ISSN: 0067-2904

Mineralogical and Geochemical analysis of the sediments surrounding the Main Drain Area, Middle of Iraq

Inass Al-Mallah*, Qusay Al-Suhail, Adel Albadran
Department of Geology, College of Science, University of Basrah, Basrah, Iraq

Abstract

Fifty five surface and subsurface soil samples were taken from the area between Tigris and Euphrates Rivers along the Main Drain course from north Baghdad to Basrah to evaluate the geochemical, physical characteristics and the probability contamination of these samples. The study area is covered by Quaternary sediments of complex alternation of sand, silt and clay. Significant variation in the textural content of the present soils is observed, where the northern and southern parts are characterized by silt predominance, while sand is prevailing in the central parts as a result of the extensive spreading of aeolian deposits represented mostly by sand dunes. Mineralogical analysis explains wide variations in the heavy minerals distribution of different origins and that all of these minerals reflect the same distribution patterns. Calcite and quartz are the minerals of non-clay fraction, whereas montmorellonite, kaolinite, and chlorite are the key clay mineral in the present soils. No geochemical anomalous concentration of the trace elements in the soils can be detected except of few locations revealing potential pollutions. Clustering technique of the surface and subsurface soils shows presence of five and six groups respectively. This confirms the complexity and diversity nature of the sedimentary environment. Discriminante analysis of the surface soils indicates that salinity and sand content are the main discriminating variables responsible for grouping the soils, whereas sand, salinity and the main oxides are the discriminating variables for grouping subsurface soils. These statistical analysis and other relations results confirm that no clear indication concerning trace element pollution can be detected in the study area soils.

Keywords: Main Drain , Mineralogy, Geochemical parameters, , Multivariate analysis, Iraq.

التحليل المعدني والجيوكيميائي لرواسب المنطقة المحيطة بالمصب العام، وسط العراق.

ايناس الملاح*، قصي السهيل، عادل البدران
قسم علم الارض، كلية العلوم، جامعة البصرة، البصرة، العراق

الخلاصة:

تم جمع 55 نموذجاً من تربة سطحية وتحت سطحية للمنطقة الواقعة بين نهري دجلة والفرات على طول مسار المصب العام من شمال بغداد الى البصرة، الغرض منها اجراء تقييم للخصائص الفيزيائية والجيوكيميائية والتلوث المحتمل لهذه الترب. تغطى منطقة الدراسة برواسب العصر الرباعي المتمثلة بتتابعات من الرمل، الغرين، والطين. هناك تغايرات واضحه بالمحتوى النسيجي لنماذج الترب قيد الدراسة حيث تميزت الاجزاء الشمالية والجنوبية من المنطقة بسيادة الغربن بينما ساد الرمل في نماذج الاجزاء الوسطية من المنطقة نتيجة للانتشار الواسع للترسبات الرملية المتمثلة بالكثبان الرملية. اوضح التحليل المعدني وجود تغايرات واسعه في توزيع المعادن الثقيلة ومن مصادر مختلفه، وبينت هذه المعادن نفس نمط التوزيع في عموم منطقة الدراسه،

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*Email: anosa1974@yahoo.com

الكالسايت والكواتز هما اهم المعادن غير الطينية بينما تميزت المونتموريلونايت ، الكاؤلينايت والكلورايت بكونها المعادن الطينية المميزة لنماذج المنطقة. لا يوجد هناك اي شذوذ جيوكيميائي في تراكيز العناصر النزرة في الترب ما عدا بعض المواقع المنفردة التي تشير الى وجود تلوث موقعي. تبين نتائج التحليل العنقودي لجميع المتغيرات الجيوكيميائية لتربة منطقة الدراسه تنوعا" واضحا" في عدد المجاميع الناتجه دالة على التنوع الكبير في ظروف ترسيب هذه الرواسب في منطقة الدراسة. بينما توضح نتائج التحليل التمييزي ان المحتوى الرملي والاملاح هي المسؤولة عن تمييز المتغيرات المسؤولة عن تغاير الرواسب السطحية لمنطقة الدراسة. اما بالنسبة للتربة تحت السطحية فأن لنسبة الرمل والاكاسيد والملوحة تأثيرا" كبيرا في تمييز وتغاير جيوكيميائية ترب المنطقة. وقد اكدت التحاليل الاحصائية عدم وجود اي تلوث بالعناصر النزرة لنماذج الترب في المنطقة.

Introduction:

Iraq's Main Drain Project (Third River) is referred to as the canal that originates from Ishaqi canal north of Baghdad and terminating at the confluence with Shat Al Basrah canal, Figure-1. It is designed primarily to washing out the salty soils of the Mesopotamia, acting as a border/barrier against the expansion of sand dunes towards the irrigated lands. The Main Drain is located in the middle of the Mesopotamia and restricted between latitudes (30˚23́36.098"E) (33˚54́47.421"E), and (43˚5́57.918"N) (47˚52́1.706"N) with total area of (60340.590km^2).It receives its water from the sub-canals and main field drains collectors distributed along its course, also receives additional pollution loads from the municipality drains (estimated at 187,500 m^3/day), based on population and water consumption [1]. There are also discharges from the small industries such as fish farms, slaughterhouse, textile factories and others, which are not regulated, licensed, or monitored. They are, needless to say, sources of the present Main Drain water pollutant, affecting also the various conditions of the surrounding environment.

In order to benefit from the Main Drain water, it has been linked to Al-Hammar Marsh to avoid its drying again by Al-Khamisiyah Canal by its entrance located at 140 km from the Main Drain. This channel has been implemented at the end of year 2009 with a capacity of (40 m^3/Sec) [2].

The study area is covered by the Holocene deposits, where the covering soil is derived mainly from the sediments of both Tigris and Euphrates Rivers, representing complex and alternating sequences of good permeable sand, silt, and clay. These sediments change in vertical and lateral directions. The dense networks of irrigated canals have significantly affecting the natural primary sedimentation patterns. The low relief of the generally flat plain controls the recent development of the region; the variation in amplitude of the land surface of only few meters can cause devastating floods [3].

This work is aimed to study the geochemistry of the surface and subsurface soils of the present area, investigate the statistical relationships between the chemical and physical characteristics of these soils, and the distribution of the probable contaminants (if any) within these soils in the area surrounding the Main Drain.

Sampling and analysis methods:

Thirty surface soil samples were taken from the whole study area Figure-2, at a depth of 20-25 cm after removing the top soil cover and then stored in a clean polyethylene container for the determination of mineralogical, chemical characteristics, and grain size analyses Table-1. Twenty four subsurface soil samples are collected from the wells currently drilled for the purpose of the present study. These wells are of total depth of 20 m where the samples are taken at the interval of 2 m. These wells are labeled as W-1 Baghdad, W-5 Diwaniya, W-6 Nassiray, and W-8, Basrah, Figure-3.

