Evaluation and Assessment of Top Soil and Herbage Pollution by Heavy Metals near Cement Plant in Rabigh, Western Coast of KSA

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Introduction

Many studies have been undertaken for many years to evaluate the deposition and distribution of heavy metals in urban soils and plants, particularly those near cement plants Heavy metals are important environmental pollutants with a well-defined toxic pathology. While some elements such as arsenic, cadmium, lead or mercury are known toxicants, essential elements such as cobalt, chromium, manganese or zinc can also have deleterious effects at certain levels Many studies have been done on ecological risk assessment by heavy metals based on different sediment quality controls and on the basis of geoaccumulation index (I geo)

1 Study area

Rabigh is a small ancient governorate on the western coast of KSA, betweed latitudes 22/23 north of the equator which it lies on the Tropic of Cancer. It is situated close to the Red Sea and 150 Km from the center of Jeddah and in a back of Arabian Cement Company (ACC) which produces 3 million tons of cement annually.

Fig. (1) Mean values of metal concentrations in soil and herbage samples

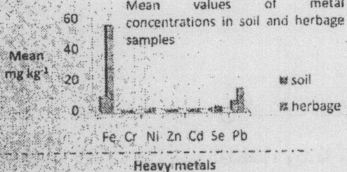


Table (1): Metals concentrations in soil and herbage samples in the studied area (mg/kg).

Element	Soil (15 cm depth) (dry weight)				Herbage (wet weight)			
	Max.	Min.	Mean	SD	Max.	Min.	Mean	SD
Fe	80.51	32.68	56.31	19.41	19.7	3.1	10.02	5.65
Cr	0.451	0.215	0.24	0.11	0.213	0.031	0.1	0.07
Ni	3.734	0.30	2.0	1.4	0.164	0.01	0.07	0.05
Zn	0.943	0.423	0.5	0.25	0.45	.0.09	025	0.17
Cd	2.334	0.095	0.85	0.7	0.257	0.009	0.18	0.2
Se	8.35	0.10	2.9	2.7	2.91	0.03	1.5	0.8
Pb	28.24	6.51	14.3	7.2	11.8	2.1	6.35	3.3

Fig.(2) Component plot in rotated space for soil samples

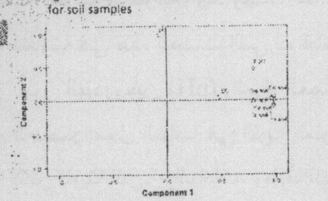
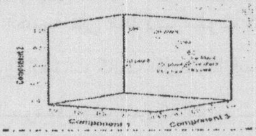
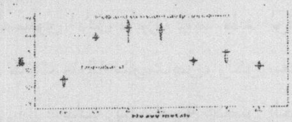


Fig. (3) Component Plot in rotated space





3- Conclusions: According to the Ministry Of Environment and Energy, Canada, Ontario Guidelins, almost all metals did not exceed their lowest effect levels (LEL) and 10% of soil samples comtaminated with Cd even exceeded (LEL). While all samples did not exceed the severe effect level (SEL). The US EPA Guideline indicated that all samples were not polluted except 7% of soil samples contaminated with Pb is moderately polluted. Igeo indicated that soil samples are unpolluted with Fe, Cd, Se and Pb, while they are unpolluted to moderately polluted with Cr, Ni and Zn. The current results show that the cement plant has a low inpact on the metal levels in the environment around the plant till now. These results should be of interest to assess future temporal variations in the levels of metals and in this area.

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تقدير وتقييم تلوث التربة وبعض النباتات الصغيرة بجوار مصنع أسمنت رابغ بالساحل الغربى للمملكة العربية السعودية

مجدى مدبولى

فى هذه الدراسة، تم أخذ ٤٥ عينة تربة سطحية من على عمق ٥ سم، و٤٥ عينة من النباتات العشوائية من المنطقة المحيطة بمصنع أسمنت رابغ، المصدر الأساسى والمتوقع للتلوث فى هذه المنطقة، وبدءًا من مسافة نصف كيلو إلى ٢٠ كيلو متر فى اتجاه الرياح للساحل الغربى للمملكة العربية السعودية، وقد وجدت عناصر الحديد، الكروم، النيكل، الخارصين، الكادميوم، والسيلينيوم بنسب متفاوتة فى هذه العينات التى تم قياسها بجهاز الامتصاص الذرى، ولقد كان لبعض صفات التربة مثل تركيز آيون الهيدروجين (pH) والمواد العضوية الكلية (TOM) والتوصيل الكهربى (EC) تأثير على حركة وتوزيع العناصر محل الدراسة فى التربة الملوثة. وقد كشفت الدراسة أن عنصرى الحديد والرصاص هما العنصران الأكثر تلويثًا للتربة وللنباتات. وطبقًا للدليل البيئى لوزارة البيئة الكندية فإن معدلات التلوث كانت أقل من المستوى الأقل تأثيرًا، بينما طبقاً لوكالة حماية البيئة الأمريكية؛ فإن العينات كانت أقل تلوثًا فيما عدا ٧٪ فقط كانت ملوثة بالرصاص، ولكن معدل التلوث كان فى المستوى المتوسط. وقد أشارت الدراسات الإحصائية إلى أن أسباب زيادة نسبة عنصر الحديد راجعة لاحتواء الصخور على هذا العنصر بنسب عالية، بينما يرجع وجود العناصر الآخرى للأنشطة الإنسانية، كما فسرت أيضًا العلاقة بين عناصر النيكل والخارصين والرصاص بخواص التربة السابق ذكرها وارتباطهم ببعضهم البعض. وقد خلصت الدراسة إلى أن مصنع الأسمنت ليس له تأثير واضح إلا عند مسافة ٠,٥ إلى ٢ كيلو متر فقط بينما لم يكن له تأثير عند المسافات الأبعد حتى الآن، وقد أوصت الدراسة بأن تتتبع الجهات المسئولة فى المستقبل تأثير المصنع على مستويات التلوث لهذه العناصر فى المنطقة المحيطة به.

