxic metals in the surface soils of the Qassim area, Central Saudi Arabia

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ABSTRACT

Metal pollution is an increasing environmental problem worldwide, especially in regions undergoing rapid development. The present work highlights the extent of metal pollution in the central part of Saudi Arabia, which is currently experiencing significant agricultural development. The study determined concentrations of Hg, Cd, Zn, As, Mo, Cu, Pb and Cr in surface soils, assessing the level of pollution and potential ecological risks using soil quality guidelines, the geo-accumulation index (I_{geo}), the Harkason potential ecological risk index (RI) and standard statistical analysis methods. Overall, the mean potential ecological risk values of metals in the surveyed soils display the following decreasing trend: Hg>Cd>Pb>As>Cu>Zn>Mo>Cr. The potential ecological risks associated with the eight investigated metals in the study area were high for Hg and Cd, and ranged from considerable too low for the rest of the analysed metals. The results also showed that surface soils in the study area are heavily affected by agricultural activities, municipal waste, local industries and quarries. These anthropogenic activities may, therefore, pose a risk to soil and water resources, and have the potential to change the physio-chemical characteristics of the associated ecosystem.

KEY WORDS: *Metals, soil pollution, potential ecological risk, central Saudi Arabia.*

INTRODUCTION

Metals have been identified as a serious threat to soil quality due to their persistency, toxicity, and bio-accumulation (MORTON-BERMEA *et alii*, 2002; ADEYI & TORTO, 2014; NAZZAL *et alii*, 2013). In contrast to organic pollutants, metals cannot be chemically or biologically degraded (AYYASAMY *et alii*, 2009). Accumulation of metals in soil adversely affects biological activities, lowers the availability of nutrients, and poses a serious threat to environmental and human health by entering into food chains and underground water supplies via the respective plant uptake and leaching processes (MAN-ZHI *et alii*, 2006).

In recent years, in order to clarify the eco-toxicological potential of soils, a large number of studies (e.g. SHEYKHI & MOORE, 2013; LIU *et alii*, 2009; CHAKRAVARTY & PATGIRI, 2009; SAKAM *et alii*, 2009) have addressed the geochemistry, distribution and sources of elements that pose a potential threat to ecosystems. Research also increasingly suggests that sediments are a major sink and source of contamination when the physical-chemical characteristics of the ecosystem change (MIL-HOMENS *et alii*, 2007; DEVESA-REY *et alii*, 2011).

Saudi Arabia's development especially in the agricultural sector over the last three decades has been astonishing on a global scale. Large areas of desert have been turned into agricultural fields – a major accomplishment in a country that receives an average of about four inches of rain a year, one of the lowest rates in the world. However, with this development comes some environmental challenges. The present paper discuss the pollution status that could be attributed to development activities. The present work uses methodology and explain processes as well as association of controlling factor of problem at hand. Those could be applied globally in areas of similar conditions to Saudi Arabia.

In developing areas like Saudi Arabia, deposition of pollutants emitted to the atmosphere from non-point sources such as agricultural activities, residential heating and industrial facilities, and mobile sources such as traffic, are the primary sources of soil pollution (HOWARI *et alii,* 2004; LOGHMAN *et alii,* 2013). Metals such as Pb, Cr, Zn, Co, Cu, Cd, Hg, Mo, and As are easily emitted from fossil fuel combustion, tire abrasion, lubricants and industrial and incinerator emissions, and can accumulate in soil.

A review of the literature indicates that there is currently only limited information about the environmental quality of soils in central Saudi Arabia and, in particular, there are no studies on metal contamination of agricultural farms in the Qassim area in central Saudi Arabia, in spit of the fact this area is a very important agricultural land in the country. Although some studies have been undertaken on the hydrochemistry of this area (NAZZAL *et alii,* 2014) the present study builds on these and it intend to achieve the following objectives:

I) Analysing the total concentration and spatial distribution of Pb, Cd, Zn, Cr, Cu, Hg, Mo, and As, in the soils of the Qassim area, Central Saudi Arabia region.

II) Carrying out a preliminary assessment of the environmental risks associated with these metals using the enrichment factor (EF) and the geo-accumulation index (Igeo).

III) Classifying these metals into distinct groups using multivariate statistical methods such as hierarchical cluster analysis (HCA) and correlation analysis (CA).

