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Vertical distribution patterns of S, Mo and some Rare Earth Elements (REE) along the soil profiles from Sulaimani governorate, Kurdistan of Iraq.

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ABSTRACT

This study was conducted to investigate the background concentrations of total S, Mo Gd, Ge, Hf, La, Sc, Th, and Y in the soil, and vertical distribution of these elements through profile depths of Sulaimani governorate, Kurdistan of Iraq. Soil samples were taken from seven different pedons in different locations; five pedons were dug from forest sites. The pedons 1, 2, 4, 5, and 7 from Cypress forest, Olive forest, Pine forest, Oak forest, and Pine forest, respectively. While the two others pedons (pedons 3 and 6) were dug from grassland sites. Soil samples were taken in each horizon. Forty-three soil samples were taken to the laboratory for this study. Soil samples were finely ground and dried at 105°C for 2 hours. Then S, Mo, Gd, Ge, Hf, La, Sc, Th, and Y were determined by ICP-OES. Principal component analysis was used to express the data in a more relevant form and to predicate a high degree of interrelations among a set of variables, also used for obtaining the most interpretable linear combinations within the dataset of total elements in the soil profiles. Results for total values of REE were La ND – 274.16, Y 15.96-32.24, Sc 10.66 -17.63, and Gd 1.10 – 6.45 mg kg^{-1}, respectively. Average total element concentrations in soil samples were in the following order: S > La > Y > Sc > Th > Ge > Hf > Gd > Mo. There are no specific pattern distributions of the studied elements in the profile depths in studied locations.

نمط توزيع العمودي لكل من الكبريت، مولبدينيم وبعض العناصر الأرضية النادرة (REE) خلال مقدات تربة من محافظة السليمانية، كردستان العراق.

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الكلمات المفتاحية:
نمط التوزيع العمودي، الكبريت، مولبدينيم، العناصر الأرضية النادرة، مقدات التربة.

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الخلاصة

أجريت هذه الدراسة للكشف عن التراكيز الاولية من S, Mo, Gd, Ge, Hf, La, Sc, Th, and Y في التربة والتوزيع العمودي لهذه العناصر خلال عمق مقد التربة في محافظة السليمانية، كردستان العراق. أخذت عينات التربة من سبعة مقدات مختلفة في مواقع مختلفة. تم حفر خمسة مقدات من مواقع الغابات. مقد 1، 2، 4، 5 و 7 من غابات السرو، غابة الزيتون، غابات الصنوبر، غابة البلوط و غابات الصنوبر، على التوالي، في حين حفرت باقي المقدات (مقد3 و6) من مواقع عشبية. أخذت عينات التربة في كل أفق. تم أخذ ثلاثة وأربعين عينة من التربة الى المختبر. جففت عينات التربة على درجة حرارة 105 م° لمدة 2 ساعة بعد عملية الطحن. ثم قدرت عناصر الكبريت (S)، والموليبدينوم(Mo) ، وغادولينيوم (Gd)، والجرمانيوم (Ge)، والهفنيوم (Hf)، واللانثانوم (La)، وسكانديوم (Sc)، والثوريوم (Th)، والإيتريوم (Y) بجهاز ICP-OES. واستخدم التحليل الأحصائيPCA لوصف البيانات في الشكل الأكثر صلة، وأعطاء درجة عالية من الترابط بين مجموعة من المتغيرات، واستخدم أيضا للحصول على أكثر التركيبات الخطية تفسيرا في مجموعة البيانات من العناصر الكلية في مقد التربة. وكانت نتائج القيمة الكلية (REE) للعناصر الأرضية النادرة هي La (0-274.16),Y (15.96-32.24), Sc (10.66-17.63), and Gd (1.10-6.45) ملغرام. كم$^{-1}$ ، على التوالي. وكان ترتيب متوسط التركيزات الكلية للعناصر في التربة كما يلي : S > La > Y > Sc > Th > Ge > Hf > Gd > Mo . ولاتوجد توزيعات نمطية محددة للعناصر المدروسة خلال عمق مقد التربة في المواقع المدروسة.

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Introduction:

Rare earth elements (REE) are a series of 17 chemical elements found in the Earth's crust, (Connelly, 2005). Which consist of the elements scandium (Sc), yttrium (Y) and the 15 so called lanthanoids which are the elements Lanthanum (La), Cerium (Ce), Promethium (Pm), Praseodymium (Pr), Neodymium (Nd), Gadolinium (Gd), Samarium (Sm), europium (Eu), Holmium (Ho), Terbium (Tb), Ytterbium (Yb), Dysprosium (Dy), Erbium (Er), Thulium (Tm), and Lutetium (Lu) (Connelly, 2005). REE are the presence in several minerals such as; granites, pegmatites, carbonatites and perovskites (Okrusch, and Matthes, 2009); also in carbonates, silicates and phosphates (Hu et al., 2006; Laveuf and Cornu, 2009).

REE is very vital to many technologies. In Chinese, they use REE as fertilizers for agricultural soils. Several studies suggested that the application of REE as fertilizers into the agricultural soils improve the quality of crops and also increase yield of the agricultural crops (Hu et al. 2004; Pang and Peng 2002; Wang and Zheng 2001; Buckingham et al. 1999). The low presence concentrations of REE in agriculture soils increase crop growth and productivity in Chinese agriculture sciences (Tyler, 2004). Some research has been done to investigate effect of REE on the biological process in plant (Brown et al., 1990). Rare earth elements are not known as essential element for plant. However, plants uptake these elements (Thomas, et al. 2014). Since total REE budgets for soils in Sulaimani are mainly unknown, this study investigates the concentrations of some REE in seven soil profiles in Sulaimani region, Kurdistan of Iraq. There was very little research on REE in the past of the studied area, so the present study may be considered as background concentrations of REE in soils.