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Fig (3)

Principal component analysis. Plot for herbage samples (21) collected at different sampling points of Rabigh.

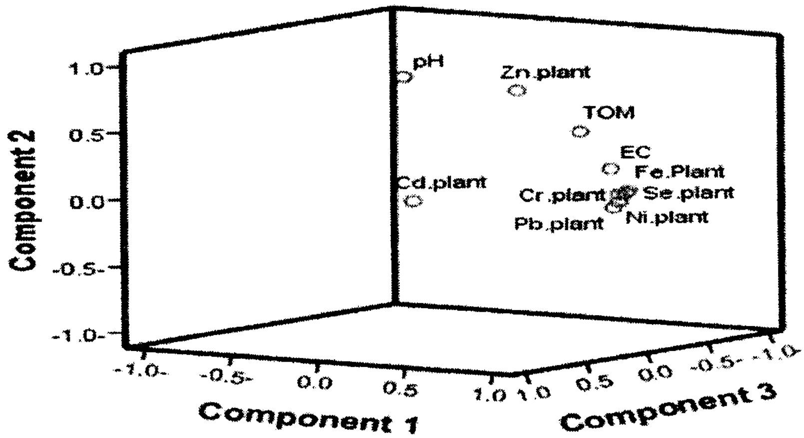

Fig (4)

Box plot for the values of heavy metals in Rabigh soil.

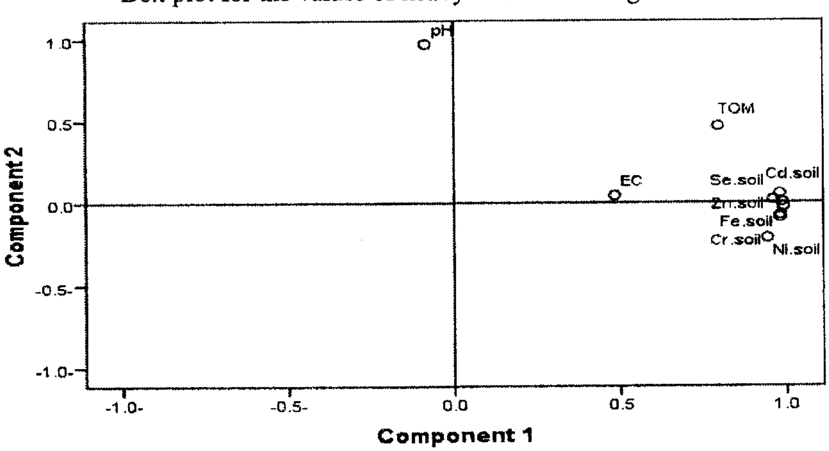

Fig (1)
Mean values of metal concentrations
in soil and herbage samples.

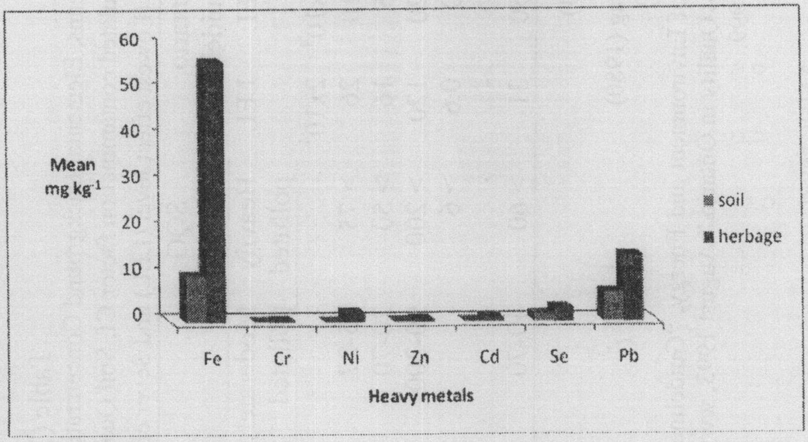

Fig (2)
Principal component analysis. Plot for soil samples
(21) collected at different sampling points of Rabigh .

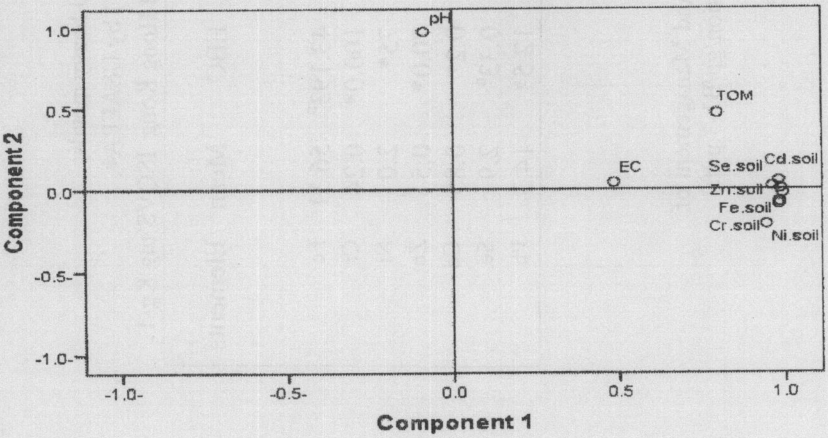

Table (7)

Means, Elemental Background Concentrations (EBC) for studied heavy metals, calculated contamination factor Cf, Soil Quality Guideline (SQG) by USAEPA*, Ontario Guidelines (Lowest effect level (LEL) and Sever effect level(SEL)) and Hong Kong ISQVS mg Kg-1.