IV) Assessing the overall degree of pollution and potential ecological risk. The results obtained here pro-

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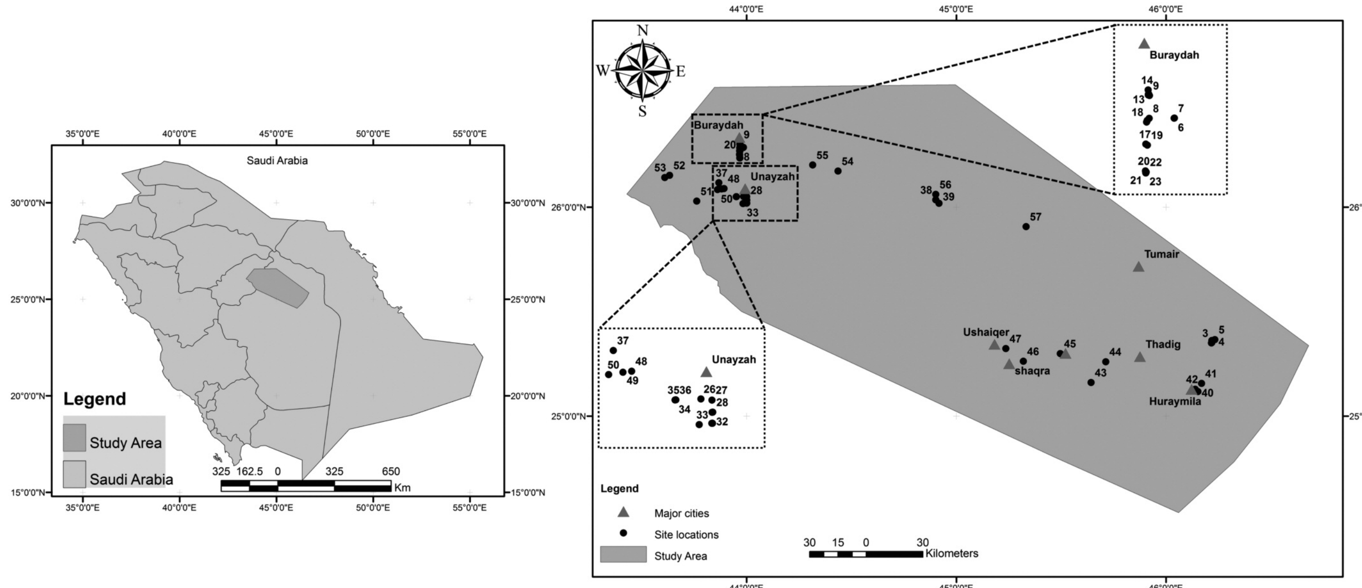

Fig. 1 - Location map of the study area.

vide a comprehensive overview of the current soil contamination status with respect to potentially toxic metals and the potential sources of such contamination in the Qassim region of central Saudi Arabia.

MATERIALS AND METHODS

Study Area

The study area is located between latitudes 25°N and 26.5°N and longitude 43.25°E and 46.25°E and forms a part of NW Riyadh and Qassim provinces in central Saudi Arabia (fig. 1). The study area represents a typical arid region with very low average annual rainfall (<150 mm) which mostly occurs between the months of November to March. Such rainfall, when it occurs, is torrential and may cause runoff to wadi channels and low lying areas. The average annual evaporation is about 3000 mm. The region is characterized by a high diurnal range of temperatures which average from 43°C to 28°C during summer and 21°C to 9°C during winter, although temperatures as low as 0°C are quite common in the area during winter months. The study area is host to a significant amount of farming with groundwater serving as the major source of irrigation, with such cultivation having developed significantly in the area over the past three decades.

Geologically, the rock formation in the study area and its vicinity ranges from the Pre-Cambrian basement rocks to the Quaternary Alluvium (fig. 1), however the major portion of the study area is covered by Mesozoic sedimentary deposits which form an important part of the Arabian platform (Chapman, 1978). The main aquifers in the study area Upper Jurassic and Lower Cretaceous Aquifers include the Saq, Khuff, Jilh, Minjur and Dhruma, Biyadh, Wasia, Aruma and Umm Radhuma aquifers. Lithologically, drilled wells in the region encounter sandstone, limestone, clay, shale, siltstone and gypsum.

Two types of soils occur in the study area, aridisols and entisols. Aridisols are mineral soils that don't have an oxic or aspodic horizon, and that have an ochric or anthropic epipedon. Entisols are mineral soils that show little or no evidence of development of pedgenetic horizons. Within the entisols, fine suborders have been identified in the study area, including psaments and orthents. The catchment of the study area has agricultural activities, municipalities, quarries, and local industries.

