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Effects of Land Uses on Soil Quality of Shwan Sub-basin, Kirkuk Governorate, Northern Iraq

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Abstract

Thirty-two soil samples were collected from the study area in October 2020 for geochemical and pollutants investigation of Shwan Sub-basin soil. All soil samples were analysed for different geochemical analyses. The analysis results revealed that the pH values in soil samples ranged from 7.12 to 7.56 with a mean of 7.327. According to the pH values detected in the soil samples, the soil is classified as neutral soil. The electrical conductivity ranged from 0.92 mmhos/cm to 7.8 mmhos/cm with a mean of 1.53 mmhos/cm. Thus, according to the detected electrical conductivity values, the soil was classified as non-saline to slightly saline. The organic matter ranged from 1.14% to 1.45% with a mean value of 1.326 %, while total organic carbon ranged from 0.66 % to 0.84 % with a mean value of 0.769 % which indicated the soil was characterized by low organic content. The results of the geochemical analysis revealed that the major and minor element mean concentrations were in the order Si> Ca> Al> Fe> Mg > K> Ti> Na> P> Mn> S> Cl> N. The average concentrations of trace elements in soil samples followed the decreasing order Sr > Cr> Ba> Zr> Ni> V> Zn> Ta> Rb> Cu> Nb> Y> Pb> Co> Ga> Mo> As> Th> Br> Sn> I. Furthermore, the comparison between heavy metal concentrations in the soil of the study area and metal concentrations in the world soil limit and Indirect Geochemical Background revealed an increase in metal concentrations of Cr, Ni, Zn, Co, As, Mo and Ta. Multivariate statistical analyses, such as Principal Component Analysis and Agglomerative Hierarchal Cluster Analysis, identified the potential sources of pollutants in the soil. Most metals are from natural sources and some of them are from anthropogenic sources mostly from agricultural activities mainly fertilizers use and the waste of animals breeding on farms. Besides industrial activities such as deposits of pollutants from emissions of petroleum refineries located inside or close to the study area. In addition, building blocks and paint factories.

Keywords: Soil quality, Shwan Sub-basin, Geochemistry, Multivariate statistical analyses.

تأثير استخدامات الارض على نوعية التربة في حوض شوان الثانوي، محافظة كركوك، شمال العراق

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الخلاصة

اثنان وثلاثون عينة تربة تم جمعها من منطقة الدراسة في شهر تشرين الاول سنة 2020 من اجل التحري الجيوكيميائي وملوثات تربة حوض شوان الثانوي. كل عينات التربة تم تحليلها لمختلف التحاليل الجيوكيميائية. نتائج التحاليل كشفت ان حامضية التربة كانت من 7.12 الى 7.56 وبمعدل 7.327 وحسب هذه القيم صنفت تربة منطقة الدراسة بأنها تربة معتدلة الحامضية. تراوحت قيم التوصيلية الكهربائية من 0.92 مليموز/سم الى 7.8 مليموز/سم وبمعدل 1.53 مليموز/سم. وحسب قيم التوصيلية الكهربائية المقاسة صنفت تربة منطقة الدراسة بالغير مالحة الى قليلة الملوحة. تراوحت قيم المادة العضوية من 1.14 % الى 1.45 % وبمعدل 1.326 %، بينما قيم الكاربون العضوي الكلي قد تراوحت بين 0.66 % الى 0.84 % وبمعدل 0.769 %، وهذه القيم تشير الى ان تربة منطقة الدراسة تتصف بمحتوى واطئ من المادة العضوية. نتائج التحليل الجيوكيميائي كشفت عن ان تراكيز العناصر الكيميائية الرئيسية والثانوية كانت بالترتيب التالي

Si> Ca> Al> Fe> Mg > K> Ti> Na> P> Mn> S> Cl> N

اما معدل تراكيز العناصر الشحيحة في عينات التربة كان Sr <Cr> Ba> Zr> Ni> V> Zn> Ta> Rb> بالترتيب التالي

Y> Pb> Co> Ga> Mo> As> Th> Br> Sn> I . مقارنة نتائج تراكيز العناصر الثقيلة في تربة منطقة الدراسة وتراكيزها في الترب

العالمية وقيم الخلفية الجيوكيميائية غير المباشرة كشفت زيادة تراكيز العناصر الثقيلة لكل من Cr, Ni, Zn, Co, As, Mo, Ta.

نتائج التحليل المتعدد المتغيرات المستخدم كتحليل العناصر الاساسية والتحليل العنقودي حدد مصادر التلوث المحتملة للملوثات بالتربة. اغلب العناصر الكيميائية نتجت من مصادر طبيعية وبعض العناصر نتجت من مصادر متمثلة بالأنشطة البشرية والتي اغلبها هي من الاسمدة وكذلك من الانشطة الصناعية المتمثلة بمصافي النفط سواء من داخل منطقة الدراسة او من المناطق المجاورة اضافة الى معامل الطابوق الاسمنتي والاصباغ.

1. Introduction

Soil is a very specific component of the biosphere because it is not only a geochemical sink for contaminants, but also acts as a natural buffer controlling the transport of chemical elements and substances to the atmosphere, hydrosphere, and biota. However, the most important role of soil is its productivity, which is essential for the survival of humans [1]. There are twelve major, minor and trace elements (Si, Al, O, Ca, Fe, K, Ti, Mg, Mn, Na, Cr, Ni) representing about 99.4% of its total composition of soil composition and at least sixty-eight trace elements account for the rest [2]. However, local or regional geochemistry plays an important role in soil composition [2]. The major elements generally occur in minerals, so they can be used as a tool for discriminating element-mineral associations [3], [4]. The parent rocks are the major controlling factor in the concentration of heavy metals. Trace elements originating from various sources may finally reach the surface soil, and their further fate depends on the soil's chemical and physical properties and especially on their speciation [1]. Heavy metals are particularly of environmental concern because of their potential toxicity and their importance as essential nutrients. The background concentration of heavy metals in soils is, therefore, important due to the recent interest in contamination potential and toxic effects of these elements on humans and the environment [5]. Soil contamination means soil whose chemical state deviates from the normal composition but does not have a detrimental effect on organisms. Pollution occurs when an element or a substance is present at greater than natural (background) concentrations as a result of human activity and has a net detrimental effect on the environment and its components [1]. Background concentrations are not necessarily equal to low concentrations and the citation of single values for a geochemical background is neither useful for the characterization of the geogenic background nor the determination of anthropogenic contamination because single values do not yield information about the natural deviation [6], [7]. Several methods have been developed to calculate the background content of trace elements in soils. There is great demand for such data as reference values because the entirely natural contents of trace elements do not currently exist. In general, these methods are based either on statistical calculations or on the relation of trace elements to various soil parameters and geologic factors [1]. Furthermore, soil contamination could affect the groundwater quality by leachate of different chemicals throughout the soil horizons until it reaches groundwater. Shwan Sub-basin is one of the important agricultural regions in north Iraq with high crop production that has been elevated in the last decades. Additionally, because the area depends on groundwater as a supply of water, it is crucial to assess soil contamination that could be a possible contamination source for groundwater by pollutants infiltration throughout the soil. While some studies have addressed hydrogeology and groundwater vulnerability assessment [8], [9], [10]. There was no study concerned with the geochemistry and soil quality of the Shwan Sub-basin soil. Additionally, they evaluate the possible sources of soil contamination. Therefore, this study aims to address the distribution, levels, and sources of chemical elements, and identify the physical properties and texture of the soil along the study area. Besides, investigate the possible influence of different land uses and land cover on the geochemical properties of the soil and estimates pollutant sources through statistical and pollution analyses.

1.1 Study area

The study area is located north of Iraq, northeast of Kirkuk Governorate between latitudes (35°32'31"-35°48'50") N and longitudes (44°06'50" – 44°37'37") E and occupies an area of 829 km^2, bordered by the northern Chamchamal Anticline from the northeast, and the Kirkuk structure, Baba Dome-Kany Domalan Mountain in the southwest. The Lesser Zab River borders the basin from the north (Figure 1). The region is characterized by variable terrain, which is between simple regressions and semi-flat terrain. Generally, elevation ranges between 200 and 850 m above sea level (ASL) (Figures 2 & 3). The main land use in the study area is agricultural. Besides, industrial activities are dominant in the southern part.