The objectives of this work were to investigate the background concentrations of total Gd, Ge, Hf, La, Sc, Th, and Y in some soil samples, and also to determine the vertical distribution of the elements through profile depths in studied locations.

Materials and Methods:

Description of Field Sampling Locations:

This study was conducted on seven agricultural locations around the Sulaimani governorate(Figure 1); soil samples were taken from seven different pedons in different locations; five pedons were dug from forest sites. The pedons (1, 2, 4, 5 and 7) from Cypress forest, Olive forest, Pine forest, Oak forest, and Pine forest, respectively. While the two others pedons (pedons 3 and 6) were dug from grassland sites. The sampling sites were located in Goizha (1) (35°34′4″N; 45°28′36″E), Goizha (2) (35°34′4″N; 45°28′39″E), Goizha (3) (35°34′08″N; 45°28′19″E), Bakhybakhtyare (4) (35°34′8″N; 45°22′8″E), Dukan (5) (35°52′56″N; 45°0′27″E), Dukan (6) (35°50′04″N; 45°05′04″E), and Khalakan (7) (35°59′18″N; 44°52′34″E).

Sample Collection:

Soil samples were collected from 7 sites in Sulaimani; soil samples were taken in each horizon after dug profiles. According to identification horizons, forty three soil samples were taken to the laboratory for this study. Collected soil samples were air dried in the laboratory for a few days and then sieved through a 2 mm sieve and saved to use.

Laboratory Analysis:

Total elemental analysis:

Soil samples were finely ground and dried at 105°C for 2 hours, then 0.1 g of sample was fused with 0.7 g of Lithium metaborate/ tetraborate flux at 1050°C for 30 min in a platinum crucible. Fusion beads were dissolved in 1 mol/L HCl, and Sulfur(S), Molybdenum(Mo), Germanium(Ge), Hafnium(Hf), Thorium(Th), Lanthanum(La), Scandium(Sc), Gd, and Yttrium(Y) were determined in the supernatant by ICP-OES (Perkin-Elmer Optima 7300DV). Data were assessed for accuracy and precision using reagent blanks and a certified reference material (OREAS-43P; Ore Research and Exploration, 1997)

Statistical analysis:

Principal component analysis (PCA) is a statistical analysis that uses an orthogonal transformation to convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables. PCA was used to express the data in a more relevant form and to predicate a high degree of interrelations among a set of variables, also used for obtaining the most interpretable linear combinations within the dataset of total elements in the soil profiles. PCA has been widely useful with the explain geochemical data (Carranza, 2008; Sadeghi et al., 2013; Agnan et al., 2014; Silva et al., 2015).

