



Spatial Distribution of Some Alkali and Alkaline Earth Metals of Selected Locations in Sulaimani Governorate, Kurdistan Region, Iraq.

Salih N. Majid¹ and Shuela M. Sheikh-Abdullah¹

1Faculty of Agricultural Science-Sulaimani University, Bakrajo Street, Sulaimani -Iraq

Corresponding author, e-mail: salih.majeed@univsul.edu.iq.

Article info	Abstract
Original: 15 October 2016 Revised: 9 December 2016 Accepted: 9 January 2017 Published online: 20 June 2017 Key Words: <i>Agglomerative Hierarchical Clustering (AHC), Alkaline earth metals, Alkali metal, principal component analysis (PCA). Sulaimani Governorate</i>	This study aimed to determine the background concentration and also to assess the distribution pattern of some alkali metals (Na and K) and alkaline earth metals of (Mg, Ca, Be, Sr and Ba) along depth increments (0 to 15 and 15 to 30 cm) of soils from ten (10) locations in Sulaimani Governorate- KRI. The soil samples were digested by aqua regia and then analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The results were statistically analyzed through both principal component analysis (PCA) and cluster analysis to show the similarity and dissimilarity of the soils among the studied locations. The results showed that there was no consistent distribution pattern for the studied metal along the selected depths due to the variation of the input sources of the metals and their quantities in the parent materials and/ or to continuous mixing by agricultural operations. It was also found that the contents of the studied metals based on the highest concentration, followed the following sequence $Ca > Mg > K > Ba > Sr > Na > Be$. According to the results of PCA analysis, the explained variation for two factors accounted for % 60.25 of the total variance. On the other hand, the agglomerative hierarchical clustering classified the soils of the ten locations into four major groups at a significant dissimilarity percent of about 57%.

Introduction

From various origins such as; lithogenic, pedogenic and anthropogenic soils get their different elements (metals, nonmetals and metalloids). Lithogenic elements inherited directly from the lithosphere (parent material). Pedogenic elements are also of lithogenic origin, but their concentration and distribution in soil layers and soil particles are changed due to pedogenic processes. Human activity and pollution are sources of anthropogenic elements which deposited directly or indirectly into soils [1].

Metals among all the other chemical contents in soil are considered to be of a specific ecological and biological significance. The metals in soil could be variously classified, one being those metals that would be identified as alkali metals and other as alkaline earth metals. Under this classification, potassium (K) and sodium (Na) as alkali metals, so calcium (Ca) and magnesium (Mg) as alkaline earth metal are the most constituent part of the lithosphere rocks and belong to the most 8 abundant elements in the Earth's crust. From a nutritional perspective the elements of K, Ca and Mg are considered as macro-elements of the essential plant nutrients, while Na is belong to beneficial elements for plant nutrition [2].

All alkali and alkaline earth metals react so readily with any water in the environment to form ions and compounds, therefore no metals of those groups would ever be found as the native metal [3]. Alkali metals

comprise the group 1 of the periodic tables, while the alkaline earth metals are referred to as group 2 of the periodic tables. Each group have six metals which they are; lithium, (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr) for group 1 since hydrogen is a nonmetal in group1, but for group 2 the metals are; beryllium (Be), magnesium Mg, calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra), [4]. However, alkali metals are characterized by the following points; they have very similar properties and of a single valence electron (form +1 ion), they are highly reactive and are never found in elemental forms in nature [5]. Furthermore, alkali metals react aggressively with the halogens to form the alkali metal halides and also react with water to form strongly alkaline hydroxides and thus should be handled with great care [6 and 7].

On the other hand, all alkaline earth metals occur in nature and have also very similar properties, but they occur in all their ores as +2 ions form (have two valence electrons) when compared to metals in group 1 [8]. All alkaline earth metals react with the halogens to form ionic halides, as well as reacting with oxygen to form oxides.

At Sulaimani Governorate, data on the concentrations and distribution patterns of alkali and alkaline earth metals elements in soils are really absent; therefore, this research aimed to determine the total concentration levels of some alkali metals (Na and K) and alkali earth metals of (Mg, Ca, Be, Sr and Ba) at (0 to 15 and 15 to 30 cm) depths of some selected locations at Sulaimani Governorate in order to establish how the lithological bedrock, or parent material affects on concentration levels of those metals in soils of the selected locations. The study also aimed to apply multivariate statistical analysis of both principal component analysis (PCA) and cluster analysis to show the similarity and dissimilarity of the soils among the studied locations.

Consequently the obtained results from the present study could help with the findings of similar future's studies to make a metal database of those groups in soils of Sulaimani Governorate.

Materials and Methods

Soil Sampling

The area under study (Sulaimani Governorate) is situated to the east of Iraqi Kurdistan Region and to the northeast of Iraq on the border with Iran. Sulaimani Governorate comprising a total area of 17,023 km² including a large area of agricultural land and has a total population of about 1.937 million. Sulaimani hosts the fertile plains of Sharazur and Bitwen, which give way to hills and the Zagros mountain range in the northeast [9].

Representative bulk soil samples were randomly collected from ten (10) locations of the surface (0-15) and subsurface (15-30 cm depth) in 2015 out of three dominant soil orders (Vertisol, Mollisol and Entisols) that occurring in Sulaimani Governorate. These depths have been established, because they are somewhat typical for tillage and seedbed preparation, as well as for nutrient supply to plants. The samples were collected in each location from a chosen square of 100 x100 m. Moreover, the GPS coordinates (latitude and longitude) were also defined for each sample location (Table 1 and Figure 1). At each sampling site a composite soil samples of about 5 kg were obtained by mixing subsamples from 6 sites using a shovel, then the composite soil samples were freed from plant roots and gravels whenever they were present.

Sample preparation

The soil samples were air-dried at room temperature for about a week, then gently crushed and sieved at 2 mm with a stainless-steel sieve to avoid any contamination and then stored for subsequent analyses. For organic carbon and metal analysis, 50 g soils of 2 mm from those samples were further pulverized to pass through a 0.50 mm sieve. Hygroscopic moisture was measured in about 10-g air-dried soil for each soil samples gravimetrically after 24 h of oven-drying at 105 °C [12].

Table 1: Locations, geographical coordinates, elevation, land use and soil orders of the studied locations.

No	Locations	geographical coordinates		Elevation (m)	Land Use	Orders	References
		Longitude	Latitude				
1	Nalparez	45° 50' 56"	35° 34' 56"	1220	Cultivated-wheat	Mollisols	[10]
2	Kanipanka	45° 42' 58"	35° 22' 56"	594	Cultivated-wheat	Mollisols	[11]
3	Qaragoll	45° 37' 18"	35° 21' 30"	606	grassland	Vertisols	[11]
4	Arbat	45° 35' 30"	35° 24' 35"	550	Cultivated -wheat	Vertisols	[11]
5	Bakrajo	45° 21' 55"	35° 32' 10"	776	Cultivated -wheat	Vertisols	[11]
6	Bakhebakhtyare	45° 22' 08"	35° 34' 08"	823	Forest-pine	Vertisols	[11]
7	Goizha	45° 28' 19"	35° 34' 08"	1076	grassland	Mollisols	[11]
8	Kani -Sard	45° 33' 59"	35° 38' 46"	1093	Grape orchards	Entisols	[10]
9	Khewata	45° 30' 50"	35° 44' 28"	959	Cultivated -wheat	Entisols	[10]
10	Dukan	45° 05' 04"	35° 50' 04"	877	grassland	Mollisols	[10]