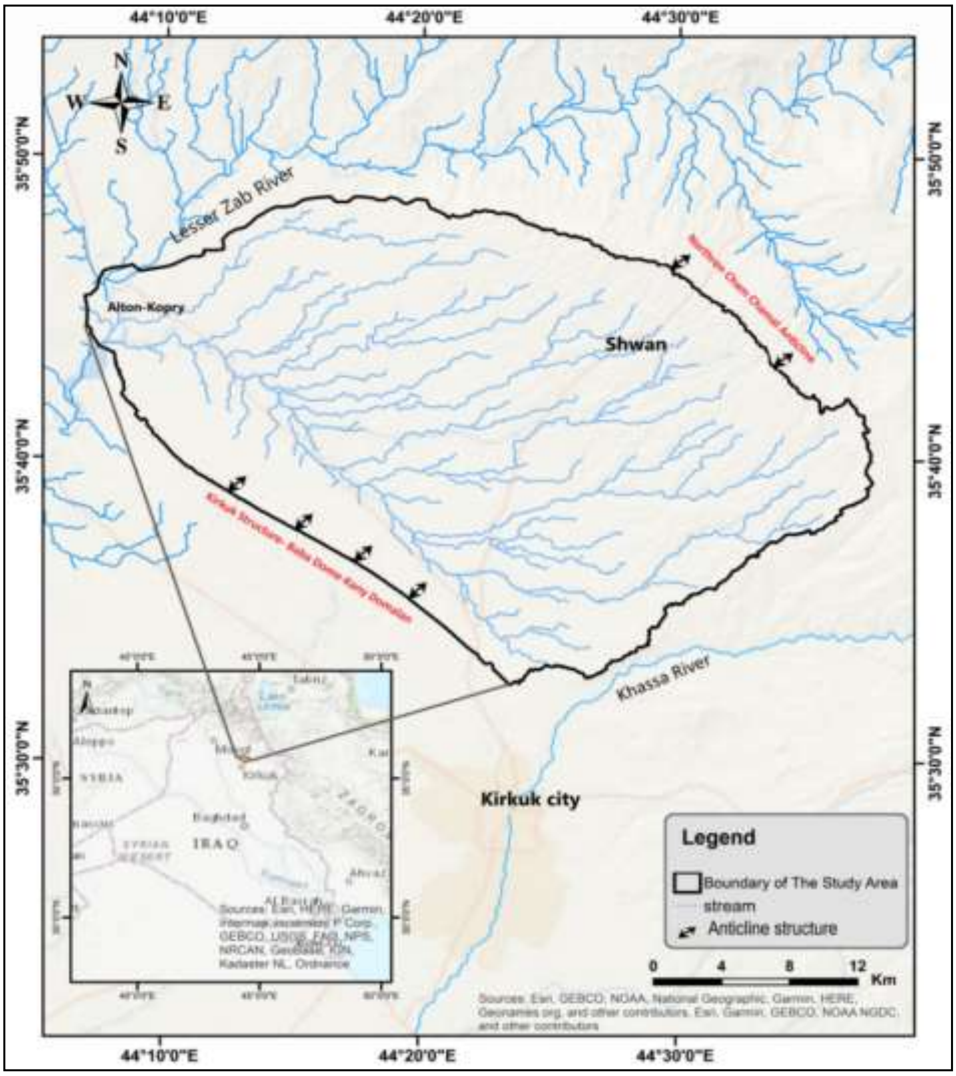

Figure 1: Location of the study area in the north of Iraq.

1.2 Geological setting

The Shwan Sub-basin is located in Iraq's folded zone of the unstable shelf and is part of the foothill zone. The unstable shelf has been the most subsiding region of the Arabian Plate [11]. The age of outcrop formations ranges from the Miocene to the Holocene [12] (Figure 2). The Kany Domalan Mountain series, a part of the Baba Dome series, forms the southwest edge of the area. The Bi-Hassan Formation is exposed in the basin's northeast along the northern Chamchamal Anticline. However, the Quaternary deposits (Pleistocene and Holocene) covered the center of the basin, known as the Julak Basin [13].

2. Materials and Methods

2.1. Materials

Sampling and analyses

Thirty-two soil samples were collected from the study area in October 2020 (Figure 3). Approximately 2-3 kg of surface soil was collected with a stainless-steel tool at a depth of 25 cm below the surface [14], and stored in polyethylene bags. All soil samples were air-dried and were sieved to remove large debris, stones and pebbles and then sieved to obtain a soil fraction less than 2 mm for geochemical analysis [14].

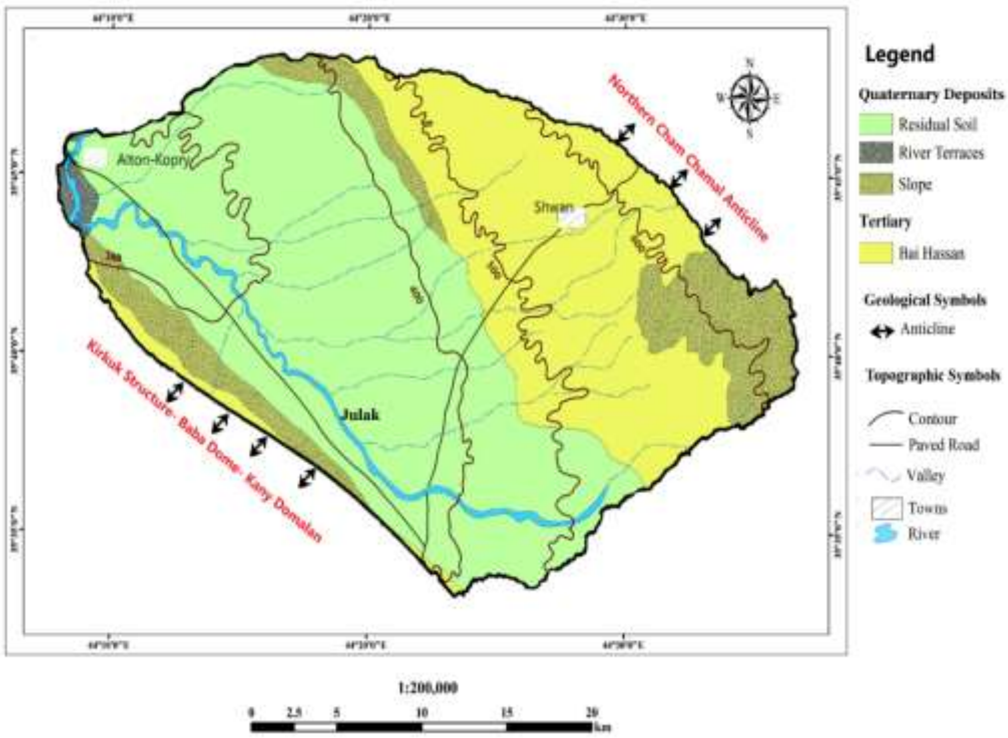

Figure 2: Geological map of the study area [15].

All soil samples were analyzed for pH and electrical conductivity (EC) was determined by soil/water suspensions. Organic matters (OM) were determined by the most common procedure involving the reduction of potassium dichromate (K_2CrO_7) by organic carbon compounds and subsequent determination of the unreduced dichromate by oxidation–reduction titration with ferrous ammonium sulfate [16]. Cation exchange capacity (CEC) was measured according to the methods of [17]. Samples were analyzed using XRF Spectrometer/SPECTRO XEPOS-2006 device at the Iraqi-German Laboratory at the University of Baghdad. Samples were sieved in a 2 mm sieve, then powdered to 0.063 μm, and 5.0 g of each sample was used to determine the element concentrations.

2.2. Methods

2.2.1 Geochemical background

The background is defined as a relative measure to distinguish between the natural element or compound concentrations and anthropologically influenced concentrations in real sample collectives, which may be determined by direct, indirect, and integrated methods [6], [18]. Several methods can be used to calculate the geochemical background value, including direct geochemical and indirect statistical methods [6], [19], [20], [21]. For the estimation of geochemical background values in the present study, the indirect geochemical method and statistical analysis are applied.

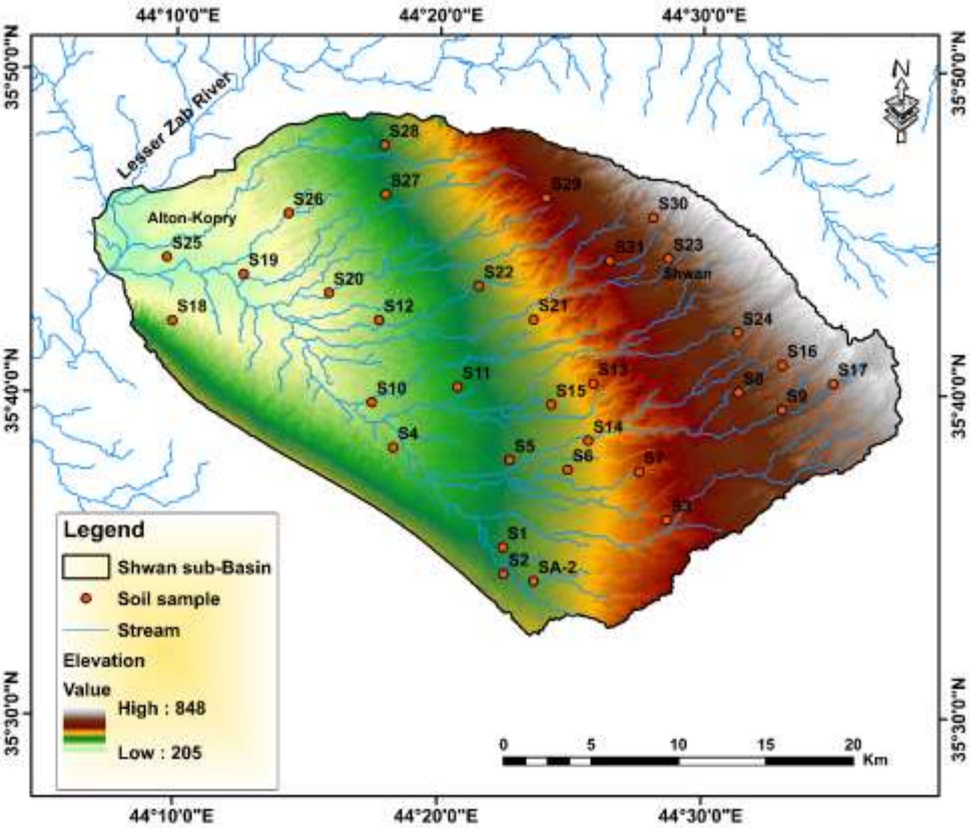

Figure 3: The soil sampling site.

Among the statistical methods, two methods were chosen. The first includes boxplot representations.

The method proposed by Tukey [22] was adopted to define background values using boxplot representations. Initially, ranges were determined by delimiting the interquartile (IQ) range augmented 1.5 times. From the range, the obtained background value was considered as the upper limit given by, where UL = upper limit and Q3 = upper quartile. The Minitab® software was used to draw the boxplot representations.

$$[UL=Q3+1/2(1.5IQ-IQ)] \qquad \text{.......................} (1)$$

UL = upper limit and Q3 = upper quartile.
The second statistical method applied in this study is an Iterative 2σ technique: according to Matschullat et al. [6].

The iterative 2σ technique (mean ± 2σ) is mainly used to define background values because it approximates the original data set to a normal distribution. In practice, the technique consists of the calculation of the mean and the standard deviation (σ) of the data set. After that, all the values outside the range (mean ± 2σ) are excluded. This procedure is repeated until all the values of the remaining data set are constrained to the range (mean ± 2σ) [23], [6]. This range is then considered the background range for the analyzed element and the background value is the upper limit of this range.