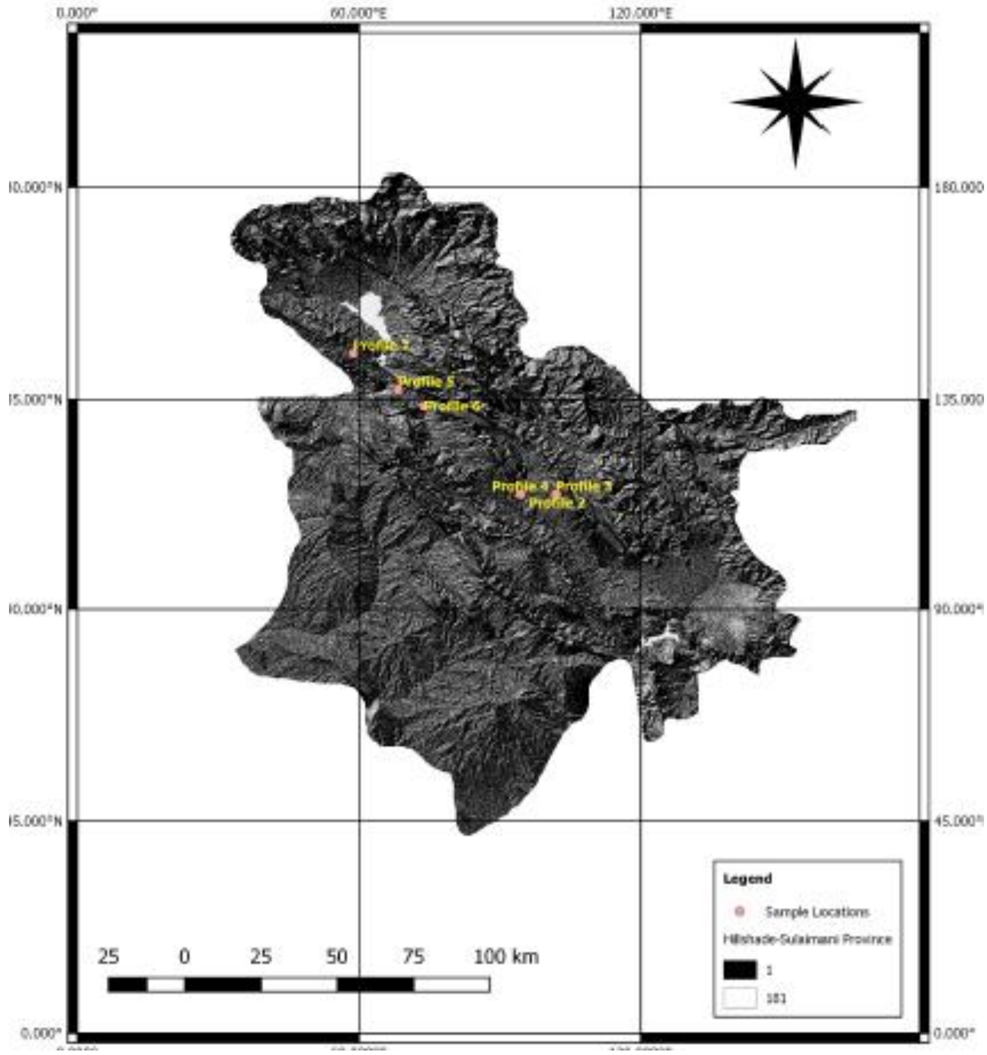

Figure 1: Locations of the studied area in Sulaimani Governorate, Kurdistan Region of Iraq.

Result and Discussions:

Some physical and chemical properties in studied soil samples are shown in Table (1). Results indicated that the values of pH were ranged between (7.34–8.36), this reflecting the calcareous parent materials. The values of Electrical conductivity (EC) ranged between (0.13-2.07 ds m^{-1}) this indicates that all soils were non-saline. The values of organic matter in studied soils ranged between (2.44 - 46.64 g kg^{-1}), the results indicates that the value of organic matter higher in the upper horizons in all pedons and decrease with soil depths, this due to the high accumulation of plant residue in the upper horizons.

Table 1: chemical and physical properties of the studied soil samples.

Profile No.	Horizon	Depth (cm)	pH	Ec (ds m^{-1})	O.M.* (g kg^{-1})	sand	silt	clay	Tex. Class*
							(g kg^{-1})		
Profile 1	A	0-15	7.71	0.29	21.53	158.7	476.7	364.6	SiCL
	B_{k1}	15-33	7.94	0.41	15.36	98.1	408.1	493.8	SiC
	B_{k2}	33-53	7.82	0.38	10.18	81.3	411.1	507.6	SiC
	C_{k1}	53-83	7.77	0.25	9.74	98.9	477.3	423.8	SiC
	C_{k2}	83-110	7.74	0.20	8.19	79.4	531.3	389.3	SiCL
	C_{k3}	+110	8.01	0.20	7.69	96.6	516.5	386.9	SiCL
Profile 2	A_1	0-15	8.07	0.23	22.70	27.2	459.5	513.3	SiC
	A_2	15-30	7.99	0.21	20.10	81.3	554.7	364.0	SiCL
	B_{K1}	30-47	7.96	0.22	15.10	91.3	567.5	341.2	SiCL
	B_{K2}	47-62	7.77	0.28	12.60	103.0	596.0	301.0	SiCL
	B_{K3}	62-89	7.70	0.24	9.40	103.0	609.0	288.0	SiCL
	C_{K1}	89-115	7.96	0.25	6.90	103.2	645.6	251.2	SiL
	C_{K2}	115-170	8.00	0.20	5.00	113.8	652.8	233.4	SiL
Profile 3	A	0-12	7.90	0.20	16.83	67.1	527.4	405.5	SiC
	B_{K1}	12-33	7.74	0.17	10.70	101.2	586.5	312.3	SiCL
	B_{K2}	33-52	7.70	0.16	12.94	108.0	610.7	281.3	SiCL
	B_{K3}	52-80	7.57	0.22	10.82	81.3	534.7	384.0	SiCL
	B_{K4}	80-99	7.69	0.17	13.17	101.4	617.4	281.2	SiCL
	C_{K1}	99-120	7.53	0.15	8.95	113.1	643.7	243.2	SiL
	C_{K2}	120-138	7.81	0.17	6.71	103.1	645.7	251.2	SiL
Profile 4	A	0-17	7.97	0.56	35.20	49.7	321.2	629.1	CL
	B_{K1}	17-30	8.28	0.35	22.70	103.0	345.3	551.7	CL
	B_{K2}	30-65	8.15	0.30	14.50	147.5	393.5	459.0	CL
	B_{K3}	65-93	8.36	0.27	11.30	140.2	473.1	386.7	SiCL
	C_K	+93	8.31	0.22	8.20	158.7	467.0	374.3	SiCL
Profile 5	A	0-25	7.61	1.06	46.64	114.1	445.9	440.0	SiC
	B_{K1}	25-40	7.70	0.34	14.01	101.5	401.6	496.9	SiC
	B_{K2}	40-56	7.35	0.24	4.87	92.9	462.4	444.7	SiC
	B_{K3}	56-83	7.50	0.20	4.81	90.9	480.6	428.5	SiC
	B_{K4}	83-103	7.57	0.20	3.05	108.0	454.5	437.5	SiC
	C_K	+103	8.02	0.13	2.44	103.6	465.9	430.5	SiC
Profile 6	A	0-20	7.45	0.89	37.16	138.4	360.9	500.7	CL
	B_{K1}	20-30	7.70	0.41	21.93	141.7	387.6	470.7	CL
	B_{K2}	30-49	7.94	0.39	12.79	170.3	392.1	437.6	CL
	B_{K3}	49-70	7.73	0.27	7.92	190.7	421.8	387.5	SiCL
	C_{K1}	70-92	7.34	0.33	4.57	181.5	444.1	374.4	SiCL
	C_{K2}	+92	7.73	0.37	4.26	176.1	464.2	359.7	SiCL
Profile 7	A	0-17	7.36	2.07	36.26	305.6	302.0	392.4	CL
	B_{K1}	17-34	7.87	0.66	16.52	215.6	306.1	478.3	CL
	B_{K2}	34-55	7.81	0.57	12.49	205.9	305.9	488.2	CL
	B_{K3}	55-78	7.58	0.42	5.48	211.5	370.0	418.5	CL
	B_{K4}	78-89	7.37	0.31	4.26	285.2	345.9	368.9	CL
	C_K	+89	7.88	0.29	3.66	339.6	349.1	311.3	CL