Hong kongISQVS[d]		Ontario Guidelines[c]		SQG			C_f	EBC	Mean	Elements
ISQV high	ISQV low	SEL	LEL	Heavily polluted	Moderately polluted	Non-polluted				
-	-	$4x10^4$	$2x10^4$	-	-	-	0.001	43,193[a]	56.31	Fe
370	80	110	26	> 75	25-27	< 25	0.002	100.0*	0.24	Cr
-	40	75	16	> 50	20-70	< 20	0.027	75*	2.0	Ni
410	200	820	120	> 200	90-200	< 90	0.007	70.0*	0.5	Zn
9.5	1.5	10	0.6	> 6	-	-	4.250	0.2*	0.85	Cd
-	-	-	-	-	-	-	8.77	0.33[a]	2.9	Se.
218	75	250	31	> 60	40-70	< 40	1.140	12.5*	14.3	Pb

* Pekey et al., (2004)

a: El-Sokkary and lag (1980)
b: Bai et al., (2011)
c:Ontario Ministry of Environment and Energy, "Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario," August 1993, www.ene.gov.on.ca/envision/gp/B1-3.pdf.
d: Chapman et al., 1999.

Table (6)
Total variance explained and rotated component matrix
for heavy metal contents in soil and in herbage.

Herbage						Soil					
Rotated Component matrix			Initial Eigen values			Rotated component matrix		Initial Eigen values			Component
PC3	PC2	PC1	Cumulative %	% of Variance	Total	PC2	PC1	Cumulative %	% of Variance	Total	
		0.978	**59.188**	**59.188**	**5.919**		**0.982**	**75.422**	**75.422**	**7.542**	Fe
		0.974	**74.220**	**15.032**	**1.503**		**0.982**	**87.687**	**12.266**	**1.227**	Cr
		0.972	85.176	10.956	1.096	-0.215	**0.944**	95.696	8.009	0.801	Ni
	0.760		91.478	6.302	0.630		**0.993**	97.784	2.087	0.209	Zn
0.801		0.337	96.816	5.338	0.534		**0.962**	99.175	1.391	0.139	Cd
		0.978	98.882	2.066	0.207		**0.981**	99.606	0.430	0.043	Se
		0.985	99.457	0.575	0.057		**0.987**	99.785	0.179	0.018	Pb
	0.866		99.835	0.378	0.038	**0.971**		99.909	0.124	0.012	pH
-0.633			99.964	0.129	0.013		0.484	99.962	0.054	0.005	EC
	0.523		100.000	0.036	0.004	0.466	**0.796**	100.000	0.038	0.004	TOM

Table (5)

Correlation matrix between metals contents and some soil properties in the studied area, cells show the Pearson correlation coefficient and the corresponding P value

EC	pH	Pb	Se	Cd	Zn	Ni	Cr	Fe	
									Soil
								0.983**	Cr
							.964**	0.983**	Ni.
						0.951**	.982**	0.983**	Zn
					.948**	0.875**	.926**	0.922**	Cd
				0.956**	.976**	0.899**	.960**	0.948**	Se
			0.988**	0.966**	.985**	0.911**	.965**	0.957**	Pb
		-0.076	-0.024	-0.071	-0.100	-0.257	-0.136	-0.155	pH
	-0.056	0.459*	0.443*	0.422	0.424	0.351	0.424	0.400	EC
0.388	0.309	0.761**	0.774**	0.764**	0.770**	0.634**	.723**	0.735**	TOM
									Herbage
								0.979**	Cr
							0.939**	0.949**	Ni.
						0.253	0.285	0.354	Zn
					0.078	0.278	0.300	0.262	Cd
				0.266	0.305	0.964**	0.979**	0.978**	Se
			0.945**	0.377	0.261	0.965**	0.959**	0.959**	Pb
		-0.184	-0.077	0.051	0.363	-0.126	-0.06	-0.082	pH
	-0.056	0.383	0.438*	-0.066	0.247	0.377	0.410	0.461*	EC
0.388	0.309	0.728**	0.753**	0.274	0.514*	0.748**	0.749**	0.738**	TOM

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

* Correlation is significant at the 0.05 level (2-tailed).

Table (4)

Statistical variation (One- way ANOVA) between metal content, soil and herbage samples.