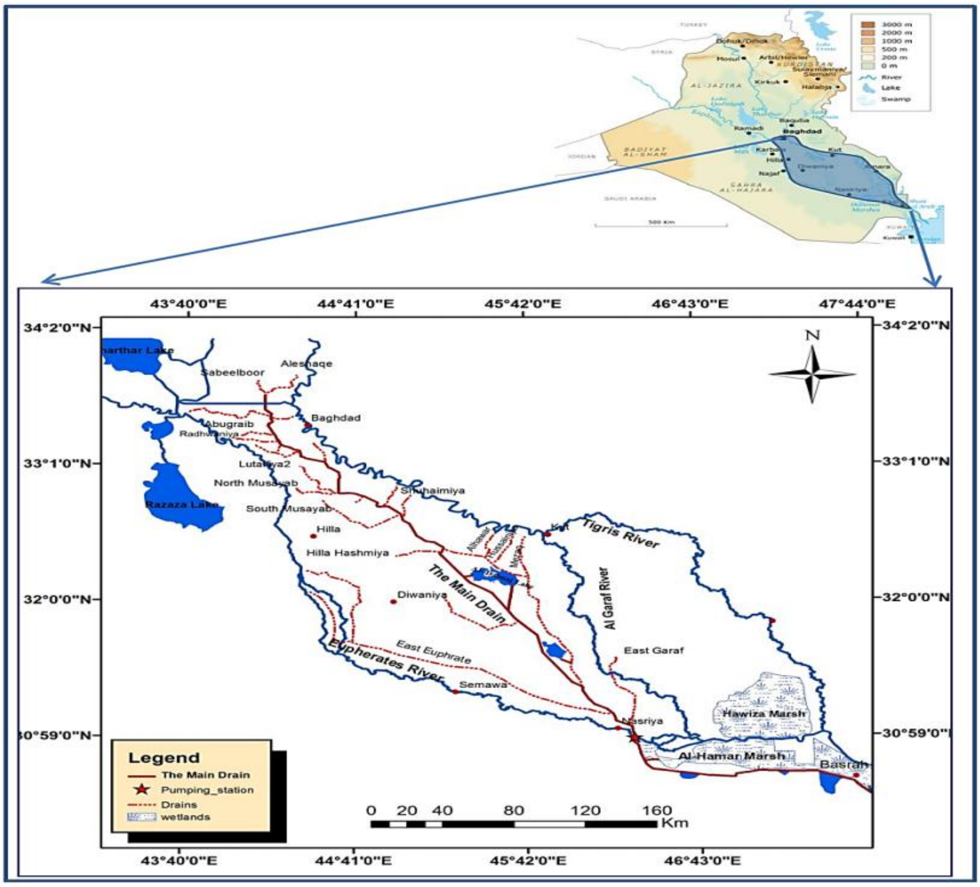


Figure 1- Location map of the study area

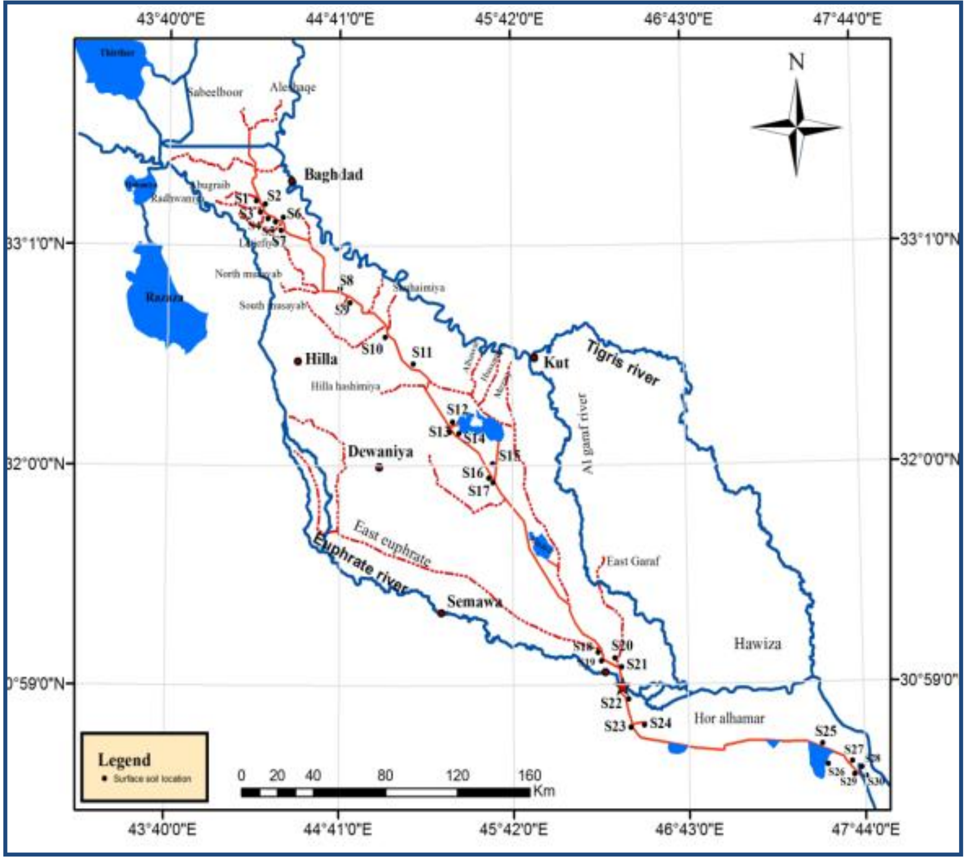


Figure 2- Location of surface soil samples.

Table 1- Summarized methods and equipment used in current study.

Chemical and mineralogical parameters	**Methods and equipment**
Al_2O_3	Chromatography analyses
Na_2O	Dissolved the sample in hydrofluoric acid (HF), then measure the Na_2O_3 by Chromatography analyses
SO_3	Titrating the sample with EDTA
SiO_2	Gravimetric method
Trace elements and Fe_2O_3	Atomic Absorption Spectrophotometer
TDS	Gravimetric method
Heavy minerals	Under the microscope after Bromoform separation according to [4]. Heavy minerals were detected by the point counting method of [4]
Clay and non-clay minerals	XRD analyzes after preparing the samples and then making three slides, Normal, Glycolated, and Heated to 550C°according to (Grim, 1968) and [4]
Grain size analyses	by MasterSizer, 2000
pH	pH –meter [5]
Organic Matter (OM)	titration with potassium dichromate [5]
Cation Exchange Capacity(CEC)	by methylene blue method [6]

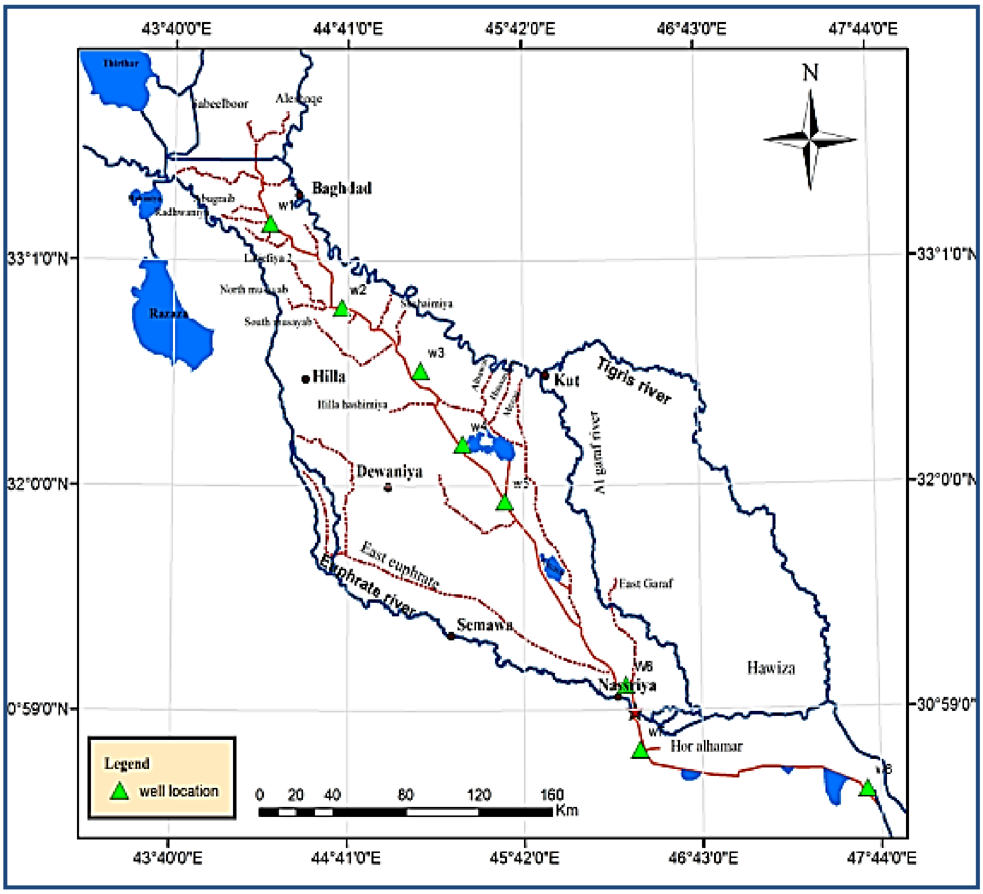


Figure 3- Location of the recent wells.

Results and discussion:

Mean values of the grain size analyses of the present study soil samples are shown in Table-2, where the mean values of silt and sand and the sand and clay are the predominant fractions in surface and subsurface soil samples respectively. Spatial distribution of the surface soil samples is shown in Figure-4, where significant variations in the sand, silt, and clay fractions of all soil samples at the downward direction can be observed. The northern and southern parts show the same distribution patterns, where the silt fraction is predominant, whereas at the middle parts, the sand fraction is predominant, due to the extensive dispersion of the aeolian deposits represented by sand dunes in this area. Shows the subsurface soil samples, where the clay fraction has the highest value at a depths of 2, 2, 4, and 4 m in the wells of Baghdad W-1, Dewaniya W-5, Nassriya W-6, and Basrah W-8 respectively, whereas the lowest value is at depths of 10, 8, 2, and 6 m at the same wells respectively, Figure- 5.

Texture names are given to the all the collected soil samples of the study area based on the web-based USDA soil texture calculator. Silty loam type is dominant in the surface soil samples, whereas the subsurface samples are characterized by clay, sandy loam, and clay, sandy clay loam types in the wells Baghdad W-1, Dewaniya W-5, Nassriya W-6, and Basrah W-8 respectively. Textural types and percentages of the surface and subsurface samples are presented in Table -2. The significant variation of the above textural types and percentages reveals the complexity of the sedimentary environments through the study area, Figure-6.

Table 2- Grain size analysis of surface and subsurface soil samples according to [4].

Surface Soil No.	Grain size analyses %			Type of soil after [6]	Subsurface Soil No.	Grain size analysis %			Type of soil after [6]
	Sand	Silt	Clay			Sand	Silt	Clay	
S1	13	75	12	Silt loam	W1-0.5m	16	25	59	Clay
S2	14	70	16	Silt loam	W1-2m	3	24	73	Clay
S3	16	25	59	Clay	W1-4m	5	23	72	Clay
S4	19	73	8	Silt loam	W1-6m	8	25	67	Clay
S5	18	65	17	Silt loam	W1-8m	18	23	59	Clay
S6	18	72	10	Silt loam	W1-10m	31	17	52	Clay
S7	11	74	15	Silt loam	W5-0.5m	48	29	23	Loam
S8	16	72	12	Silt loam	W5-2m	25	36	39	clay loam
S9	60	18	22	Sandy clay loam	W5-4m	74	12	14	sandy loam
S10	65	18	25	Sandy clay loam	W5-6m	79	10	11	sandy loam
S11	82	14	4	Loamy sand	W5-8m	95	2	3	Sand
S12	82	14	4	Loamy sand	W5-10m	93	3	4	Sand
S13	13	71	16	Silt loam	W6-0.5m	36	22	42	Clay
S14	26	65	9	Silt loam	W6-2m	48	17	35	sandy clay loam
S15	33	60	7	Silt loam	W6-4m	11	35	54	Clay
S16	27	55	18	Silt loam	W6-6m	14	35	51	Clay
S17	48	29	23	Loam	W6-8m	13	33	54	Clay
S18	36	55	9	Silt loam	W6-10m	34	27	39	clay loam
S19	35	56	9	Silt loam	W8-0.5m	55	21	24	sandy clay loam
S20	36	22	42	Clay	W8-2m	56	18	26	sandy clay loam
S21	20	69	11	Silt loam	W8-4m	54	17	29	sandy clay loam
S22	12	76	12	Silt loam	W8-6m	62	15	23	sandy clay loam
S23	22	65	13	Silt loam	W8-8m	55	18	27	sandy clay loam
S24	3	62	35	Silty clay loam	W8-10m	51	23	26	sandy clay loam
S25	14	61	25	Silt loam	Mean	41.00	21.25	37.75	
S26	6	65	29	Silty clay loam					
S27	55	21	24	Sandy clay loam					
S28	6	67	27	Silty clay loam					
S29	13	70	17	Silt loam					
S30	17	49	34	Silty clay loam					
Mean	27.87	53.60	18.80						