Sampling and analysis

A total of 57 soil samples were collected during August 2013 from a number of farming areas located in the Qassim region of Central Saudi Arabia (fig. 1). The samples were collected from the upper 10 cm section of soil and stored in labelled polyethylene bags. After grinding and sieving through 2 mm mesh in the laboratory, these samples were re-stored in plastic bags. Samples were prepared by accurately weighing around 200 mg of sieved materials into dry and clean Teflon digestion beakers. Following this, all samples were digested by adding 6 ml HNO_3, 2 ml HCl and 2 ml HF. The digested samples were then heated on a hot plate at 120-150°C for about 40 minutes. The samples were filtered through Whatman filter paper No. 42. Following this, the filtered digest was transferred to a 50 ml plastic volumetric flask and filled up to the mark by deionized water. The selected metals were measured with an ICP-MS (Inductively Coupled Plasma-Mass Spectrometer), NexION 300D model, from Perkin Elmer, USA.

The accuracy and precision of the analytical methods used for the multi-element determination of soil samples were evaluated by analysing a Certified Reference Material (CRM), namely IAEA SOIL-7, which was obtained from International Atomic Energy Agency (IAEA), Vienna, Austria. Tab. 1 illustrates the recovery (%) results. Recoveries ranging between 97% and 109% is a good indication of how accurate the method employed was. Statistical applications in geochemical and hydrochemical studies was carried out by many researches e.g, Zhang *et alii* (2008), Cloutier *et alii* (2008), and Garcia *et alii* (2001). All those studies applied the statistical methods to link between the chemical elements and sources of pollutions. A multivariate analysis was performed on 57 samples using the SPSS software to study the metal contamination in the collected soils. The metals examined were Pb, Cd, Zn, Cr, Cu, Hg, Mo, and As Data normality was checked before starting the statistical analyses on the samples, and it was observed that the data followed Gaussian distribution and therefore, no further normalization was required.

Potential ecological risk

From a soil contamination point of view, the potential ecological risks were assessed using the method suggested by Hankanson (1980). His study suggested equation 1 below as a means of assessing soil contamination. The equation was applied successfully by Jinmei & Xueping (2014).

$$C_j^i = \frac{C_D^i}{C_R^i} \quad (1)$$

Where C_D^i is the mean concentration of an individual metal and C_R^i is the soil background values for that metal. C_f^i is the single element index. The sum of the contamination for all of the metals examined is defined as the contamination degree (C_d) for the environment, Eq. 2:

$$C_D = \sum_{i=1}^{m} \times C_f^i \quad (2)$$

Where E_r^i is the potential ecological risk index for an individual metal, calculated using Eq. 3

$$E_r^i = T_r^i \times C_f^i \quad (3)$$

Where T_r^i is the toxic response factor for metals, provided by Hakanson (1980). The potential ecological risk index (RI) is the sum of the E_r^i values, Eq. 4:

$$RI = \sum_{i=1}^{m} E_r^i \quad (4)$$

Hankanson definitions of the E_r^i and RI categories are shown in tab. 2.

Table 1

The accuracy and precision of the analytical method applied for the multi-element determination of soil samples.

Element	*Mass*	*Certified Value (mg/Kg)*	*Measured Value (mg/Kg)**	*Recovery (%)*
Cr	52	60	61.71	102.85
Mn	55	631	641.1	101.6
Co	59	8.9	9.76	109.66
Ni	60	26	26.76	102.92
Cu	63	11	10.82	98.36
Zn	66	104	101.94	98.02
As	75	13.4	14.01	104.01
Cd	111	1.3	1.31	100.77
Pb	208	60	61.6	102.67

* The mean of five consecutive samples.

Table 2

Risk grade indexes and grades of Potential Ecological risk of metal pollution.

Er	*Risk Grade*	*RI*	*Risk Grade*
<40	Low potential ecological risk	<150	Low potential ecological risk
40-80	Moderate potential ecological risk	150-300	Moderate ecological ecological risk
80-160	Considerable potential ecological risk	300-600	High potential ecological risk
160-320	High potential ecological risk	≥600	Significantly high potential ecological risk
≥320	Significantly high potential ecological risk		

RESULTS AND DISCUSSION

Geochemical results

The chemical characteristics of the soils of the Qassim area are outlined in tab. 3. In most stations, the soils are com-

Table 3

Metals concentration in study area soils.