df within group	df between group	herbage Sig.	F	Mean squares within groups	Mean squares Between groups	Sum of squares within groups	Sum of squares Between groups	Soil Sig.	F	Mean squares within groups	Mean squares Between groups	Sum of squares within groups	Sum of squares Between groups	
														pH
18	2	0.101	2.614	25.220	65.916	453.951	131.832	0.030	4.274	224.859	1169.283	4047.454	1922.267	Fe
18	2	0.049	3.583	0.003	0.012	0.061	0.024	0.025	4.578	0.010	0.047	0.185	0.094	Cr
18	2	0.055	3.434	0.002	0.008	0.040	0.015	0.021	4.853	1.401	6.798	25.215	13.596	Ni
18	2	0.374	1.040	0.030	0.031	0.531	0.061	0.062	3.262	0.049	0.160	0.883	0.320	Zn
18	2	0.682	0.391	0.050	0.020	0.899	0.039	0.064	3.210	0.362	1.162	6.514	2.323	Cd
18	2	0.069	3.118	0.694	2.164	12.490	4.327	0.053	3.483	5.802	20.206	104.427	40.412	Se
18	2	0.035	4.051	8.211	33.264	147.805	66.528	0.050	3.563	41.561	148.085	748.094	296.170	Pb
														EC
18	2	**0.006**	6.889	18.433	126.994	331.795	253.989	0.011	5.796	201.731	1169.283	3631.156	2338.565	Fe
18	2	0.015	5.364	0.003	0.016	0.053	0.032	**0.005**	7.317	0.009	0.063	0.154	0.125	Cr
18	2	0.023	4.711	0.002	0.010	0.036	0.019	0.015	5.325	1.355	7.214	24.383	14.427	Ni
18	2	0.160	2.036	0.027	0.055	0.483	0.109	0.011	5.919	0.040	0.239	0.725	0.477	Zn
18	2	0.858	0.154	0.051	0.008	0.923	0.016	**0.009**	6.225	0.290	1.807	5.224	3.613	Cd
18	2	**0.008**	6.374	0.547	3.486	9.845	6.973	**0.008**	6.390	4.706	30.069	84.702	60.138	Se
18	2	0.016	5.290	7.499	39.673	134.987	79.345	**0.007**	6.739	33.174	223.566	597.131	447.132	Pb
														TOM
18	2	**0.005**	7.262	18.010	130.798	324.187	261.597	**0.003**	8.130	174.251	1416.601	3136.520	2833.201	Fe
18	2	**0.004**	7.843	0.003	0.020	0.046	0.040	**0.003**	7.925	0.008	0.065	0.148	0.131	Cr
18	2	**0.003**	8.407	0.002	0.013	0.029	0.027	0.017	5.165	1.370	7.075	24.660	14.151	Ni
18	2	0.176	1.917	0.027	0.052	0.489	0.104	**0,002**	8.948	0.034	0.300	0.603	0.600	Zn
18	2	0.159	2.038	0.043	0.087	0.765	0.173	**0.002**	8.891	0.247	2.196	4.445	4.391	Cd
18	2	**0.004**	7.519	0.509	3.827	9.163	7.655	**0.003**	8.404	4.161	34.970	74.899	69.941	Se
18	2	**0.005**	7.399	6.535	48.351	117.631	96.701	**0.003**	8.327	30.134	250.926	542.411	501.853	Pb

- The mean difference is significant at a level of 0.01.
- df: Degree of freedom.
- F: Factor.
- Bold numbers are significant.

Table (2)
Max., Min., Mean and Standard deviation
for the descriptive parameters of the 21 soil samples.

SD	Mean	Min.	Max.	Factors
0.49	8.0	6.5	8.6	pH
320.4	406.8	105	1100	EC µs/cm
1.46	3.08	1.2	5.2	TOM%

Table (3)
Comparison of the heavy metals concentration
(mg Kg-1) in soil in different cities and Rabigh.

Reference	Pb	Se	Cd	Zn	Ni	Cr	Fe	City
Thornton (1991)[59].	294	-	1	183	-	-	-	London
Paterson et al., (1996) [60].	94.4	-	-	58.5	-	23.9	-	Aberdeen
Wong et al., (1996)[61].	100	-	1.89	93.9	-	-	-	Hong kong
Li et al., (2001)[62].	93.4	-	2.18	168	-	-	-	Hong kong
Banat et al. (2005)[63].	62.17	-	4.98	146.94	-	83.93	-	Central Jordon
Al-Khashman and Shawabkeh (2006)[64].	55	-	5.0	44.51	-	22.18	24.18	Southern Jordon
This study	14.3	2.9	0.85	0.5	2.0	0.24	56.31	Rabigh

5. Conclusions

Results obtained in this study showed that Fe has the highest mean value, followed by Pb, Se, Ni, Cd, Zn and Cr in surface soils and herbage samples. By comparing the concentrations of heavy metals in surface soils with several SQGs, Fe, Cr are identified as metal pollutants of primary concern, and Ni, Cd, Pb, Zn, and are of moderate concern. Almost all heavy metals in soil profiles did not exceed the LEL. The output of the PCA revealed that Fe is produced from natural sources and that all the other metals were produced from anthropogenic activities such as industrial, construction and traffic emissions. The current results show that the cement plant has a low impact on the metal levels in the environment around the plant till now. These results should be of interest to assess future temporal variations in the levels of metals and in this area.

Table (1)
Metals concentrations in soil
and herbage samples in the studied area (mg/kg).

Herbage (wet weight)				Soil (1-5 cm depth), (dry weight)				Element
SD	Mean	Min.	Max.	SD	Mean	Min.	Max.	
5.65	10.02	3.1	19.7	19.41	56.31	32.68	80.51	Fe
0.07	0.1	0.031	0.213	0.11	0.24	0.215	0.451	Cr
0.05	0.07	0.01	0.164	1.4	2.0	0.30	3.734	Ni
0.17	0.25	0.09	0.45	0.25	0.5	0.423	0.943	Zn
0.2	0.18	0.009	0.257	0.7	0.85	0.095	2.334	Cd
0.8	1.5	0.03	2.91	2.7	2.9	0.10	8.35	Se
3.3	6.35	2.1	11.8	7.2	14.3	6.51	28.24	Pb

index (Igeo) introduced by Muller 1969[51]. The method has been widely employed in European trace metal studies since the late 1960s[52]. The I geo is used to assess metal contamination in urban soils by comparing current and pre-industrial concentrations, although it is not always easy to reach pre-industrial sediment layers. It is also employed in pollution assessment of heavy metals in urban soil. The geo accumulation index is computed using the following equation[53]:

$$I_{geo} = \log_2 \left[\frac{Cn}{1.5Bn} \right]$$

Where Cn represents the measured concentration of the element n and Bn is the geo chemical background value of the element in sediment. In the study, because there are no available elemental background concentration of heavy metal in Saudi soils, the EBC for the studied metals have been taken from the average concentration of trace elements in the earth crust[54] except for Fe that has been taken from the background values of metals in soil in Delta region, Egypt[55].The constant 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to litho logic variations in the sediments[56] and allows us to analyze natural fluctuations in the content of a given substance in the environment and to detect very small anthropogenic influences[57]. The following classification is given for geo accumulation index[58]: <0 = practically unpolluted, 0-1= unpolluted to moderately polluted, 1-2 = moderately polluted, 2-3 = moderately to strongly polluted, 3-4 = strongly polluted, 4-5 = strongly to extremely polluted and > 5 extremely polluted. From the calculated values of I_{geo}, heavy metals can be divided into two groups: the first group includes Fe, Cd, Se and Pb and is characterized by I_{geo} values lower than -5.0 in all the investigated samples which indicates that the soil samples are unpolluted with these metals. The second group includes Cr, Ni, Zn. In this group, calculated values of Igeo ranged from unpolluted to moderately pollute for all the investigated samples (Fig 4).