2.2.2 Statistical analyses

Statistical analyses were performed using JMP® Pro 16.0.0 (512257) software, the statistical methods used were principal component analysis (PCA) and Agglomerative Hierarchal Cluster Analysis (AHCA). PCA is a dimensionality-reduction method that reduces the number of variables in a data set naturally comes at the expense of accuracy, but the trick in dimensionality reduction is to trade a little accuracy for simplicity. Because smaller data sets are easier to explore and visualize and make analyzing data much easier and faster for machine learning algorithms without extraneous variables to process. Varimax rotation was employed because orthogonal rotation minimizes the number of variables with high loading on each component and therefore facilitates the interpretation of PCA results [24], [25], [26], [27]. This can be accomplished by converting the initial variables to a new small group of variables without missing the most important information in the initial data set. Factor loading values of between 0.3 - and 0.5, between 0.5 - and 0.75, and > 0.75 are classified as weak, moderate, and strong, respectively, based on their absolute values [28]. AHCA applying the ward's method was performed on the results of geochemical results in soil samples.

3. Results and discussion

3.1 Geochemical background of Shwan Sub-basin soils

The geochemical background in this study was assumed from the mean values of the boxplot method [22] and Iterative 2σ; technique [6] and statistical methods have been defined as indirect geochemical background (IGB) (Table 2).

Table 1: Indirect geochemical background (IGB) of the Shwan Sub-basin soil.

Element (ppm)	Statistical technique			Element (ppm)	Statistical technique		
	UL*	Iterative 2σ**	IGB***		UL*	Iterative 2σ**	IGB***
Na	4172.96	4497.51	4335.24	Cu	35.97	38.15	37.06
Mg	21480.17	22967.45	22223.81	Zn	89.56	91.29	90.42
Al	51430.53	54151.45	52790.99	Ga	14.16	14.94	14.55
Si	192158.75	203334.60	197746.70	As	7.81	8.70	8.26
N	99.63	107.93	103.78	Br	5.91	5.95	5.93
P	983.39	977.08	980.24	Rb	53.17	57.59	55.38
S	624.90	419.36	522.13	Sr	310.07	334.27	322.17
Cl	207.97	207.79	207.88	Y	21.65	23.46	22.56
K	11649.74	13114.78	12382.26	Zr	167.75	175.99	171.87
Ca	184361.36	204662.75	194512.10	Nb	10.38	10.84	10.61
Ti	5508.67	5867.99	5688.33	Mo	15.19	18.38	16.78
V	108.64	115.11	111.87	Ba	271.33	287.58	279.45
Cr	301.29	244.33	272.81	Ta	71.77	74.16	72.97
Mn	818.28	896.39	857.34	Pb	13.58	14.37	13.97
Fe	39109.94	41769.20	40439.57	Th	6.71	7.20	6.95
Ni	145.65	156.23	150.94				

*Ul; The upper limits which are considered as the background value of elements are calculated according to the adopted method of Tukey [22].

** Iterative 2σ; technique means that all the values outside the range of (mean ± 2σ) are excluded. Hence, this procedure is repeated until all the values of the remaining data set are constrained to the range (mean ± 2σ) [6].

*** IGB; Indirect geochemical background values obtained from the mean value of both methods.

3.2 Geochemistry of Shwan Sub-basin soil

3.2.1 Chemical properties of soil

The pH values in the current study ranged from 7.12 to 7.56 with a mean of 7.327 (Table 4). According to pH values detected in the soil samples, the soil is classified as neutral soil (Table 2) [29], [30]. Soil pH affects the solubility of chemicals in soils by influencing the degree of ionization of compounds and their subsequent overall charge. Thus, soil pH may be critical in affecting the transport of potential pollutants through the soil [29],[30]. In the present study, the salinity degree of soil was expressed

Table 2: Soil type based on PH Regime [29]

Soil	PH Regime
Acidic	>5.5
Neutral	6-8
Alkaline	>8.5

as EC. The EC ranged from 0.92 mmhos/cm to 7.8 mmhos/cm with a mean of 1.53 mmhos/cm (Table 4). After comparison, the EC results in soil samples with the USDA [31] the soils are classified as non-saline to slightly saline (Table 3).

Table 3: Soil classification based on soil salinity as EC [30]

Salinity class	mmhos/cm
Non-saline	0-2
Very slightly saline	2-4
Slightly saline	4-8
Moderately saline	8-16
Strongly saline	>16

The CEC values in the soil samples ranged from 10.7 to 13.3 meq/100g with a mean value of 12.175 meq/100g (Table 4). The detailed CEC values for all soil samples were presented in appendix 1

The OM was measured for all soil samples, and it is necessary to convert the organic matter content to total organic carbon content. Traditionally, for soils, a conversion factor of 1.724 has been used to convert OM to organic carbon based on the assumption that organic matter contains 58% organic carbon (i.e.g., organic matter/1.724 = g organic carbon) [32] (Table 4).

In the current study, The OM ranged from 1.14% to 1.45% with a mean value of 1.326 %, while TOC ranged from 0.66 % to 0.84 % with a mean value of 0.769 % (Table 4). The soil of the study area showed low OM content (Appendix 1). In arid areas with high rates of decomposition and low inputs of plant residues, values are usually less than 1% [30] and the location of the study area within the region of arid and semi-arid climate [33], which explained the low OM content in the soil of the study area. OM can complex or chelate heavy metals, and sorb organic contaminants. This retention affects their availability to plants and soil microbes as well as their potential for transport into the subsurface [30].

3.2.2 Distribution of Major and minor elements

The results of chemical analysis in the present study revealed that the major and minor element mean concentrations were in the order Si> Ca> Al> Fe> Mg > K> Ti> Na> P> Mn> S> Cl> N (Table 4). The summary statistics of all measured elements with ranges, means, standard deviations, Indirect Geochemical Background (IGB), and World soil limit [1] are all presented in Table (4). The elements' spatial distribution in Shwan Sub-basin soils is illustrated in Figure 4 which showed the most abundant element is silicon (Si) with a mean of 174,803.57 ppm. Consequently, all Si concentration values were within the IGB except samples SA-2, S13, and S14, which had concentrations greater than the IGB (Table 4 and Appendix 2). While the next abundant element was calcium (Ca) with a mean value of 155371.31 ppm (Table 4). All Ca concentration values within the IGB except S12, S26 and S29, whereas all concentrations were exceeded the WBA except SA-2, S7, S9, S10, S13, S14, S15, S21, S22 and S31 (Table 4 and Appendix 2).

Table 4: Summary statistics of the geochemical analyses of soil samples from Shwan Sub-basin

Parameter	Min	Max	Mean	SD	IGB*	WBA** [34]	Word soil limit [1]
pH	7.12	7.56	7.3275	0.123			
EC (mmhos/cm)	0.92	7.8	1.535	1.199			
OM %	1.14	1.45	1.326	0.0699			
TOC%	0.661	0.841	0.769	0.0405			
CEC (meq /100g)	10.7	13.3	12.175	0.6701			
Na (ppm)	2,841.32	5,230.11	3,704.66	561.21	4335.238	9644.18	
Mg (ppm)	7,960.92	22,610.22	19,078.50	2,919.08	22223.81	9046.5	
Al (ppm)	33,453.89	60,175.73	46,268.19	5,763.74	52790.99	79387.5	
Si (ppm)	115,457.68	222,548.18	174,803.57	19,718.37	197746.7	280464	
Fe (ppm)	23,969.47	41,714.01	35,564.27	3,804.16	40439.57	34971.5	
P (ppm)	297.03	1951.67	800.8812	332.7936	980.2353	741.914	
N (ppm)	65.00	106.00	88.13	10.28	103.776	1700	
S (ppm)	258.40	2,181.87	569.08	443.54795	522.1279		
Cl (ppm)	104.10	499.80	160.26	70.059495	207.8819		
K (ppm)	4,565.88	12,933.89	9,800.51	1857.4571	12382.26	13282.56	
Ca (ppm)	79,689.05	248,215.30	155,371.31	32320.868	194512.1	14294	
Ti (ppm)	2,774.53	5,755.90	4,746.30	678.57935	5688.331	4016.717	
V (ppm)	50.42	123.24	95.98	15.27119	111.8739		129
Cr (ppm)	106.19	501.24	253.39	77.83604	272.8096		59.5
Mn (ppm)	550.8	877.46	731.25	87.03103	857.3378		488
Co (ppm)	3.07	18.95	12.78	6.46			11.3

Ni (ppm)	48.96	155.28	126.53	22.29	150.9382	29
Cu (ppm)	21.09	39.86	31.47	4	37.0588	38.9
Zn (ppm)	59.37	122.03	83.59	12.87	90.42375	70
Ga (ppm)	9.4	16.1	12.72	1.61	14.54928	15.2
As (ppm)	2.04	8.63	6.8	1.29	8.257732	6.83
Br (ppm)	3	9.3	5.28	1.55	5.929794	10
Rb (ppm)	23.68	57.52	46.79	7.13	55.38102	68
Sr (ppm)	138.34	417.98	265.9	68.31	322.1684	175
Y (ppm)	12.4	23	19.53	2.42	22.55607	23
Zr (ppm)	65.44	188.85	142.9	26.49	171.8668	267
Nb (ppm)	3.84	411.49	22.42	71.25	10.60633	12
Mo (ppm)	3.4	55.4	11.83	8.86	16.78186	1.1
Sn (ppm)	<3.071835	5.277255	4.332075	1.478947		2.5
I (ppm)	<3	7.9	3.66	2.48		2.8
Ba (ppm)	145.7	316.3	236.63	36	279.4515	460
Ta (ppm)	59.54	73.63	68.75	3.24	72.96569	1.39
Pb (ppm)	9.44	49.53	13.79	6.83	13.97314	27
Th (ppm)	3.9	7.5	6.03	0.82	6.952311	9.2
U (ppm)	<1	<1	<1	-		3

* IGB: Indirect Geochemical background. **WBA: World Background Average [34].