Descriptive Statistics	*N*	*Minimum*	*Maximum*	*Mean*	*Std. Deviation*	*Skewness*		*Kurtosis*	
	Statistic	*Statistic*	*Statistic*	*Statistic*	*Statistic*	*Statistic*	*Std. Error*	*Statistic*	*Std. Error*
As	57	8.6	27.2	14.419	3.0714	1.222	.316	4.045	.623
Cd	57	.07	1.20	.3733	.28096	1.158	.316	.740	.623
Cr	57	3.2	45.2	29.791	9.1296	-.751	.316	.256	.623
Cu	57	3.3	27.3	11.321	4.4998	.951	.316	2.109	.623
Hg	57	.6	1.9	1.330	.3919	-.357	.316	-1.054	.623
Pb	57	2.6	46.0	25.828	11.3456	-.539	.316	-.414	.623
Zn	57	17.9	173.6	72.395	28.3102	.826	.316	3.037	.623
Mo	57	.3	1.1	.646	.1928	.433	.316	-.354	.623
Sand	57	81.93	99.60	94.6707	4.07791	-1.422	.316	1.991	.623
Silt	57	.02	7.91	3.0369	2.11968	.903	.316	-.004	.623
Clay	57	.04	13.01	2.2360	2.59683	2.783	.316	8.814	.623
ValidN (listwise)	57								

TABLE 4

Index of geo-accumulation (I_{geo}) and contamination level for mean metal concentrations in the soils of the study area.

Metal	I_{geo}	*Contamination level*
Pb	-0.47	uncontaminated
Cd	-0.68	uncontaminated
Zn	-1.11	uncontaminated
Cr	-2.28	uncontaminated
Mn	-3.39	uncontaminated
Cu	-2.69	uncontaminated
Co	-3.02	uncontaminated
Hg	1.08	moderately contaminated
Mo	0.04	uncontaminated/moderately contaminated

TABLE 5

Standard geo-accumulation index (I_{geo}) for contamination levels in soil (presented by Muller, 1981).

I_{geo} *class*	I_{geo} *value*	*Contamination level*
0	$I_{geo} \leq 0$	uncontaminated
1	$0 < I_{geo} < 1$	uncontaminated/moderately contaminated
2	$1 < I_{geo} < 2$	moderately contaminated
3	$2 < I_{geo} < 3$	moderately contaminated/strongly contaminated
4	$3 < I_{geo} < 4$	strongly contaminated
5	$4 < I_{geo} < 5$	strongly contaminated/extremely contaminated
6	$5 < I_{geo}$	extremely contaminated

posed of sand (in the range of 81.93 to 99.6%) with a mixture of clay (0.04 to 13.01%) and silt (0.02 to 7.91%) (tab. 3). The estimated average concentrations (ppm) of metals in the studied soil samples are as follows: Zn (72.39), Cr (29.79), Pb (25.83), Cu (11.32), Hg (1.33), Mo (0.65), and Cd (0.37).

Metals concentration in the study area (tab. 4) were compared to the standard of the geo-accumulation index in order to determine their compliance. This comparison showed that values of Pb, Cd, Hg and Mo are higher than the world average shale concentrations reported for these metals (TUREKIAN & WEDEPOHL, 1961). It was also evident the concentrations of Cd, Hg, and Pb in the study area are above the average values reported by BOWEN (1979) for normal soils. The studied metals values were below the levels permitted by the Canadian Council of Ministers for the Environment's soil quality guidelines (CA-SQG, 2010). The relative dominance of the most potentially toxic metals in the soils of the Qassim area decrease in the following order Hg>Cd>Zn>As>Mo>Cu>Pb>Cr.

Tab. 3 shows a summary of the concentrations of the metals included in the present study (As, Cd, Cr, Cu, Hg, Pb, Zn and Mo). Two approaches to assessing sediment quality are considered in this present study (MCDONALD *et alii*, 2002; SHEYKHI & MOORE, 2013). The first approach is the threshold effect level (TEL). TEL is the concentration level below which adverse biological effects would rarely be expected to occur (SHEYKHI & MOORE, 2013). The second approach is the probable effect level (PEL). PEL is the concentration level above which adverse effects would often be expected to occur (SHEYKHI & MOORE, 2013). These two quality guidelines were first introduced by the Australian and New Zealand Environment and Conservation Council (ANZECC, 1997).

