

Environmental Significance of Major and Trace Elements in the Soils of Selected Areas in Erbil City, Kurdistan Region, Northern Iraq

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ABSTRACT

Thirty five elements were analyzed in twenty seven soil samples from six different sites in Erbil city to investigate the possible pollution by heavy metals in these areas. These sites are North Industrial, South Industrial, Erbil Citadel and three sites outside the city as background. Fe, K, Al, Na, P, Li, Be, B, Sc, V, Cr, Ga, As, Se, Rb, Sr, Y, Zr, Mo, Sn, Cd, Cs, Ba, La, Ce, Th, and U have higher concentrations than those of the local background but still have not reached the pollutant levels when compared with the international standards. The concentrations of Ni, Cu, and Zn have exceeded pollutant levels but still cannot be considered toxic or hazardous because of their immobile nature under the current oxidizing environmental conditions. Meanwhile, Co, Mn and Pb have reached critical levels in the industrial areas; while Ni, Cu, Co, and Mn have critical values in the Citadel soils. The concentration of Ca in all studied areas is higher than those of international soil standards, while Mg is lower. There are high concentrations of P in the Erbil Citadel soil samples which are considered pollutant.

Keywords: Major Trace Elements, Erbil Soil , Kurdistan, Iraq.

الأهمية البيئية للعناصر الرئيسية والأثرية في ترب مناطق مختارة في مدينة أربيل، إقليم

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compared with the international soil standards. Erbil city is the capital of Iraqi Kurdistan region located between Longitudes 43°57'59" - 44°03'04" E and Latitudes 36°09'04" - 36°13'13" N , with an area of about 92 km² and a population of ~1 million. There are many factories and car repair shops in the two industrials parts of the city which are possible heavy metal pollution sources. The ancient citadel was inhabited for centuries by many generations which might also caused some pollution (Fig. 1).

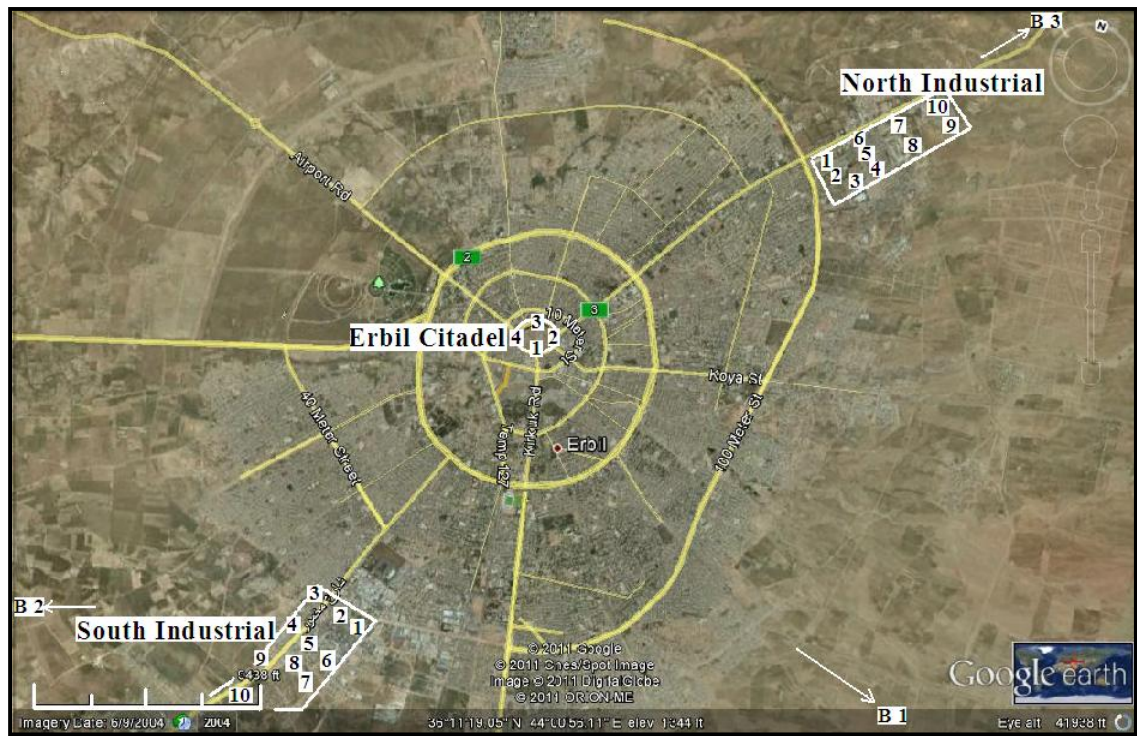


Fig. 1: Google Earth Map of Erbil City Showing the Studied Areas and Sample Locations. B1, B2, and B3 Represent the Location of Background Samples which lie Outside the Map Area in the Direction of Arrows.

SAMPLING AND ANALYTICAL METHODS

Twenty seven in-situ soil samples were collected for this study. Twenty of them were collected by scraping the soil to a depth of 25cm in South and North Erbil Industrial districts and four samples from the deeper horizons at a depth below 25cm in different localities of the ancient Erbil citadel (Fig. 1).The remaining three samples were collected as background samples from fresh soils out of Erbil city municipal which were obtained with a hand auger at a depth of about 25cm within the A-horizon below the organic layer.

The samples were analyzed by ICP-MS (Inductive Coupled Plasma Mass Spectrophotometer) in ALS laboratory group at Seville in Spain (Table 1). The mineralogical studies were carried out at the Department of Earth Sciences, Dalhousie University in Canada. Phillips XRD machine was used in analyzing the bulk soil samples. Whole rock powder mount analysis was performed under the following working conditions: 40 kV voltage, 40 mA current, Cu K α radiation, Ni filter, 2 Soller slits, 1° divergence slit, 1° and 0.1° receiving slits, 0.02 °2 θ step at a range of 5 to 85.20° and counting time of 5 s/step. The machine was provided with an automatic X' Pert search-match software for interpreting the results.