Aluminium (Al) with a mean value of 46268.19 ppm, all Al concentration values were within the IGB and the WBA, except samples SA-2, S13 and S31, which were more than the IGB. The maximum detected Al value was in sample S13 (Figure 4 and Appendix 2). Magnesium (Mg) also recorded the highest value in soil sample S13 (Figure 6 and Appendix 2), the high value at this site was due to an increase in animal breeding at this agricultural village. All of the Mg concentration values were higher than the WBA except S29 had a value of 7960.92 ppm within this background. While most of the Mg concentration values were within the IGB except S4 and S13 which were higher than this background (Table 4). The mean value of phosphorous (P) concentrations was 800.88 ppm. P concentration values were exceeded the WBA in samples of S2, SA-2, S3, S7, S9, S10, S11, S13, S14, S15, S17, S21, S30, and S31. Whereas P showed concentrations exceeded the IGB in soil samples of S3, S10, S13, S14 and S15 (Appendix 2). Sulfur (S) recorded a mean value of 569.08 ppm, and concentrations exceeded the IGB in soil samples S2, S3, S7, S10, S14, S15, S18, S20, S26, S30 and S31, while the rest of the samples were within the IGB. The highest S value was detected in soil sample S15 (Appendix 2). This increase in S concentrations at these soil sites was a result of the land uses effect which was mainly agricultural use, the application of fertilizers was the main source for elevated S concentrations. On another hand, the lowest value was detected in S29 (Figure 4 and Appendix 2).

However, the minimum values of most elements were detected in soil sample S29. The land uses on this site are agricultural and grazing practices with very limited use of fertilizer. Titanium (Ti) was detected with a mean of 4746.30 ppm. All Ti concentration values were within the IGB**,** except SA-2 and S11, which exceeded the IGB (Appendix 2). After comparing Ti concentrations within the WBA, the results showed that all Ti concentrations were greater than this background except for the soil samples S20, S29 and S30 (Appendix 2).
The results revealed that the alkali contents of sodium (Na) and potassium (K) in the soil of the study area were low. The Na concentrations in the soil had a mean value of 3704.66 ppm, All Na concentration values were within the WBA and the IGB except concentration values in soil samples S2, S3, S15, and S18 were greater than the IGB (Table 4 and Appendix 2).

Potassium (K) had a mean concentration value of 9800.51 ppm (Table 4). All K concentration values were within the IGB except K values in the soil samples S7, S9 and S14 exceeded the IGB, while after a comparison of the world background average and the K concentrations, have been concluded that all values of K were within this background (Table 4 and Appendix 2).

Iron (Fe) had a mean of 35,564.27 ppm (Table 4). Fe concentrations in most samples were within the IGB except for soil samples S13 and S16, where recorded values exceeded this background. and after comparison with the WBA, the Fe concentrations exceeded this background in most soil samples except S2, S3, S5, S10, S12, S15, S18, S20, S23, S26, S29, and S30 were within the world background average.

Manganese (Mn) concentrations ranged from 550.80 to 877.46 ppm with a mean of 731.25 ppm. Mn concentration values were all less than the world soil background [1] and the IGB except for the soil samples SA-2, S21, and S3 which were greater than the latter background. Nitrogen (N) had a mean value of 103.77 ppm (Table 4). All N concentration values were within The IGB except soil samples SA-2 and S14, which recorded N values greater than the IGB. The major and minor element sources were considered naturally, except for some increases in some elements that resulted from effects of land use such as agricultural activities, animal breeding and grazing.

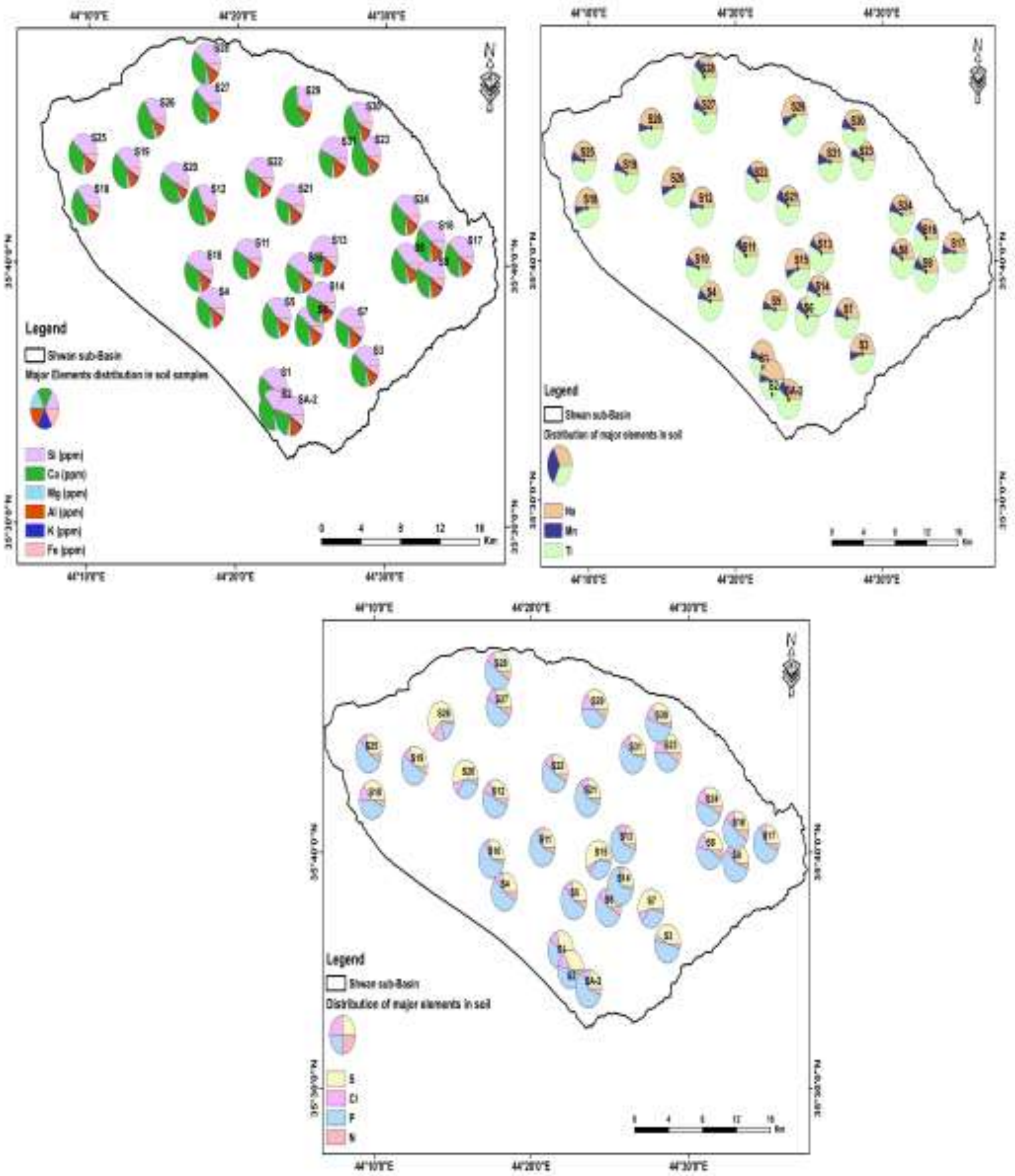

Figure 4: Spatial distribution maps of major and minor elements in soil samples of Shwan Sub-basin.

3.2.3 Spatial distribution of trace elements

The average abundance of trace elements in soil samples of Shwan Sub-basin follows the decreasing order of Sr> Cr> Ba> Zr> Ni> V> Zn> Ta> Rb> Cu> Nb> Y> Pb> Co> Ga> Mo> As> Th> Br> Sn> I (Table 4). Trace element concentrations showed obvious variation in the spatial distribution of Sr, Zr, Ba, Y, Zn, Rb, Cu, Mo, As, Br, Pb and Nb in the soils of different land use land cover (Table 4 and Figure 5). The rest of the trace elements showed no significant variation along with the sub-basin samples. Trace element concentrations from the soil samples of the Shwan Sub-basin were compared with the world soil limit [1] and indirect geochemical background (IGB) (Table 4) and this comparison revealed that all V concentrations within the world soil limit and the IGB, except S7 and S28, exceeded the IGB. All Cr concentrations exceeded the world soil limit, whereas most Cr concentrations were within the IGB, except for soil samples S1, SA-2, S4, S6, S8, S11, S13, S21, S25 and S30 (Table 4 and Appendix 2). The Co concentrations exceeded the world soil limit in soil samples SA-2, S9, S13, S14, S21 and S25 (Table 4 and Appendix 2). All Ni concentrations exceeded the world soil limits, while the Ni concentrations exceeded the IGB in soil samples S21 and S25 (Table 4 and Appendix 2).

All Cu concentrations were within the IGB and world soil limit except for soil sample S14, which was higher than all limits with a concentration value of 39.862 ppm. All Zn values were within the IGB except for soil samples S3, S10, S14 and S15. Whereas most Zn concentrations exceeded the world soil limit in most samples except soil samples S5 and S29 were within this limit. Ga exceeded the IGB and world soil limit just in samples SA-2, S14 and S16. Furthermore, the value of Ga in soil sample S28 exceeded the IGB. As exceeded the IGB in soil sample S16, and exceeded the world soil limits in soil samples S1, S3, S10, S11, S13, S14, S15, S18, S19, S20, S29 and S31(Table 4 and Appendix 2).