(SQTs) of China and the proposed Interim Sediment Quality Values (ISQVs) of Hong Kong (see Table 7). According to the Ontario guidelines[49] the 21 soil samples did not exceed the lowest effect level (LEL, below which no effects on the majority of sediment microorganisms are expected) for Fe, Cr, Ni, Zn and Pb, except for Cd where there were 10% exceeded the LEL. These demonstrated that adverse toxic impact to the area around the cement factory might not be expected now. In addition, all samples did not exceed the severe effect level (SEL), above which seriously effects on the majority of sediment micro organisms are expected). The US EPA guidelines, on the other hand, indicated that all samples were not polluted except for 7 % of soil samples contaminated with Pb is moderately polluted. Comparing metal data with the ISQVs-low values of HongKong revealed that about 8% of the samples were contaminated by Cd. While, with the ISQVs- high values all samples under the limits, except for sites contaminated by Cd, about 6% exceeds the limits.

4.2 Assessment of heavy metal contamination by the contamination factor (C_f).

Hakanson, 1980 and Pekey 2004[50] used C_f to describe the contamination of a given toxic substance in a sediments, where C_f was calculated by dividing the mean content of the substance by elemental background concentration of the elements (EBC). The following terminologies are used to describe the contamination factor: $C_f < 1$ low contamination factor; $1 \leq C_f < 3$ moderate contamination factors; $3 \leq C_f < 6$ considerable contamination factors; $C_f \geq$ very high contamination factor. As shown in Table (7) the contamination factor are low for Fe, Cr, Ni and Zn, moderate for Pb and considerable for Cd. This means that the mean total concentrations for all elements and sampling areas were within the limits for land use, with the exception of Cd and Pb.

4.3 Assessment of heavy metal contamination by geo accumulation Index (I_{geo}) and Enrichment factor (EF).

The contamination levels of heavy metals in urban soils, urban road dusts and agricultural soils are assessed by using ageo accumulation

Factor analysis was used to give information about the distribution and source identification of metal pollution based on Eigen values (Eigen value >1)[43]. The rotation of PCA was carried out by the varimax method. The factor loadings obtained for various metals are tabulated in Table (6). The loadings having a greater than 0.7 are marked bold in the table. For soil samples, PC sare accounting for 87.687 % of the total variance. Factor 1 explaining 75.422% of the total variance, was strongly and positively related to Fe, Cr, Ni, Zn, Cd, Se, Pb and TOM (Table 6). The relation of these metals with PC1 can be indicated by their anthropogenic influence and the effect of TOM on them[44], while Fe, Cr and Niare well known to be geogenic[45]. Factor 2 explaining 12.266 % of the total variance showed highly positive factor loading on soil characteristics pH[46]. This factor is insignificant and represents the physicochemical source of the variability[47].

The PCA also determines if elements are clustered in groups (Fig. 2). A diagnostic assessment of the scatter plots indicated two groupings: (a) two soil properties pH and EC (b) TOM and all elements. This suggests the significant influence of TOM on these metals. For herbage samples, PCs are accounting for 74.220 % of the total variance. Factor 1 explaining 59.188 % of the total variance, was strongly and positively related to Fe, Cr, Ni, Se and Pb (Table 6). Factor 2 explaining 15.032 % of the total variance showed highly positive factor loading on Zn and soil characteristics pH (Fig. 3).

A diagnostic assessment of the scatter plots indicated three groupings: (a) Fe, Cr, Se, Ni, and Pb (b) two soil properties TOM and EC (c) Zn and pH. This suggests the insignificant influence of soil characteristics, especially TOM and EC on metal uptake by herbage.

4. Assessment of heavy metals in soils samples

4.1 Assessment of heavy metal pollution by sediment quality guidelines (SQGs)

Bai et al., 2011[48], assessed the extent of metal pollution by comparing metal concentrations in surface soils to the sediment quality guidelines (SQGs) developed by US EPA, the Ministry of Environment and Energy, Ontario, Canada, soil quality thresholds generated by dissolution of organic matter[36]. The high correlation between Fe and Zn (r = 0.983), Zn and TOM (r = 0.770) may be attributed to the adsorption of Zn in Fe-oxides due to weathering of iron artifacts, and the strong specific adsorption affinity of poorly crystalline oxides for heavy metals[37]. Moreover, Zn is easily bounded organically with TOM in neutral or alkaline soil[38], (Table 5). The results of the ANOVA showed significant difference in metals between sites for all soil samples which confirm their probable common natural or anthropogenic origin. For herbage samples, the significant difference was found only for Fe vs. Cr, Ni, Se and Pb (r = 0.979, 0.949, 0.978 and 0.959 respectively) and Cr vs. Ni, Se and Pb (0.939, 0.979 and 0.959 respectively) and Ni vs. Se and Pb (0.964 and 0.965 respectively) and Se vs. Pb (0.945) (Table 5).

3.4.2 Correlation matrix (CM)

Table (6) shows the relationship between heavy metals in all samples and selected soil properties. Results obtained by PCA are confirmed by analyzing the CM. Total organic matter (TOM) exhibited a positive linear relationship with Cd, Cr, Ni, Pb, Zn ($P<0.05$), Some researchers[39] have proved that TOM can act as a major sink for heavy metals (i.e., Cd, Cr, Ni, Pb and Zn) due to its strong complexion capacity for metallic contaminants. Fe has well significantly positive correlations with TOM suggesting that the TOM might be mainly imported by external source with such heavy metals i.e., Cd, Cr, Pb and Zn in the study area.