GEOLOGICAL SETTING

Erbil city is located within the foothill zone which is part of the stable shelf tectonic unit of Iraq. Geomorphologically the area is flat lying with sporadic low lying hills. Stratigraphically the area is covered by Quaternary and Pleistocene deposits which are dominated by clays, silt and sand (Jawad *et al.*, 1982), (Fig. 2a, b). The age of these deposits are Pleistocene to Holocene (Buday and Jassim, 1987). The Quaternary deposits include river terraces, slope deposits, polygenetic deposits and flood plain deposits (Sissakian and Youkhana, 1978). The Quaternary sediments unconformably overly the Bai-Hassan (formerly Upper Bakhtiary) formation (Pliocene) which is dominated by thick conglomerate units alternating with clayctones, siltstones and sandstones (Buday, 1980) exposed to the east of the studied area, near Basstowra valley .

SOIL OF THE AREA

Internationally the soils of the world are classified into eleven orders: alfisols, andisol, aridisol, entisol, histosol, inceptisol, mollisol, oxisol, spodosol, ultisol, and vertisols (Soil Survey Staff, 1975; in Foth, 1990). The soils of the studied areas in Erbil City are of the aridisols order - orthids suborder (Kahraman, 2004). This is also indicated in the schematic map of soil orders and suborders of the world given in Foth (1990, p290). This type of soil includes most of the soils of the arid regions of the world which are characteristic of dry climates; in the absence of groundwater, the soil layers remain dry throughout most of the year; and will not be subjected to intensive leaching. They have an ochric epipedon, light colour and low organic matter content. They may have a calcic, gypsic, or salic horizon. Orthids suborder soils are common and do not have an argillic horizon. Argids is the other suborder of aridisols which have an argillic horizon. The studied soils are of calcic character, slightly argillic, poor in organic matter, and ochric as indicated from field observations and X-ray diffraction analyses (Fig. 3).

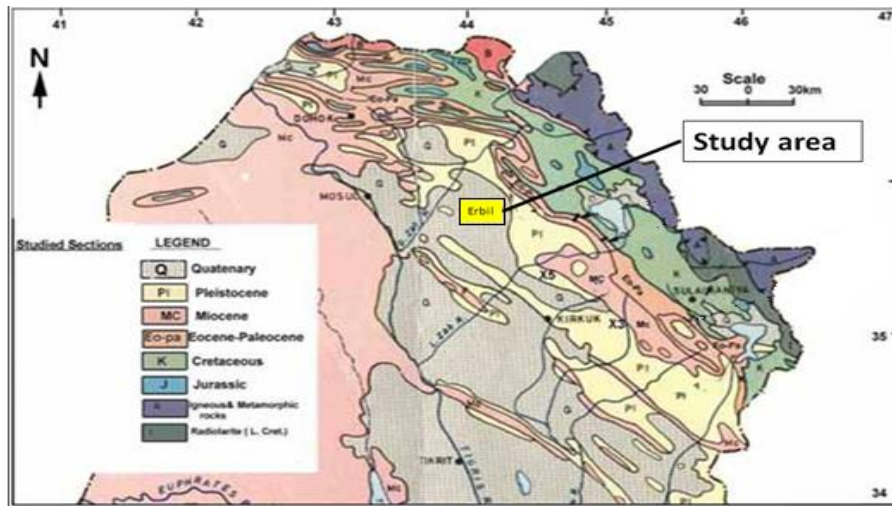


Fig. 2a: Geological Map of Northern Iraq (Buday and Jassim, 1987) Showing the Location of Studied Area in Erbil City.

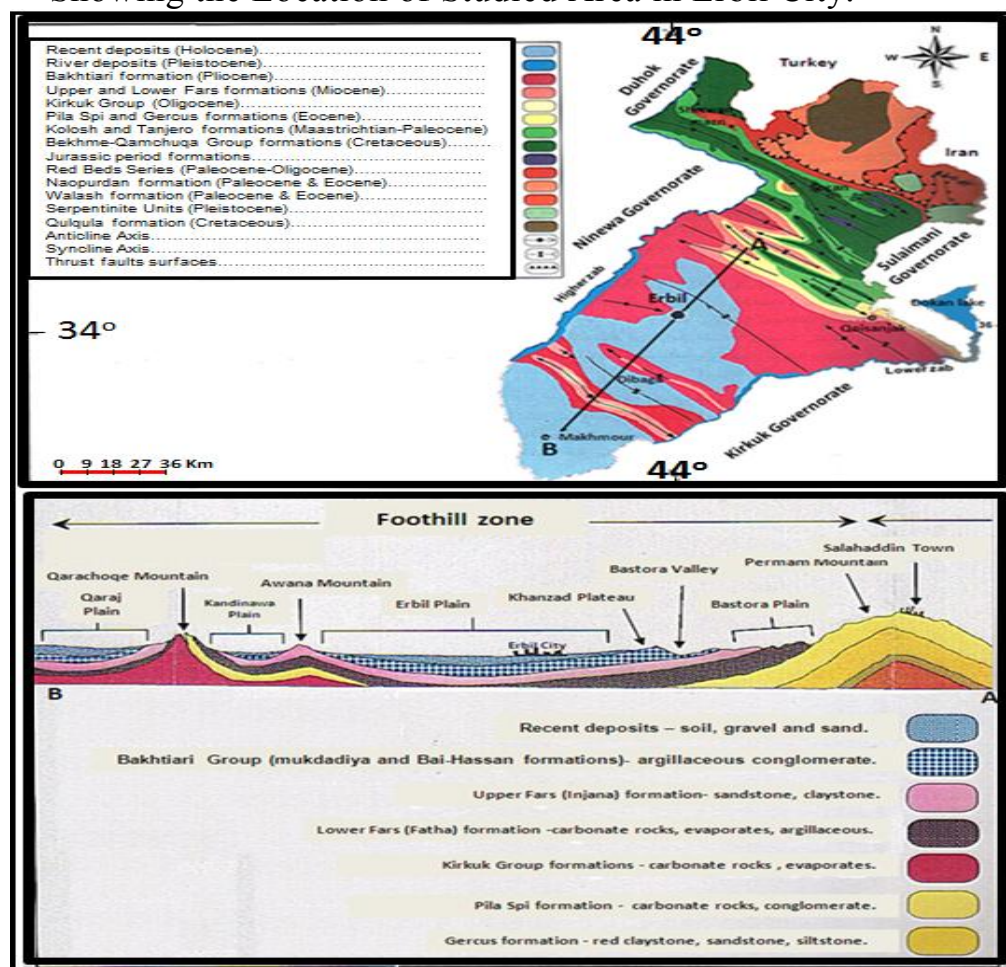


Fig. 2b: Detailed Geologic Map and Schematic Cross-Section (not to scale) of the Erbil Governorate Including the Studied Area (After Ali Surdashi 2003, in Kahraman, 2004).