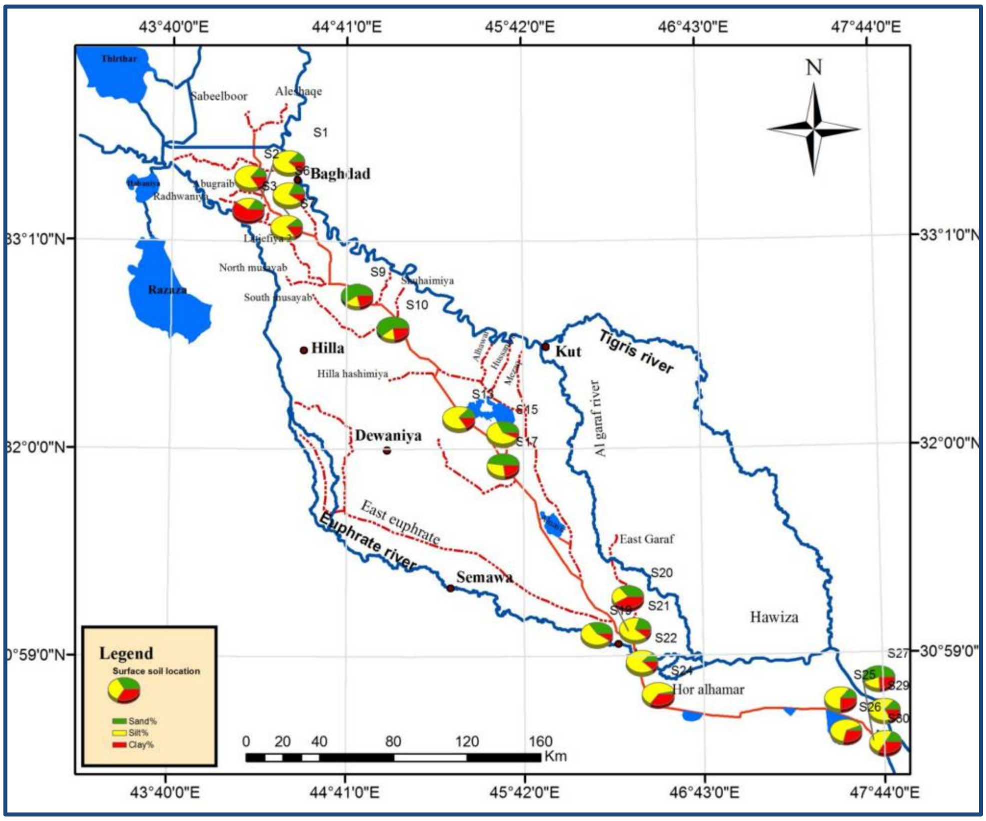


Figure 4- Grain size distribution of the study area samples.

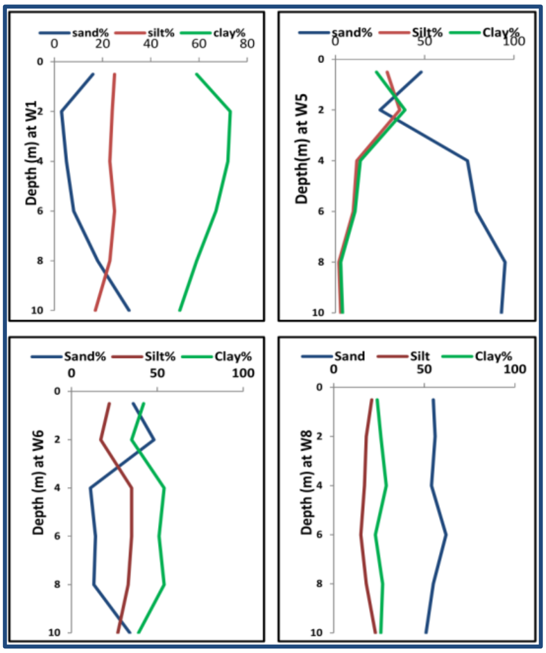
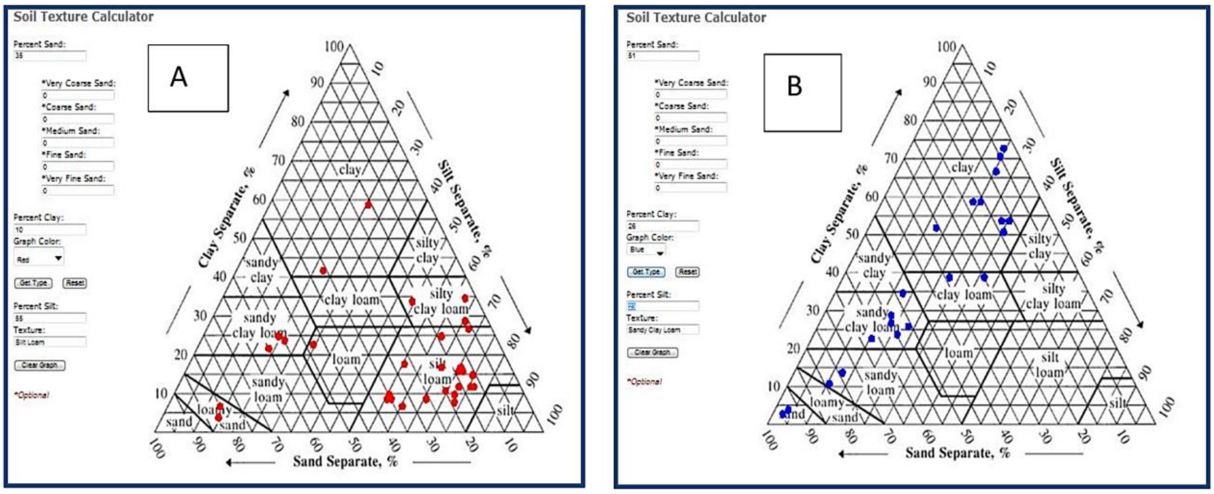


Figure 5- Vertical distribution of grain size of subsurface soil samples at the wells (W1, W5, W6, W8) drilled in the study area.



Soil Texture Calculator

Percent Sand: 35

*Very Coarse Sand: 0

*Coarse Sand: 0

*Medium Sand: 0

*Fine Sand: 0

*Very Fine Sand: 0

Percent Clay: 10

Graph Color: Red

Percent Silt: 55

Texture: Silt Loam

*Optional

Soil Texture Calculator

Percent Sand: 51

*Very Coarse Sand: 0

*Coarse Sand: 0

*Medium Sand: 0

*Fine Sand: 0

*Very Fine Sand: 0

Percent Clay: 26

Graph Color: Blue

Percent Silt: 23

Texture: Sandy Clay Loam

*Optional

Figure 6- Grain size classification of the **A**-surface soil samples, and **B**-subsurface soil samples according to [4].

Heavy minerals:

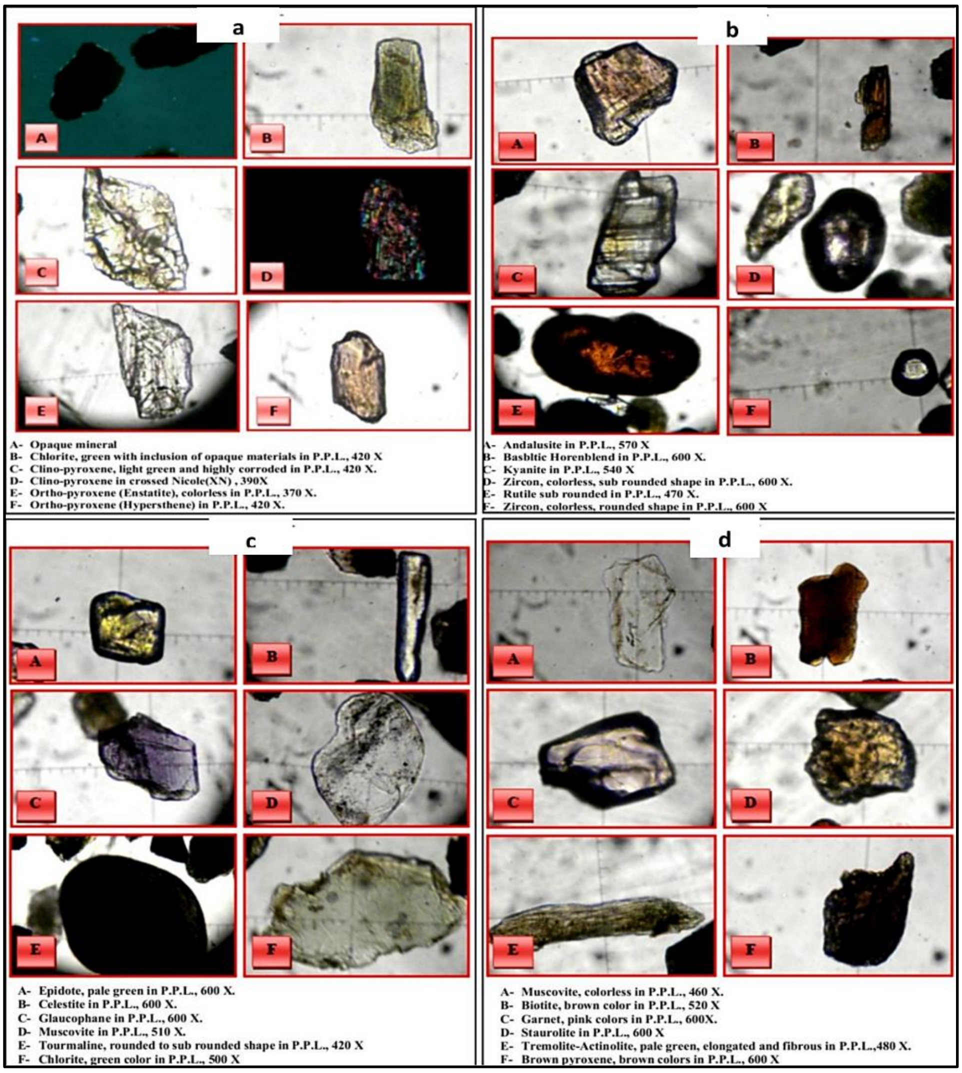
Heavy minerals are considered as the most important factor controlling the presence of trace elements in the soils [7]. Identified heavy minerals of the present study are shown in Plate (1)**.** Distribution of heavy minerals in the surface soil samples is shown by Figure-7, whereas Figure-9, shows the vertical distribution of these minerals to a depth of 10m in the currently drilled wells.