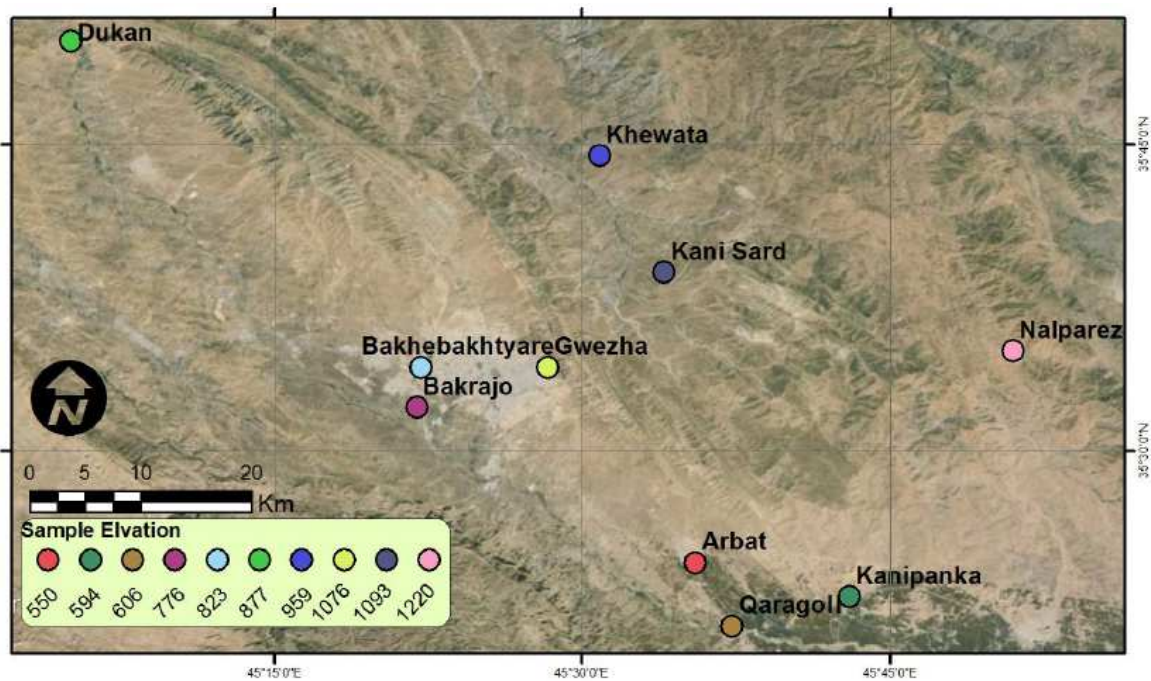


Figure 1: Location map showing the sampling sites and their elevations.

Analytical methods of the soil samples;

pH-value: Soil pH was measured in a saturated soil paste extract according to [12]. After leading the saturated soil paste stand for four hours to reach the equilibrium state, the pH-values were measured by using a portable pH-meter (model WTW 330i/ Germany).

ECe-Value at 25 °C: EC of extract from soil saturated paste was measured as described by [12] using a portable EC-meter (model WTW 330i/ Germany).

Organic matter (OM) content: Firstly the content of organic carbon (OC) in soil samples were determined by Walkley-Black method (wet oxidation by potassium dichromate $K_2Cr_2O_7$ and concentrated H_2SO_4) as described by [13], then the content of organic matter (OM) was calculated as follows;

$$\% \text{ Organic matter} = \% \text{ organic carbon} \times 1.724 \text{ (factor)}$$

Percent of carbonate minerals (equivalent $CaCO_3$ percent): $ECaCO_3$ in soil samples were determined by the acid-neutralization method according to the method 23c of U.S. Salinity Laboratory Staff, 1954 [14].

Total content analysis of alkali and Alkaline earth metal: The total content of the 7 metal of alkali metals (Na and K) and alkali earth metals of (Mg, Ca, Be, Sr and Ba) in soil sample were determined in the aqua regia extractions, following the procedure recommended by the [15] as follows: A 1.0-g of thoroughly mixed air dry soil (< 0.5 mm size diameter) was digested from each sample with 20 ml of aqua

regia mixture (HCl of 37% and HNO₃ of 70% in a ratio of 3:1) at room temperature for 16 hour. Then the mixtures were heated at 130 °C for 2 hour using the automated Kjeldahl digester (model Tecator Digestion System Unit 2540 Auto/ Denmark-Sweden). The obtained suspension was then filtered through an ashless Whatman 42 filter paper, diluted to 100 ml with 0.5 M HNO₃, and stored in polyethylene bottles at 4 °C for element analysis. All used glass and plastic-wares were previously soaked in 10% HNO₃ and rinsed thoroughly with deionized water. The metals were analyzed by using inductively coupled plasma-optical emission spectroscopy ICP-OES (model PerkinElmer, precisely Optima 2100/USA). Duplicate soil samples were analyzed for each soil sample and the average values for each parameter were taken out, additionally, the analytical calculation for the soil parameters were conducted on oven-dry weight base.

Statistical analysis

Statistical analysis for all measured variable was performed using Excel software. Correlations between the soil chemical parameters and the metals and also among the metals themselves were carried out. Multiple comparisons tests (Duncan's test) were also performed to find out the significance differences between the average concentrations of the studied alkali and alkaline earth metals for the studied locations.

To interpret the data in a more relevant form and to predicate a high degree of interrelations among a set of variables, principal component analysis (PCA) also called factor analysis was used for obtaining the most interpretable linear combinations within the dataset of metals results and the chemical studied parameters through the studied locations. Principal component analysis (PCA) is a multivariate technique that analyzes a data by several inter-correlated quantitative dependent variables. Conceptually the goal of PCA is to reduce the number of variables of interest into a smaller set of components, or its goal is to extract the important information from the observation of a table, to represent it as a set of new orthogonal variables called principal components, and to display the pattern of similarity of the observations and of the variables as points in maps [16].

Also in current study, Agglomerative Hierarchical Clustering (AHC), as one of the most statistic popular clustering methods of multivariate statistical analysis has been used for clustering (or classification) the soils of the studied locations into groups by using the XLSTAT statistical software. AHC as iterative classification method (successive clustering operations or dendrogram) works from the similarity or dissimilarities between the objects to be grouped together.

Results and Discussions

Table (2) shows the results of the chemical properties for the soils samples at the studied locations. The pH of soil is considered to be one of the most important properties of soils, because it controls the concentration of toxic metals and also the availability of nutrients such as; iron, manganese, zinc, copper, boron and phosphorus to plants. In this study the pH values for the soil saturation extract had generally a slight alkaline reaction and ranged between 7.70- 8.32 and 7.83-8.19 for the surface and subsurface samples respectively. The differences in pH range for both surface and subsurface samples were 0.62 and 0.36 respectively. Although the surface range was higher as compared with the subsurface range, but the differences were relatively not too high among the locations. In locations; 1, 6, 7 and 10 the pH values for surface samples were a little bit higher than in subsurface samples. The alkalinity of the soil samples might be due to the presence of high calcium carbonates minerals and this was to be expected simply because the studied soils are calcareous and contained more than 5% carbonate [17]. These results were in very close agreement with [18], who reported that in countries with Mediterranean, arid and desert climates, soils containing calcium carbonate in one or several of their horizons are frequent.

The Electrical Conductivity (ECe) readings of the saturated paste extract showed that the soils were not non-saline since the ECe of them were less than 4000 $\mu\text{S cm}^{-1}$. In general, the values ranged between 147 to 389 and 150 to 335 $\mu\text{S cm}^{-1}$ for the surface and subsurface samples at studied locations. The relative variations in ECe values among the locations might be due the fact that these were correlated with soil properties that affect crop productivity, including soil texture, cation exchange capacity (CEC), drainage conditions, organic matter level, salinity, and subsoil characteristics [19].