RESULTS

The soil samples were studied mineralogically and geochemically. The mineralogical studies by XRD showed that they consist of quartz, calcite, and clay minerals. The clay minerals are nontronite, illite, chlorite and/or kaolinite (Fig. 3).

The geochemical studies included the analysis of 8 major and 28 trace elements. The major elements are Fe, Ca, K, Al, Mg, Na, P and Mn; the trace elements are Li, Be, B, Sc, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Mo, Sn, Cd, Cs, Ba, La, Ce, Pb, Th, and U (Table 1).

All geochemical data for the soil samples were statistically treated using correlation coefficient and factor analysis programs. The results were compared with international standards given by Kabata-Pendias, and Pendias (1992), Van loon and Duffy (2005) and Kabata-Pendias, and Mukherjee (2007) to determine the possible pollutant elements in the studied soil samples (Table 1).

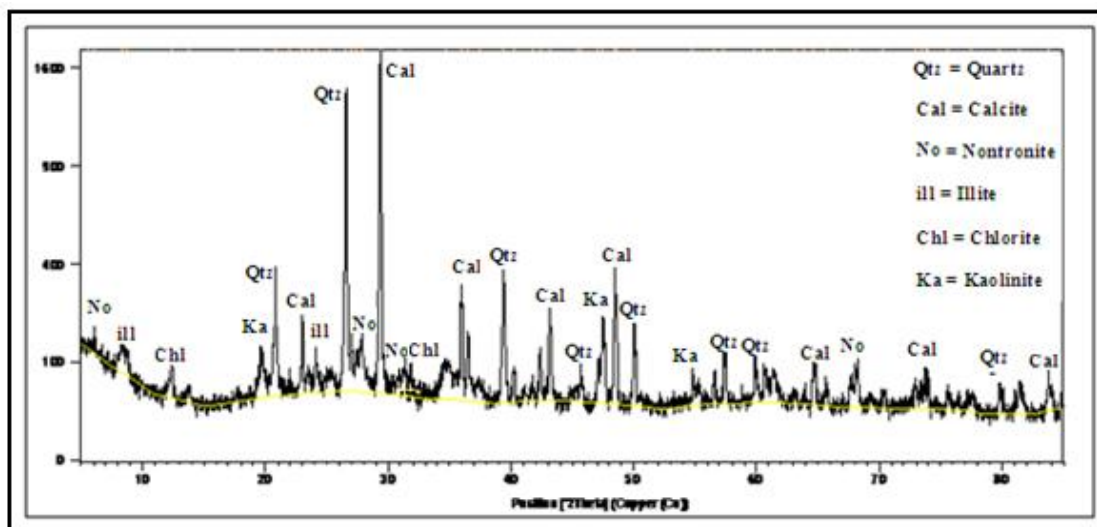


Fig. 3: X-Ray Diffractogram of a Representative Soil Sample from Erbil Industrial Area.

Table 1. Major, Minor and REE Elements concentrations of the studied soil samples (The major elements Fe, Al, Ca, K, Mg, Na are in %; the rest are in ppm).