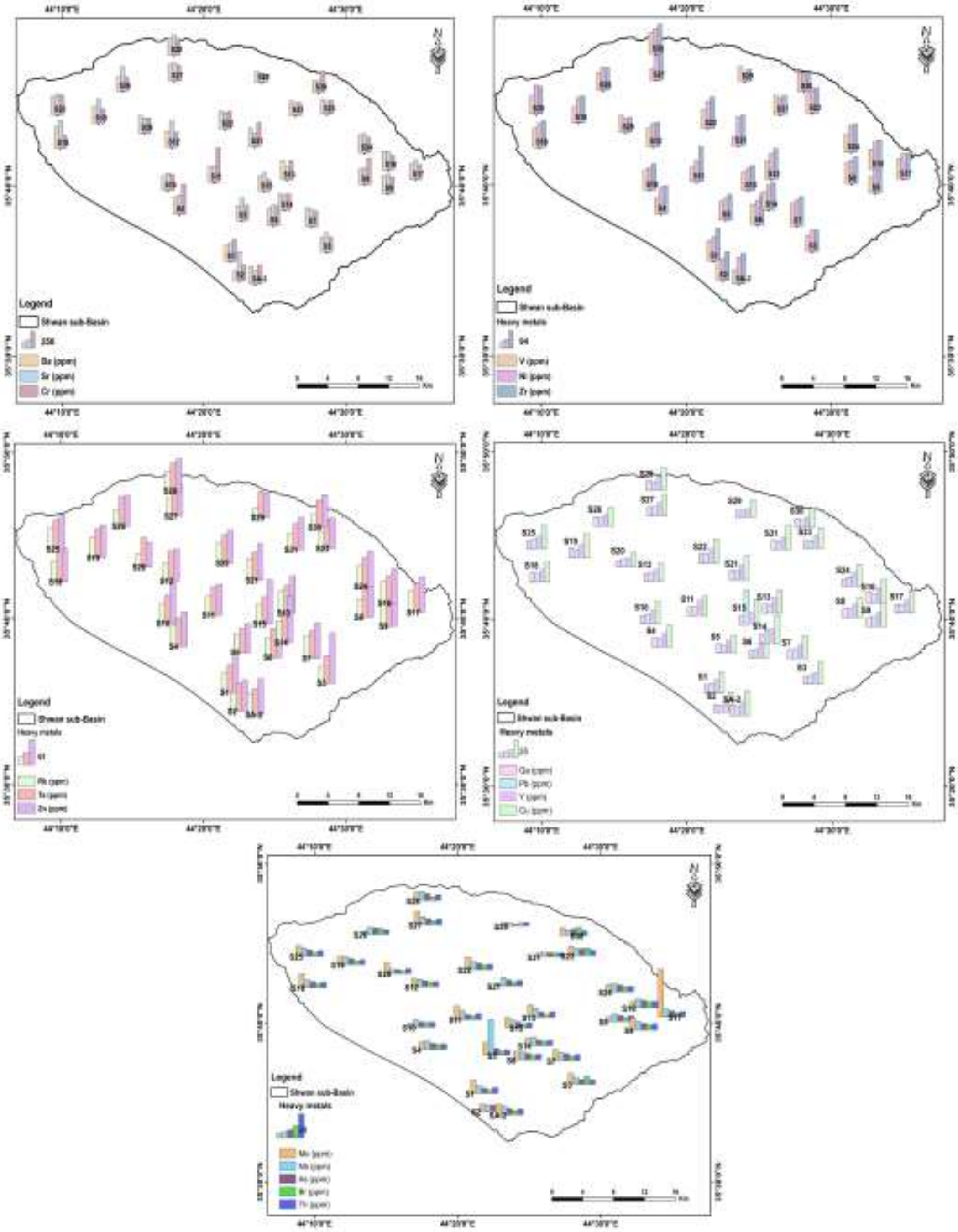

Figure 5: Spatial distribution of trace elements in soil samples.

Br All concentration values were within the world soil standard, while it exceeded the IGB in soil samples S3, S9, S16, S23, S26 and S30. Rb was all within the world soil standard and

IGB, except soil sample S9, which exceeded the IGB. All Sr concentration values exceeded the world soil limit except S29 and S30, whereas soil samples S2, S5, S12, S18, S19 and S26 exceeded the IGB (Table 4 and Appendix 2). All Y concentrations were within the world soil limit. The soil samples S11, S13 and S16 exceeded the IGB. All Zr concentration values were within the world soil limit. While soil samples S1, and S11 were detected with Zr concentration values that exceeded the IGB. The soil samples S16 and S14 and S26 recorded in general higher metal concentrations than other samples. Nb detected values exceeded the IGB in soil samples S5 and S16 and exceeded the world soil standard in S5. All Mo concentrations exceeded the world soil limit. While Mo exceeded the IGB in soil sampled just in sample S17. Sn was more than the world soil limit in S7, S10, S11 and S29. Iodine exceeded the world soil standard in soil samples S3, S6, S17, S18, S23, S24, S26, S30 and S31 (Table 4 and Appendix 2). All Pb concentrations were within the IGB except for soil samples S9, S14 and S15, while Pb concentration exceeded the world soil limit in sample S15. All Ba concentrations were within the world soil limit but exceeded the IGB in soil sample S18 (Table 4 and Appendix 2). All Ta concentration values were greater than the world soil limit, whereas it had values that exceeded the IGB in soil samples S8, S12 and S18. Th and U were all recorded concentrations within the world soil limit and IGB (Table 4 and Appendix 2).

3.3 Statistical analysis

3.3.1 Principal component analysis (PCA)

After applying PCA in the chemical analysis [24], [25], [35]. results principal components with eigenvalues greater than 1 (Kaiser Criterion) were extracted into six PCs, which explained about 83.299 % of the total variation (Table 5). The factor loadings of the different variables are presented in Table (6). In detail, the first principal component (PC1) with an Eigenvalue of 11.369 accounted for 43.728% of the total variance (Table 5) and had a strong factor loading of Mg (0.857), Al (0.85), Si (0.78), Fe (0.901), Ti (0.94), Ni (0.80), Rb (0.82), Zr (0.9) and Y (0.93) (Table 6), quite explained the natural sources of these elements from rock weathering. Furthermore, PC1 had a moderate factor loading of K (0.733), Mn (0.735), Cr (0.585), Cu (0.545), Ba (0.686) and As (0.621) (Table 6). Most of these were probably derived from natural sources for K, while Mn, Cr, Cu and As were derived from natural and anthropogenic sources. Oil production activities from the Kirkuk oil fields could be considered the source of these metals by aerial transport then deposited in the close regions, as well as the Shwan Sub-basin.

The second principal component (PC2) with an Eigenvalue of 3.85 explained 14.8 % of the total variance (Table 5) which had strong factor loadings of P (0.891), and moderate for Mn (0.513), Cu (0.64), CEC (0.51012) and Zn (0.72) accounts for 14.81% of the total variance, PC2 source could be considered from agriculture activities, Fertilizers, and livestock manure are known to be a significant source of these elements [30], [36]. The third principal component (PC3) with an Eigenvalue of 2.38 explained 9.17% (Table 5) of the total variance had a strong factor loading of N (0.881), CEC (0.594) and TOC (0.831) and moderate factor loading of Pb (0.509). PC3 sources were mainly derived from the decomposition of plants and animal waste or anthropogenic sources such as chemical contaminants, fertilizers, or organic-rich waste [37]. The fourth principal component (PC4) with an Eigenvalue of 1.5726, explained 6.04% of the total variance had a strong factor loading of S (0.836), Cl (0.924), and moderate factor loading Na (0.566) (Table 6). Fertilizers and animal waste are sources of S and Cl. This finding is consistent with Pepper et al. [30] who stated that most animal wastes are high in TDS (Na, Cl, Ca, Mg, K, and soluble N and P forms and for S). While the fifth principal component (PC5) with an Eigenvalue of 1.34 explained 5.164% of the total variance (Table 5) had a strong factor loading Br (0.836), Br might be of agricultural source [38], [1]. The sixth principal component (PC6) with an Eigenvalue of 1.13 explained 4.364 % of the total variance and had a strong factor loading of Vanadium (0.893). Vanadium is mainly derived from phosphorus fertilizers commonly used in the study area that riches in trace elements such as As, Cd, Cr, Hg, Pb, Se, U and V [39].

Vanadium mainly accumulates from aerial transport as an atmospheric deposition [37] derived from fuel combustion operations at the refineries in the south of the sub-basin and the Kirkuk oil field near the study area. Petroleum refinery is a major source of pollution in areas where they are established. The refineries are major sources of toxic air pollutants including BTEX compounds, carbon monoxide, particulate matter, and sulfur dioxide [36]. Vanadium is also present in crude oil. However, this effect is quite noticeable not just in the soil it also clears in groundwater from the study region who recorded high V concentrations.

Table 5: Eigenvalues of total variance explain the six components selected.

Number	Eigenvalue	Percent	Cumulated Percent
1	11.3694	43.728	43.728
2	3.8529	14.819	58.547
3	2.3856	9.175	67.723
4	1.5726	6.048	73.771
5	1.3425	5.164	78.935
6	1.1347	4.364	83.299

Table 6: Loadings of experimental geochemical variables on significant principal components for the Shwan Sub-basin soil samples. Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization.

Element	PC1	PC2	PC3	PC4	PC5	PC6
Na	-0.258956	0.084297	0.309569	0.566215	-0.430234	0.229765
Mg	0.857582	0.049054	0.329424	0.084891	-0.095834	0.108095
Al	0.850810	0.332667	-0.121905	-0.070718	0.072552	0.047490
Si	0.780043	0.422767	-0.085211	-0.004478	-0.133793	-0.099112
Fe	0.901480	0.206572	0.165461	-0.131201	0.192801	0.069802
N	0.274246	0.162863	0.881655	0.098834	0.108071	-0.054401
P	0.126380	0.891818	0.116514	0.113736	-0.071506	0.005539
S	-0.247377	0.225316	0.311593	0.836183	-0.036475	0.076756
Cl	0.018862	-0.067141	-0.103757	0.924361	0.196740	-0.032287
K	0.733781	0.487251	0.078392	0.069706	-0.233641	0.052687
Ca	-0.692660	-0.611693	-0.127269	-0.013143	0.122226	0.049645
Ti	0.944011	0.031158	0.056679	-0.117956	0.026956	0.022666
Mn	0.735885	0.513412	-0.021384	-0.119119	0.076205	-0.214037
V	0.037157	0.029495	-0.098853	0.104410	0.096323	0.893540
Cr	0.585444	-0.121983	-0.190711	-0.085369	-0.054896	-0.334862
Ni	0.806606	-0.042074	0.482394	-0.074838	0.157767	0.077122
Cu	0.545568	0.649393	0.339441	-0.125234	0.162927	-0.026319
Zn	0.166403	0.720565	0.492508	0.088408	0.138813	0.070090
Sr	0.04706	0.30313	0.66684	0.42255	0.22753	0.14722
As	0.621486	-0.252285	0.415924	0.006877	0.382914	0.347649
Mo	0.15509	0.06362	0.20021	0.32252	-0.51252	0.14426