*O.M. → organic matter *Tex.class → Texture class

Particle size distribution was measured as physical properties. The texture of the soils ranged from clay loam to silty clay loam. Results indicates that the values of clay, silt, and sand ranged between (233.4 -629.1), (302-652.8), and (27.2- 339.6) g kg^{-1}, respectively. In general, the amount of clay in all pedons is at its maximum in the B_{k1} horizon. Clay contents tend to decrease with depth, then increase in the B_{k1} horizon, and decrease in the C_k horizons. This may be due to the effect of eluviations of clay from surface horizons, and illuvial deposition of clay in B_k horizons (Aziz, 2006). Silt and sand did not show specific pattern of distribution with depth in all studied pedons

Total concentrations of essential elements (S and Mo) in studied soil samples shown in Table (2). Results indicated that the values of S were ranged between (0.00 – 380.22) mg kg^{-1}, and the lowest value was in B_{K3} and C_K horizons of profile7, while the highest value was in A horizon of profile 5. This due to the effects of plant residues, types of minerals, and atmospheric deposition to adding sulphur in to the soils (Edwards, 1998). Forest covers cause to increase sulphur deposition in the soils (Moldan and Cerny 1994)

Results in Figure 2 shows that there was no specific pattern distribution for S values with depth in studied profiles. In general, in pedons 4, 5, 6 and 7 there was a high amount of total S in the surface horizon; this is maybe due to the high amount of organic matter in the upper surface of the agriculture soil, Table (1). Sulphate is leaching following water movement through soil depths (Harward and Reisenauer, 1966).

Molybdenum is a trace element found in the soil and is required for growth of most biological organisms including plants and animals. Also, is found in alkaline soils. Table (2) shows the total concentrations of Molybdenum in soil samples. Results showed that the value of total Mo ranged between (0.00 – 3.35) mg kg^{-1}, and the lowest value was in B_{K1} and B_{K3} horizons in profile 4, while the highest value was in A_1 in profile 2. The content of molybdenum in most agricultural soils is usually between 0.6 and 3.5 mg kg^{-1}(Mengel, and Kirkby, 2001). The amount of total Molybdenum varied between soil profiles was highest at surface soil and decreased with depth in the profile 1, 2, 3, and 7. The soil water budget has an effect on controlling differences between moving elements downward and upward concentrations of the element in the soils (Rate, and Sheikh-Abdullah, 2017).

The concentrations of total REE in studied soils samples.

The concentrations of some REE in soil samples from studied locations shown in Table (3). Values of REE differed among the soil samples which may be due to the differences of types of minerals and tree growing in these locations. Several studies have mentioned that the land use with different type of tree affects the REE content in soil locations (Hu, Haneklaus, Sparovek and Schnug, 2006).

Lanthanum is a light rare earth element (LREE). The concentrations of total La were ranged between (*ND* – 274.16) mg kg^{-1}, and the highest value was in the B_{K3} horizon in profile 6. The average La concentrations (24.60) mg kg^{-1} were higher than the Mo were found in the same soils (Table 3).

Yttrium, Scandium and Gadolinium are heavy rare earth elements (HREE). The concentrations of total Y were ranged between (15.96-32.24) mg kg^{-1}, and the lowest value was in the B_{K4} horizon in profile 5, while the highest value was in the A_1 horizon in profile 2.

The concentrations of total Sc were ranged between (10.66 -17.63) mg kg^{-1}, and the lowest value was in B_{K4} horizon in profile 5, while the highest value was in A horizon in profile 1, whereas, concentrations of total Gd were ranged between (1.10 – 6.45) mg kg^{-1}, and the lowest value was in the B_{K1} horizon in profile 4, while the highest value was in the A horizon in profile 3.

Concentrations of total Ge were ranged between (1.98 - 9.50) mg kg^{-1}, and the lowest value was in the B_{K3} horizon in profile 2, while the highest value was in the B_{K3} horizon in profile 7, whereas concentrations of total Hf were ranged between (2.86 – 6.73) mg kg^{-1}, and the lowest value was in the B_{K1} horizon in profile 1, while the highest value was in A horizon in profile 1. Concentrations of total Th were ranged between (3.81-10.37) mg kg^{-1}, and the lowest value was in the B_{K2} horizon in profile 5, while the highest value was in the A horizon in profile 1.

Table 2: Concentrations of total Sulfur and Molybdenum in some soil profiles.