The organic matter content was varied from 14.7 to 50.4 and 7.1 to 32.8 g kg⁻¹ for the surface and subsurface samples respectively. Both the upper limits of organic matter content for surface and subsurface samples were found in location 1 and this can be attributed to high precipitation rate and consequently much vegetations covers at this location. In general, the organic matter content in surface samples was higher than those of subsurface samples at all the studied locations except location 4 which was somewhat similar at both depths. However, the surface soil contains generally a relatively more organic matter than the other soil layers. In a research study by [20], it has been found that significant quantities of alkali metal cations associated with humic acid fraction of the organic matter.

Table 2: Some chemical properties for the soil samples of the studied Locations.

No.	Locations	Depth (cm)	pH	ECe ($\mu\text{S cm}^{-1}$)	O.M. (g kg ⁻¹)	ECaCO ₃ (g kg ⁻¹)	
1	Nalparez	S	0-15	7.85	281	50.4	48.6
		Sub	15-30	8.10	303	32.8	41.7
2	Kanipanka	S	0-15	7.70	218	14.8	208.3
		Sub	15-30	7.83	150	13.5	206.0
3	Qaragoll	S	0-15	7.81	160	19.0	115.8
		Sub	15-30	7.95	189	14.1	120.4
4	Arbat	S	0-15	7.90	191	20.1	189.8
		Sub	15-30	7.95	155	20.7	199.1
5	Bakrajo	S	0-15	7.84	174	14.7	254.6
		Sub	15-30	7.95	205	8.6	231.5
6	Bakhebakhtyare	S	0-15	8.25	272	30.7	217.6
		Sub	15-30	8.13	243	17.3	226.9
7	Goizha	S	0-15	8.32	147	15.5	134.3
		Sub	15-30	8.13	172	7.1	282.4
8	Kani-Sard	S	0-15	7.86	182	19.0	187.5
		Sub	15-30	7.95	335	14.8	217.6
9	Khewata	S	0-15	8.05	203	16.9	60.2
		Sub	15-30	8.12	156	16.6	69.5
10	Dukan	S	0-15	8.27	389	38.3	78.7
		Sub	15-30	8.19	248	24.8	152.8

As it is shown in Table 2, the equivalent calcium carbonate content was relatively high and the values were varied too much among the studied locations and ranged between 48.6 to 254.6 and 41.7 to 282.4 g kg⁻¹ in surface and subsurface samples respectively. The lower values for both surface and subsurface samples found in location 1 and this might be due to the high precipitation rate at this location which led to remove calcium carbonate from surface layers. On the other hands, the results showed that in all the studied locations except location 1 and 2, the calcium carbonate was predominantly higher in the layers lying below the surface layers, and this may be attributed to the effect of the parent material which contains high percent of calcium minerals or due the effect of rainfall because the studied soils could be classified between calcareous to extremely calcareous soil. Since the ECaCO₃ of some samples were more than 105 or 100g per kg soil.

Our findings for the above mentioned soil parameters were relatively close and in the same range with the values reported by [21 and 22].

The total concentration of (Na and K) as alkali metals and (Mg, Ca, Be, Sr and Ba) as alkaline earth metals at the studied locations are presented in Table (3).

Sodium (Na) is one of the most widely spread metal in soils; its content varies within 5900–8600 $\mu\text{g g}^{-1}$ [1]. This element is important for the soil forming process, because it affects the state of the soil adsorption complex [23]. In this study Na was found in the range (92 to 106) and (90 to 104) $\mu\text{g g}^{-1}$ soil for surface and subsurface soil samples respectively. Both the lowest values for surface and subsurface soils were revealed at location 9, furthermore, the lowest values for the surface layer was also repeated at location 4, while the highest values for surface and subsurface layers were observed at location 5 and 7 (Table 3 and Fig. 2).

Table 3: Total concentration of some alkali and alkaline metals for soil samples of the studied Locations.

No.	Locations	Depth (cm)	Alkali metals		Alkaline earth metals					
			Na	K	Mg	Ca	Be	Sr	Ba	
			$\mu\text{g g}^{-1}$	%	%			$\mu\text{g g}^{-1}$		
1	Nalparez	S	0-15	98	0.49	0.84	2.32	0.9	61	136
		Sub	15-30	92	0.52	0.80	1.92	1.0	52	140
2	Kanipanka	S	0-15	104	0.49	1.37	8.42	1.1	167	297
		Sub	15-30	95	0.40	1.31	8.21	1.1	161	272
3	Qaragoll	S	0-15	103	0.68	1.85	5.54	1.2	143	192
		Sub	15-30	95	0.50	1.77	5.62	1.1	141	175
4	Arbat	S	0-15	92	0.48	1.63	8.71	1.1	156	142
		Sub	15-30	95	0.50	1.62	8.80	1.0	155	143
5	Bakrajo	S	0-15	106	0.40	1.54	10.9	0.9	220	142
		Sub	15-30	101	0.43	1.49	11.5	0.9	209	133
6	Bakhebakhtyare	S	0-15	105	0.51	1.42	11.3	0.9	203	141
		Sub	15-30	101	0.53	1.41	11.3	0.9	200	134
7	Goizha	S	0-15	104	0.50	1.57	7.06	1.2	122	161
		Sub	15-30	101	0.49	1.39	12.60	1.0	173	146
8	Kani-Sard	S	0-15	96	0.48	1.45	9.04	1.1	151	190
		Sub	15-30	94	0.44	1.36	10.1	1.0	154	192
9	Khewata	S	0-15	92	0.43	1.61	4.08	1.2	76	156
		Sub	15-30	90	0.42	1.53	3.82	1.2	72	155
10	Dukan	S	0-15	97	0.49	1.98	7.05	0.9	95	123
		Sub	15-30	95	0.48	2.01	7.43	0.9	99	126

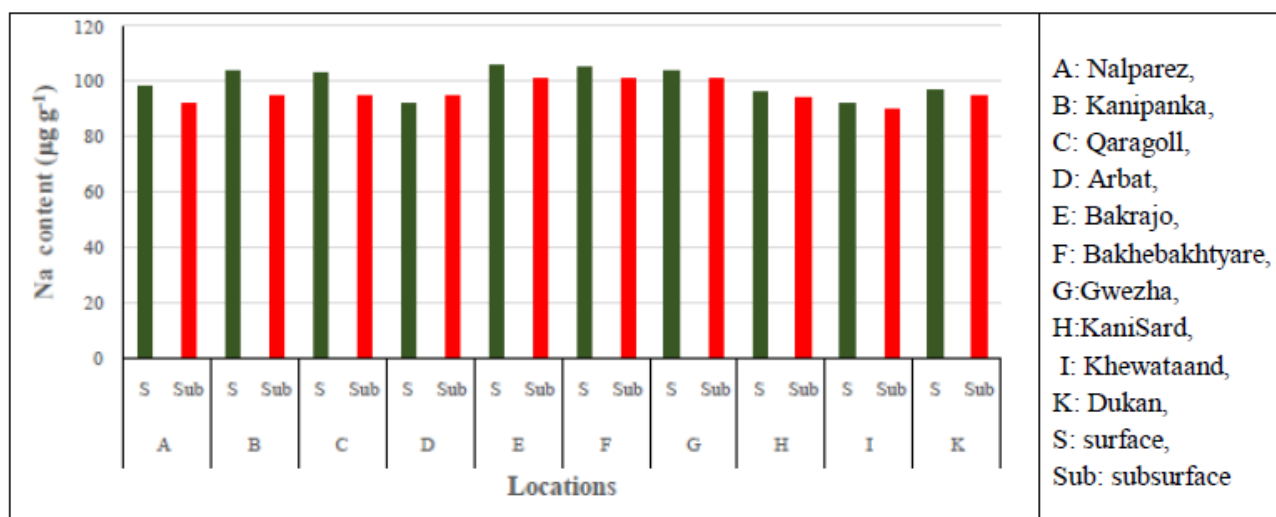


Figure 2: Total concentration of sodium (Na) in surface and subsurface samples at the studied locations.