Br	-0.125168	0.028420	0.206951	0.097849	0.836537	0.105780
Rb	0.820094	0.173039	0.401899	-0.045865	-0.116787	0.187087
Zr	0.904456	-0.066495	0.189334	-0.113224	-0.084927	0.003944
Ba	0.68640	0.02465	0.22774	0.07341	-0.21299	-0.22526
Pb	-0.087897	0.417496	0.509252	0.319969	-0.307347	0.106013
Y	0.930171	0.052476	0.174713	-0.189066	0.011574	0.027153
Nb	0.185747	-0.269296	0.182207	-0.192151	-0.202587	0.299844
Th	0.74872	-0.18665	0.24636	-0.04516	-0.26215	-0.26215
CEC	0.41012	0.59430	0.19070	-0.42448	-0.21699	-0.06496
Ph	0.36693	0.44942	0.00694	0.25831	-0.47300	0.02312
TOC	0.229134	0.190423	0.831054	0.057223	0.119856	-0.037311

3.3.2 Agglomerative Hierarchal Cluster Analysis (AHCA)

The results of the geochemical analysis are illustrated in the dendrogram (Figure 6). AHCA highlighted [25], [35], [40]. six specific soil response patterns (R1, R2, R3, R4, R5, and R6) were identified from clustering samples based on geochemical variables (Figure 6). The distance cluster represents the degree of association between sampling sites depending on geochemical variables, where clusters with smaller or shorter distances between them are more similar to each other than clusters with larger or longer distances between them [40]. From the dendrogram cluster, R2 had the shortest distance (2.185) and highest similarity to cluster R1, whereas cluster R3 was the least similar and has the greatest distance to R1 (15.144) (Figure 6 and Table 7).

Table 7: Detail distance between the different clusters.

Number of Clusters	Distance	Leader	Joiner	Number of Clusters	Distance	Leader	Joiner
31	2.18549248	S6	S24	15	4.54921118	S4	S16
30	2.39075239	S22	S28	14	4.72234250	S2	S12
29	2.50320357	S4	S25	13	5.01526071	SA-2	S14
28	2.53625651	S19	S27	12	5.51824633	S2	S17
27	2.56331257	SA-2	S21	11	5.53507105	S1	S31
26	3.13072940	S7	S9	10	5.58045540	S3	S15
25	3.19992588	S6	S8	9	6.13832483	S23	S26
24	3.37302625	S4	S22	8	6.15135406	S20	S29
23	3.57345585	S1	S10	7	6.55497670	S2	S5
22	3.61938021	S12	S18	6	6.82492107	S1	SA-2
21	3.62819786	S4	S6	5	7.15359639	S2	S23
20	3.96357639	S7	S13	4	7.53271119	S1	S4
19	3.98877768	S23	S30	3	8.93703890	S2	S3
18	4.00041566	S4	S19	2	11.95012900	S2	S20
17	4.23140545	S1	S11	1	15.14440539	S1	S2
16	4.53404828	SA-2	S7				

Cluster R1 involved ten samples (S1, S10, S11, SA-2, S31, S21, S7, S9, S13, and S14) (Figure 6), this cluster was subdivided into two sub-cluster, the first groups including S1, S31, S10, and S11. Soil sample S1 was taken from urban and built-up lands, while the rest of the samples were from agricultural land. Another sub-cluster in R1 includes soil samples SA-2, S21, S7, S9, S13, and S14 (Figure 6) which represent agricultural land. Furthermore, SA-2 is very close to the refinery and may have a direct effect on this sample. The representative variables with high concentrations in R1 were Al, Si, Fe, K, Ti, Mn, Cr, Co, Cu, Ga, Rb, Zr and Y (Table 8). Cluster R2 included ten samples (S4, S25, S22, S28, S6, S24, S9, S8, S19, S27 and S16 (Figure 8) whereas the representative variables in R2 are M g, Ni, Ba, Th. All high variables in clusters R1 and R2 were dominant in the PC1 (Table 6) indicating natural and anthropogenic sources. Cr, Ni, Cr, Ni, Zn, As, and Br (Table 8) were derived from fertilizers and supplies from an oil refinery located south of the study. Besides, pollutants from emissions from the Kirkuk oil refinery located far away from the study area about a distance of 27 Km, could be transported by winds to the study area.

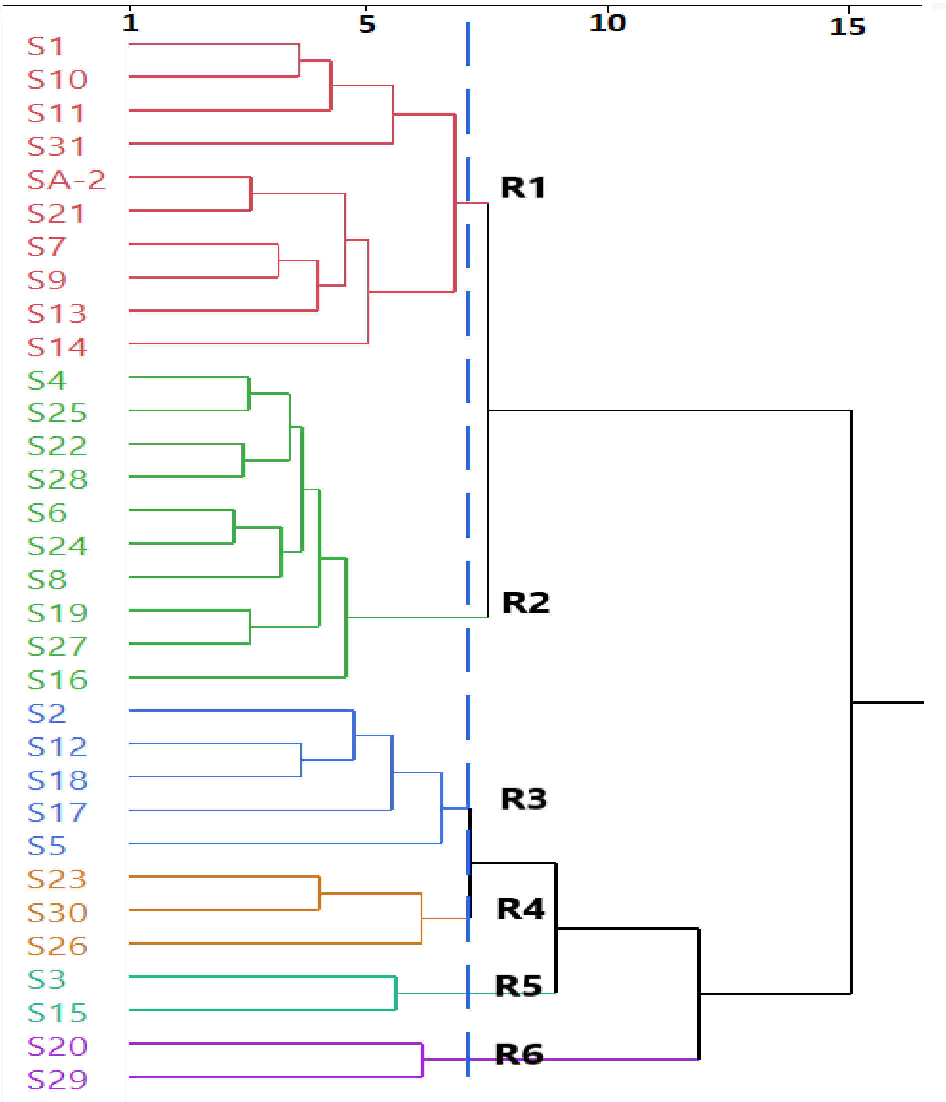

Figure 6: Dendrogram showing clustering of soil sample sites

Cluster R3 involved five soil samples (S2, S12, S17, S18 and S5) (Figure 8), these samples were taken from agricultural lands. The representative variables in R3 are Sr, Mo and Nb (Table 8) that were dominant in PC3. The source of high concentrations of these elements was the use of fertilizers. Cluster R4 involves S23, S30 and S26 (Figure 8). The representative variables with high concentrations were Cl, V, As, Br, and Ta (Table 8) indicating mainly natural sources and anticipated sources from fertilizer uses. The cluster R5 involved S3 and S15 (Figure 6), the land uses in these two sites are agriculture and grazing lands. The representative variables in R5 were Na, N, P, S, Zn, Pb, pH, CEC, and TOC (Table 8) which were dominant in PC2, PC3, and PC4 (Table 6). The grouping of these elements with pH, CEC and TOC indicate the direct effect between the increase in concentrations of Na, N, P, S, Zn, and Pb at samples S3 and S15 and these parameters. Mostly the CEC showed an increased pattern with the increase of OM and TOC in Fertilizers and animal manures are most probably the sources of increasing the variable concentrations in R5. Cluster R6 involved samples S20 and S29 (Figure 6). The representative variable in R6 was Ca (Table 8), such an increase in this element is mostly from a natural source.

Table 8: Representative mean of variables in red line for each of six clusters.