Profile No.	Horizon	Depth (cm)	Total S	Total Mo
			mg kg^{-1}	
Profile 1	A	0-15	137.50	2.92
	B_{k1}	15-33	144.91	0.88
	B_{k2}	33-53	163.05	1.28
	C_{k1}	53-83	132.15	1.72
	C_{k2}	83-110	149.99	2.02
	C_{k3}	+110	159.20	0.69
Profile 2	A_1	0-15	84.62	3.35
	A_2	15-30	79.38	2.26
	B_{K1}	30-47	105.27	1.97
	B_{K2}	47-62	103.28	0.67
	B_{K3}	62-89	125.33	1.41
	C_{K1}	89-115	123.85	0.08
	C_{K2}	115-170	119.84	1.83
Profile 3	A	0-12	104.55	2.30
	B_{K1}	12-33	98.20	1.10
	B_{K2}	33-52	95.48	0.75
	B_{K3}	52-80	97.89	1.64
	B_{K4}	80-99	87.56	0.89
	C_{K1}	99-120	124.51	0.0
	C_{K2}	120-138	102.45	1.93
Profile 4	A	0-17	253.58	0.44
	B_{K1}	17-30	136.01	0.0
	B_{K2}	30-65	160.57	1.03
	B_{K3}	65-93	108.82	0.00
	C_K	+93	122.81	1.62
Profile 5	A	0-25	380.22	1.06
	B_{K1}	25-40	137.31	1.83
	B_{K2}	40-56	129.76	0.19
	B_{K3}	56-83	132.71	1.61
	B_{K4}	83-103	169.21	2.22
	C_K	+103	136.89	0.99
Profile 6	A	0-20	245.76	1.47
	B_{K1}	20-30	193.74	1.79
	B_{K2}	30-49	93.15	2.01
	B_{K3}	49-70	54.30	0.18
	C_{K1}	70-92	55.53	0.87
	C_{K2}	+92	68.97	0.30
Profile 7	A	0-17	312.59	2.28
	B_{K1}	17-34	125.84	1.00
	B_{K2}	34-55	59.07	1.97
	B_{K3}	55-78	0.00	0.56
	B_{K4}	78-89	2.89	0.55
	C_K	+89	0.00	1.67
Mean			127.80	1.26

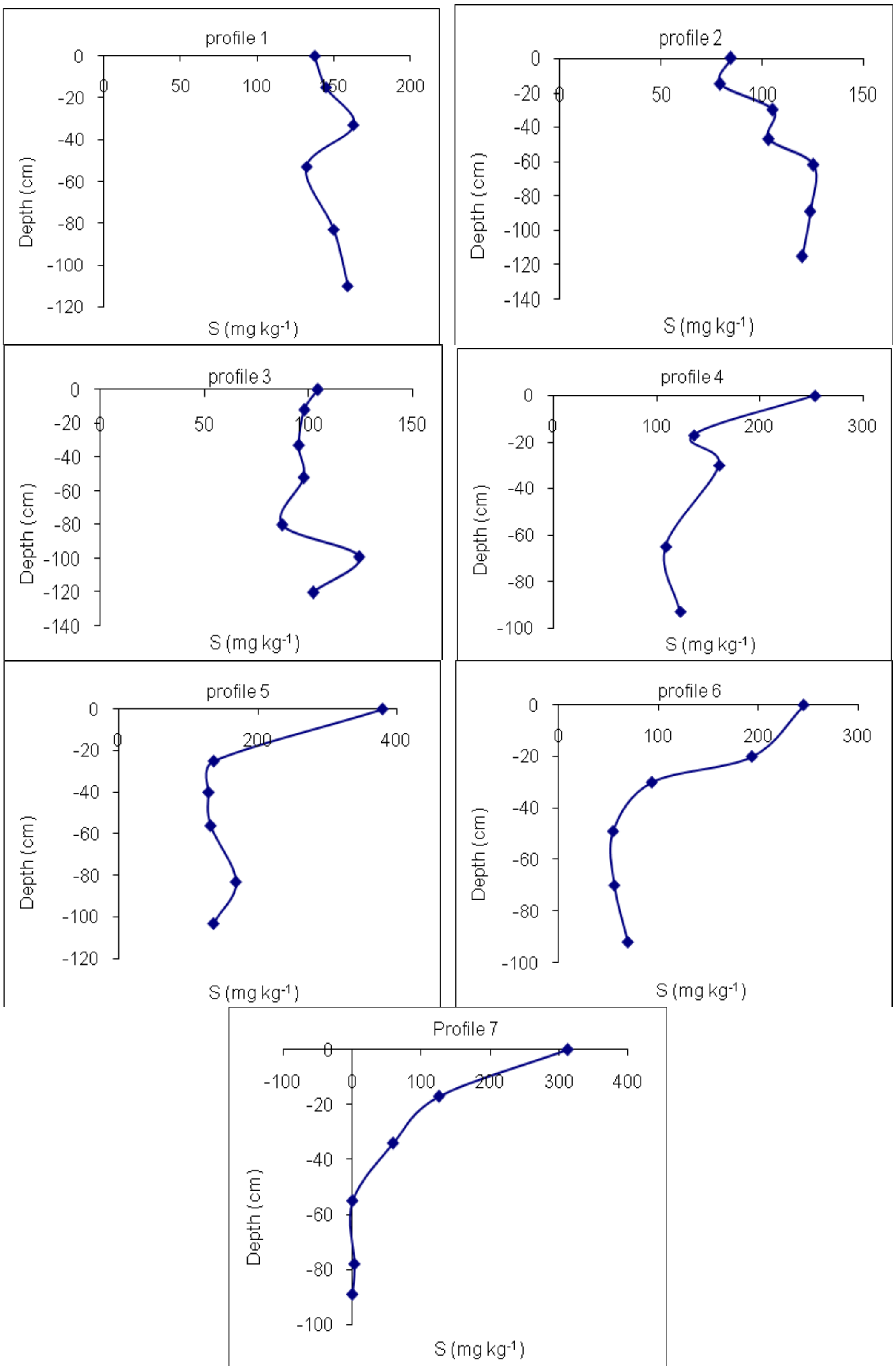

Figure 2: Vertical distribution of Sulfur in soil profile depths in studied locations.