Sodium (Na) was found in higher concentration in the surface layers rather than the subsurface ones at all locations except location 4 (Fig. 2). This trend was entirely similar to the trend of organic matter, thus significant quantities of alkali metal cations might be associated with humic acid fraction of the organic matter in the surface layer [20]. Similar trend and pattern of Na distribution was reported by [24] in soils and rocks of the southern Cis-Ural region. Conversely, Na had an increasing trend with depth in the wetland sediment of a monsoonal wetland in INDIA [25].

Duncan test revealed significant differences for the average concentrations of sodium (Na) among locations 5, 6 and 7 as compared to location 4 and 9 (Table 4). Additionally, Na was positively correlated with each of; CaCO_3 content, Ca and Sr concentration ($r = 0.491$, $r = 0.510$ and $r = 0.627$ at the level of significance alpha (α) = 0.050 respectively).

Other researchers have published a wider concentration ranges for sodium in their studies, as an examples, [25] found sodium to be in the range of 41-690 $\mu\text{g g}^{-1}$ in the wetland sediment of a monsoonal wetland in India. Additionally, [24] reported a wide range of Na content from (0.1 to 12270) and (41 to 690) $\mu\text{g g}^{-1}$ in soil and rocks of the southern Cis-Ural region.

Table 4: Multiple comparisons tests (Duncan’s test) between the average concentrations of the studied alkali and alkaline earth metals among the studied locations.

No	Location	Na ($\mu\text{g g}^{-1}$)	K (%)	Mg (%)	Ca (%)	Be ($\mu\text{g g}^{-1}$)	Sr ($\mu\text{g g}^{-1}$)	Ba ($\mu\text{g g}^{-1}$)
1	Nalparez	95.000ab*	0.505ab	0.820g	2.120e	0.950bc	56.500d	138.000cd
2	Kanipanka	99.500ab	0.445b	1.340f	8.315abc	1.100ab	164.000b	284.500a
3	Qaragoll	99.000ab	0.590a	1.81b	5.580cd	1.150a	142.000b	183.500b
4	Arbat	93.500 b	0.490ab	1.625c	8.755ab	1.050abc	155.500b	142.500cd
5	Bakrajo	103.500a	0.415b	1.515cde	11.200a	0.900c	214.500a	137.500cd
6	Bakhebakhtyare	103.000a	0.520ab	1.415ef	11.300a	0.900c	201.500a	137.500cd
7	Goizha	102.500a	0.495ab	1.480de	9.830ab	1.100ab	147.500b	153.500c
8	Kani -Sard	95.000ab	0.460b	1.405ef	9.570ab	1.050abc	152.500b	191.000b
9	Khewata	91.000b	0.425b	1.570cd	3.950de	1.200a	74.000cd	155.500c
10	Dukan	96.000ab	0.485ab	1.995a	7.240bc	0.900c	97.000c	124.500d

Note: * Similar letter or letters means no significance difference between them was present..

Potassium (K) like Na is also widespread in the earth’s crust and its main source in soil is potash rock, a group of sedimentary substances often found in association with rock salt, gypsum, and dolomite. Furthermore, potassium is a component of many of Earth’s minerals, including muriate of potash or sylvite (KCl), carnallite ($\text{KCl} \times \text{MgCl}_2 \times 6\text{H}_2\text{O}$), lang beinite [$\text{K}_2\text{Mg}_2(\text{SO}_4)_5$], and polyhalite [$\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \times 2\text{H}_2\text{O}$], [3]. Potassium is one of the essential nutrients in plants and its uptake by crops under good growing conditions is high, often equal to nitrogen (N) uptake and several times the quantity of phosphorus (P) uptake. Potassium is used in photosynthesis, sugar transport, water and nutrient movement, protein synthesis, and starch formation by plants [26].

In current study, the minimum and maximum total concentrations of K were 0.40 to 0.68% for surface samples and 0.40 to 0.53% for the subsurface soil samples (Table 3). There were no obvious significant differences for K percent between surface and subsurface samples among all the locations except location 3. K showed a completely different trend for its distribution along the depth at studied locations; for example in location 2, 3, 7, 8, 9 and 10 potassium showed a trend to decrease downwards to the subsurface, while for the other locations the distribution was on the contrary (Figure 3).

Potassium was not significantly correlated with any of the other examined metals and chemical properties in this study. However, Duncan test in table (4) showed that there was a significant difference between the average concentrations of K at location 3 and that at locations 2, 5, 8 and 9.

Generally, the obtained range concentration of 0.40 to 0.68% which equivalent to (4000 to 6800) $\mu\text{g g}^{-1}$ for potassium metal by this study is higher than the ranges of (77 to 1802), (180 to 775) and (0.1 to 6213) $\mu\text{g g}^{-1}$ soil which reported by [27], [25] and [24] respectively.

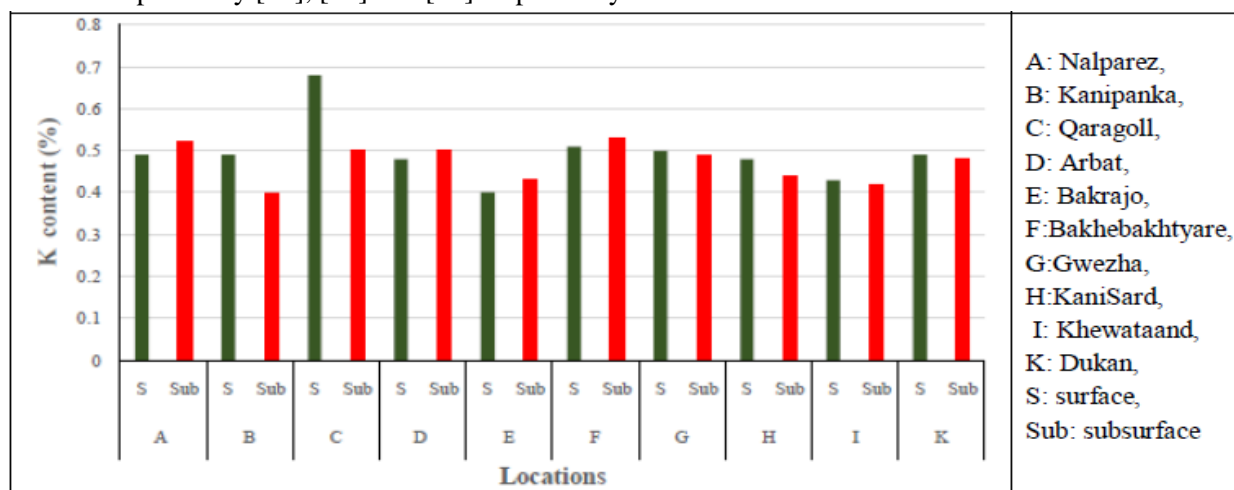


Figure 3: Total concentration of potassium (K) in surface and subsurface samples at the studied locations.