Table-3 illustrates the mean, and the range of heavy minerals in the studied soil samples. Heavy minerals of all the surface and subsurface soil samples seems to be of same distributions indicating that they are deriving mostly from igneous, metamorphic, and old sedimentary source rocks transported by the rivers to the central parts of the study area due to erosion and abrasion processes. Opaque groups have the highest percentage as compared with the other minerals. There exist slightly increasing trends in their percentages towards the southern parts of the study area, Figure-8.

Pyroxene, hornblend, chlorite, and garnet from igneous, metamorphic, and old sedimentary source rocks are also show high contents. Regarding the ultra-stable heavy minerals, zircon has the highest values as compared with the remaining minerals. Generally, types and percentages of all the heavy minerals seem to be of similar distribution patterns, and having slight variations towards downward direction indicating the same sedimentary environmental conditions.

Table 3- Mean and range (%) of the heavy minerals in the study area.

Mineral	Surface soil samples		Subsurface soil samples	
	Range%	Mean%	Range%	Mean%
Light fraction	85.67 - 98.87	94.035	85.43 - 99.10	94.671
Heavy fraction	1.13 - 14.33	5.965	0.9 - 14.57	5.327
Opaque	10.53 - 37.19	24.437	12.73 - 38.02	27.412
Alterite	0.31 - 1.18	0.643	0.31 - 1.71	0.821
Ziosite epidote	0.37 - 7.41	3.151	1.05 - 9.71	3.885
Hornbland	4.44 - 28.79	17.385	5.71 - 31.64	19.280
Ortho-pyroxene	0.38 - 10.0	5.106	1.24 - 12.50	5.237
Clino-pyroxene	10.94 - 36.88	25.716	10.94 - 33.66	22.892
Zircon	0.31 - 4.94	1.020	0.31 - 3.02	1.039
Rutile	0.41 - 2.48	1.045	0.35 - 1.21	0.648
Tourmaline	0.41 - 4.66	1.448	0.0 - 3.14	0.943
Garnet	1.49 - 17.56	5.348	1.49 - 10.42	5.593
Staurolite	0.31 - 4.07	0.931	0.3 - 2.07	0.795
Chlorite	0.72 - 30.0	8.46	0.87 - 10.97	5.950
Kyanite	0.38 - 1.06	0.569	0.35 - 0.54	0.447
Biotite	0.41 - 5.79	1.708	0.3 - 4.66	2.027
Barite-celestite	0.31 - 3.31	1.612	0.31 - 2.30	0.860
Tremolite-actinolite	0.37 - 4.78	1.930	0.41 - 3.98	1.694
Glaucophane	0.37 - 0.59	0.470	0.26 - 0.65	0.430
Basaltic-hornbland	0.31 - 1.04	0.579	0.26 - 1.15	0.760
Titanite	0.38 - 1.18	0.672	0.38 - 1.14	0.853
Muscovite	0.37 - 3.33	1.318	0.41 - 5.30	2.166
Brown-pyroxene	----	-	0.31 - 0.87	0.557



a:
A- Opaque mineral
B- Chlorite, green with inclusion of opaque materials in P.P.L., 420 X
C- Clino-pyroxene, light green and highly corroded in P.P.L., 420 X.
D- Clino-pyroxene in crossed Nicole(XN) , 390X
E- Ortho-pyroxene (Enstatite), colorless in P.P.L., 370 X.
F- Ortho-pyroxene (Hypersthene) in P.P.L., 420 X.

b:
A- Andalusite in P.P.L., 570 X
B- Basbltic Horenblend in P.P.L., 600 X.
C- Kyanite in P.P.L., 540 X
D- Zircon, colorless, sub rounded shape in P.P.L., 600 X.
E- Rutile sub rounded in P.P.L., 470 X.
F- Zircon, colorless, rounded shape in P.P.L., 600 X

c:
A- Epidote, pale green in P.P.L., 600 X.
B- Celestite in P.P.L., 600 X.
C- Glaucophane in P.P.L., 600 X.
D- Muscovite in P.P.L., 510 X.
E- Tourmaline, rounded to sub rounded shape in P.P.L., 420 X
F- Chlorite, green color in P.P.L., 500 X

d:
A- Muscovite, colorless in P.P.L., 460 X.
B- Biotite, brown color in P.P.L., 520 X
C- Garnet, pink colors in P.P.L., 600X.
D- Staurolite in P.P.L., 600 X
E- Tremolite-Actinolite, pale green, elongated and fibrous in P.P.L.,480 X.
F- Brown pyroxene, brown colors in P.P.L., 600 X

Plate 1- The identified heavy minerals of the present study are shown in (a, b, c, and d)

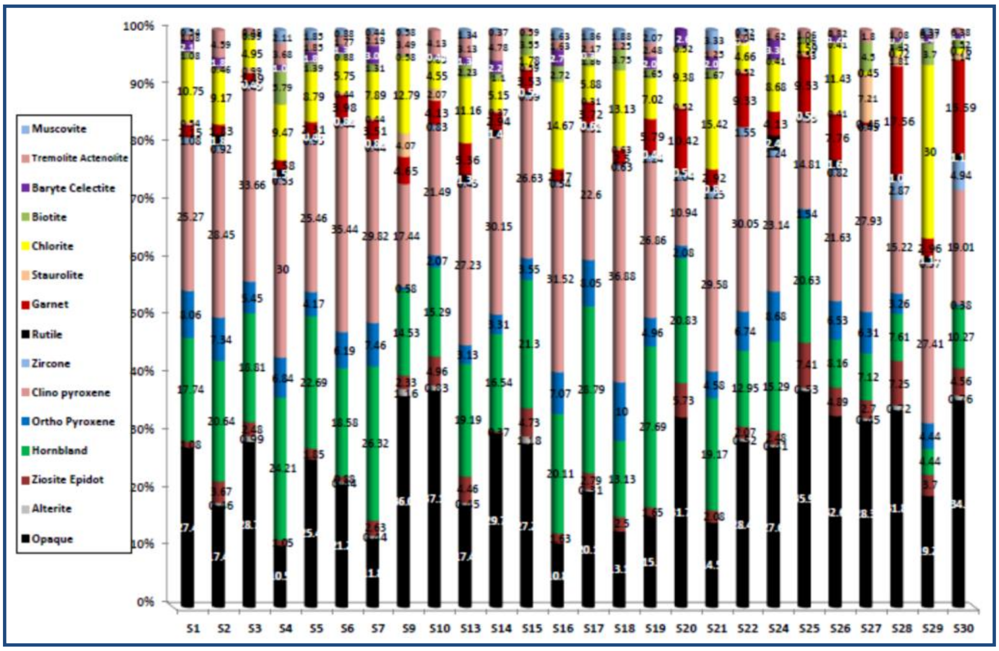


Figure 7- Distribution of the heavy minerals in the surface soil samples.

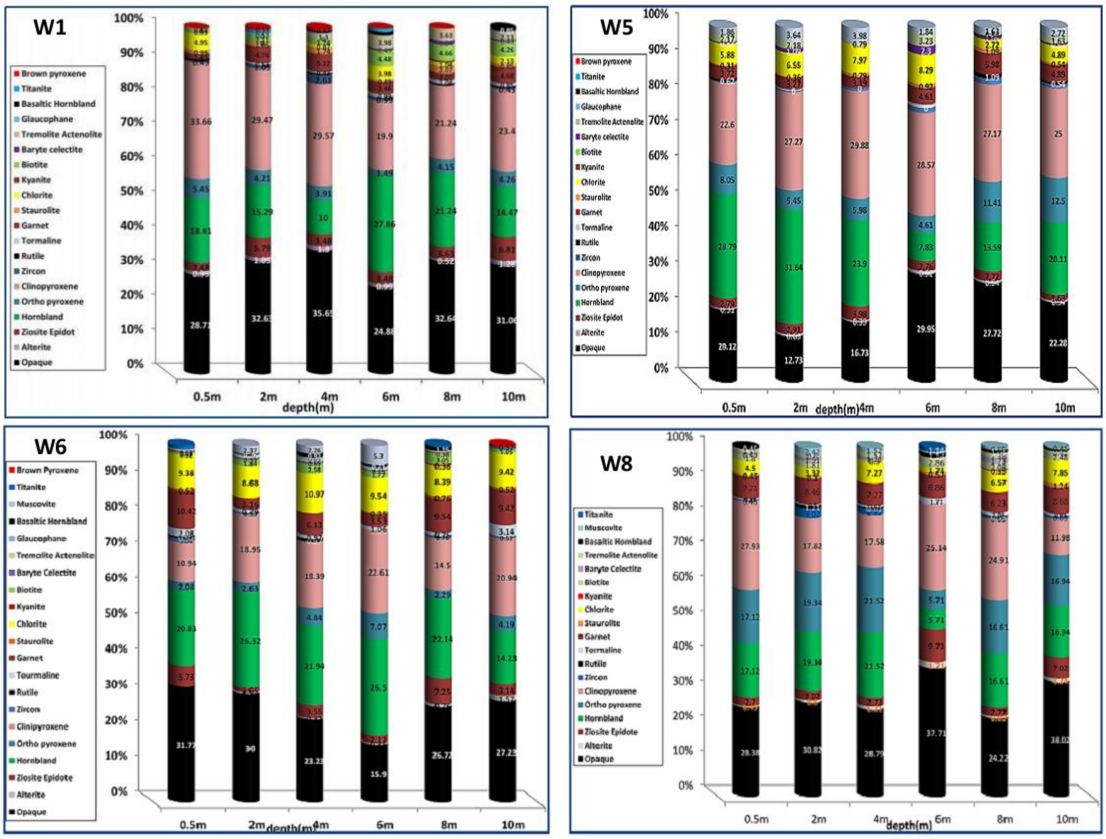


Figure 8- Vertical distribution of the heavy minerals in Baghdad well (W1), Dewaniya well (W5), Nassriya well (W6), and Basrah well (W8)

X-Ray Diffraction (XRD) analyses:

Clay minerals are important means of studying the ancient sediments and identifying the conditions of the depositional environment [8].The diversity of the clay minerals is due to many reasons like the source rocks, basin sediments, water chemistry, and human and industrial activities, [9]. Thirteen surface soil samples and twenty four subsurface soil samples are tested by X-ray Diffraction to identify their mineralogical contents. Calcite and quartz are the main non-clay minerals in these samples, whereas the other non-clay minerals vary from one site to another. Gypsum appears in the wells (W1, W6, W8) with three percentages and disappears in the well (W5). Dolomite and feldspar are appearing in all depths of these wells.