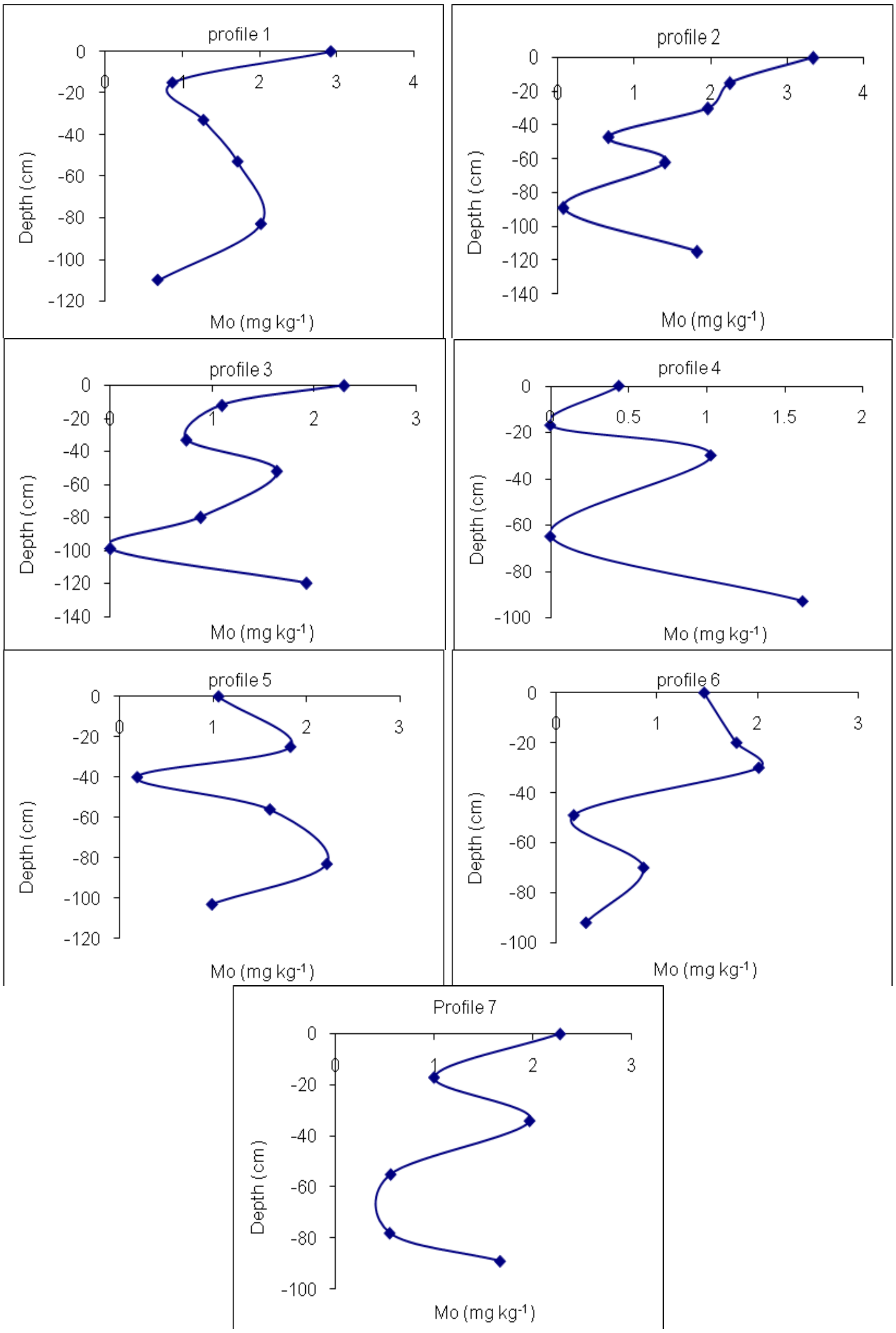

Figure 3: Vertical distribution of Molybdenum in soil profile depths in studied locations.

Table 3: Concentrations of some REE in studied soil samples.