Of the studied alkaline earth metals **magnesium (Mg)** is essential to both plants and animals as a component of chlorophyll in green plants, bones in animals, and numerous enzymes in a variety of living organisms. Magnesium also helps protein building and facilitates DNA replication. Magnesium is a bivalent cation and mined in significant quantities from the minerals dolomite [$\text{CaMg}(\text{CO}_3)_2$] and magnesite (MgCO_3) and in smaller quantities from brucite ($\text{Mg}(\text{OH})_2$) and carnallite [$\text{KMgCl}_3 \times 6(\text{H}_2\text{O})$]. Magnesium makes up about 2.4 percent of Earth's crust [3]. However, magnesium content in soils varies from 1000 to 11700 $\mu\text{g g}^{-1}$ [28]. High Mg content is normally typical of the calcareous rocks such as; limestone, dolomite, and multicolored marl [24].

In the present investigation, maximum concentrations of Mg (1.98 and 2.01%) at both surface and subsurface samples were observed at location 10, while a minimum concentration of 0.84 and 0.80% were found at location 1 for the surface and subsurface samples respectively (Table 3). Magnesium exhibited considerable variation between these two locations and this might be due to the fact that many factors play their roles in abundance of certain elements in soils and other surficial materials such as; the bedrock or other deposits from which the materials originated, climatic and biological factors as well as agricultural and industrial operations that have acted on the materials for various periods of time [29]. But all the other locations except location 3 showed relatively a close concentration for Mg content (Figure 4).



Figure 4: Total concentration of magnesium (Mg) in surface and subsurface samples at the studied locations.

As it is reported for Na, the concentration of Mg at surface samples was either higher than or similar with the concentration of Mg in the subsurface samples and this might be attributed to the high content of organic matter in surface samples as compared with the subsurface depth.

Like potassium correlation, no significant correlation was observed between Mg and the other studied metals and chemical properties in this study. Nevertheless, Duncan test revealed significant differences for the average concentrations of magnesium (Mg) among locations 1, 3 and 10 as compared to the other locations (Table 4).

Some studies have dealt with the concentration of magnesium metal in soil and the findings were as follow; 230.3 to 5654.0 $\mu\text{g g}^{-1}$ in soils of a wetland–terrestrial ecosystem complex in India [27], 185.2 to 5147.7 $\mu\text{g g}^{-1}$ in wetland sediment [25] and were 4163 to 30845 $\mu\text{g g}^{-1}$ in soils of the Southern Cis-Ural region [24]. Anyhow, the finding of Mg concentrations range (8000 to 20100 $\mu\text{g g}^{-1}$) in the present investigated soils was not completely consistent with the reported results. Among the studied metals in the present study, Mg was the second most abundant metal after calcium in soil samples of all the locations.

Calcium (Ca) like Mg is well known to most people because it is an essential element to both plants and human. The most sedimentary materials that contain calcium are; calcite, limestone, marble, chalk, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and dolomite [$\text{CaMg}(\text{CO}_3)_2$] which they are relatively insoluble forms. Moreover, sea water

is also a main source of calcium [3]. Calcium plays an important role in soil forming process. It determines optimum physicochemical soil properties and affects agrophysical parameters and humus status of soils [23]. In the present study, the total Ca concentration varied from 2.32 to 12.60% and 1.92 to 11.5% in soil samples of surface and subsurface depth respectively (Table 3). Overall, Ca showed considerable difference between the locations (Figure 5), since its content in soils depends on climatic conditions and the amount of Ca carbonates in the parent material which varies within a wide range [23]. Contrary to Na and Mg the concentration of Ca at surface samples was mostly lower than the subsurface samples and this might be due to the presence of high calcium carbonates minerals in the originated parent material, since soils at Sulaimani Governorate are mostly calcareous and contained more than 5% carbonate [17]; as a result Ca concentration was the first most abundant metals among the studied metals at the location's samples.

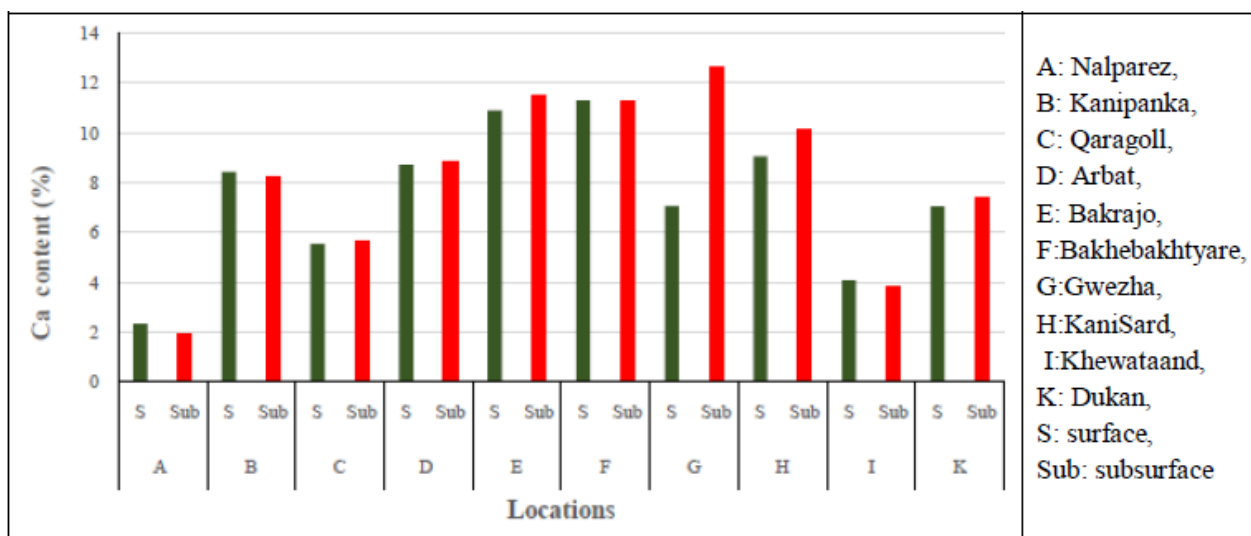


Figure 5: Total concentration of calcium (Ca) in surface and subsurface samples at the studied locations.

Significant positive correlations were found between calcium and each of strontium, sodium and CaCO_3 content ($r = 0.902$, $r = 0.510$ and $r = 0.954$) at the level of significance alpha (α) = 0.050 respectively, while significant negative correlation ($r = -0.525$ at the level of significance alpha (α) = 0.050) was found between Ca and organic matter content. On the other hand, Duncan test indicated significant differences for the average concentrations of Ca between location 9 and the other locations (Table 4).

The results of Ca content in soils by the present study were somewhat agreed with those obtained by [24].

Beryllium (Be) as one of alkaline earth metal is found in the smallest quantity (about 4 - 6 $\mu\text{g g}^{-1}$) in Earth's surface rocks and its relative abundance rank is 47th. Beryllium is a constituent of about 100 minerals out of about 4000 known minerals, the most important of which are beryllium silicate ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$), bertrandite [$\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$], phenacite (Be_2SiO_4), and chrysoberyl (BeAl_2O_4). Beryllium is also present in solid and liquid fossil fuels. The burning of coal and oil emits beryllium particulates that may continue to circulate in the air for some time or settle into waterways [3 and 30].

The results of beryllium are shown in Table (4) and had a narrow range of variation (0.9 to 1.2) $\mu\text{g g}^{-1}$ at both surface and subsurface depths. The minimum and maximum values of the surface depth were revealed in many locations, similar cases were obtained for the minimum values of the subsurface depth, while the maximum value of the surface depth occurred only at location 9 (Figure 6). Beryllium like Na and Mg, its concentration at surface samples was either higher than or similar with the concentration of Be in the subsurface samples at all locations except location 1 and this might be due to the high content of organic matter in surface samples as compared with the subsurface depth or might be due to the anthropogenic activity through the deposition of emitted Be from burning of oil. Beryllium has a toxic effect on plant when its concentration in the soil solutions varied between 2–16 $\mu\text{g g}^{-1}$, and it is able to replace Mg^{2+} in some plants [1]. Fortunately, there was a lower concentration range of Be in the studied soil.

