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GEOCHEMICAL DISTRIBUTION AND BACKGROUND VALUES OF SOME MINOR AND TRACE ELEMENTS IN IRAQI SOILS AND RECENT SEDIMENTS

Khaldoun S. Al-Bassam[1] and Munaf A. Yousif[2]

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ABSTRACT

The analysis of about 21000 soil and recent sediments samples collected by Iraq Geological Survey in the seventies and eighties of the last century from the Western and Southern deserts and from the Mesopotamia plain analysed for some minor and trace elements (P_2O_5, K_2O, Al_2O_3, Fe_2O_3, TiO_2, SO_3, Cu, Pb, Zn, U, Cr, Ni and V) are statistically treated in this study to extract natural background values for these terrains which represent about 70% of Iraq area. The results are compared with soil analysis in other areas in Iraq of various physiographic, climatic and source rocks conditions, as well as with reported range values for the soil of the world.

Natural (geogenic) background range values are presented in two ways: the first involved all analytical results including natural anomalous values and the second after removing values above the statistically calculated threshold. The concentration range values for the desert and Mesopotamia are comparable to those reported for world soil with some exceptions. Higher upper range values are noticed for Cr, Ni and V, but the median values are within the world range.

The results also indicate significant influence on the background values by various factors including source rocks and pedogenic processes controlling soil development and maturity such as climate, vegetation, and drainage. The distribution of the elements analysed varies between normal and log-normal, higher concentration outlayers are noticed in most trace elements distribution patterns as well as in SO_3 distributions.

The distribution of minor elements (TiO_2, Al_2O_3, Fe_2O_3, K_2O and P_2O_5) is largely controlled by parent rocks. Some trace elements are also related to source rocks, especially U, Cr and Ni. Sulfate is enriched by authigenic processes.

This study clearly emphasizes the impact of various soil-forming processes, parent rocks, physiography and climate on the geogenic background range of the analysed elements. It also suggests that local environmental studies to demonstrate pollution cases should consider comparison with backgrounds of the uncontaminated soil related to the same physiographic terrain instead of making conclusions based on comparison with world averages for soil, shale or Earth crust.

[1] Chief Researcher, e-mail: albassam703@gmail.com
[2] Senior Geologist, Iraq Geological Survey

الانتشار الجيوكيميائي وقيم الخلفية الطبيعية لبعض العناصر الكيميائية الثانوية والشحيحة في الترب والرواسب الحديثة العراقية

خلدون صبحي البصام و مناف عبد الجبار يوسف

المستخلص

أجريت معالجة إحصائية لنتائج تحليل ما يقرب من 21000 عينة تم جمعها من قبل فرق المسح الجيولوجي العراقية في عقدي السبعينات والثمانينات من الترب والرواسب في الصحراء الغربية والجنوبية والسهل الرسوبي وجرى تحليلها للعناصر (P_2O_5، K_2O، Al_2O_3، Fe_2O_3، TiO_2، SO_3، Cu، Pb، Zn، U، Cr، Ni و V). استهدفت المعالجة استخراج المدى الطبيعي للخلفية الجيوكيميائية لهذه العناصر في المناطق التي جرى مسحها والتي تمثل حوالي 70% من مساحة العراق ومقارنتها مع تحليلات ترب في مناطق أخرى في العراق ذات طبيعة فيزيوغرافية ومناخية وصخور مصدرية مختلفة فضلا عن مقارنتها مع المديات الطبيعية لهذه العناصر في الترب العالمية.

تم تقديم البيانات المستخلصة للخلفية الجيوكيميائية الطبيعية (الجيولوجية) بطريقتين: الأولى شملت كافة النتائج بضمنها القيم العالية الشاذة طبيعيا والثانية بعد حذف تلك الشواذ المحسوبة إحصائيا. توضح النتائج تقارب القيم المستحصلة لمديات الخلفية الجيوكيميائية للعناصر المستهدفة مع المديات والمعدلات الموثقة عن ترب العالم مع ملاحظة وجود قيم أعلى نسبيا للعناصر الكروم والنيكل والفناديوم غير أن المعدل الوسطي يقع ضمن المديات العالمية.