Cluster	1	2	3	4	5	6
Count	10	10	5	3	2	2
Na	3571	3430	4235	3492	**4833**	3609
Mg	20255	**20302**	19346	16776	18006	10937
Al	**51138**	48297	41990	42153	41144	33769
Si	**193604**	176561	159434	156265	164843	148202
Fe	**37826.6**	37641.2	33548.9	33346.5	32478	25319.4
N	85	94	86	82	**106**	70
P	1072	623	712	587	**1269**	407
S	529	359	437	933	**1609**	566
Cl	162	134	150	**273**	171	129
K	**11611**	9442	9852	7618	9410	6070
Ca	124994	155433	176802	193898	140081	**210872**
Ti	**5151.47**	5099.73	4494.05	4214.16	4186.98	2941.5
Mn	**819.58**	746.688	658.183	655.012	681.951	558.657
V	93.324	97.47	100.27	**101.017**	93.828	85.706
Cr	**284.347**	277.019	215.879	236.574	191.508	161.3
Co	**11.206**	2.669	1.892	1.375	1.375	1.375
Ni	130.866	**140.06**	124.886	118.452	117.326	62.592
Cu	**34.1588**	32.7049	28.1994	27.9864	33.7115	23.0069
Zn	89.1339	81.3492	78.3928	76.0256	**114.8418**	60.1322
Ga	**13.4**	13.008	12.4	12.533	12	9.6
As	6.567	7.498	7.15	**7.523**	6.211	3.105
Br	4.8	5.18	4.8	**8.267**	6.95	3.2
Rb	**50.219**	49.323	48.153	38.192	45.035	28.164
Sr	226.474	279.873	**365.329**	237.019	275.451	178.293
Zr	**156.724**	154.614	140.081	120.868	125.26	72.884
Mo	10.67	10.29	**20.88**	7.633	12.45	8.45
Ba	247.22	**252.79**	228.48	196.567	213.6	206.3
Ta	67.7698	69.6206	69.2357	**70.1311**	67.0736	67.7288
Pb	13.6334	12.8646	11.6774	11.2882	**30.9939**	10.4124

Th	6.36	**6.43**	5.58	5.5667	5.5	4.8
Y	**21.05**	20.57	19.04	17.27	17.45	13.35
Nb	9.3	9.7	**15.2**	7.6	8.5	4.4
Ph	7.3	7.3	7.4	7.2	**7.5**	7.2
CEC	12	13	12	12	**13**	11
TOC	0.758121	0.792343	0.7529	0.750193	**0.835267**	0.716357

Conclusions

The soil of the study area generally was characterized by high concentrations of Ta, Mo, Ni, Cr and As in most sampling sites, whereas some sample sites showed high concentrations of Co, Nb, Sr, Zn and Mn. The applied multivariate statistical techniques, such as PCA and AHCA, identified the possible sources of contaminants in the soil. Some metals were from anthropogenic sources (mainly fertilizers and petroleum extraction emissions), and others were from natural sources.

Most geochemical elements were derived from natural sources, and some heavy metals were derived from anthropogenic activities. The dominant land use in the study area was agricultural activities. The farmers were depending greatly on fertilizers to enhance crop production. The consequences of fertilizer application remarkably affected soil quality. Besides, industrial activities, whether inside or outside of the study area, these activities were represented by oil production activities that released significant air pollutants such as metals that are transported and deposited on the soil of the study area. Many other industrial activities, such as blocks and painting factories in the southern part of the sub-basin could be sources of increased metals in this part.

This study established geochemical background that could be the geochemical reference for future geochemical and environmental studies for the regions located close to the study area.

Competing interests

The authors declare no conflict of interest.

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Appendices

Appendix 1: Results of chemical analyses for Shwan Sub-basin soils

Station	Land Use Land Cover	EC (ds/m)= mmhs/cm	Ph	OM %	CEC (centmol. Kg-1)	TOC %
S1	Urban and Built-up Land	1.24	7.16	1.2	11	0.696056
S2	Urban and Built-up Land	1.2	7.18	1.23	11.2	0.713457

SA-2	Agricultural Land	1.1	7.23	1.32	12	0.765661
S3	Agricultural Land	1.2	7.41	1.43	13.2	0.829466
S4	Urban and Built-up Land	1.12	7.37	1.37	12.5	0.794664
S5	Urban and Built-up Land	1.18	7.34	1.32	12.2	0.765661
S6	Agricultural Land	1.24	7.3	1.34	12.3	0.777262
S7	Agricultural Land	2.2	7.33	1.36	12.7	0.788863
S8	Agricultural Land	1.64	7.38	1.31	12	0.759861
S9	Agricultural Land	1.5	7.41	1.29	11.8	0.74826
S10	Agricultural Land	2	7.44	1.26	11.4	0.730858
S11	Agricultural Land	1.28	7.42	1.27	11.5	0.736659
S12	Agricultural Land	1	7.47	1.25	11.3	0.725058
S13	Agricultural Land	1.04	7.52	1.31	12.1	0.759861
S14	Agricultural Land	1.14	7.49	1.41	12.9	0.817865
S15	Agricultural Land	2.6	7.56	1.45	13.3	0.841067
S16	Barren land	1.22	7.51	1.42	13	0.823666
S17	Agricultural Land	1.46	7.46	1.33	12.2	0.771462
S18	Agricultural Land	1.3	7.41	1.36	12.3	0.788863
S19	Agricultural Land	1.4	7.37	1.37	12.7	0.794664
S20	Agricultural Land	1.08	7.34	1.33	12.1	0.771462
S21	Agricultural Land	1.2	7.3	1.35	12.4	0.783063
S22	Barren land	1.12	7.28	1.37	12.5	0.794664
S23	Agricultural Land	1.24	7.31	1.35	12.2	0.783063
S24	Agricultural Land	1.06	7.25	1.36	13.3	0.788863
S25	Urban and Built-up Land	1.14	7.17	1.38	12.7	0.800464
S26	Barren land	7.8	7.2	1.33	12	0.771462
S27	Agricultural Land	1.2	7.23	1.39	12.9	0.806265
S28	Agricultural Land	1.04	7.18	1.35	12.1	0.783063
S29	Barren Land	0.92	7.12	1.14	10.7	0.661253
S30	Barren Land	1.6	7.15	1.2	11.3	0.696056

S31	Agricultural Land	1.66	7.19	1.3	11.8	0.75406
Min		0.92	7.12	1.14	10.7	0.661253
Max		7.8	7.56	1.45	13.3	0.841067
Mean		1.535	7.3275	1.3265625	12.175	0.769468
SD		1.199290113	0.123419034	0.06995895	0.670098693	0.040579

Appendix 2: Chemical elements concentrations in (ppm) for Shwan Sub-basin soils.

Sample	Na	Mg	Al	Si	Fe	N	P	S	Cl	K
S1	4,184.09	20,638.08	49,437.24	183,096.25	36,797.01	76	732.3128	405.6964	151.2	10,352.1
S2	4473.416	19685.18	42281.78	165707.48	32537.48	88	765.9171	550.6738	199.2	10401.9
SA-2	2997.114	21615.1	53348.4	198428.28	40329.13	83	937.4302	350.7892	128.5	12078.8
S3	4436.323	17700.99	39762.55	161079.82	31852.04	105	1202.774	1035.267	138.6	8401.21
S4	3976.37	22302.64	48040.02	184498.57	36999.85	98	673.8325	348.0659	136.6	11090.9
S5	3746.393	19727.4	43610.2	166595.62	33257.9	84	606.6238	298.2049	114.2	8982.33
S6	3256.765	20776.8	49426.66	181834.16	37216.67	87	671.214	349.828	128.8	9845.69
S7	4020.881	21024.07	51559.54	189079.48	38391.71	96	773.7727	1226.701	190.3	12485.6
S8	3605.44	18159.34	46637.51	166595.62	36496.26	85	502.7558	378.0225	148.2	8063.34
S9	3516.416	20752.67	48749.22	185994.38	37174.7	82	900.3345	444.9444	150.2	12809.3
S10	3687.044	17960.32	44853.94	178749.06	34453.92	77	1319.298	568.2953	139.5	11032.8
S11	3212.254	18901.15	48765.1	194642.02	35202.31	80	874.1493	318.8301	114.9	11066.0
S12	3983.788	19486.16	37412.68	141914.78	31593.25	78	599.6411	380.1852	128.5	9106.85
S13	3746.393	22610.22	60175.73	222548.18	41714.01	83	1029.515	328.0814	201.9	12327.8
S14	3279.021	21832.22	49135.57	199456.65	38146.91	103	1951.67	605.5409	155.3	12933.8
S15	5230.113	18310.12	42525.24	168605.61	33104.02	106	1335.009	2181.87	202.6	10418.5
S16	2952.603	18599.6	50405.77	173840.94	40895.67	101	548.1435	299.0058	121	8899.31
S17	4035.718	18539.29	44123.57	163650.74	35726.88	86	898.1524	383.9498	108.7	11248.6
S18	4933.369	19293.17	42519.95	159303.55	34628.78	94	692.1621	574.3027	201.8	9521.93

S19	3427.393	20179.73	44896.28	166829.34	35880.76	96	707.0004	407.6988	138.6	9521.93
S20	3635.114	13913.52	33453.89	180946.02	26669.27	74	517.1577	873.4687	153.7	7574.38
S21	3204.835	20246.07	50257.58	192117.84	39874.5	93	918.2277	378.5031	157.1	11373.1
S22	3301.277	21633.2	52358.7	194922.48	39475.83	95	670.7775	360.401	151	10385.3
S23	3167.742	16380.2	42001.28	158836.11	34495.89	89	381.9111	340.8971	123.1	6556.60
S24	3687.044	18394.55	48389.33	171830.94	38510.62	91	543.7793	364.4859	153.4	9023.83
S25	3961.532	21488.45	46759.24	171597.22	37622.34	99	729.2578	366.5685	109	10161.1
S26	4228.602	19769.62	42059.5	156358.68	32894.19	89	536.3602	1894.718	499.8	8148.85
S27	3293.858	19781.68	45621.35	170802.58	35454.11	98	622.3349	379.224	139.3	8625.36
S28	2841.324	21699.54	50437.53	182862.53	37860.15	90	562.9818	335.2902	115.5	8807.99
S29	3583.184	7960.92	34083.7	115457.68	23969.47	65	297.0275	258.3961	104.1	4565.88
S30	3078.719	14178.88	42398.22	153600.78	32649.39	69	841.4178	564.2904	197.4	8149.68
S31	3865.091	16971.23	55094.93	191930.86	36181.51	80	1285.257	658.4056	226.3	9654.76
Min	2,841.32	7,960.92	33,453.89	115,457.68	23,969.47	65.00	297.03	258.40	104.10	4,565.88
Max	5,230.11	22,610.22	60,175.73	222,548.18	41,714.01	106.00	1,951.67	2,181.87	18,612.72	12,933.8
Mean	3,704.66	19,078.50	46,268.19	174,803.57	35,564.27	88.13	800.88	569.08	738.06	9,800.51
SD	561.21	2,919.08	5,763.74	19,718.37	3,804.16	10.28	332.79	443.55	3,262.50	1,857.46