Montmorellonite is the major clay mineral in the surface and subsurface soil samples with percentages of 48 and 61 except for surface soil samples (S2, S5, S6, S10, S13, S22, S29, S30), W1 at 2meter, W5 at 4,8meter, and W8 at 8m depths, whereas the kaolinite was predominant with the percentages of 33 and 30 in the surface and subsurface soil samples respectively. Palygorskite, illite, and chlorite appear in all depths with variable percentages as explained by Figures-9 and 10.

The absorption of cations onto the surface and interlayer's of clays is an important sink for toxic metals [10]. Measured Cation Exchange Capacity,(CEC) of the present study samples explains that they are very close to each other where, the mean values of the surface and subsurface samples are 13.79 and 13.84 meq/100 gm respectively, Table-4. CEC mean values show significant variation from site to another. It decreases with the all depth of W1 and W5, and increases in the subsurface soil samples of W6 and W8 at depths of 4, 6 and 8 m. The soil samples tend to be sensitive to the pollution due to this increasing of cation exchange capacity values.

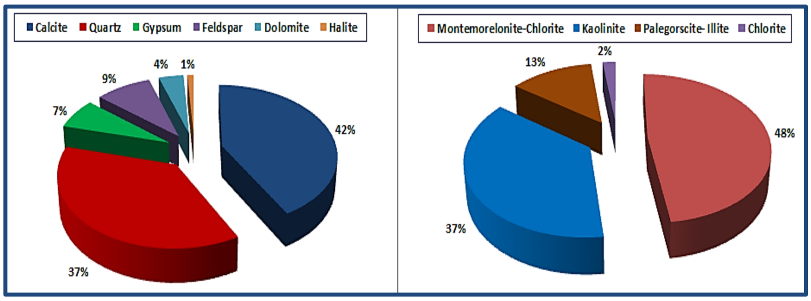


Figure 9- Clay and non-clay minerals percentages of the surface soil samples

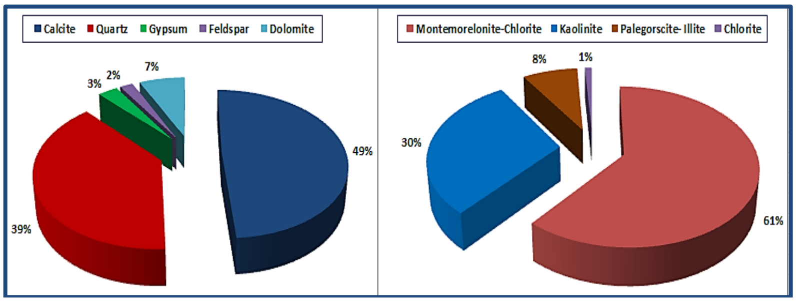


Figure 10- Clay and non-clay minerals percentages of the subsurface soil samples

Table 4- Cation exchange capacity (meq/100gm) of the surface and subsurface soil samples according to [11].

Surface sample no.	CEC(meq/100gm)	Subsurface sample no.	CEC(meq/100gm)
S1	20.32	W1-0.5m	18.76
S2	17.19	W1-2m	26.57
S3	18.76	W1-4m	25.57
S4	12.5	W1-6m	18.76
S5	15.63	W1-8m	20.32
S6	20.32	W1-10m	17.19
S7	15.63	W5-0.5m	10.94
S8	---	W5-2m	14.07
S9	12.5	W5-4m	9.38
S10	18.76	W5-6m	9.38
S11	---	W5-8m	4.9
S12	---	W5-10m	6.25
S13	14.06	W6-0.5m	9.38
S14	17.19	W6-2m	9.38
S15	12.5	W6-4m	14.07
S16	15.63	W6-6m	14.07
S17	0.94	W6-8m	10.94
S18	6.25	W6-10m	4.69
S19	7.81	W8-0.5m	14.07
S20	9.38	W8-2m	14.07
S21	15.63	W8-4m	14.07
S22	15.63	W8-6m	15.63
S23	---	W8-8m	15.63
S24	20.32	W8-10m	14.07
S25	12.15	Mean	13.8400
S26	17.19		
S27	14.07		
S28	9.37		
S29	9.37		
S30	9.4		
Mean	13.7885		

-Geochemical parameters:

Mean values of the main geochemical parameters of the present study soil samples are shown in Table-5. pH mean value of the present surface soil samples is 8.54, whereas in the subsurface soil samples, the mean value is 8.6. It has a relatively high value in depths of 8m, W5, 2 and 4 m in W6, 2m and 10m of W8. Values of pH decreased in the depth of 0.5 m in W5, 8 m in W6, and 4, 6and 8m in W8, Figure-11. Mean values of the organic matter of the surface and subsurface soil samples are 0.47% and 0.36% respectively. The organic matter is increased at the surface soil samples of W1 and then decreasing with increasing the depths, whereas it increased at depths of 0.5 and 2m and then decreasing with the depths in the W5. At W6 site, the organic matter decreased at depth of 4m, whereas increased at depths of 4 and 6 m of W8, Figure-11.

Mean values of the total dissolved solids of the surface and subsurface soils samples are 3.44% and 1.34% respectively. The vertical distribution of TDS values is the same in well W1, while it increases in surface soil of W5 and then decreasing with depth. In W6, it decreased in the depth of 4 m and then increased after 6m at the same well. At W8 site, TDS values are increased in the depths of 6 and 8 m and then decreased below depth of 10m. The nature of the salinity values variation seems to be related to the variation of the salts outwash from the soils at the different locations, Figure-11.

Table 5- Mean values of the geochemical parameters of the soil samples.

Geochemical parameters	Surface soil samples		Subsurface soil samples	
	Range	Mean	Range	Mean
pH	8.01 - 8.97	8.548	8.30 - 8.80	8.589
O.M	0.12 - 0.90	0.470	0.03 - 0.97	0.364
CEC	0.94 - 20.32	13.788	4.69 - 26.57	13.840
TDS	0.44 - 16.60	3.441	0.40 - 3.64	1.342
SiO_2	27.64 - 46.70	38.998	23.86 - 54.32	38.929
Al_2O_3	6.02 - 10.79	8.654	0.64 - 9.93	7.932
Fe_2O_3	2.80 - 6.40	5.017	2.70 - 5.40	4.208
Na_2O	0.84 - 2.60	1.270	0.64 - 1.50	1.039
SO_3	0.12 - 7.00	1.402	0.12 - 0.96	0.394

The major oxides values show that the mean value of silicon oxide is about 40% in the surface soil samples, whereas it is 39% in the subsurface soil samples. The vertical distribution of these oxides shows increasing patterns at the depth of 0.5meter in W1, 8 m in W5, and decreasing at depth of 4m in W6, no specific pattern in W8 site can be observed**.** Mean values of Al_2O_3 in the surface and subsurface soil samples of the present study are 8.654% and 7.932% respectively, Figure-11.

There is a systematic vertical distribution in Al_2O_3% in the subsurface soil samples at all the recently drilled wells in the study area except its absence in the depth of 8m at W1. Mean value of the Iron oxides is 5.01% in the surface soil samples, whereas it is 4.20% in the subsurface soil samples. No changes in the vertical distribution of the iron oxides with depths of W1, W5, and W8 can be noticed, while it increased with increasing the depth at W6. Mean values of Na_2O are 1.27% and 1.04% in the surface and subsurface soil samples respectively. There are no significant changes with the depths at all wells drilled in the study area except the small decreasing in the percent of sodium at the depths of 4 m of W6, and small increasing at depths of 6 and 8m at W8, whereas, the mean values of the SO_3 are 1.402% and 0.394% in the surface and subsurface soil samples respectively, and it has a similar vertical distribution to that of Na_2O.

Trace elements have a great ecological significance due to their toxicity and accumulation behavior [12]. The descriptive statistics of the trace element of the surface and subsurface soil samples are shown in Table-6. It appears that there are similar patterns of Fe_2O_3, Al_2O_3, and SO_3 with Mn, Zn, Cu, Ni and Co, while no specific relationship between these oxides and Sr in all wells can be observed. Na_2O has a similar relationship with Ni at W1 and Cr, Ni, Cu, Zn, Co, at W6. The same behavior is also noticed at W5 and W8. SiO_2 is correlated with Sr in W1, Co in W5, and Co, Zn, in W6, while they have different behavior as compared with trace elements in W8, Figure-11.

The distribution of the trace elements in the surface soil samples are shown in Figure-12. It is clear that the northern parts of the study area surface soil samples have the highest concentration of Mn and tend to decrease downward direction. Significant increasing of Mn concentration at Al-Khamesiya marsh and the second balancing basin was noticed. Sr has a different trend as compared with manganese, it increases at the middle stations of Dewaniya and Nasiriya and decreasing downward with obvious increasing in the second balancing basin. Ni, Cr, and Zn have the highest concentrations in the northern parts of the study area and they tend to decrease downward with remarkable increasing in Al-Khamessiya marsh. No significant changes in Co concentration along the study area surface soil samples can be detected.