Profile No.	Depth (cm)	Gadolinium (Gd)	Germanium (Ge)	Hafnium (Hf)	Lanthanum (La)	Scandium (Sc)	Thorium (Th)	Yttrium (Y)
		mg kg^{-1}						
Profile 1	0-15	4.06	4.11	6.73	10.03	17.63	10.37	31.64
	15-33	4.25	6.67	2.86	1.63	14.57	8.49	23.73
	33-53	4.85	6.67	3.92	0.57	12.57	5.60	20.00
	53-83	3.68	5.79	4.53	*ND*	11.75	5.37	18.31
	83-110	2.22	2.86	3.19	3.76	11.59	4.06	18.71
	+110	3.32	4.78	4.26	*ND*	11.61	4.86	19.17
Profile 2	0-15	5.69	3.36	6.28	11.18	17.24	8.99	32.24
	15-30	5.39	8.57	4.60	90.25	17.38	9.24	30.95
	30-47	3.20	6.21	5.73	5.16	16.04	9.06	26.42
	47-62	2.54	4.44	4.35	5.87	14.20	6.77	22.98
	62-89	4.60	1.98	4.49	24.58	13.24	7.04	20.61
	89-115	3.82	3.97	4.84	0.01	12.68	5.54	19.46
	115-	3.35	6.50	4.37	3.56	13.53	6.13	20.84
Profile 3	0-12	6.45	5.98	4.69	7.44	15.16	8.62	24.69
	12-33	3.84	6.28	4.16	0.32	12.68	5.04	19.21
	33-52	5.39	4.27	4.75	*ND*	13.01	6.14	20.41
	52-80	1.97	5.75	3.64	0.08	12.78	6.23	20.03
	80-99	3.05	5.20	4.03	*ND*	13.05	5.45	20.62
	99-120	3.71	3.25	4.41	10.34	12.83	5.47	20.36
	120-	1.63	7.12	5.07	5.64	12.79	6.33	20.11
Profile 4	0-17	3.73	4.02	4.25	*ND*	12.26	4.32	19.07
	17-30	1.10	5.20	4.99	8.31	12.15	4.91	19.02
	30-65	2.96	6.08	4.38	3.01	11.79	4.74	17.96
	65-93	3.02	4.33	4.11	*ND*	11.15	3.85	16.59
	+93	5.21	6.05	4.65	0.26	12.19	4.41	18.49
Profile 5	0-25	4.22	8.73	4.09	21.41	12.45	3.86	19.57
	25-40	4.22	4.54	3.47	0.08	12.63	5.12	19.58
	40-56	2.44	4.21	2.88	*ND*	12.03	3.81	18.31
	56-83	3.38	8.29	4.46	3.99	11.38	4.87	16.99
	83-103	3.45	5.80	2.92	*ND*	10.66	5.39	15.96
	+103	3.22	7.37	3.31	*ND*	10.70	4.70	16.43
Profile 6	0-20	4.47	5.21	4.76	34.99	15.04	7.25	22.97
	20-30	5.46	4.10	3.72	80.22	15.01	6.65	21.79
	30-49	4.73	5.80	4.61	*ND*	14.04	5.18	20.07
	49-70	2.91	4.68	4.03	274.16	13.17	5.40	18.69
	70-92	3.50	5.51	4.29	*ND*	12.95	4.15	18.68
	+92	4.35	3.50	2.91	1.43	12.80	4.83	18.81
Profile 7	0-17	4.18	6.23	4.96	*ND*	11.39	6.01	19.31
	17-34	3.19	6.24	5.01	2.57	14.73	6.99	25.75
	34-55	3.93	6.57	5.05	1.59	14.92	6.53	24.70
	55-78	5.12	9.50	5.88	214.50	14.90	7.51	24.00
	78-89	5.67	8.56	5.24	220	13.95	5.71	21.89
	+89	5.34	3.46	4.40	7.53	12.93	5.50	19.26
Mean		3.86	5.53	4.39	24.60	13.22	5.89	20.88

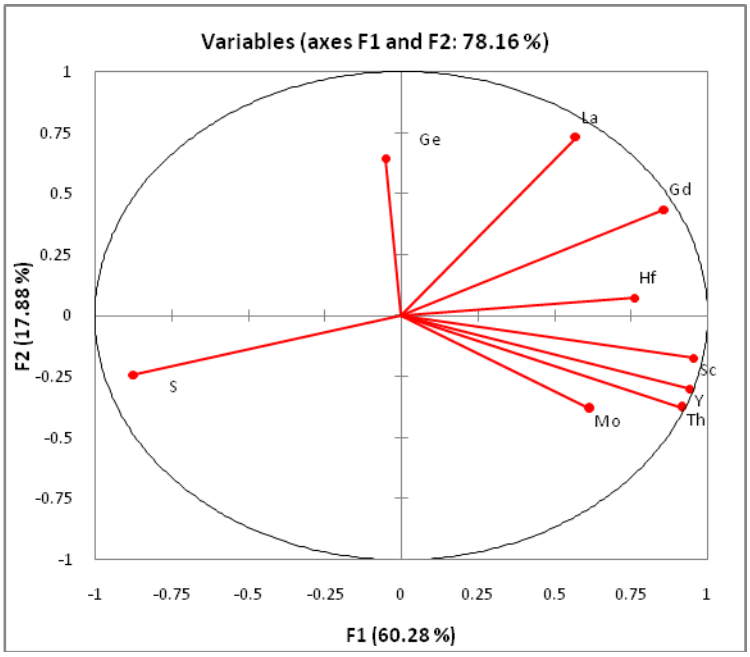

Figure 4: Principle component analysis (PCA) plot showing the distribution of the different total S, Mo, and REE in soils samples.