Soils recovered from site 4 display the highest contamination for As with 27.2 ppm. This is higher than the background value found in natural soils. The highest level of contamination for Cd occurs at site number 55 with 1.20 ppm, which is twice as high as the average background value (0.3 ppm). The average natural abundance of cadmium in the earth's crust has most often been reported from 0.1 to 0.5 ppm (COOK & MORROW, 1995). The highest values for Hg were found at sites 6 and 9, with 1.9 ppm (which is six times the background value). The highest contamination value for Zn, meanwhile, was found at site 51, with 173.6 ppm, this is higher than the background value. The highest contamination value for Mo was found at site number 23, with 1.1 ppm, almost higher than the background value. The mean concentrations of As and Hg in the soils studied from the Qassim area are above the TEL, and the mean concentration of Hg is also higher than the PEL (tab. 3). The spatial correlation shows that, the increase in the levels of the metals included in the present study attributed to the agricultural activities in one side specially the use of chemical, and organic fertilizers and pesticides. In the other hand municipalities, quarries, local industries, and runoff contribute in the metals levels increase.

INDEX OF GEO-ACCUMULATION (I_{geo})

The following formula is used to calculate the Index of geo-accumulation (I_{geo}) values:

$$I_{geo} = \mathrm{Log}_2 \left(\frac{C_n}{1.5Bn} \right)$$

Where Cn is the metal content in the soil, Bn is the geochemical background value in shale (TUREKIAN & WEDEPOHL, 1961), and the factor 1.5 is used for possible changes in the background data due to lithological variations.

MULLER (1969) first proposed the use of a geo-accumulation index consisting of a seven point scale (0-6) for the quantification of metal accumulation in sediments, where 0 represents unpolluted and 6 represents very highly polluted (tab. 5). Variations in the calculated I_{geo} value of soils in the Qassim area of central Saudi Arabia are presented in tab. 4. This shows that As, Cr, Cu, Zn and Mo fall within a range of <1, indicating that there is no pollution from these metals in Qassim area soils. Cd and Pb, meanwhile, fall within the class 1 range indicating unpolluted to moderately polluted soil. The I_{geo} of Hg is in class 2, indicating that the soil is moderately polluted with Hg. Fig. 2 shows the calculated geo-accumulation index (I_{geo}) for the various surveyed metals.

POTENTIAL ECOLOGICAL RISK EVALUATION

With the aim of achieving a broader assessment of metal pollution in the surface soils of the Qassim area of central Saudi Arabia, the potential risk factor (E_i) and the potential ecological risk index (RI) of HAKANSON (1980) were used. The metal concentrations were evaluated using the potential ecological risk index for each metal (tab. 2 and fig. 2), and fig. 2 shows that the potential ecological risk is high for Hg and Cd. It is further evident that the E_i values of Mo, Zn, Pb, Cu, Cr and As were lower than 40% indicating that, these metals cause low potential ecological pollution risk for Qassim surface soils. Overall, the mean potential ecological risk values of metals

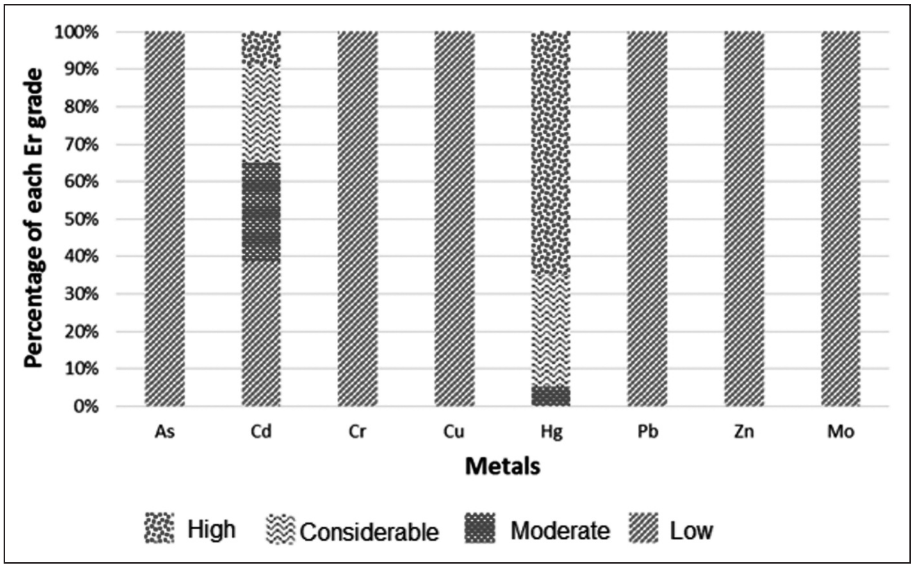

Fig. 2 - Potential ecological risk index and its grading in the analyzed samples in study area.