Table 6- Descriptive statistics of the surface and subsurface soil samples

Geochemical parameters	Surface soil samples		Subsurface soil samples	
	Range	**Mean**	**Range**	**Mean**
pH	8.01 - 8.97	8.548	8.30 - 8.80	8.589
O.M%	0.12 - 0.90	0.470	0.03 - 0.97	0.364
CEC (meq/100gm)	0.94 - 20.32	13.788	4.69 - 26.57	13.840
TDS%	0.44 - 16.60	3.441	0.40 - 3.64	1.342
SiO_2%	27.64 - 46.70	38.998	23.86 - 54.32	38.929
Al_2O_3%	6.02 - 10.79	8.654	0.64 - 9.93	7.932
Fe_2O_3%	2.80 - 6.40	5.017	2.70 - 5.40	4.208
Na_2O%	0.84 - 2.60	1.270	0.64 - 1.50	1.039
SO_3%	0.12 - 7.00	1.402	0.12 - 0.96	0.394

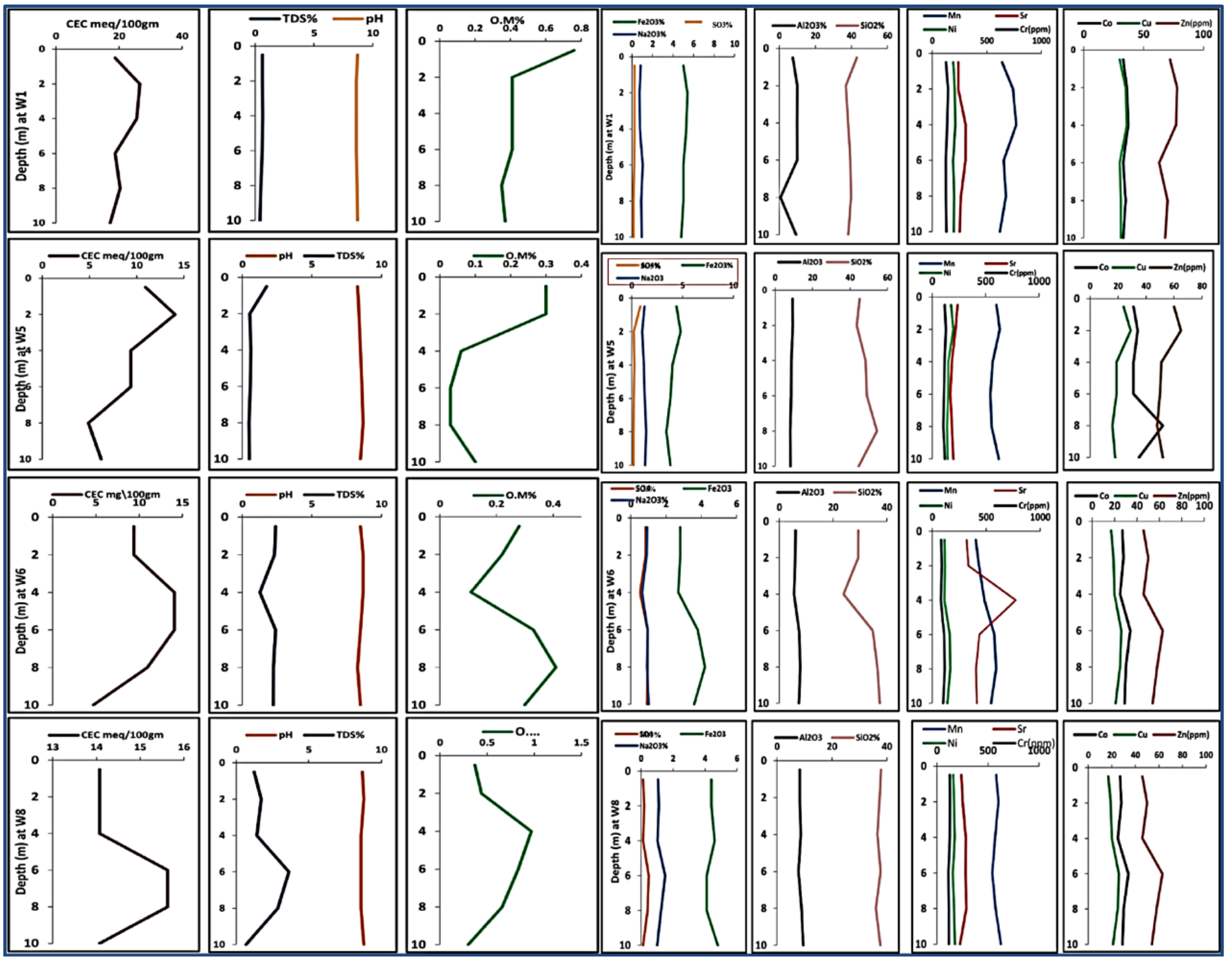


Figure 11- Vertical distribution of geochemical parameters of the subsurface soil samples at the wells drilled in the study area (W1, W5, W6, W8).

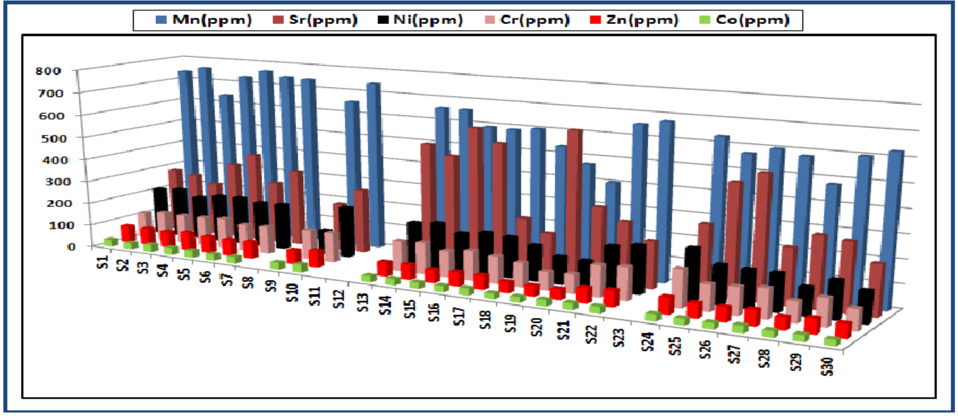


Figure 12- Spatial distribution of trace elements (ppm) in surface soil samples.

Statistical analysis of the present soil samples

a- Geochemical anomalies:

The geochemical anomalies can be identified by setting threshold values, which are the upper and lower limits of the normal variations for the particular population of data. Values within the threshold values are referred to as background values and those above and below as anomalies [13]. The threshold value can be estimated by [14]:-

Threshold = Mean ± 2 standard deviation **(1)**

The positive and negative output of the above equation refers to the upper and lower threshold values respectively.

The background and threshold values of the present study data are shown in Table-7, whereas the distribution of the anomalies values of the trace elements in the surface soil samples are shown in Figure-13. The results show that no significant differences in the distribution of the background values along the flow path of the Main Drain can be seen. Except of the positive anomalies of Mn in the sample S20, Sr in S19, Co in S10, Cu in S20, Cr in S14, and Zn in S18, S19, and S20, no anomalous values between the upper and lower parts of the Main Drain area can be noticed. Ni shows no significant anomaly along the area. From the above figures, it seems that the concentrations of Sr, Co, and Cr in S19, S10, and S24 are above the threshold value. This can be regarded as signs of local potential pollution. Mn, Cu, Cr, and Zn in S20, S19, S19, and S18, S19, S20, S28 are below the threshold.

Table 7- Thresholds and background of the trace elements of the surface soil samples.

Elements (ppm)	Mean	Standard deviation	Background	Threshold	
				Lower	Upper
Mn	632.19	93.43	636	445.31	819.06
Sr	343.61	132.02	293	79.57	607.65
Co	28.73	2.89	28	22.94	34.51
Cu	26.80	4.86	26.5	17.07	36.53
Zn	64	9.38	64	45.22	82.77
Ni	176.46	35.60	186.5	105.26	247.66
Cr	119.42	18.88	123	81.64	157.19

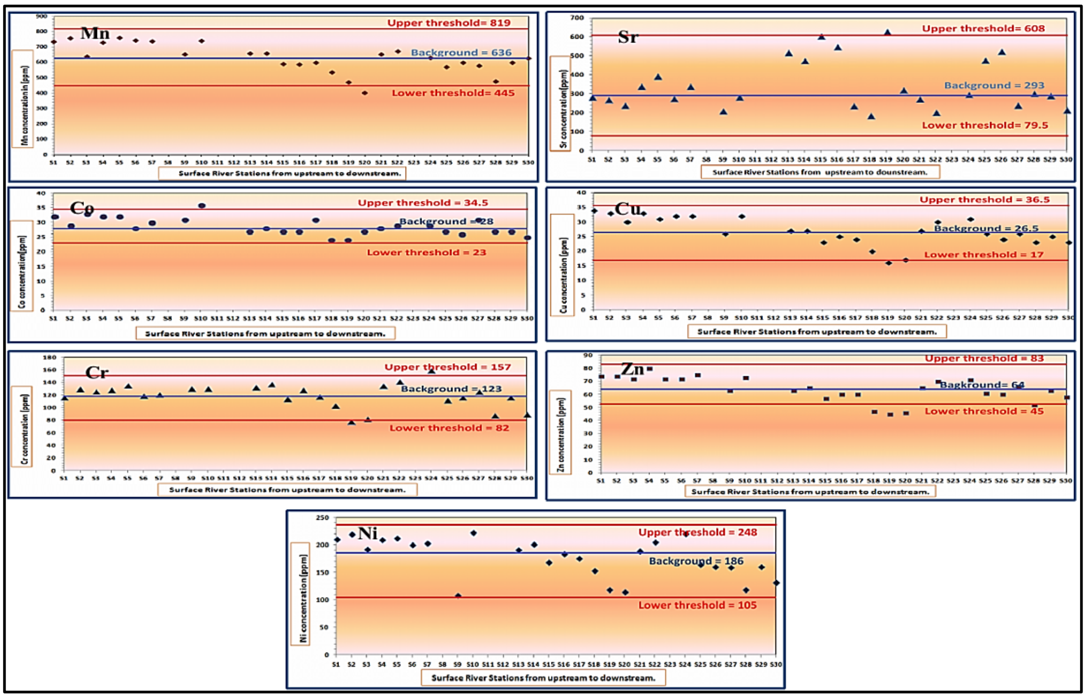


Figure 13- Ni values of the soil samples downstream direction.