No.	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	AV S	N1	N2	N3	N4	N5	N6	N7	N8	N9	N10	AV N	AV N S	Cl	C2	C3	C4	AV C	B1	B2	B3	AV B	AV All	Soil*	Soil Δ	Soil Ω
Fe	1.9	2.9	2.2	2.4	2.6	2.4	2.1	2.6	2.7	2.3	2.41	2.4	2.5	2.1	1.6	2.1	2.7	2.6	2.6	2.8	2.4	2.38	2.4	2.2	1.9	2.3	2.1	2.1	2.1	1.7	1.5	1.77	2.3			
Ca	18	11	17	16	14	14	15	14	13	17	14.9	16	15	18	19	18	12	14	15	11	15	15.3	15	14	19	16	18	16.8	17	19	20	18.7	15.7			
K	0.2	0.4	0.2	0.2	0.4	0.5	0.2	0.3	0.4	0.3	0.31	0.3	0.3	0.2	0.1	0.2	0.4	0.4	0.3	0.5	0.2	0.29	0.3	1.4	0.3	0.4	0.2	0.58	0.3	0.1	0.1	0.17	0.33			
Al	1.1	2.1	1.4	1.6	2	2	1.3	1.6	1.9	1.5	1.65	1.7	1.8	1.3	0.9	1.3	1.8	1.7	1.6	2.1	1.7	1.59	1.6	1.8	1.3	1.5	1.3	1.48	1.5	1	0.8	1.1	1.5			
Mg	1.4	1.1	1.3	1.4	1.6	1.8	1.4	1.2	1.1	1.6	1.39	1.5	1.4	1.7	1.8	1.7	1	1.3	1.4	0.8	1.7	1.43	1.5	1.7	1.9	1.5	1.7	1.7	0.9	1.8	1.9	1.5	1.46			
Na	0	0.1	0.1	0	0	0	0.1	0.1	0.1	0.1	0.06	0.1	0.1	0.1	0	0.1	0.1	0.1	0.1	0.1	0.1	0.09	0.7	0.1	0.06	0.08	0.04	0.7	0.03	0.01	0.09	0.04	0.064			
P	590	660	600	540	900	640	500	650	680	600	636	630	645	580	450	590	680	670	657	710	640	626	631	3080	2800	3090	3070	3010	400	450	425	425	960.6			
Li	1.1	2.2	1.7	1.3	2.1	1.9	1.2	1.3	2.0	1.5	1.63	1.2	2.3	1.7	1.3	1.0	1.1	2.1	1.7	1.4	1.9	1.57	1.6	1.5	1.6	1.4	1.5	1.5	1.5	1.6	1.4	1.5	1.65			
Be	0.3	0.6	0.5	0.4	0.6	0.5	0.3	0.2	0.3	0.4	0.41	0.5	0.4	0.6	0.5	0.3	0.2	0.3	0.2	0.5	0.4	0.39	0.4	0.5	0.6	0.4	0.5	0.5	0.4	0.3	0.5	0.4	0.42			
B	8	11	8	9	11	7	8	9	11	8	9	9	6	7	10	8	11	8	9	10	7	8.5	9	10	9	8	9	9	9	7	8	8	8.1			
Sc	3.7	5.9	5.5	6	5.4	5.2	4.6	4.7	4.9	5.5	5.14	6	3.4	4.2	4.6	3.7	5.8	5.6	5.5	6.4	6.2	5.14	5.5	5	6	10	7	7	4.5	5.5	6.4	5.47	5.4			
V	45	56	57	59	54	54	51	56	57	59	54.8	54	54	45	56	53	52	58	44	56	46	51.5	53	45	46	43	44	44.5	49	50	48	49	51.41			
Cr	56	77	67	87	70	70	65	63	71	63	68.9	65	67	65	59	64	76	70	76	81	65	68.8	69	62	61	68	61	63	50	63	49	54	66.3			
Mn	446	627	531	525	603	574	480	613	623	591	561	605	613	564	460	553	623	612	615	717	616	598	580	606	528	591	545	568	562	478	463	501	569			
Co	11	16	14	14	16	14	11	17	18	15	14.6	16	16	12	8	11	12	17	16	20	15	14.3	15	14	10	15	14	13.3	13	9	8	10	13			
Ni	65	109	81	75	102	97	69	97	99	77	87.1	78	83	69	45	71	98	93	95	100	77	80.9	84	21	23	18	22	21	17	23	20	20	17.8			
Cu	46	59	83	69	31	93	92	87	67	43	67	41	63	47	57	66	47	61	71	53	65	57.1	62	36	33	27	36	33	19	21	20	20	53.1			
Zn	102	138	117	92	122	93	100	123	125	117	113	120	122	100	93	99	127	121	124	133	119	116	114	45	39	47	41	43	72	65	61	66	98.41			
Ga	2.9	5.1	3.1	4	4.9	4.8	3.3	3.3	5.1	3.1	3.96	4	4.5	4.8	4.3	4.6	3.1	3.8	5.1	3.1	4.8	4.21	4.1	4.1	4.3	4.2	4.3	4.4	4.3	3.8	3.6	3.7	3.7			
As	9	18	9	10	12	11	8	12	14	10	11.3	11	12	9	6	9	15	12	13	16	11	11.4	11	4	2	6	3	3.8	7	6	5	6	9.63			
Se	0.3	0.3	0.4	0.3	0.3	0.3	0.3	0.2	0.3	0.4	0.31	0.3	0.2	0.4	0.3	0.2	0.3	0.4	0.3	0.2	0.3	0.29	0.3	0.4	0.3	0.5	0.4	0.4	0.3	0.3	0.2	0.27	0.32			
Rb	5.7	13	7.3	5.5	12	11	7.5	5.3	12	7.1	8.64	5.6	12	11	7.4	5.3	7.2	7.1	5.2	7.1	5.1	7.3	7.8	13	12	12	13	12.5	7.9	7.8	7.6	7.77	8.6			
Sr	267	391	285	272	445	366	291	273	329	253	317	375	354	295	439	339	285	241	319	271	322	324	321	511	371	281	337	375	396	237	330	321	322.8			
Y	6.9	10	8.2	9.2	10	9.5	7.9	6.7	9.7	8.2	8.63	9.1	10	8.5	7.9	6.8	9.8	8.3	9.4	10	7.5	8.73	8.7	8.9	8.7	8.8	8.4	8.7	7.8	6.8	7.6	7.4	8.76			
Zr	4.2	5.1	4.3	4.6	5.6	5.4	4.5	4.1	5.2	4	4.7	4.9	6	5	4.3	3.9	4.8	4.4	4.4	4.7	4.9	4.73	4.7	4.6	4.8	4.5	4.3	4.6	4.2	4	4.1	4.1	4.2			
Mo	1.3	0.8	1.1	0.8	1	0.7	0.8	1.7	0.8	1.3	1.03	0.9	1.2	0.5	0.6	0.9	1.6	0.8	1.2	0.9	1.1	0.97	1	1.1	0.9	1.2	0.8	1	0.7	0.8	0.6	0.7	0.97			
Cd	0.1	0.8	0.2	0.3	0.6	0.3	0.3	0.5	0.6	0.3	0.4	0.4	0.2	0.1	0.2	0.7	0.5	0.7	0.5	0.7	0.3	0.4	0.4	0.2	0.1	0.3	0.2	0.2	0.3	0.2	0.1	0.2	0.35			
Sn	1.9	1.2	1.3	1.6	0.8	1.2	1.4	1.9	1.7	1.5	1.45	1.3	0.8	1.2	1.3	1.9	1.1	1.3	1.5	0.9	1.7	1.3	1.4	1.2	1.3	1.1	1.5	1.3	0.5	0.7	0.6	0.6	1.27			
Cs	0.4	0.9	0.7	0.5	0.6	0.8	0.4	0.5	0.8	0.4	0.62	0.7	0.6	0.5	0.4	0.6	0.9	0.4	0.5	0.8	0.6	0.6	0.5	0.8	0.6	0.5	0.6	0.5	0.6	0.6	0.57	0.63				
Ba	80	120	111	100	140	120	140	131	135	112	119	123	97	93	87	94	93	132	122	130	120	109	114	120	122	123	119	121	114	114	114	120.2				
La	7	12	8	9	12	12	9	7	11	6	9.3	9	11	10	9	8	11	8	10	11	12	9.9	9.6	10	11	9	14	11	9.8	10.4	8.6	9.6	9.97			
Ce	14	23	16	17	24	23	16	15	18	15	18.1	24	23	25	17	18	15	24	23	15	24	19.9	19	20	19	23	22	21	19	18	20	19	19.5			
Pb	14	40	30	34	37	33	15	36	38	31	30.8	34	35	25	16	26	37	34	35	40	33	31.5	32	10	8	13	9	10	11	10	8	9.7	25.63			
Th	1.6	2.9	1.7	2	3.2	2.8	1.9	1.5	2.6	2.1	2.21	2.3	3.4	2.6	1.7	1.3	2.2	1.6	1.8	3.1	2.2	2.22	2.2	2.3	2.3	2.2	2	2.1	2.1	2.1	2.32					
U	0.6	1	0.7	0.8	1.1	1	0.8	0.6	1	0.5	0.81	0.9	1.2	1	0.7	0.4	0.8	0.7	0.8	1	0.9	0.84	0.8	0.7	0.6	0.6	0.5	0.6	0.9	0.7	0.8	0.8	0.97			