in the surveyed soils display the following decreasing trend: Hg>Cd>Pb>As>Cu>Zn>Mo>Cr. The potential ecological index E_i values for As range from 5.752 to 18.193, for Cd from 13.548 to 212.903, for Cr from 0.620 to 2.597, for Cu from 1.15 to 6.825, for Hg from 74.303 to 235.294, for Pb from 1.60 to 23.00, for Zn from 0.378 to 3.472 and for Mo from 0.9 to 3.30. The RI values for the Qassim area soils, meanwhile, show that 13 stations have a high level of potential ecological risk (which implies an RI grade of 300-600) with values ranging from 312.55 to 484.60. Forty stations exhibit a moderate level of potential ecological risk (an RI grade of 150-300). The actual values for these stations range from 151.066 to 296.31, while four stations exhibit a low level of potential ecological risk (an RI grade of <150) with actual values that range from 131.06 to 150.17. The high potential ecological risk due to Hg and Cd can be attributed to the presence of agricultural activities, municipal solid waste, quarries and local industries in proximity to the parent rocks (tab. 6).

TABLE 6

Potentially pollution sources for Qassim area, Central Saudi Arabia.

Zone	*Sample locations*	*Coordinates*	*Elevation (meters)*	*Potential pollution source*
A	1-7	N25°21'44.9''–25°22'65'' E46°13'7.7''–46°14'48''	640	Agricultural
B	5-38	N26°07'49''–26°17'08' E43°52'47''–43°59'06''	680	Agricultural/ Industry/ Quarries
C	38	N26°01'17''–26°02'06'' E44°54'16''–44°55'49''	687	Agricultural

CORRELATION ANALYSIS (CA)

Generally, metals in soils are characterized by complicated relationships. Tab. 7 represents the results of a Pearson's correlation coefficient matrix for the metals in the studied soil samples. Examination of the matrix provides evidence that some variables are related and reveals information about the carrier substances and chemical association of metals in the study area. Positive correlations were found between Cd and Cu (*r*=0.41), Cd and Mn (*r*=0.61), Cd and Pb (*r*=0.50), and Cr and Pb (*r*=0.40) at 0.05 levels. The Hg values, however, show negative correlations with Cd. The high positive correlation between most of the studied metals may reflect nearly similar levels and sources of contamination in the study area.

CLUSTER ANALYSIS

Prior to the cluster analysis, the metal concentrations were standardized using z-scores and squared Euclidean

TABLE 7

Pearson's correlation matrix for the concentrations of the sampled metal.

	Cd	*Co*	*Cr*	*Cu*	*Hg*	*Mn*	*Mo*	*Pb*	*Zn*
Cd	1.000								
Co	0.318	1.000							
Cr	0.220	0.214	1.000						
Cu	0.417	0.106	0.245	1.000					
Hg	-0.097	0.051	0.119	0.057	1.000				
Mn	0.610	0.223	0.234	0.379	-0.103	1.000			
Mo	0.357	-0.047	0.201	0.267	-0.047	0.234	1.000		
Pb	0.504	0.254	0.402	0.141	-0.012	0.305	0.079	1.000	
Zn	0.275	0.020	-0.063	0.192	0.125	0.336	0.159	0.037	1.000

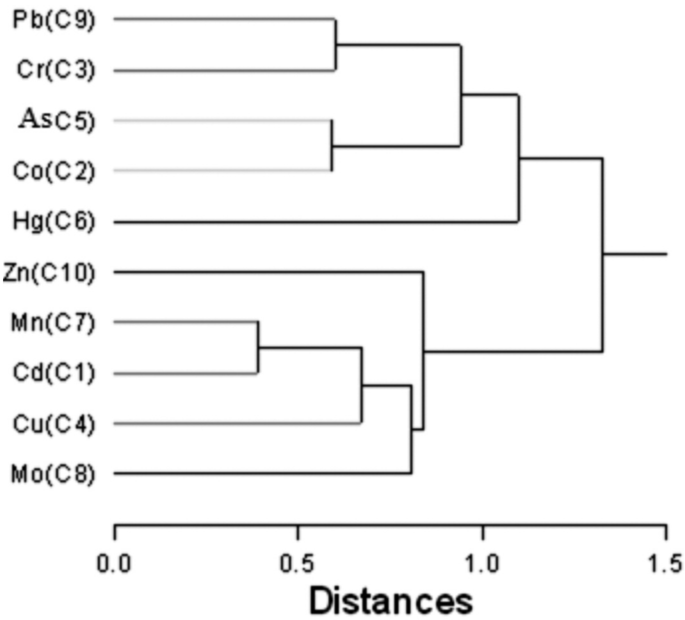

Fig. 3 - Cluster classification of the sampled elements using Ward minimum variance method.