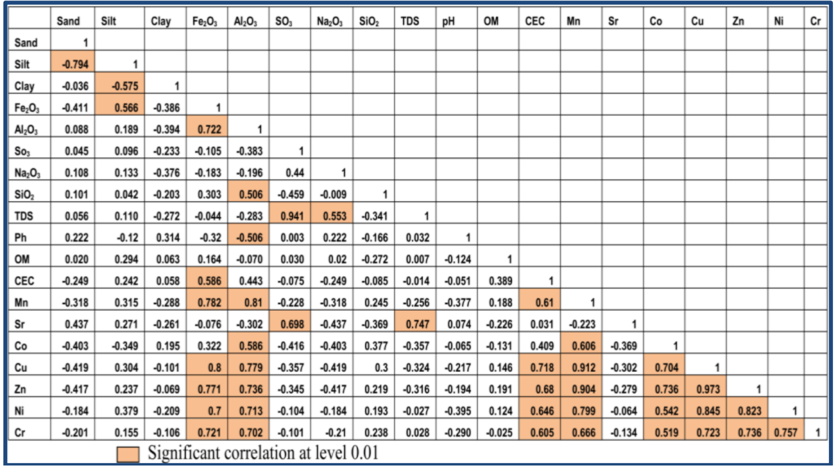
b- Multivariate Analyses:

Multivariate analysis is an important statistical technique used for analyzing and interpreting of randomly distributed data set. These data should be normally distributed and have the same scale of measurement. For the purpose of the present study, correlation coefficients, cluster analyses, and discriminate analyses were used to analyze the present surface and subsurface soil samples. The variables used in this study are soil textural, main oxides, TDS, pH, O.M, CEC, and trace elements. To eliminate the scale difference among these data, standardization of these parameters is applied and then applying the above mentioned analysis.

Correlation coefficients matrix of the surface soil samples show high and significant values between sand and silt, as well as the relation among the oxides such as Fe_2O_3, Al_2O_3, SO_3, and Na_2O_3 with Al_2O_3 and TDS, Table-8. For the subsurface soil samples, the same relationships can be noticed as well as the significant correlation between OM with both Cu and Zn. Clay contents has a significant correlation with Cu, Ni, and CEC, and Na_2O_3, Table-9.

Cluster analysis technique is used to investigate the main assemblages based on their characteristics into many groups. The dendrograms of the surface and subsurface soil samples shows five and six groups are obtained respectively. These grouping patterns will be used later in the discriminant analysis of the same data, Figure-14.

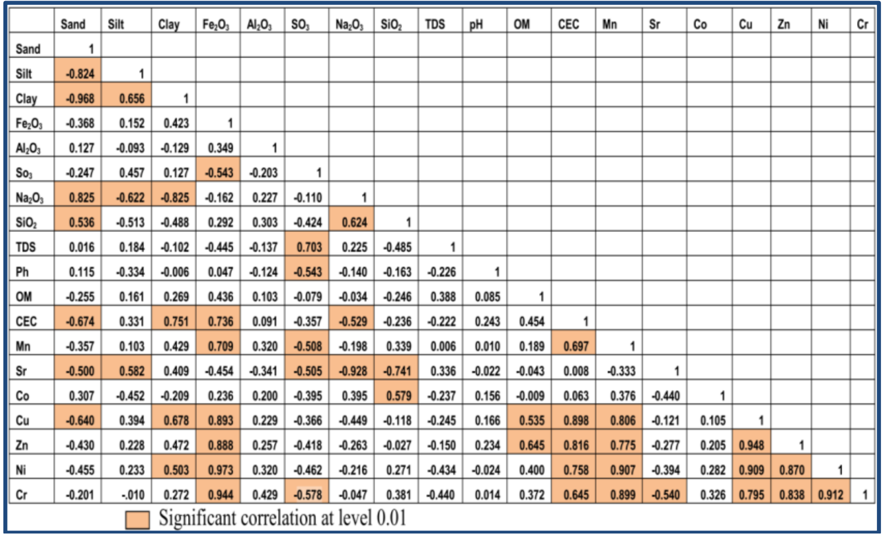
Table 8- Correlation coefficient matrix of the surface soil samples



	Sand	Silt	Clay	Fe_2O_3	Al_2O_3	SO_3	Na_2O_3	SiO_2	TDS	pH	OM	CEC	Mn	Sr	Co	Cu	Zn	Ni	Cr
Sand	1																		
Silt	**-0.794**	1																	
Clay	-0.036	**-0.575**	1																
Fe_2O_3	-0.411	**0.566**	-0.386	1															
Al_2O_3	0.088	0.189	-0.394	**0.722**	1														
So_3	0.045	0.096	-0.233	-0.105	-0.383	1													
Na_2O_3	0.108	0.133	-0.376	-0.183	-0.196	0.44	1												
SiO_2	0.101	0.042	-0.203	0.303	**0.506**	-0.459	-0.009	1											
TDS	0.056	0.110	-0.272	-0.044	-0.283	**0.941**	**0.553**	-0.341	1										
Ph	0.222	-0.12	0.314	-0.32	**-0.506**	0.003	0.222	-0.166	0.032	1									
OM	0.020	0.294	0.063	0.164	-0.070	0.030	0.02	-0.272	0.007	-0.124	1								
CEC	-0.249	0.242	0.058	**0.586**	0.443	-0.075	-0.249	-0.085	-0.014	-0.051	0.389	1							
Mn	-0.318	0.315	-0.288	**0.782**	**0.81**	-0.228	-0.318	0.245	-0.256	-0.377	0.188	**0.61**	1						
Sr	0.437	0.271	-0.261	-0.076	-0.302	**0.698**	-0.437	-0.369	**0.747**	0.074	-0.226	0.031	-0.223	1					
Co	-0.403	-0.349	0.195	0.322	**0.586**	-0.416	-0.403	0.377	-0.357	-0.065	-0.131	0.409	**0.606**	-0.369	1				
Cu	-0.419	0.304	-0.101	**0.8**	**0.779**	-0.357	-0.419	0.3	-0.324	-0.217	0.146	**0.718**	**0.912**	-0.302	**0.704**	1			
Zn	-0.417	0.237	-0.069	**0.771**	**0.736**	-0.345	-0.417	0.219	-0.316	-0.194	0.191	**0.68**	**0.904**	-0.279	**0.736**	**0.973**	1		
Ni	-0.184	0.379	-0.209	**0.7**	**0.713**	-0.104	-0.184	0.193	-0.027	-0.395	0.124	**0.646**	**0.799**	-0.064	**0.542**	**0.845**	**0.823**	1	
Cr	-0.201	0.155	-0.106	**0.721**	**0.702**	-0.101	-0.21	0.238	0.028	-0.290	-0.025	**0.605**	**0.666**	-0.134	**0.519**	**0.723**	**0.736**	**0.757**	1

▨ Significant correlation at level 0.01

Table 9- Correlation coefficient matrix of the subsurface soil samples



	Sand	Silt	Clay	Fe_2O_3	Al_2O_3	SO_3	Na_2O_3	SiO_2	TDS	pH	OM	CEC	Mn	Sr	Co	Cu	Zn	Ni	Cr
Sand	1																		
Silt	**-0.824**	1																	
Clay	**-0.968**	**0.656**	1																
Fe_2O_3	-0.368	0.152	0.423	1															
Al_2O_3	0.127	-0.093	-0.129	0.349	1														
So_3	-0.247	0.457	0.127	**-0.543**	-0.203	1													
Na_2O_3	**0.825**	**-0.622**	**-0.825**	-0.162	0.227	-0.110	1												
SiO_2	**0.536**	-0.513	-0.488	0.292	0.303	-0.424	**0.624**	1											
TDS	0.016	0.184	-0.102	-0.445	-0.137	**0.703**	0.225	-0.485	1										
Ph	0.115	-0.334	-0.006	0.047	-0.124	**-0.543**	-0.140	-0.163	-0.226	1									
OM	-0.255	0.161	0.269	0.436	0.103	-0.079	-0.034	-0.246	0.388	0.085	1								
CEC	**-0.674**	0.331	**0.751**	**0.736**	0.091	-0.357	**-0.529**	-0.236	-0.222	0.243	0.454	1							
Mn	-0.357	0.103	0.429	**0.709**	0.320	**-0.508**	-0.198	0.339	0.006	0.010	0.189	**0.697**	1						
Sr	**-0.500**	**0.582**	0.409	-0.454	-0.341	**-0.505**	**-0.928**	**-0.741**	0.336	-0.022	-0.043	0.008	-0.333	1					
Co	0.307	-0.452	-0.209	0.236	0.200	-0.395	0.395	**0.579**	-0.237	0.156	-0.009	0.063	0.376	-0.440	1				
Cu	**-0.640**	0.394	**0.678**	**0.893**	0.229	-0.366	-0.449	-0.118	-0.245	0.166	**0.535**	**0.898**	**0.806**	-0.121	0.105	1			
Zn	-0.430	0.228	0.472	**0.888**	0.257	-0.418	-0.263	-0.027	-0.150	0.234	**0.645**	**0.816**	**0.775**	-0.277	0.205	**0.948**	1		
Ni	-0.455	0.233	**0.503**	**0.973**	0.320	-0.462	-0.216	0.271	-0.434	-0.024	0.400	**0.758**	**0.907**	-0.394	0.282	**0.909**	**0.870**	1	
Cr	-0.201	-.010	0.272	**0.944**	0.429	**-0.578**	-0.047	0.381	-0.440	0.014	0.372	**0.645**	**0.899**	**-0.540**	0.326	**0.795**	**0.838**	**0.912**	1