* (Kabata-Pendias and Pendias 1992); Δ (Van loon and Duffy 2005); Ω (Kabata-Pendias and Mukherjee 2007).
 S= South Industrial samples; N= North Industrial samples; C= Citadel samples; B= Background samples; Av = average.

CORRELATION COEFFICIENT

The correlation coefficients for the analyzed elements are shown in (Table 2) Regression accordance tests were run to understand the meanings of the interpretations of the correlation coefficients. The majority of the correlation coefficients were significant with a 95% and 99% probability. The trace elements such as Mn, Co, Ni, Zn, As, Cd, Pb, Cr, and U, have significant positive correlations with most major elements. These groups of trace elements have significant positive correlations with Fe, Al, Na; and significant negative correlation with Ca and Mg. The important heavy trace metals V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb and to some degree U have significant positive correlations with each other.

The lanthanides (La, Ce) and actinides (U and Th) have significant positive correlations with Y and Zr indicating their common host mineral which is most probably zircon; all these elements also have significant positive correlations with Li and to a lesser degree with Ga, Rb, Sr, Be and Cs.

P shows significant positive correlation at the 0.01 level with Rb, Sc, and significant positive correlation at the 0.05 level with K, Se, and significant negative correlation at the 0.01 level with Zn, As, V, and significant negative correlation at the 0.05 level with Pb.

FACTOR ANALYSIS

Factor analysis was intended to show the dependant structures among grouped variables (Maiz, *et al.*, 2000; Arik and Nalbantplar 2005). The recognition of these associations allows for the creation of a small number of hypothetical variables known as factors, with the aim of finding a simple order related to the observed variables. The grouping of major and trace elements which behave coherently, enables an assessment to be made of the geochemical processes (factors) acting in the environment pollution of the study areas (Yaldiz, 2007). Factor analysis in the present study was conducted using the components of distinct groups which have a high positive correlation in the soils. The R-mode factor analysis results for 36 elements, including varimax factor rotation of the factor matrix, were used. All of the variables have significant extraction values in terms of the principal component analysis (Table 3).

There are eight factors with initial Eigenvalues >1 in the factor analysis of the soil samples. These factors represented 85.04% of the total variation. The weights of the remaining factors, which have 14.96% of the total change, are low, and therefore were ignored in the factor analysis (Table 3). Among these eight factors, the first four

factors represent 70.26% of the total variation and each has >7% variance which were taken into consideration.

The first factor has two opposing poles comprising 30.63% of the total variation. The first pole is represented by significant positive weights of Fe, Al, Na, K, Cd, Ni, Co, Mn, As, Pb, Zn, Cr, U, Y, V, Th, Cu, Li, Mo, Cs and Ga which are in inverse relation with second pole represented by significant negative weights of Ca and Mg (Table .3; Fig. 3).

The second factor has 23.19 % of the total variation with two opposing poles. The first pole is represented by significant positive weights of Al, Mg, K, Th, Zr, La, Rb, Be, Li, Y, Sr, Ce, P, Ga, Ba, Cs, U, Sc, B and Se. which are in inverse relation with the second pole. The second pole of the second factor shows significant negative weights of Fe, Sn, Cu, Zn, Mo, V, Pb, Cr and Ni (Table 3; Fig. 3).

The third factor has 9.42% of the total variation and is represented by significant positive factor weights of P together with the K, Na, Se, Sc, Mo, Sn, Ni, Co, Mn, B and Rb elements which are in inverse relation with U, V, Zn, Th, Cs, Y, and Zr (Table 3).

The forth factor has 7.02% of the total variation and is represented by significant positive factor weights of Mg, Ga, Cu, Sn, Sr, Be, Rb, Li, Ce, Pb and U which are in inverse relation with Ba, B, Cs, Sc, Y and Cd.

Table 2: Correlation Coefficients of the Analyzed 35 Elements in 27 Soil Samples.