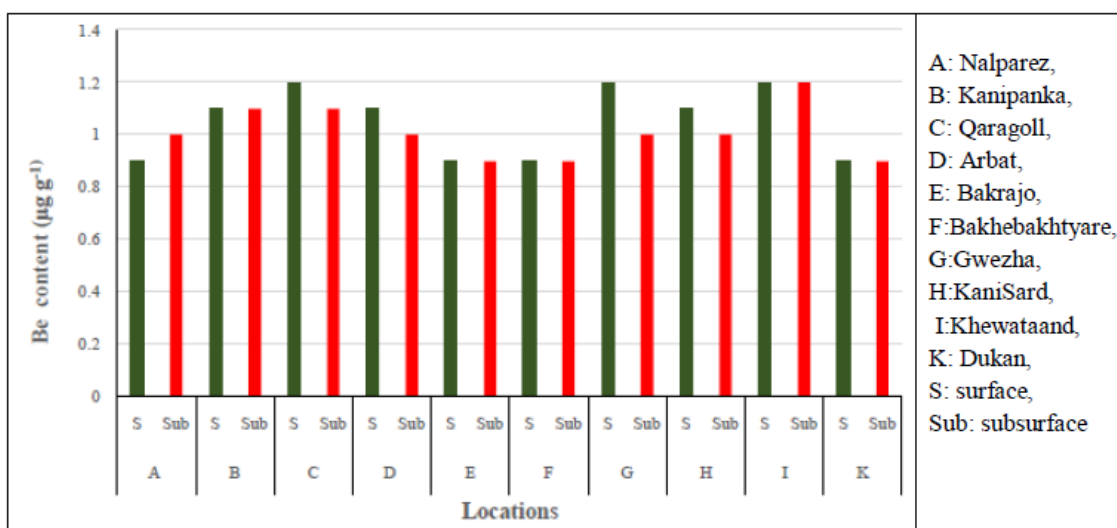


Figure 6: Total concentration of beryllium (Be) in surface and subsurface samples at the studied locations

There were a significant positive correlation ($r = 0.466$ and $r = 0.501$ at the level of significance $\alpha = 0.050$) between Be concentration with each of barium contents and pH respectively. Additionally Be showed a significant negative correlation ($r = -0.572$ at the level of significance $\alpha = 0.050$) with EC. No significant differences were appeared according to Duncan test among the average concentration of Be in soils of the studied locations (Table 4).

Our results for Be concentrations were much lower than those found by [24], who reported a range of 2–6 $\mu\text{g g}^{-1}$ in soils and rocks of the southern Cis-Ural region.

Strontium is averaging 0.034 % in all igneous rock and it is the 16th most abundant element on Earth. Celestite as the form of the sulfate mineral (SrSO_4) and the carbonate strontianite (SrCO_3) are the principal sources of Sr [3 and 30]. According to [31], the mean concentration of Sr in soils is about 350 $\mu\text{g g}^{-1}$. Strontium is assigned to be the third hazard category according to the current State Standard of Russia and therefore requires special attention [32]. Strontium has moderate mobility in soils and sediments and sorbs moderately to metal oxides and to the surface of clays and other minerals [33].

Strontium content in soils of this study varied considerably and ranged from (61 to 220) and (52 to 209) $\mu\text{g g}^{-1}$ in surface and subsurface samples respectively (Table 3). Both the upper levels of Sr for the surface and subsurface samples were recorded at location 5, while both the lower levels of Sr for the surface and subsurface samples were revealed at location 1. The great variation of Sr concentration between location 1 and 5 might be either due the relative abundance of Sr minerals at the two locations or any other affecting sources of Sr concentration.

As it is shown in Figure (7), Sr like Na and Mg was found to be distributed more in the surface depth rather than the subsurface depth at all locations except location 8 and 10.

Strontium was positively correlated with Ca, Na and CaCO_3 ($r = 0.902$, $r = 0.627$ and $r = 0.913$ respectively at the level of significance $\alpha = 0.050$). The high positive correlation of Sr with each Ca and CaCO_3 may be due to the fact that on calcite (calcium carbonate), low concentrations of the Sr^{2+} cation may sorbs by electrostatic attraction as hydrated ions, or higher concentrations may precipitate as strontianite (strontium carbonate), thus reducing mobility [34]. Conversely, there was a significant and negative correlation between Sr and organic matter content at the studied locations. Moreover, Duncan test showed in Table (4) that there were significant differences among the following locations (5, 6) with (2, 3, 4, 7, 8), then with (10) and finally with location (1 and 9). [24] have reported that in the arable soils the accumulation of Sr may be related to the application of the high rates of phosphorus fertilizers and lime. However, they found the range of 122 to 135 $\mu\text{g g}^{-1}$ for Sr concentration in soils of the southern Cis-Ural region and these results are somewhat close to the findings of Sr concentration by this study.

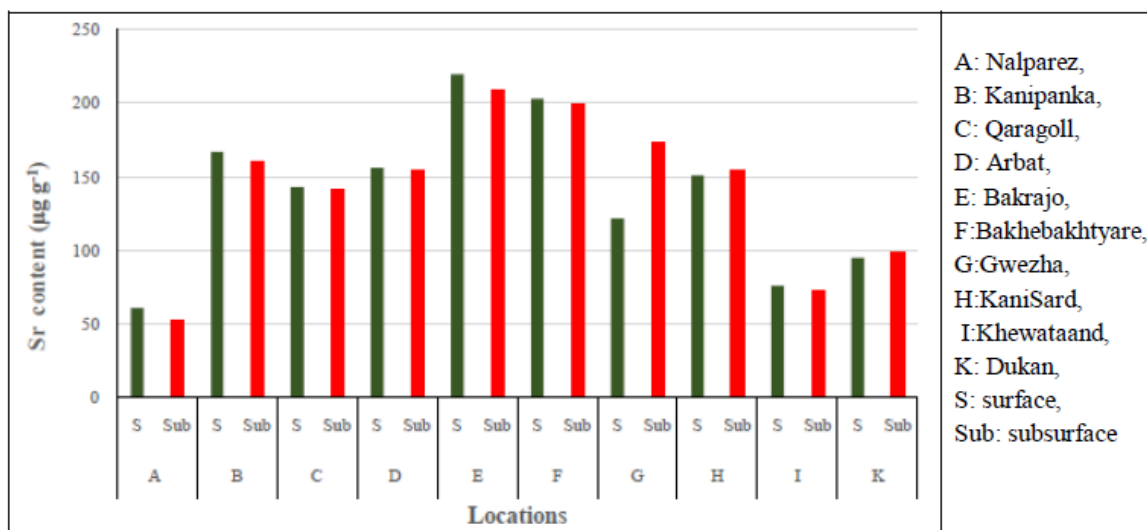


Figure 7: Total concentration of strontium (Sr) in surface and subsurface samples at the studied locations.

Barium (Ba) metal ranks 14th in abundance and it is probably best known in the form of barium sulfate, BaSO₄ (Barite,) and barium carbonate, BaCO₃ (Witherite). However some sediment may contain the only known streaks of sanbornite, a rare barium silicate (BaSi₂O₅). Ba is also characterized by its reactivity with air so as water, therefore it is never found in nature in its pure form [3]. Neither metals of Ba nor Sr have any biological importance under natural conditions; in some cases, however, strontium can be of concern in regards to human health [30]. The researcher [35] has pointed out that the Ba content in earth's crust is about 0.05%.