The positive relationships between Cr and TOM ($P<0.05$) showed that the reduction of Cr from its toxic and mobile hexavalent form Cr (VI) to a rather stable Cr (III) could be accelerated by the presence of organic matter[40]. Additionally, Cr and Pb were negatively correlated with electrical conductivity (EC) while Ni and Zn were negatively correlated with soil pH values ($P<0.05$). However, no significant correlations were observed between heavy metals and soil pH and EC. Although most heavy metals are not significantly correlated with soil pH due to the narrow range of pH, their mobility is usually the lowest in these soils with slightly alkaline pH[41] and the lowest mobility would favor metal accumulation in the soil[42].

the heavy metals analysis indicated that the herbage species had good metal accumulation and we recommend, in future, to make more studies about the herbage species in the study area and their ability for metal accumulation.

3.3 Physico-chemical factors

The characteristics of soil samples, pH, electrical conductivity (EC) and total organic matter (TOM) are given in Table (2). The pH values ranging in narrow interval (7.23 to 8.15), which suggests neutral to little alkaline conditions for all the soil samples. Also, high electrical conductivity values are found close to the cement factory with mean value 406.8 µs/cm. The total organic matter in the soil ranges from 1.2% to 5.2%, with a mean value of 3.08%. The highest values of organic matter found very close to the cement plant.

3.4 Statistical data treatment

3.4.1 One way ANOVA analysis

The statistical analysis of the results (ANOVA) shows significant differences between the concentrations of metals in the soil and herbage samples and the physico-chemical parameters collected at many sites ($P< 0.01$)Tables (4).All metal contents in soil and herbage do not correlate with pH, owing to the narrow range of pH (6.5-8.6) measured in the soil and herbage samples. This means that pH has limited importance on the metal mobility and distribution [34]. For EC, Cr, Cd, Se and Pb had significantly higher concentrations in soil samples at some sites, While, Fe and Se had significantly higher concentrations in herbage samples at some sites. For soil and herbage, there were no samples showing higher levels in metal content. Moreover, decreasing in metal concentrations according to the distance of the sampling points to the facility was noted. The presence of anthropogenic contamination in the studied area far from the cement factory is explained by the correlation between metals-metals and metals-soil characteristics. Binding with TOM can lead to increased metal mobility at higher pH[35].The significant difference between the samples and the TOM% may reflects that some of the heavy metals like Cr and Ni could have been mobilized by chelation

Among the heavy metals, lead is the most immobile element and Pb content in soil is closely associated with clay minerals, Mn-oxides, Aland Fe hydroxyls, and organic material[31]. In general, the highest Pb concentrations are recorded in organic-material-rich soils and Pb behaves as adsorbent in soils contaminated by organic material[32]. In this study, Lead concentrations were in the range of 6.51–28.24mgkg^{-1}dry weight. The mean concentration of lead was found to be (14.02mgkg^{-1}dry weight) while, the highest value was 28.24mgkg^{-1}dry weight. This lead concentration was found at site one located 0.5 km away from the factory while the lowest lead concentration (6.51mgkg^{-1}dry soil) was found at site 21. The highest lead concentration in the soil samples was recorded close to the cement plant. This could be attributed to the cement industry in which the process and production of cement industry require a substantial amount of energy supplied by burning fossil fuel and traffic activity in the plant[33].

Compared to mean concentrations in urban soils in the world (Table 3), the mean values of all metals in the analyzed soils are much lower than those reported for the ones from different cities in the world (i.e. London, Aberdeen, urban playground in Hong Kong, Hong Kong and central Jordan, southern Jordan). In this study, it has been noted that the concentrations of heavy metals are highest only around the cement plant and decrease gradually as the sample sites become far from the plant.

3.2 Heavy metal distribution in herbage

Heavy metals levels in herbage samples collected from the studied area near the cement plant are also shown in Table (1). The highest levels corresponded again to Fe, Pb and Se. The concentrations ranged between 19.7 and 3.1mg/kg wet weight and 11.8 and 2.1mg/kg wet weight with a mean value of 10.02 and 6.35mg/kg wet weight, respectively. By contrast, the levels of Cr, Ni, Zn and Cd were the smallest in all samples. The mean values were 0.01, 0.07, 0.25 and 0.18mg/kg wet weight, respectively. In general, as soil samples, the metal concentrations in the herbage samples are low. In the study area, Cr concentration in soil samples ranges from 0.22 to 0.45 mg kg^{-1}dry soil with mean value of 0.24 mg kg^{-1}dry soil, Fig (1). The presence of Cr metal around the cement plant may be attributed to the fact that in the cement industry the linings for the rotaries contain Cr which could be liberated by wear and friction(26). The mean concentration of Ni was 2 mg kg^{-1} dry soil, where the maximum value was 3.743mg kg^{-1} dry soil (0.5 km far the plant) and the minimum value was 0.3mg kg^{-1} dry soil at site 21. The presence of Ni in soil samples is highly dependent on the content of parent rocks and also reflects the additional impacts of both soil forming processes and pollution like fuel combustion and industrial activities(27). Regarding Zn, the mean concentration was almost low. The highest concentrations were also near the cement plant. Zinc can have a lithogenic source as it forms a number of soluble salts (e.g. chlorides, sulfates and nitrates) or insoluble salts (e.g. silicates, carbonates, phosphates, oxides and sulfides) depending on the prevailing pedogenic processes(28). Zn particles may also derive from industrial sources or the abrasion of motor vehicle tires(29).Cadmium concentration was found to be higher than Zn and Cr and lower than the other studied elements with mean concentration of 0.85mg kg^{-1} dry soil. Cd is emitted into the atmosphere from natural sources, mainly basaltic rocks and from anthropogenic sources. Metal production (drying of zinc concentrates and roasting, smelting, and refining of ores) is the largest source of anthropogenic atmospheric cadmium emissions, followed by waste in cineration and by other sources, including the production of batteries, fossil fuel combustion and generation of dust by industrial processes such as cement manufacturing(30).