Fe	Ca	K	Al	Mg	Na	P	Li	Be	B	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Ga	As	Se	Rb	Sr	Y	Zr	Mo	Cd	Sn	Cs	Ba	La	Ce	Pb	Th	U		
1	-.91**	0.33	.92**	-.68**	-.55**	-0.09	0.23	-0.16	0.03	0.04	0.36	.74**	.87**	.94**	.93**	.39*	.68**	0.21	.84**	-0.12	0.12	-0.1	0.36	0.01	.39*	.90**	0.15	0.11	-0.05	0.12	0.14	.85**	0.17	.43**		
		1	-.49**	-.91**	-.54**	.46*	0.08	-0.19	0.14	-0.18	0	-0.32	-.68**	-.80**	-.85**	-.38*	-.61**	-0.12	-.80**	0.16	-0.17	-0.02	-.47*	-0.08	-0.32	-.90**	-0.03	-0.14	-0.04	-0.19	-0.08	-0.73**	-0.26	-.49**		
			1	.53**	-0.1	.45*	0.26	0.14	0.28	0.04	-0.12	0.15	.47*	0.37	.55**	-0.07	-0.14	0.13	0.02	0.18	.43*	.51**	0.25	0.22	0.19	0.21	-0.08	-0.05	0.04	0.09	0.11	0.03	0.25	0.1	K	
				1	-.55**	.50**	0.02	0.36	0.08	0.06	0.02	0.31	.66**	.87**	.93**	0.29	.52**	0.3	.71**	-0.11	0.3	.51**	.50**	0.25	0.24	.80**	-2	-0.27	0.02	0.28	0.26	.74**	0.4	.56**	Al	
					1	-0.34	0.3	0.1	0.34	-0.1	0.1	-0.29	-0.41	-.56**	0.21	.58**	0.26	.69**	0.21	0.18	0.25	-0.27	0.12	-0.32	.72**	0.02	-0.05	-0.07	0.04	0.22	.52**	-0.1	-0.32	Mg		
						1	0.15	0.17	-0.12	-0.01	0.19	0.01	0.26	.69**	.63**	.50**	0.09	0.3	0.02	.39**	-0.16	0.05	-0.05	0.24	0.06	0.38	0.47	0.04	-0.12	0.07	-0.07	0.17	.47*	0.14	0.2	Na
							1	0.31	0.28	0.28	.56**	-0.1	0.08	0	0.05	-0.36	-.7**	0.17	-.56**	.48*	.61**	0.33	0	-0.24	0.1	-0.23	0.02	-0.33	-0.09	0.25	0.21	-.48*	0.16	-0.36	P	
								1	.40*	0.04	0.17	0.08	0.05	0.29	0.19	0.31	-0.15	-0.11	.56**	0.01	0.27	.70**	0.3	.47*	.65**	-0.21	0.18	-0.37	.47**	0.32	.55**	.64**	0.06	.62**	.43**	Li
									1	0.1	0.16	-0.06	-0.09	-0.01	-0.19	-0.08	-0.3	-0.25	0.31	-0.23	0.14	.56**	0.32	.52**	-0.17	-0.37	.50**	0	0.36	0.25	-0.14	.57**	0.3	.36*	Be	
										1	0.33	-0.01	0.09	0.06	0.04	0.14	-0.45*	-0.2	0.02	-0.03	0.06	0.25	0.32	0.37	0.16	-0.03	0.3	-0.23	0.31	0.35	0.33	-0.02	-0.14	0.21	-0.06	B
											1	-0.24	0.16	0.1	0.12	0.01	-0.36	-.40*	0.03	-0.21	.52**	0.24	-0.11	0.23	0.12	0.03	0.06	-0.18	-0.2	0.27	0.16	0.34	-0.19	0.12	-0.22	Sc
												1	0.37	-0.17	-0.29	0.26	.44*	.59**	-0.17	.50**	-0.25	-0.19	-0.16	0.08	-0.26	0.01	.39*	0.23	0.05	0.05	-0.31	-0.19	.61**	-0.14	0.17	V
													1	.55**	.64**	.61**	.43*	.50**	0.18	.66**	-0.01	0.22	-0.25	0.35	-0.08	0.14	.66**	0.13	0.05	-0.23	0.12	-0.03	.72**	0.1	0.32	Cr
														1	.91**	.83**	0.14	.49**	0.24	.65**	-0.1	0.18	0.04	.40*	0.13	0.32	.78**	-0.23	0.17	0.05	0.2	0.21	.70**	0.29	.39*	Mn
															1	.38**	0.26	.60**	0.06	.74**	-0.05	-0.09	-0.15	0.35	0.01	.46*	.83**	-0.03	0.07	-0.01	0.09	0.1	.77**	0.18	0.37	Co
																1	0.34	.53**	0.23	.71**	-0.06	0.27	0.1	0.38	0.09	.48*	.83**	0.09	0.12	0.03	0.17	0.16	.72**	0.24	.39*	Ni
																	1	.51**	0.05	.44*	-0.28	-0.23	-0.23	-0.29	-.40*	0.16	0.21	.56**	-0.22	-0.3	-0.24	-0.22	.54**	-0.33	0.11	Cu
																		1	0.01	.92**	-0.38	-0.34	-0.27	0.08	-0.29	0.29	.70**	0.22	0.02	-0.22	-0.21	-0.13	.90**	-0.1	.45**	Zn
																			1	0.1	0.01	.49**	.51**	0.29	0.44	-0.37	0.14	0.03	0.15	-0.02	.52**	.63**	0.18	0.33	.38*	Ga
																				1	-0.35	-0.16	-0.24	0.31	-0.11	0.27	.88**	0.11	0.19	-0.12	0	-0.02	.92**	0.09	.53**	As
																					1	0.32	-0.1	-0.06	-0.02	-0.06	-0.22	-0.04	-0.1	0.02	-0.02	0.11	-0.31	-0.08	-0.29	Se
																						1	.49**	.44*	.67**	-0.22	0.07	-0.29	0.16	0.05	.53**	0.31	-0.15	.63**	0.28	Rb
																							1	0.29	.46*	-0.25	-0.08	-0.25	0.05	0.04	0.37	.39*	-0.2	.39*	0.24	Sr
																								1	.71**	-0.24	.50**	-0.71**	0.33	.58**	.39*	0.24	.79**	.70**	Y	
																									1	-0.29	0.08	-0.68**	.46*	0.33	.71**	-0.14	.93**	.66**	Zr	
																										1	0.28	0.33	-0.03	-0.25	-0.35	-0.26	0.29	-0.29	-0.25	Mo
																										1	-0.08	0.25	0.14	0.23	0.12	.78**	0.26	.50**	Cd	
																											1	-0.35	.51**	.49**	0.24	0.13	.47*	0.27	Cs	
																												1	0.33	.49**	0.24	0.13	.47*	0.27	Cs	
																													1	0.31	.50**	-0.05	.72**	.48*	Ia	
																														1	0.03	.47*	0.33	Cc		
																															1	0.04	.48*	Pb		
																																	1	.75**	Th	
																																		1	U	

**Correlation is significant at the 0.01 level (2-tailed) shown in bold numbers.

*Correlation is significant at the 0.05 level (2-tailed). shown in bold italic numbers.

Table 3: The R-mode Factor Analysis of the Studied Soil Samples.