The distribution of Ba with depth is presented in Table (3) and varied considerably from (123 to 297) and (126 to 272) µg g⁻¹ for the surface and subsurface soil samples respectively at the studied locations. Both the maximum levels of the surface and subsurface samples were revealed at location 2, while both the lower limits of the surface and subsurface samples were occurred at location 10 and this would be either attributed to the relative abundance of Ba bearing minerals at the two depths [3 and 30] or due to the fact that many factors play their roles in abundance of certain elements in soils and other surficial materials such as; the bedrock or other deposits from which the materials originated, climatic and biological factors as well as agricultural and industrial operations that have acted on the materials for various periods of time [29].

Irregular distribution of Ba down the depth was observed among the locations, hence at locations 2, 3, 5, 6, 7 and 9 the surface concentrations of Ba were more than at the subsurface depths, while the other locations showed the converse case (Figure 8).

Barium exhibited a significant correlation only with Be in this study ($r = 0.466$ at the level of significance $\alpha = 0.050$), and no further significant correlation was found between Ba and the other studied metals or with the studied chemical parameters. Additionally, Duncan test showed significant differences among location 2 with (3, 8) and then with (1, 4, 5, 6, 7, 9 and 10), (Table 4).

According to [36], the Ba concentrations in surface soils of 12 sampling sites in Malaysia were in the range of 63.72 to 382.01 µg g⁻¹ and these results are close to our findings by the present study. However, [24] have reported a much wider variation range of Ba concentration (16 to 4730 µg g⁻¹), in different soils and parent material of the southern Cis-Ural region.

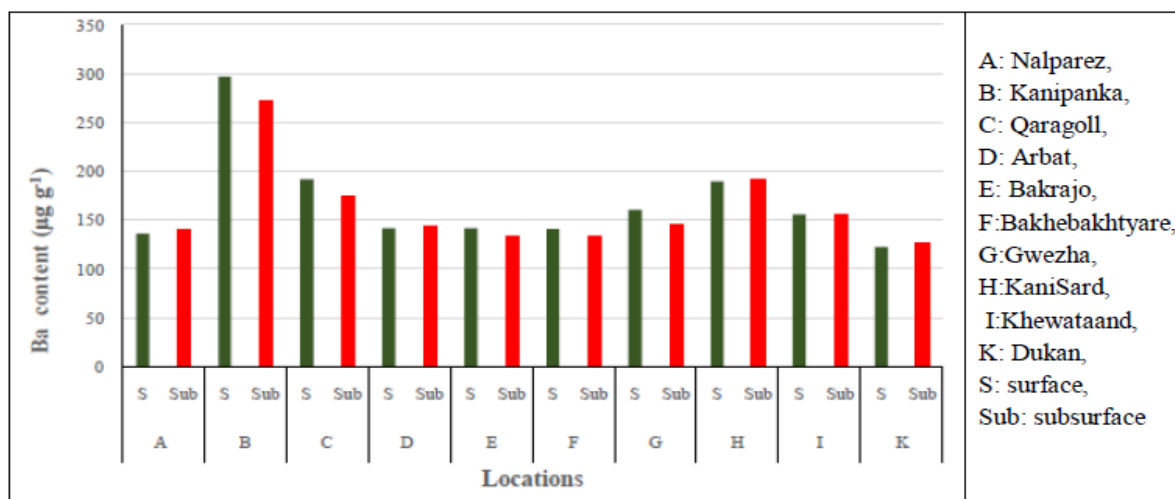


Figure 8: Total concentration of barium (Ba) in surface and subsurface samples at the studied locations.

In general, based on the highest concentration, the studied metals in current study followed the following sequence $Ca > Mg > K > Ba > Sr > Na > Be$.

For giving a good description in the variation of the metal background concentration among the studied locations, principle component analysis (PCA) was used to interpret the relations between the studied alkali and alkaline earth metals and consequently using the obtained results for assessing the relations among the soils of the studied locations. As it is shown in the plots of Figure (9 and 10), x-axis explains 39.44 % of the variation among the metals and this regarded as the first component (principle component) because the greatest variance of the data set comes to lie on the first axis, while y-axis explains 20.81 % of the variation. Thus, the cumulative explained variance among the metals or namely among the soils of the studied locations was % 60.25.

The cosines of the angles between the vectors of the metals in Figure (9) express an approximation of the correlation between the studied metals. A small angle (less than 90° degree); such as the angles between the vectors of Sr, Ca, Na and Mg indicates that the metals are positively correlated. An angle of ninety (90°) degree between the metals Na and Ba indicate that the metals are not correlated. The cosine of 0 (zero) is equal one and this means that the variables are high significantly and positively correlated. On the other hand an angle of more than (90°) degree; such as the angel between the vector of Be with the vectors of each Sr, Ca, Na and Mg and the angle between the vectors of Ba and K express a negative correlation between the metals. If the angle is approaching 180° degree, the relation then expresses a strong negative correlation between them.

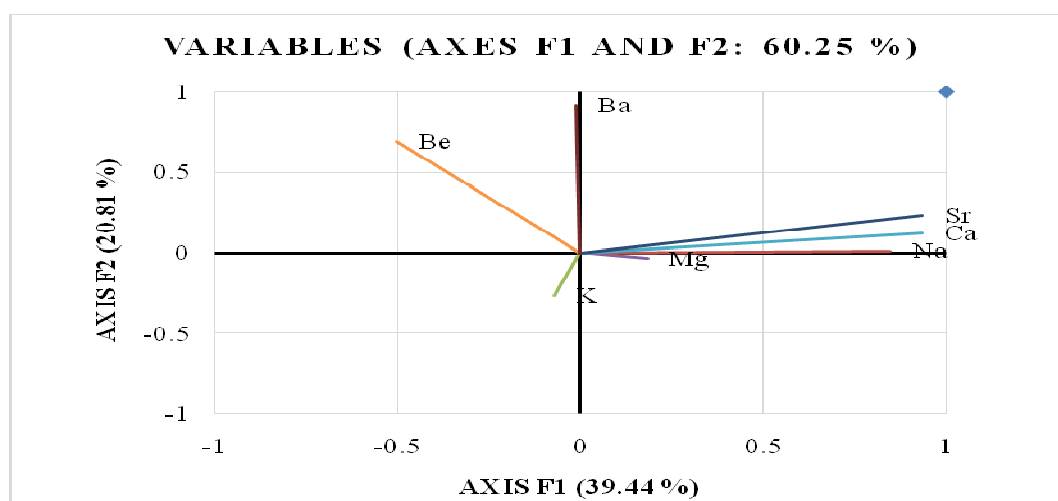


Figure 9: Principle component analysis (PCA) plot showing distribution of the different alkali metals and some alkaline earth metals in soils of the studied locations.

The agglomerative hierarchical clustering classified the soils of the ten locations into four major groups at a significant dissimilarity percent of about 57% (Figure 11). The first group composed only of location 2 (Kanipanka). The second group included three locations (1, 9 and 10 which stand for Nalparez, Khewata and Dukan respectively). The third group covered location 5 and 6 which stand for Bakrajo and Bakhebakhtyare respectively, while the last group comprised four locations and they were 3, 4, 7 and 8 which stand for Qaragoll, Arbat, Goizha and Kani-Sard respectively. All the major hierarchy groups except group 1 were clustered into subgroups and the subgroups in turn were also clustered into sub-subgroups of about 20 % dissimilarity (Figure 11).