Selenium occurs naturally in a number of inorganic forms, including selenide, selenate, and selenite. In soils, selenium most often occurs in soluble forms such as selenate. Natural sources of selenium include certain selenium-rich soils, and selenium that has been bioconcentrated by certain plants. Anthropogenic sources of selenium include coal burning and the mining and smelting of sulfide ores. In this study, the mean concentration of Se was 2.9 mgkg^{-1}dry weights.

relationships present in the original data[21]. For comparison of the heavy metal and soils and herbages data, statistical significance was computed by ANOVA. Differences are considered to be significant if $P < 0.05$[22]. In order to look for a possible linear dependence between the different heavy metal homologues in soil and herbage samples, obtained soil and herbage heavy metals and other soil properties were tested for correlations between them using Pearson's correlation coefficient based on the assumption that the data were normally distributed.

3.Results and discussions

3.1 Heavy metal distribution in soil

The descriptive statistics in Table (1) summarizes the concentrations of a number of metals found in 21 soil samples collected in the vicinity of the cement plant. The highest levels corresponded to Fe, Pb and Se, followed by Ni. By contrast, the levels of Cd, Zn and Cr were the smallest in all samples. The metal concentrations in the soil samples are generally low. These metals are distributed in soil due to the atmospheric deposition depending on the distance from the cement plantand the size of particles. The concentration of these metals in soil can vary greatly according to the strength and direction of wind, type of soil and pH. Usually pH affects the heavy metal mobility and distribution in the soil samples and proved to be the major controlling factors for the stabilization of trace elements[23]. Additionally, some differences between these heavy metals can be attributed to tidal inundation, salinity changes, wind and waves[24]. Iron is one of the principle element in the earth crust and is mainly associated with the coarse atmospheric particles, if associated with other sources,it is generally deposited in the neighborhood of the emission sources [25]. In the study area the higher levels were observed at 0.5 km away from the cement plant (80.51 $mgkg^{-1}$dry soil), but the lowest value of iron was observed at site 21 (3.3$mgkg^{-1}$dry soil). However, higher levels were also observed by the influence of the already mentioned cement plant and mechanical traffic places in the factory.

soil and herbages samples. Samples were placed into an acid washed PTFE digestion vessel to which 5 ml of 1:1 nitric acid (HNO_3, Merck) were added, and the vessel covered with a glass watch. The sample was placed on a hotplate at 95°C and refluxed for 5 to 10 min. The vessel was then removed from the hotplate and allowed to cool. After cooling, 2.5 ml of concentrated nitric acid (HNO_3) was addedand the reflux was repeated until brown fumes were no longer visible. The solution was evaporated to approximately 5 ml at 95°C, without boiling, for one hour. After cooling, 1 ml of water and 3 ml of 30% H_2O_2 were added and the solution heated slowly to start the peroxide reaction. The vessel was then cooled and 30% H_2O_2 in 1 ml aliquots added (less than a total of 10 ml). This was repeated until the appearance of digested samples was unchanged. Acid-peroxide digested samples were heated at 95°C without boiling for one hour and 5 ml of concentrated HCl added to the sample digest and covered with a glass watch. The sample was placed on the hotplate at 95°C for 15 min. After cooling, sample was transferred into a 50 ml volumetric flask, diluted to 50 ml with Milli-Q deionized water (analytical grade), and the flask was transferred to a 125 ml high density polyethylene (HDPE) sample bottle for storage. Sample solutions were analyzed for trace elements by AAS. Analyses were assessed using duplicates. The recoveries of samples spiked with standards ranged from 95 to 105%. Total organic matter (TOM) was measured using dichromate oxidation[(20)]. Soil pH was measured with a Hach pH meter (Hach Company, Loveland, USA). Electrical conductivity (EC) was determined in supernatant of 1:5 Soil/water mixtures using a VWR Scientific conductivity meter (VWR Scientific, West Chester, Pennsylvania, USA).

2. 3 Statistical analysis

All multivariate statistical analyses, including principal component analysis (PCA), correlation matrix (CM), and one-way analysis of variance (ANOVA), were conducted using SPSS 16.0 for windows. Principal component analysis (PCA), is generally employed to reduce the dimensionality of a data set while attempting to preserve the temperature degree in 45°C in August and rises somewhat in winter. The climate is characterized by high relative humidity, especially in the summer and also we can not say that there is a special season for falling rains in Rabigh. The prevailing wind direction is from westerly to northwesterly. Rabigh town population is around 180, 352 according to the most recent government census and it includes many small villages (Sa'aber and Kiellaya). The surroundings are essentially rural consisting of open areas with little scattered houses at distance varying from 30-50 meters in these villages. Rabigh is situated close to the Red Sea and 150 Km from the center of Jeddah and in a back of Arabian Cement Company (ACC). (ACC) founded in 1956, built its Rabigh plant in 1984 and expanded it in 1996-1997. The plant currently produces three million tons of cement annually. And now, ACC is planning to add a new 7,000 tons of cement per day production line.