Element	Component			
	1	2	3	4
Fe	0.957	- 0.156		
Ca	- 0.936		- 0.155	
K	0.352	0.305	0.561	
Al	0.939	0.127		
Mg	- 0.684	0.269		0.396
Na	0.563		0.346	
P		0.485	0.804	
Li	0.303	0.694		0.274
Be		0.67		0.309
B		0.342	0.202	- 0.46
Sc		0.355	0.516	- 0.314
V	0.411	- 0.366	- 0.358	
Cr	0.709	- 0.179		
Mn	0.873		0.266	
Co	0.903		0.285	
Ni	0.907	- 0.121	0.286	
Cu	0.359	- 0.56		0.474
Zn	0.712	- 0.516	- 0.354	
Ga	0.236	0.439		0.681
As	0.868	- 0.346	- 0.244	
Se		0.26	0.559	
Rb		0.735	0.612	0.313
Sr		0.587		0.357
Y	0.534	0.63	- 0.234	- 0.228
Zr		0.875	- 0.228	
Mo	0.279	- 0.427	0.469	- 0.249
Cd	0.933			- 0.205
Sn		- 0.698	0.343	0.432
Cs	0.255	0.429	- 0.243	- 0.35
Ba		0.427		- 0.515
La	0.236	0.74		
Ce		0.582		0.223
Pb	0.861	- 0.353	- 0.291	0.158
Th	0.366	0.826	- 0.257	
U	0.621	0.388	- 0.547	0.124
Eigen value	11.026	8.349	3.392	2.526
% variance	30.629	23.192	9.423	7.016
Cumulative%	30.629	53.821	63.243	70.260

DISCUSSION

Based on correlation coefficient and factor analysis results of soil samples, five element groups were recognized.

The first group is represented by Fe, Al, Na, K, Cd, Ni, Co, Mn, As, Pb, Zn, Cr, U, Y, V, Th, Cu, Li, Mo, Cs and Ga element assemblages. This group represents clay minerals which exist in the soil samples representing the first pole of the first factor (Table 3; Fig. 3). The concentrations of these elements in both industrial areas are higher than those in the local background and ancient Erbil Citadel soil samples. Most of these elements have not reached the pollutant levels when compared with the international standards except Ni, Cu, Zn, Co, Mn and Pb (Table 1). The concentrations of Ni, Cu, and Zn are about 4-, >2-, and 1.5-times their values in the international standards which means that they are of pollutant levels.

The source of Ni could be from ultrabasic rocks, serpentinite or low grade metamorphic rocks (Burt *et al.*, 2001), or from anthropogenic sources such as smelting, mining and industrial activities. It can form organic complexes, or soluble complexes with sulfates, carbonates and bicarbonates (Sposito, 1989). The concentration of Ni in the studied soils of Citadel and the background samples are normal and about the same as those in the international standards; however its concentration in both industrial areas is about four times as those of the local background and the international standards (Table 1). This indicates that the main source of this excess Ni in the two industrial districts are from the industrial activities rather than the natural lithological sources such as the ultrabasics, serpentinites and the low grade metamorphic rocks which are exposed in the border zones of northeastern Iraq. Ni functions as exchangeable cation bound by oxides, and is mobile under reducing conditions (Lee *et al.*, 2001). The studied soils are of oxidizing nature which means that they have reduced mobility. For this reason, and in spite of the pollutant levels of Ni in the industrial districts of Erbil City, it still cannot be considered toxic or hazardous but it should be monitored and listed among the possible pollutant heavy metals in the area.

The concentration of Cu in the studied soils of Citadel and the background samples are close to those of the international standards; however its concentration in the two industrial areas is about three times as much (Table 1). This indicates that the main source of this excess Cu in the two industrial districts is from the anthropogenic and industrial activities. Normally such activities involve municipal sludge, wastes from smelting industries and poultry (Reed and Martens, 1996). Copper in soil can be absorbed by carbonates, clay and oxides (Romkens and Salomons, 1998). It may be present as exchangeable adsorbed cation involving site exchanges in acid soil conditions (Kabata-Pendias and Pendias, 2001). There are copper occurrences related to serpentinites, ultramafics, gabbros, metavolcanics and/or hydrothermal quartz veins in Penjween, Mawat and Bulfat massifs of north eastern Iraq (Al-Bassam and Hak, 2006) which could be the source of natural copper background

levels in the studied soils. Copper is generally immobile element due to its adsorption on organic materials and mineral surfaces (Reed and Mrtens. 1996, Kabata-Pendias and Pendias. 2001) and for this immobile nature of copper, it cannot be hazardous or highly toxic in the studied areas.

The concentration of Zn in the studied background samples is similar to those of the international standards, slightly less in the Citadel soils, while it is ~1.8 times in the soils of the two industrial districts (Table 1). This suggests that the anthropogenic and industrial activities are the source of excess Zn concentrations in the two industrial districts. There are many Zn-Pb mineralization occurrences in northeastern part of Iraq which are the probable source of the natural concentrations of Zn and many other associate dmetals (Pb, Cu, Mn, Cd, ..) in the studied soils. The most prominent mineralized area is that of Marapasta which occurs within basic, ultrabasic rocks, phyllites, limestones and skarns (Al-Bassam and Hak, 2006). The behavior of Zn is generally similar to that of Cu in many aspects including reactivity in soil (Romkens and Salomons.1998), mobility (Reed and Martens, 1996; Kabata-Pendias and Pendias, 2001), and sources of pollution (Reed and Martens, 1996). For these reasons, its relatively higher concentration in the soils of the industrial districts is still not of toxic or hazardous levels.

Meanwhile Co, Mn, and Pb have close concentrations to those of the international standards which are in critical status of pollution but still have not exceeded pollutant levels. The source of these metals are the same as that mentioned above for Ni, Cu and Zn; mineralized areas in northeastern Iraq which is part of the Zagros Suture Tectonic Zone of Iraq. The trace elements of this group have significant positive correlation with Fe and Al (Table2); (Myers and Thorbjornsen, 2004) have recognized similar relation between these elements. The high concentrations of these elements can be partially attributed to the human activities in the industrial area. Leaching process of these elements from their potential industrial sources is the main reason for their enrichment in the local soils (Papastergios *et al.*, 2004).