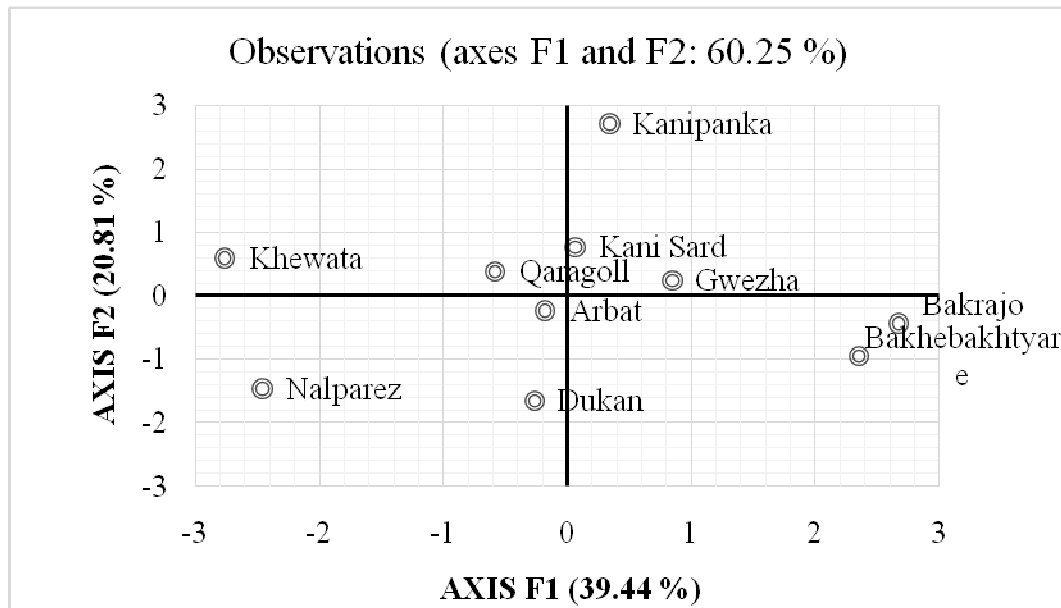


Figure 10: Principle component analysis (PCA) plot showing distribution of the studied soils on scatter plot based on the metal results.

Based on the average values of 7 metals in surface and subsurface depths, cluster analysis as a method of multivariate analysis was performed by using Euclidean distance coefficient and UPGMA method (Figure 11). The maximum distance of (181.872) was appeared between location 1(Nalparez) and location 2 (Kanipanka), this means that highest dissimilarity was occurred between those two locations. This can be mainly attributed to the difference in parent material, relative abundance of the metal-bearing minerals and also to the type of the mineral content at these two locations, though the findings of most of the studied metals showed a significant difference between them. Contrary to that, high similarity was found between location 5 (Bakrajo) and location 6 (Bakhebakhtyare) and the minimum distance coefficient was 13.011 between these two locations, this might be due to the similarity of the parent materials and the other soil forming factors for location 5 and 6. The divergence between the highest and the lowest dissimilarity values (Euclidean distance coefficients) confirms variation among the soils of the ten locations. Also, the dendrogram establish the results of PCA in the classification of soils into groups at the studied locations.

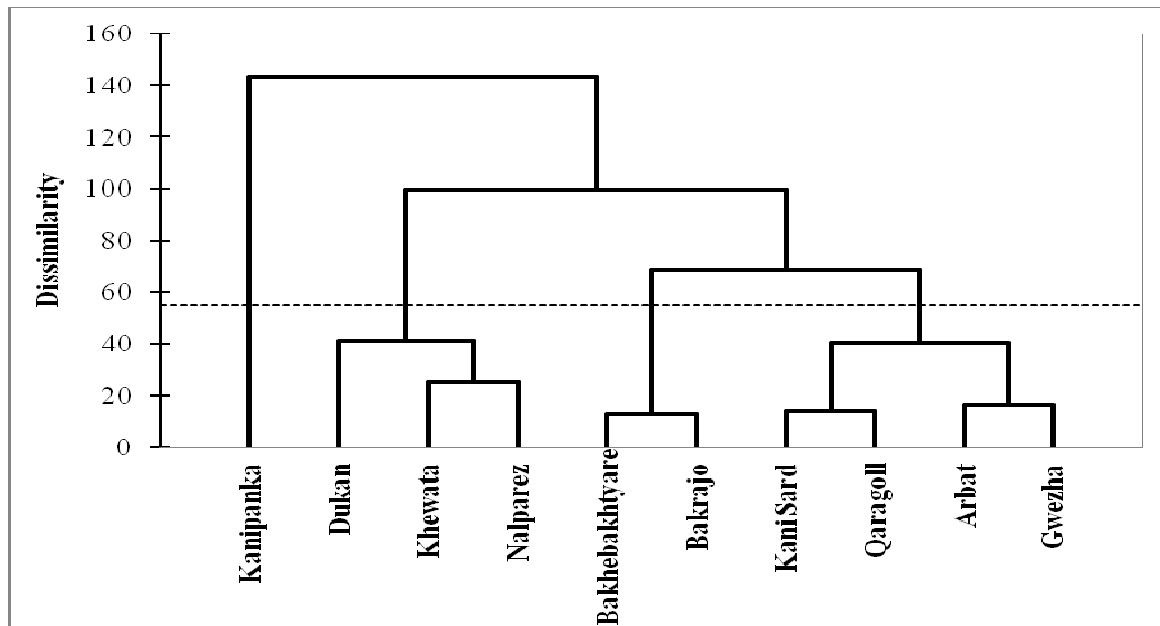


Figure 11: Agglomerative Hierarchical Clustering (AHC) analysis of the studied soil locations depending on metal results by using Euclidean distance and unweighted pair-group method average (UPGMA).

Table 5: Euclidean distance coefficients values showing dissimilarity among the soils of ten locations based on some alkali and alkaline earth metals.

Locations	Arbat	Bakhe-bakhtyare	Bakrajo	Dukan	Goizha	Kani-Sard	Kani-panka	Khewata	Nalparez	Qaragoll
Arbat	0									
Bakhe-bakhtyare	47.305	0								
Bakrajo	60.100	13.011	0							
Dukan	61.278	105.618	118.522	0						
Goizha	16.346	56.342	68.905	58.656	0					
Kani-Sard	48.623	73.009	82.348	86.656	38.569	0				
Kani-panka	142.382	151.778	155.511	173.502	132.078	94.320	0			
Khewata	82.708	129.531	142.384	39.065	74.653	86.430	157.583	0		
Nalparez	99.339	145.512	158.491	43.024	92.938	109.913	181.872	25.149	0	
Qaragoll	43.631	75.533	86.164	74.282	30.995	14.093	103.407	73.992	97.003	0

Conclusions

The total metal concentrations of the studied soils had no specific pattern distribution at the selected depths due to the variation in the heavy metal sources and their quantities in the parent materials. The obtained data on the contents of these metals showed that the highest concentration followed the following sequence $Ca > Mg > K > Ba > Sr > Na > Be$. The findings of Ca, Mg and Sr showed relatively wide ranges for their concentrations among the studied locations. The high content of Ca in soils of the study locations might be due to the presence of high calcium carbonates minerals in the originated parent material. The results may help us also for making better qualitative soil assessment and land evaluation for supply the plants with the essential studied alkali and alkaline earth elements.

PCA and agglomerative hierarchical clustering analysis indicated that multivariate statistical analyses were useful in classification the soils of locations into four major groups at a significant dissimilarity percent of about 57% based on the studied metal contents.

Similar studies are suggested to be carried out in examining the alkali and alkaline earth metal enrichment at deeper depths and other location of Sulaimani Governorate because a more complete study of amount and relative proportion of metals in soils contribute for better establishing the background levels and also for reflecting the soil's parent materials as well as the anthropogenic impact and fertility limiting.

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