▨ Significant correlation at level 0.01

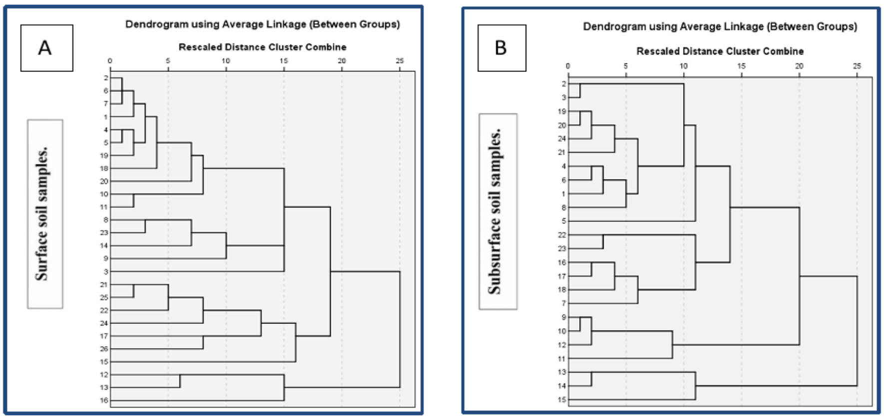


Figure 14- Dendrograms of **A**-surface soil samples and **B-** subsurface soil samples.

c- Discriminant analysis:

Discriminant analysis (DA) involves the determination of a linear equation like regression that will predict which group the case belongs to. The form of the equation is, [15]:

$$\mathbf{D=v_1X_1+v_2X_2+v_3X_3\ \ldots\ldots=v_iX_i+a} \qquad \mathbf{(1)}$$

Where,D=discriminant function. v=the discriminant coefficient or weight for that variable.
X=respondents score for that variable. a= constant. i= the number of predictor variable.

The v’s are un-standardized discriminant coefficient analogue to the b’s in the regression equation. The v’s maximize the distance between the means of the criteria (dependent). Standardized discriminant coefficient can also be used like beta weight in the regression. The number of discriminant functions is one less than the number of groups [16]. Discriminant analysis is applied to the above variables using stepwise method to determine the most discriminating parameters. In this analysis, Wilk’s lambda shows the significance of the discriminate functions and provides the proportions of the total variability not explained, i.e. it is the converse of the squared canonical correlation.

By application of DA, four steps were achieved to classify the present study surface soils. The minimum value of the Wilk’s Lambda was recorded whereas four discriminately functions were obtained. These four functions have eigen-values accounting of 100% of the total variance where the canonical correlations among these functions shown to be of high values. All of the obtained functions are significant in the discriminating processes as appeared from Table-10, The standardized canonical function and discriminant function coefficients show that sand% and Al_2O_3 have the highest weights on the first function; clay and TDS have the highest weights on the second function whereas the third function has highest weights of Al_2O_3 and clay content was the highest on the fourth function. Classification results show that 96.2% of the original grouped cases are correctly classified, whereas 76.9% of the cross-validated are correctly classified, Table-11.

Wilk's Lambda values and the discriminating functions obtained where the variance of the subsurface soil samples are explained by four discriminating functions, Table-12. The canonical correlations of the obtained discriminating functions were of high values. Wilk's Lambda table shows that these functions are significant in interpreting the data variability. Standardized canonical coefficient of the above functions reveals that sand%, oxides content, and salinity of the subsurface soils have the highest weights in discriminating the previously identified groups. Classification results show that 100% of the original grouped cases are correctly classified, whereas 95.8% of the cross-validated are correctly classified, Table-13.

Table 10- Outline of the canonical discriminant functions of the surface soil samples.

Eigenvalues				
Function	**Eigenvalue**	**Variance %**	**Cumulative %**	**Correlation**
1	**7.041**	**43.8**	**43.8**	**0.936**
2	**5.850**	**36.4**	**80.2**	**0.924**
3	**2.673**	**16.6**	**96.8**	**0.853**
4	**0.516**	**3.2**	**100**	**0.583**
Wilks' Lambda				
Test of Function(s)	**Wilks' Lambda**	**Chi-square**	**df**	**Sig.**
1 through 4	**0.003**	**114.521**	**20**	**0.000**
2through4	**0.026**	**72.831**	**12**	**0.000**
3 through4	**0.180**	**34.345**	**6**	**0.000**
4	**0.660**	**8.324**	**2**	**0.016**
Discriminant function coefficients				
	function			
	1	**2**	**3**	**4**
Sand	**0.916**	**0.341**	**0.350**	**-0.118**
Clay	**-0.172**	**0.789**	**0.224**	**0.651**
Al_2O_3	**0.626**	**0.160**	**-0.686**	**0.537**
TDS	**0.325**	**-0.798**	**0.255**	**0.556**

Table 11- Classification results of the present surface soil groups.

			Group	**Predicted group membership**						**Total**
				1	**2**	**3**	**4**	**5**	**6**	
original	**count**	**1**	**1**	**10**	**0**	**0**	**0**	**1**	**0**	**11**
		2	**2**	**0**	**4**	**0**	**0**	**0**	**0**	**4**
		3	**3**	**0**	**0**	**1**	**0**	**0**	**0**	**1**
		4	**4**	**0**	**0**	**0**	**0**	**0**	**0**	**6**
		5	**5**	**0**	**0**	**0**	**0**	**1**	**0**	**1**
		6	**6**	**0**	**0**	**0**	**0**	**0**	**3**	**3**
	%	**1**	**1**	**90.9**	**0**	**0**	**0**	**9.1**	**0**	**100**
	%	**2**	**2**	**0**	**100**	**0**	**0**	**0**	**0**	**100**
	%	**3**	**3**	**0**	**0**	**100**	**0**	**0**	**0**	**100**
	%	**4**	**4**	**0**	**0**	**0**	**100**	**0**	**0**	**100**
	%	**5**	**5**	**0**	**0**	**0**	**0**	**100**	**0**	**100**
	%	**6**	**6**	**0**	**0**	**0**	**0**	**0**	**100**	**100**
Cross-validated	**count**	**1**	**1**	**9**	**0**	**0**	**1**	**1**	**0**	**11**
		2	**2**	**0**	**4**	**0**	**0**	**0**	**0**	**4**
		3	**3**	**0**	**0**	**0**	**1**	**0**	**0**	**1**
		4	**4**	**0**	**0**	**1**	**5**	**0**	**0**	**6**
		5	**5**	**1**	**0**	**0**	**0**	**0**	**0**	**1**
		6	**6**	**0**	**0**	**0**	**0**	**1**	**2**	**3**
	%	**1**	**1**	**81.8**	**.0**	**.0**	**9.1**	**9.1**	**.0**	**100**
	%	**2**	**2**	**.0**	**100**	**.0**	**.0**	**.0**	**.0**	**100**
	%	**3**	**3**	**.0**	**.0**	**.0**	**100**	**.0**	**.0**	**100**
	%	**4**	**4**	**.0**	**.0**	**16.7**	**83.3**	**.0**	**.0**	**100**
	%	**5**	**5**	**100**	**.0**	**.0**	**.0**	**.0**	**.0**	**100**
	%	**6**	**6**	**.0**	**.0**	**.0**	**.0**	**33.3**	**66.7**	**100**
Correctly classified original grouped cases = 96.2% **Correctly classified cross-validated grouped cases =76.9 %**										

Table 12- Outline of the canonical discriminant functions of the present subsurface soil samples.

Eigenvalues				
Function	**Eigenvalue**	**Variance %**	**Cumulative %**	**Correlation**
1	31.519	62.7	62.7	0.985
2	12.450	24.8	87.4	0.962
3	5.267	10.5	97.9	0.917
4	1.065	2.1	100	0.718
Wilks' Lambda				
Test of Function(s)	**Wilks' Lambda**	**Chi-square**	**df**	**Sig.**
1 through 4	0.000	155.539	20	0.000
2through4	0.006	92.866	12	0.000
3 through4	0.077	46.084	6	0.000
4	0.484	13.049	2	0.001
Discriminant function coefficients				
	Function			
	1	2	3	4
Sand	1.521	0.009	-0.368	-0.198
Fe_2O_3	1.075	-0.813	0.710	-0.028
Al_2O_3	-0.240	1.151	0.257	-0.111
SiO_2	0.644	0.090	-0.067	0.680
TDS	-1.206	-0.211	0.719	0.708

Table 13- Classification results of the present subsurface soil groups.

			Group	Predicted group membership					Total
				1	2	3	4	5	
original	count	1	1	11	0	0	0	0	11
		2	2	0	1	0	0	0	1
		3	3	0	0	5	0	0	5
		4	4	0	0	0	4	0	4
		5	5	0	0	0	0	3	3
	%	1	1	100	.0	.0	.0	.0	100
	%	2	2	.0	100	.0	.0	.0	100
	%	3	3	.0	.0	100	.0	.0	100
	%	4	4	.0	.0	.0	100	.0	100
	%	5	5	.0	.0	.0	.0	100	100
Cross-validated	count	1	1	11	0	0	0	0	11
		2	2	1	0	0	0	0	1
		3	3	0	0	5	0	0	5
		4	4	0	0	0	4	0	4
		5	5	0	0	0	0	3	3
	%	1	1	100	.0	.0	.0	.0	100
	%	2	2	100	.0	.0	.0	.0	100
	%	3	3	.0	.0	100	.0	.0	100
	%	4	4	.0	.0	.0	100	.0	100
	%	5	5	.0	.0	.0	.0	100	100
Correctly classified original grouped cases = 100% Correctly classified cross-validated grouped cases = 95.8%									

Conclusions:

Several conclusions can be drawn from the present work as:

- Great variation in the lateral and vertical distribution of the soil textures is noticed. This reflects the complexity and diversity of the sedimentary environments of the study area.
- The sedimentary environments variations are highly reflected in the nature of the main minerals distribution, i.e. clay and non-clay minerals.
- Trace elements concentrations values show that they are within the threshold values where no geochemical anomalies can be detected, except of locations that reflecting potential local pollution.
- Clustering and discriminate analyses explain presence of five and six groups for surface and subsurface soils respectively, where the sand, salinity and the main oxides distribution are the main discriminating variables responsible for study area grouping. This confirms the complexity of the study area geological conditions. No significant signs of trace elements pollution can be observed.

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