distances of similarity. Cluster analysis was performed on the resulting standardized data using Ward's method, and this in general agreed with the results obtained from the correlation analysis. The aim of performing CA was to identify the relationship among various metals. Two distinct clusters of the constituent metals were observed in the dendrogram (fig. 3). One cluster consisted of Pb, Cr, and Co, while the second was composed of Zn, Mn, Cd, Cu and Mo. In addition, these metals could be classified into further sub-clusters, such as Pb-Cr, Mn-Cd, Zn, Cu, and Mo. A remarkable difference was evident in terms of Euclidian distances between these two integrated clusters.

CONCLUSIONS

In the present study, the concentrations of Pb, Cr, Zn, Co, Cu, Cd, Hg, Mo, and As were surveyed. The distribution, pollution level and potential ecological index of these metals were assessed using statistical analyses, geo-accumulation index and Hakansons ecological risk index. The mean concentrations of As, Cd, Cr, Cu, Hg, Pb, Zn and Mo were found to be 14.41 ppm, 0.373 ppm, 29.79 ppm, 11.32 ppm, 1.33 ppm, 25.82 ppm, 72.39 ppm, and 0.646 ppm, respectively. The cluster analysis demonstrates that association exists between Pb, As, Cr, and between Zn, Cd, Cu and Mo. The geo-accumulation index, meanwhile, shows that As, Cr, Zn and Mo falls within a class of less than one, indicating no pollution from these metals. Cd and Pb fall within class one, and thus include both unpolluted and moderate levels of pollution. The results show that potentially toxic metal pollution in the study area surface soils, is related to five anthropogenic sources: agricultural activities, municipalities, quarries, and local industries, and possibly runoff. The results of the present study indicate that monitoring and management options should be considered to avoid further pollution by potentially toxic metals in the soils of central Saudi Arabia.

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REFERENCES:

Adeyi A. & Torto N. (2014) - *Profiling heavy metal distribution and contamination in ....*

Anzec C. (1997) - *Basis for a national agreement on environmental impact assessment, Australian and New Zealand Environment and Conservation Council*.

Ayyasamya P.M., Rajakumarb S., Sathishkumarc M., Swaminathanck., Shanthid K., Lakshman Aperumalsamye P. & Leea S. (2009) - *Nitrate removal from synthetic medium and groundwater with aquatic macrophytes*. Des alination **242** (2009), 286-296.

Bowen H.J.M. (1979) - *Environmental chemistry of the element*. Academic press, 333p.

CA-SQG. (2010*) - Soil Quality Guidelines Task Group (SQGTG)*. On-line available; http://www.ccme.ca/ourwork/ soil.html,category_id=44S.

Chakravarty M. & Patgiri A.D. (2009) - *Metal pollution assessment in sediments of the Dikrong River, NE India*. Journal of Human Ecology, **27**, 63-67.

Chapman R.W. (1978) - *Geology*. In Quaternary Period in Saudi Arabia (pp. 4-19).

Cloutierl V., Lefebvre R., Therrien R. & Savard M. (2008) - *Multivariate statistical analysis of geochemical data as indicative of the hydrogeochemical evolution of groundwater in a sedimentary rock aquifer system*. Hydrogeology Journal, **353** (3-4), 294-313.

Cook M.E. & Morrow H. (1995) - *Anthropogenic Sources of Cadmium in Canada,* National Workshop on Cadmium Transport Into Plants, Canadian Network of Toxicology Centres, Ottawa, Ontario, Canada, June 20-21, 1995.

Devesa-Rey R., Diaz-Fierros F. & Barral M.T. (2011) - *Assessment of enrichment factors and grain size influence on the metal distribution in riverbed sediments (Anllóns River, NW Spain)*. Environmental Monitoring and Assessment, **179** (1-4), 371-388. doi: 10.1007/s10661-012-2785-8.