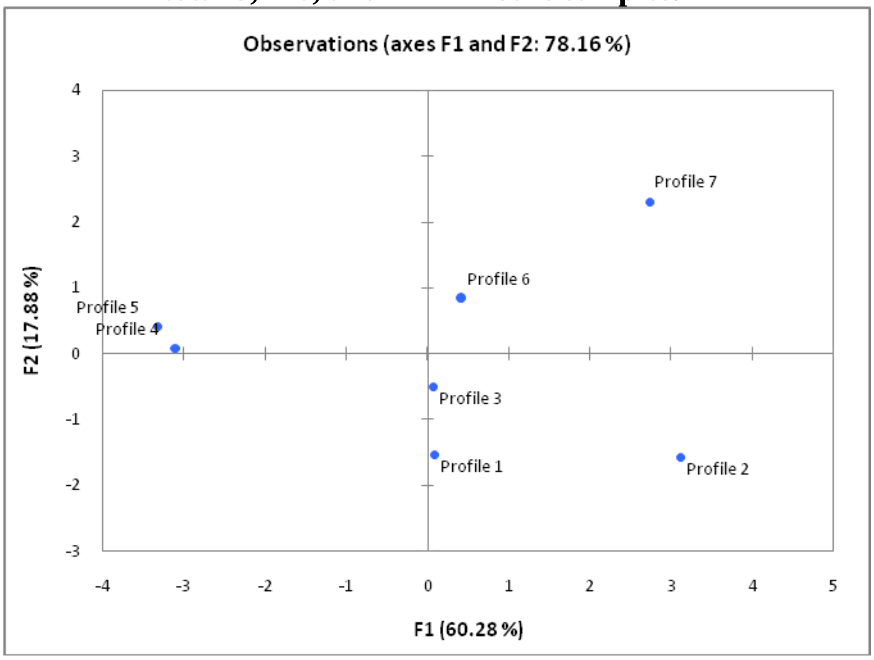

Figure 5: Principle component analysis (PCA) plot showing the distribution of the studied soils on scatter plot based on the total elements results.

The original of REEs in soils is from parent materials (Liu 1998). Parent material and soil type are sources to the concentration of REEs (Hu et al., 2006).

Results shown that means values of La, Y, Sc, Th, Ge, Hf, and Gd are (24.60, 20.88, 13.22, 5.89, 5.53, 4.39, 3.86 mg kg^{-1}), respectively. These results reveal that the La, Y, and Gd content in studied soils is lower than that in the earth's crust. (Vinogradov 1959)

No specific pattern distributions in REE were seen in the profile depths in studied locations; this may be due to the effect of types of parent materials, also clay content, and organic matter on the concentrations REE in soils. Also there are interactions between REE and biological systems (Tyler, 2004).

In general, based on the highest concentration, the total elements in the study followed the following sequence: S > La > Y > Sc > Th > Ge > Hf > Gd > Mo. Principal component analysis (PCA) was used to clarify the relations between the S, Mo and some REE in studied soil samples and consequently using the obtained results for assessing the relations among the soil profiles of the studied locations. As shown in the plots of Figure (4 and 5), x-axis explains 60.28 % of the variation among the total elements, while y-axis explains 17.88 % of the variation. Thus, the cumulative explained variance among the total elements or namely among the soils of the studied locations was % 78.16.

Figure 6 shows the Biplot (axes F1 and F2:78.16%) in the studied soil samples. There is a high positive correlation from Gd, Hf, and La. The vectors of Gd and S express a negative correlation between the elements. There is a high positive correlation between profile 7 and Gd element.

The PCA appears to represent a multivariate signal from differences between Profiles 2 and profiles 4 and 5, with the greatest positive loadings in PCA from Sc, Y, Th and Mo (Fig 6). Also, there is a high positive correlation between Sc, Y, Th, and Mo elements.

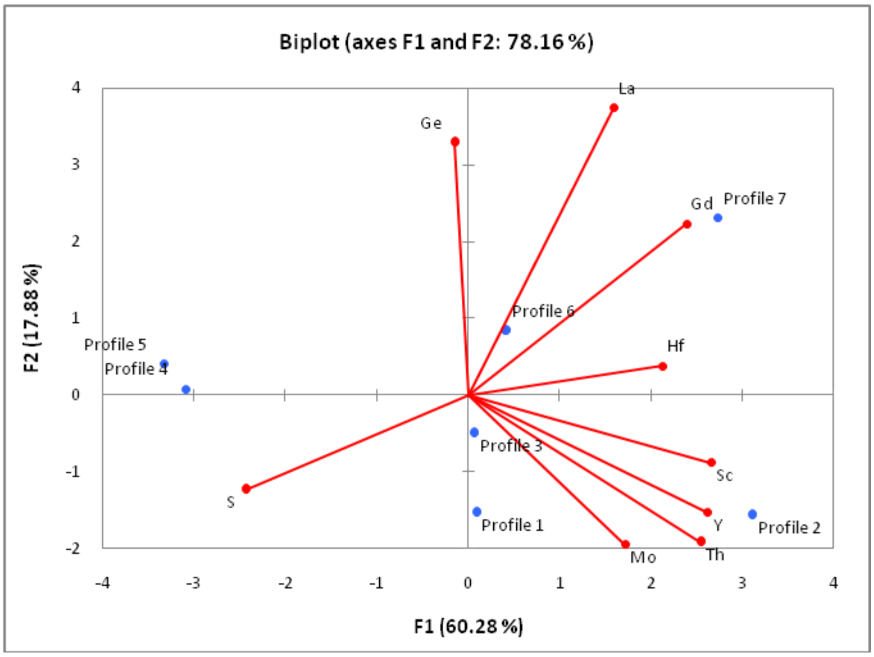

Figure 6: Principal component analysis biplot for components 1 and 2.

Conclusions and Recommendations:

Average total S, Mo, and some REE concentrations in Sulaimani soil profile were in the following order: S > La > Y > Sc > Th > Ge > Hf > Gd > Mo. The average La concentrations (24.60) mg kg^{-1} was higher than the Mo found in the same soils. These results reveal that the La, Y, and Gd content in studied soils is lower than that in the earth's crust. Principal Component Analysis shows that there was a great positive correlation between Sc, Y, Th, and Mo elements; whereas there was a negative correlation between profile 2 and profile 4 and 5. There are no specific pattern distributions of the studied elements in the profile depths in studied locations. Further research suggested on the determining REE in agricultural soil in Kurdistan region, especially in rhizosphere zone.

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