Appendix 2: Continued

Sample	V	Cr	Co	Ni	Cu	Zn	Ga	As	Se	Br	
S1	107.5526	317.4004	9.75235	130.1351	31.07527	84.59486	12.9	6.05912	<0.5	3.9	47
S2	87.94669	232.0806	<3.067272	116.3043	28.35918	75.83813	11	7.270944	<0.5	4.6	46
SA-2	75.62295	277.3747	18.95417	142.9443	36.66722	88.04935	15.6	7.195205	<0.5	4.8	51
S3	86.26618	210.5283	<3.067272	113.7896	32.11377	122.0319	11.1	5.756164	<0.5	9.3	41

S4	87.38652	437.1354	<3.067272	143.18	32.03389	84.19318	13.4	7.119466	<0.5	5.6	53
S5	101.9509	225.0334	3.067272	118.2689	25.72297	69.73252	13.6	7.801117	<0.5	4.8	45
S6	111.4738	291.7429	<3.067272	133.6714	32.43331	82.02408	9.89	7.5739	<0.5	5.4	48
S7	123.2374	223.8702	7.235616	138.9365	33.71147	86.60329	13.7	8.255551	<0.5	5.3	54
S8	111.4738	379.731	<3.067272	126.9917	29.07814	77.52521	12.4	7.043727	<0.5	4.9	44
S9	89.6272	241.9331	13.37016	140.5082	35.30917	87.48699	12.8	7.725378	<0.5	6.3	57
S10	108.1128	232.9017	<3.067272	120.7836	32.19366	98.73417	11.9	6.05912	<0.5	5.6	47
S11	78.4238	501.2449	<3.067272	115.5185	28.03964	75.19543	11.8	5.680425	<0.5	4.2	46
S12	100.8306	220.5861	<3.067272	123.927	26.36205	77.76622	11.5	6.967988	<0.5	5.1	44
S13	100.2704	281.4799	17.6958	140.6654	33.71147	89.25441	13.9	6.286337	<0.5	3.2	54
S14	98.02975	235.228	18.95417	133.8286	39.86262	113.8375	12.9	6.362076	<0.5	5.3	52
S15	101.3908	172.4868	<3.067272	120.8622	35.30917	107.6516	12.9	6.665032	<0.5	4.6	48
S16	106.9925	212.6494	<3.067272	148.6023	34.51032	83.87183	16.1	8.634246	<0.5	7.2	52
S17	106.9925	215.8651	<3.067272	135.7146	31.63446	87.08531	12.3	7.119466	<0.5	4.8	52
S18	103.6315	185.8287	<3.067272	130.2137	28.91837	81.54206	13.6	6.589293	<0.5	4.7	50
S19	85.14584	213.2651	<3.067272	136.8147	33.87124	78.8106	14.1	6.740771	<0.5	4.2	48
S20	90.74754	216.4125	<3.067272	76.22648	21.08964	60.89545	9.4	4.165645	<0.5	3	32
S21	50.4153	346.8894	12.26909	155.282	35.86837	88.69205	14.4	7.119466	<0.5	4.7	51
S22	100.2704	257.875	<3.067272	143.6516	34.90975	80.01565	13.7	7.422422	<0.5	5.7	51
S23	103.6315	197.597	<3.067272	131.3924	29.87699	74.39206	12	7.876856	<0.5	8.6	39
S24	95.78907	226.1965	<3.067272	144.6731	31.954	86.04093	10.19233	8.028334	<0.5	5.8	51
S25	99.15009	290.1692	13.7634	154.8105	34.59021	85.23756	12.5	7.346683	<0.5	4.2	51
S26	95.78907	204.7811	<3.067272	123.6912	26.92125	74.63307	13.2	7.195205	<0.5	6.9	41
S27	60.49836	225.786	<3.067272	132.1783	31.15515	77.92689	12.9	7.043727	<0.5	4.8	44

S28	116.5154	235.6385	<3.067272	136.0289	32.5132	77.84655	14.9	8.028334	<0.5	4	47
S29	80.66448	106.1878	<3.067272	48.95783	24.92412	59.36904	9.8	2.044953	<0.5	3.4	23
S30	103.6315	307.3426	<3.067272	100.2732	27.1609	79.05161	12.4	7.498161	<0.5	9.3	33
S31	101.9509	185.1445	<3.067272	90.05726	35.1494	78.89093	14.1	4.923035	<0.5	4.7	39
Min	50.42	106.19	3.07	48.96	21.09	59.37	9.40	2.04	<0.5	3.00	2
Max	123.24	501.24	18.95	155.28	39.86	122.03	16.10	8.63	<0.5	9.30	5
Mean	95.98	253.39	12.78	126.53	31.47	83.59	12.72	6.80	<0.5	5.28	4
SD	15.27	77.84	6.46	22.29	4.00	12.87	1.61	1.29	-	1.55	

Appendix 2: Continued

Sample	Zr	Mo	Ag	Cd	I	Ba	Ta	Hg	Sn	Pb	Th	Y	Nb
S1	175.1574	15.6	<2	<2	<3	235.9	68.384	<1	<3.071835	13.33174	6.8	20.5	9.43704
S2	152.8	8.3	<2	<2	<3	145.7	67.97451	<1	<3.071835	9.439264	3.9	19.3	7.549632
SA-2	164.6449	12.3	<2	<2	<3	262.1	63.55207	<1	<3.071835	12.45594	6.6	21.8	9.996272
S3	115.4143	12.8	<2	<2	5.3	206.3	67.64692	<1	<3.071835	12.45594	5.1	17.1	8.178768
S4	151.0232	8.9	<2	<2	<3	252.5	69.12107	<1	<3.071835	11.96938	6.3	20.1	9.996272
S5	137.8457	15.2	<2	<2	<3	213.2	59.53912	<1	<3.071835	11.09357	6.1	19.3	41.16446
S6	164.6449	10	<2	<2	3.4	248.3	70.43142	<1	<3.071835	12.164	6.4	20.7	10.06618
S7	157.7601	13.6	<2	<2	<3	275.9	67.31933	<1	3.62319	13.52637	7	21.6	9.3
S8	146.0632	5.3	<2	<2	<3	224	73.6254	<1	<3.071835	13.13712	6.5	19.9	9.297232
S9	161.9058	13.8	<2	<2	<3	258.5	70.34952	<1	<3.071835	14.30486	7	21	9.716656
S10	141.3992	4.3	<2	<2	<3	214.2	69.53055	<1	4.804665	13.23443	5.7	19.3	9.157424
S11	188.8531	15.9	<2	<2	<3	230.9	68.3021	<1	3.62319	12.164	6.9	22.9	10.20598
S12	131.1829	9.6	<2	<2	<3	235	73.54351	<1	<3.071835	12.26131	5.7	17.8	8.668096
S13	165.1632	14.2	<2	<2	<3	279.2	67.40123	<1	<3.071835	13.13712	6.5	23	10.4856

S14	144.3605	8.9	<2	<2	<3	239.3	70.84091	<1	<3.071835	18.97584	6	20.5	9.646752
S15	135.1066	12.1	<2	<2	<3	220.9	66.50036	<1	<3.071835	49.53181	5.9	17.8	8.807904
S16	155.9833	7.4	<2	<2	<3	268.3	65.92709	<1	<3.071835	13.03981	7.5	22.9	10.62541
S17	135.8469	55.4	<2	<2	5.4	232.2	71.74177	<1	<3.071835	12.45594	6.3	19.4	9.367136
S18	142.7318	15.9	<2	<2	7	316.3	73.37971	<1	<3.071835	13.13712	5.9	19.4	9.227328
S19	144.1384	9.6	<2	<2	<3	245.3	70.43142	<1	<3.071835	12.164	5.4	19.3	9.017616
S20	80.32364	12.9	<2	<2	<3	256.1	72.31505	<1	<3.071835	11.09357	5.6	14.3	5.033088
S21	164.867	3.5	<2	<2	<3	268	68.05641	<1	<3.071835	13.23443	6.4	22.2	10.13608
S22	169.0128	14.5	<2	<2	<3	265.9	69.28486	<1	<3.071835	13.52637	6.4	21.9	9.506944
S23	135.6248	10.6	<2	<2	3.8	208.8	71.0047	<1	<3.071835	11.28819	6.1	19.1	8.248672
S24	151.1713	8.9	<2	<2	6	259.1	69.61245	<1	<3.071835	13.33174	6.4	21.3	9.78656
S25	148.136	12.4	<2	<2	<3	270.7	71.57798	<1	<3.071835	13.91562	6.4	19.5	9.646752
S26	123.0395	3.4	<2	<2	7.9	210.5	72.80643	<1	<3.071835	11.77475	5.3	17	8.108864
S27	154.8729	15.8	<2	<2	<3	246.3	67.31933	<1	<3.071835	13.13712	6.6	19.7	9.017616
S28	161.0915	10.1	<2	<2	<3	247.5	68.87538	<1	<3.071835	12.26131	6.4	20.4	10.27589
S29	65.4434	4	<2	<2	<3	156.5	63.14259	<1	5.277255	9.7312	4	12.4	3.84472
S30	103.9395	8.9	<2	<2	6.4	170.4	66.58226	<1	<3.071835	10.80163	5.3	15.7	6.361264
S31	103.1252	4.6	<2	<2	3.2	208.2	63.96156	<1	<3.071835	11.96938	4.7	17.7	5.312704
Min	65.44	3.40	<2	<2	<3	145.70	59.54	<1	<3.071835	9.44	3.90	12.40	3.84
Max	188.85	55.40	<2	<2	7.90	316.30	73.63	<1	5.277255	49.53	7.50	23.00	41.16
Mean	142.90	11.83	<2	<2	3.66	236.63	68.75	<1	4.332075	13.75	6.03	19.53	9.85
SD	26.49	8.86	-	-	2.48	36.00	3.24	-	1.478947	6.72	0.82	2.42	5.9399001