Garcia M.G., Del Hidalgo M. & Blesal M. (2001) - *Geochemistry of groundwater in the alluvial plain of Tucuman province, Argentina*. Hydrogeology Journal, **9**, 597-610.

Hakanson L. (1980) - *An ecological risk index for aquatic pollution control. A sedimentological approach*. Water Research, **14** (8), 975-1001.

Howari Fares., Abu-Rakah Y. & Goodell P.C. (2004) - *Heavy metal pollution of soils along North Shuna-Aqaba Highway, Jordan*. International Journal of Environment and Pollution, **22** (5), 597-607.

Jinmei B. & Xueping L. (2014) - *Heavy metal pollution in surface soils of Pearl River Delta, China*. Environ Monit Assess, **186**, 8051-8061. doi: 10.1007/s10661-014-4050-9.

Liu J., Li Y., Zhang B., Cao J., Cao Z. & Domagalski J. (2009) - *Ecological risk of heavy metals in sediments of the Luan river source water*. Ecotoxicology, **18**, 748-758.

Loghman K.A., Amiri F., Sefiyanian A., Abdul Rashid B., Sharif M., Tabalabie T. & Pradhan B. (2013*) - Spatial patterns of heavy metals in soil under different geological structures and land uses for assessing metal enrichment*. Environmental Monitoring and Assessment, **185**, 9871-9888.

Man-Zhi T., Fang-Ming X., Jie C., Xue-Lei Z. & Jing-Zhong C. (2006) - *Spatial prediction of heavy metal pollution for soils in peri-urban Beijing, China based on fuzzy set theory*. Pedosphere, **16**, 545-554.

Mathis B.J. & Cummings T.F. (1973) - *Selected metals in sediments and biota in Illinois River*. Journal of the Water Pollution Control Federation, **45**, 573-583.

McDonald D.D., Ingersoll C.G. & Berger T.A. (2002) - *Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems*. Archives of Environmental Contamination and Toxicology, **39**, 20-31.

Mil-Homens M., Stevens R.L., Cato I. & Abrantes F. (2007) - *Regional geochemical baselines for Portuguese shelf sediments*. Environmental Pollution, **148** (2), 418-427.

Morton-Bermea O., Alvarezl H., Gaso I. & Segovia N. (2002) - *Heavy metal concentrations in surface soils from Mexico City*. Bulletin of Environmental Contamination and Toxicology, **68**, 383-388.

Muller G. (1969) - *Index of geo-accumulation in sediments of the Rhine River*. Geology Journal, **2** (3), 108-118.

Muller G. (1979) - *Schwermetalle in den sediment des Rheins, Veranderungem Seit 1971*. Umschau, **79**, 778-783.

Müller G. (1979) - *Schwermetalle in den Sedimenten des Rheins-Veränderungen seit (1971)*. Umschau, **24**, 778-783.

Nazzal Y. & Habes Ghrefat Marc A. Rosen (2013) - *Application of multivariate geostatistics in the investigation of heavy metal contamination of roadside dusts from selected highways of the Greater Toronto Area, Canada*, Environmental Earth Sciences/Springer. doi: 10.1007/s12665-013-2546-1.

Nazzal Y., Ahmed I., Al-Arifi N., Ghrefat H., Batayneh A., Abuamarah B. & Zaidi F. (2014) - *A combined Hydrochemical-statistical analysis of Saq aquifer, northwestern part of the Kingdom of Saudi Arabia*. Geosciences Journal. doi: 10.1007/s12303-014-0016-8.

Sakam S.M., Dordevic D.S., Manojlovic D.D. & Predrag P.S. (2009) - *Assessment of heavy metal pollutants accumulation in the Tisza river sediments*. Journal of Environmental Management, **90**, 3382-3390.

Sheykhi & Moore (2013) - *Evaluation of potentially toxic metals pollution in the sediments of the Kor River, southwest Iran*. Environ Monit Assess **185**, 3219-3232.

.... & .... (0000) - *Soil of old power generation station in Lagos, Nigeria. American Journal of Science and Springer Vienna*. Technology, **1** (1), 1-10.

Turekian K.K. & Wedepohl K.H. (1961) - *Distribution of the elements in some major units of the earth's crust*. The Geological Society of America, **72**, 175-192.

Zhang C.S., Deirdre Fasy., David McGrath., Eamonn Grennan. & Owen T. Carton. (2008) - *Statistical analysis of geochemical variables in soils of Ireland*. Geoderma, **146**, 378-390.

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