Human activities in industrial sites are among the reasons causing soil pollution by high concentrations of heavy metals such as Ni, Cu, Pb,.. as reported by (Chen, 2000) in industrial locations of Taiwan city. Similarly pollution by trace elements such as Ni, Zn, Co, Pb,.. close to soils of highways can be caused by vehicle exhausts and oil trash burning among other factors (Howari *et al.*, 2004). The excess of Cu concentration in soils is also attributed to the burning of wood, coal and plastic materials which increases the Cu levels in air that ultimately precipitate on ground and pollute soils; meanwhile the burning of vehicle oil rich in Cu and Pb also pollute soils (Baird, 2001). Among the reasons of excess Zn concentration in soil samples is the acidity of such soils because it can dissolve easily in acidic solution products coming from factories.

Soil pollution by Pb, Cu, and Zn can also originate from metal processing factories (U.S.EPA, 2005).

The second group is represented by Ca and Mg as a second pole of the first factor (Table 3; Fig. 3). The concentrations of these two elements in both industrial areas are less or equal to those in the local background and ancient Erbil Citadel soil samples (Table 1). They show significant positive correlation with each other, but have negative correlation with all other elements (Table 2). This group represents calcite which is a dominant constituent in the studied soils. The concentrations of Ca in all studied areas are higher than those of international soil standards. This is because these soils are of calcareous types (Kahraman, 2004).

The third group includes Al, Mg, K, Th, Zr, La, Rb, Be, Li, Y, Sr, Ce, P, Ga, Ba, Cs, U, Sc, B and Se element assemblages which represent heavy minerals fraction. The concentrations of these third group elements in both industrial areas are less than those in the ancient Erbil Citadel soil samples except Al, Li, and U. The concentrations of the elements of this group in both industrial areas are equal or higher than those of the local background soil samples (Table 1). The elements with nearly equal concentrations are Mg, Zr, La, Rb, Be, Sr, Ba, Cs, Sc, B and Se; while those with higher concentrations are Al, K, Th, Li, Y, Ce, P, Ga and U. However these higher concentrations still have not reached the pollutant levels in comparison with the international standards levels (Table 1). There is an overlap between this group and the first group of the first factor due to the presence of Al or clay minerals in both. This group represents first pole of the second factor (Table 3; Fig. 3).

The fourth group represents Sn, Cu, Zn, Mo, V, Pb, Cr and Ni. The concentrations of these elements in both industrial areas are higher or close to those in the local background and the ancient Erbil Citadel soil samples (Table 1). It may indicate the effect of manufactured metals and alloys derived from car repair shops and other metal-dealing local industries.

This group represents the second pole of the second factor (Table 3; Fig. 3). Excluding Sn, there is an overlap between this group and the first group of the first factor.

The fifth group represents P together with K, Na, Se, Sc, Mo, Sn, Ni, Co, Mn, B and Rb represented by some samples rich with phosphorous taken from the ancient Erbil Citadel (Table 1). The P and most elements of this group are in inverse relation with U, V, Zn, Th, Cs, Y, and Zr (Table 2). This group can be called as the paleo-anthropogenic group since the existence of phosphorus and the associated elements might be due to the human and/or domesticated animal remains that inhabited the ancient site of the Erbil Citadel during the historic times thousands of years ago. Such remains include bones and household metal utensil. Traces of tiny bones were found within the sampled soils which could belong to the graveyards or domestic animals

used by the inhabitants (Tables 1 to 3). The concentration of P in the Erbil Citadel samples are about three-times as those of international standards and seven-times as those of local backgrounds which means that they are pollutant; while those of the industrial areas are about half that of international standards and 1.5 that of local background levels (Table 1).

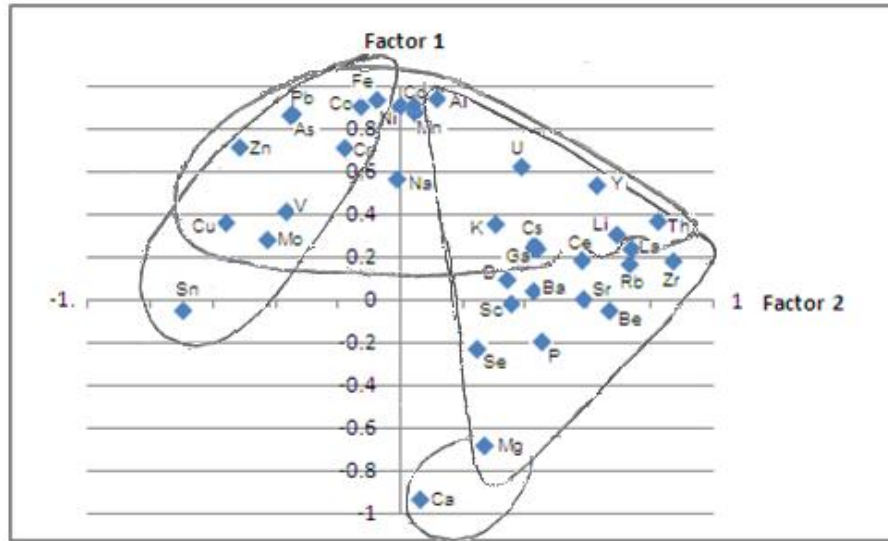


Fig. 3: Relationship between Factor 1 and Factor 2 to all Variants.

CONCLUSIONS

The following conclusions can be drawn from the study results:

1. The investigated elements are isolated into five groups. The elements of the first two groups are attributed to the predominant minerals forming the bulk of the studied soils, the clays and carbonates, respectively.
2. The third group can be attributed to the heavy mineral fractions within the soils.
3. The fourth and fifth groups are attributed to the anthropogenic factors.
4. The trace elements Ni, Cu, and Zn can be considered pollutant since their concentrations are about 4-, >2-, and 1.8-times their value in the international standards. However, they are still not of toxic or hazardous levels because of their immobile nature under the current oxidizing environmental conditions but should be

monitored in future. The closely related Co, Mn, and Pb have concentrations close to those of the international standards which are in critical status of pollution but still have not exceeded the limit.

5. The concentration of P in the Erbil Citadel samples are three-times as those of international standards and seven-times as those of local backgrounds which means that they are pollutant; while those of the industrial areas are about half that of international standards and 1.5 that of local background levels.
6. The source of most trace elements in the studied soil are basic/ultra basic igneous rocks and metamorphic rock units exposed in the ophiolitic thrust zone of northeastern Iraq which also contains some mineralized occurrences.

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