2.2 Sample collection and analysis

During late August of 2010, 21 sampling sites around the plant were identified. The samples were collected near the gate of the plant (500 m far) and then with increasing distance from the cement plant. The top 5 cm soils and the herbages with three replicates were collected in each sampling site and mixed to form a composite sample. All soil samples were then placed into polyethylene bags, and brought to the laboratory. For the purposes of determining soil chemical properties, all soil samples were air dried at room temperature and sieved through a 2-mm nylon sieve to remove coarse debris. All the air-dried soil samples were then ground with a pestle and mortar until all particles passed a 0.149-mm nylon sieve. In turn, approximately 10g of herbage samples was obtained by cutting at a height of approximately 4cm from the soil. Subsequently, herbage samples were dried at room temperature, kept in a double aluminum foil, packed in labeled plastic bags, and stored at room temperature until analysis. About 5g (dry weight) of soil and herbage samples were used for analytical purposes. The US EPA Method 3050B (hotplate digestion technique US EPA, 1999)[19] was used to digest and analyze Fe, Cd, Cr, Zn, Ni, Se and Pb

Many studies have been done on ecological risk assessment by heavy metals based on different sediment quality controls. Pekey et al., 2004,[13] used the Sediment Quality Guidelines (SQG) of US EPA to assess the toxicity of heavy metals in surface sediment of Izmit bay of Turkey. Khan et al 2008,[14] evaluated the healthy risks of heavy metals posed by contaminated soil and food crops irrigated with wastewater in Beijing of China using the permissible limits. Chen et al., 2008[15] identified the trace element sources and associated risk assessment in vegetable soils of the urban-rural transitional area of Hangzhou, China. Lu et al., 2009 [16] assessed the contamination level of heavy metal on the basis of geo accumulation index (I geo), enrichment factor (EF), pollution Index (PI) and integrated pollution index (IPI) in street dust in Baoji, China. Bai et al., 2011[17] assessed the heavy metals in wetland soil from the young and old reclaimed regions in the Pearl River estuary, south China. Khairy et al., 2011[18] assessed the trace of metal in road dust in Delta region, Egypt by using a geo accumulation index (Igeo).

Since there are no previous data concerning the concentrations of heavy metals in the soils and plants of Rabigh governorate, important goals of this investigation are to be established, if the area is affected by environmental pollution, the amount of heavy metals in order to compare the present results with data obtained in future surveys and, eventually, to allow the competent authorities to take any technical and policy decisions to protect the area. As a result of the fact that some environmental groups argue that the cement production causes the deterioration of environmental quality of Rabigh area. This study examines and assesses the influence of the cement plant on the level and distribution of heavy metals in Rabigh governorate.

2.Materials and methods

2.1 Study area

Rabigh is a small ancient governorate on the western coast of KSA, between latitudes 22/23 north of the equator which lies on the Tropic of Cancer. The climate is extremely hot on the summer and the temperature ranges from 36-38°C and ends of the maximum

As well known, Portland cement results from the grinding of a clinker. The clinker is produced by burning a mixture of limestone, clay and gypsum at high temperatures (1450–1600°C for the materials, and approximately 2000°C for the combustion fumes). Cement is manufactured in three basic steps: extraction and preparation of raw materials, calcining, and finally grinding of the clinker(3). Portland cement dust is a gray powder with an aerodynamic diameter ranging from 0.05 to 5 mm. This size is within the range of sizes of respirable particles. Therefore, exposure to Portland cement dust has been long associated with respiratory symptoms(4). Data on environmental levels and health risks for populations living near cement plants are very scarce(5). Moreover, studies simultaneously assessing health risks due to emissions from criteria pollutants and toxicants are also scarce.

Cement kilns are sources of hazardous air pollutants emissions, which include a number of heavy metals (mainly adhered to particles), NOx, SO_2, CO_2 and lower amounts of CO, organic compounds such as PCDD/Fs and PAHs, as well as other minor pollutants(6). While, heavy metals are present at low concentrations in the raw material and in the fuel used for clinker production, heavy metals can cross environmental - media boundaries, becoming distributed in soils, vegetation, water, biota, etc. As a result, human health can be indirectly affected through different pathways such as drinking water or ground water, skin absorption of the chemicals present in water and soil, and by eating contaminated food stuffs(7). Heavy metals are important environmental pollutants with a well-defined toxic pathology. While some elements such as arsenic, cadmium, lead or mercury are known toxicants, essential elements such as cobalt, chromium, manganese or zinc can also have deleterious effects at certain levels(8).The deposition of cement dust on the surface of leaves has a physical effect on the growth of plants(9) and variation of stomata activities(10) and chemical effects on the nutrient absorption from the soil(11) and cause significant reduction in the size of soil microbial biomass(12).

Evaluation and Assessment of Top Soil and Herbage Pollution by Heavy Metals near Cement Plant in Rabigh, Western Coast of KSA*

Magdy Madbouly**

Forty-two topsoil (0-5 cm) and herbage samples were collected in Rabigh area, KSA. The possible metal pollution source for these samples was a cement plant. The elements Fe, Cr, Ni, Zn, Cd, Se and Pb were measured using atomic absorption spectroscopy. Physicochemical factors believed to affect the mobility of metals in soil of the study area were examined such as; pH, EC, and TOM. Several statistics were performed to the data set in order to accomplish the objectives of the study. Fe and Pb were identified as metal pollutants of primary concern and had higher contributions to the total toxic units compared to other metals. According to the ministry of environment and energy, Canada, Ontario guidelines almost all metals did not exceed their lowest effect levels (LEL) while, the US EPA indicated that all samples were not polluted except for 7 % of soil samples contaminated with Pb is moderately polluted. Multivariate analysis shows that Fe is controlled by parent rocks and other metals mainly originate from anthropogenic source. A correlation analysis showed that total organic matter and pH had strong associations with Ni, Pb, and Zn. The contribution of cement industry is significant only in the zone located at about 0.5 to 2 km around the cement plant. The current results show that the cement plant has a low impact on the metal levels in the environment around the plant till now. These results should be of interest to assess future temporal variations in the levels of metals and in this area.

1. Introduction

Many studies have been undertaken for many years to evaluate the deposition and distribution of heavy metals in urban soils and plants, particularly those near cement plants(1) and those in roadside settings(2).

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