تبين النتائج أيضا وجود تأثير مهم نسبيا على مديات الخلفية الجيوكيميائية من عدة عوامل بضمنها الصخور المصدرية والعمليات المؤثرة على تطوير التربة ونضوجها بما فيها العوامل المناخية والغطاء النباتي والتصريف المائي. إن توزيع العناصر التي شملتها الدراسة يتراوح بين طبيعي ولوغارتمي حيث لوحظ وجود استطالات ذات تراكيز أعلى من النمط الطبيعي في معظم العناصر الشحيحة وكذلك في توزيع الكبريتات (SO_3). سيطرت طبيعة الصخور المصدرية على انتشار تراكيز العناصر الثانوية (TiO_2، Al_2O_3، Fe_2O_3، K_2O و P_2O_5) فضلا عن بعض العناصر الشحيحة خاصة (U، Cr و Ni) في حين تحكمت عوامل الإغناء المتأخرة في توزيع الكبريتات.

وضحت هذه الدراسة دور العمليات المتحكمة بتكون التربة ودرجة نضوجها ونوع الصخور المصدرية والطبيعة الفيزيوغرافية والمناخية في اختلاف التوزيع والتركيز والخلفية الجيوكيميائية الجيولوجية الطبيعية للعناصر الكيميائية موضوع الدراسة في مناطق العراق المختلفة وتؤكد أهمية تناول الدراسات البيئية الموقعية موضوع المقارنة مع مديات الخلفية الطبيعية للترب غير الملوثة المقاربة في طبيعتها لمناطق الدراسة بدلا من اعتماد المعدلات العالمية المنشورة لترب العالم أو معدل السجيل أو معدل القشرة الأرضية للوصول الى استنتاجات تحدد درجة التلوث في التربة.

INTRODUCTION

The term "geochemical background" became an important reference with increasing environmental awareness. However, there seems to be no clear definition or agreement on the use of this term. 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 for the determination of an anthropogenic contamination, because single values do not yield information about the natural deviation (Matschullat *et al*., 2000). Moreover, comparing local results of soil analysis with global averages such as "shale" of Turekian and Wedepohl (1961), or "soil" of Hawkes and Webb (1962) or those of Aubert and Pinta (1977), among other global averages reported for soil, may be misleading when dealing with local surveys. In addition, almost all soil analysis reported in the literature on geochemistry, report total (or nearly so) element concentrations in the samples, including structurally bound, exchangeable, adsorbed and other types of bonded elements to soil components. What is important for the environment is the concentrations of these elements in the soil water that may be available to plants under various pH and Eh conditions or can be mobilized to surface or groundwater resource.

About 70% of the Iraqi territory has been covered by geochemical soil sampling over two decades; the seventies and eighties of the last century by Iraq Geological Survey. About 20000 samples were collected from top soil, covering about 305000 Km^2. Two main physiographic province of Iraq were covered by this survey; the Desert (western and southern deserts) and the Mesopotamia Plain. In addition, local and isolated small areas in the Fold Thrust Belt were also covered by soil sampling. All samples were collected from pollution – free areas; away from anthropogenic activities, and before the Gulf wars on Iraq, providing an excellent opportunity to drive natural (geogenic) geochemical background values for 13 chemical elements in top soil and sediments in various physiographic terrains of Iraq.

In this work, two major physiographic provinces in Iraq are considered: the desert plateau and the Mesopotamia plain. Local surveys in the North of Iraq located in folded and imbricate terrains were included for comparison to show the influence of parent rocks, physiography, climate and natural geogenic contamination on the background values (Fig.1).

The Desert terrain was dealt with collectively as one physiographic province as well as sub provinces divided according to dominating bed rock lithology, to show the influence of parent rocks on the elements concentration in the overlying soil.

The Mesopotamia plain was dealt with as one entity since it is the product of the collective sedimentation of Euphrates and Tigris Rivers and their tributaries in one flood plain basin. Since flooding of these rivers was stopped more than half a century ago, the upper horizon of these sediments has undergone salinization.

To achieve the goals of this study, one area in the folded terrain of Iraq located East of Erbil city and two areas located in the imbricate terrain of extreme north of Iraq (Serguza and Berzanik) with Zn – Pb – pyrite mineralization, were selected for comparison of background concentration range of elements. Areas covered by sampling are shown in Fig.1. Area, number of samples and sampling density are given in Table 1. The elements included in this study are TiO_2, Al_2O_3, Fe_2O_3, K_2O, P_2O_5, SO_3, Cu, Pb, Zn, Cr, Ni, V and U. Uranium was analysed in the desert samples mainly, with minor area coverage in the Mesopotamia plain.

The main aim of this work is to present geogenic geochemical background range values for the above chemical elements in the Desert and Mesopotamia provinces in comparison with other localities in Iraq of different climate, soil conditions and parent rocks, in order to show the influence of climate, physiography, source rocks and natural (geogenic) contamination by mineralization on the geochemical distribution and background concentration of elements in soil and sediments.

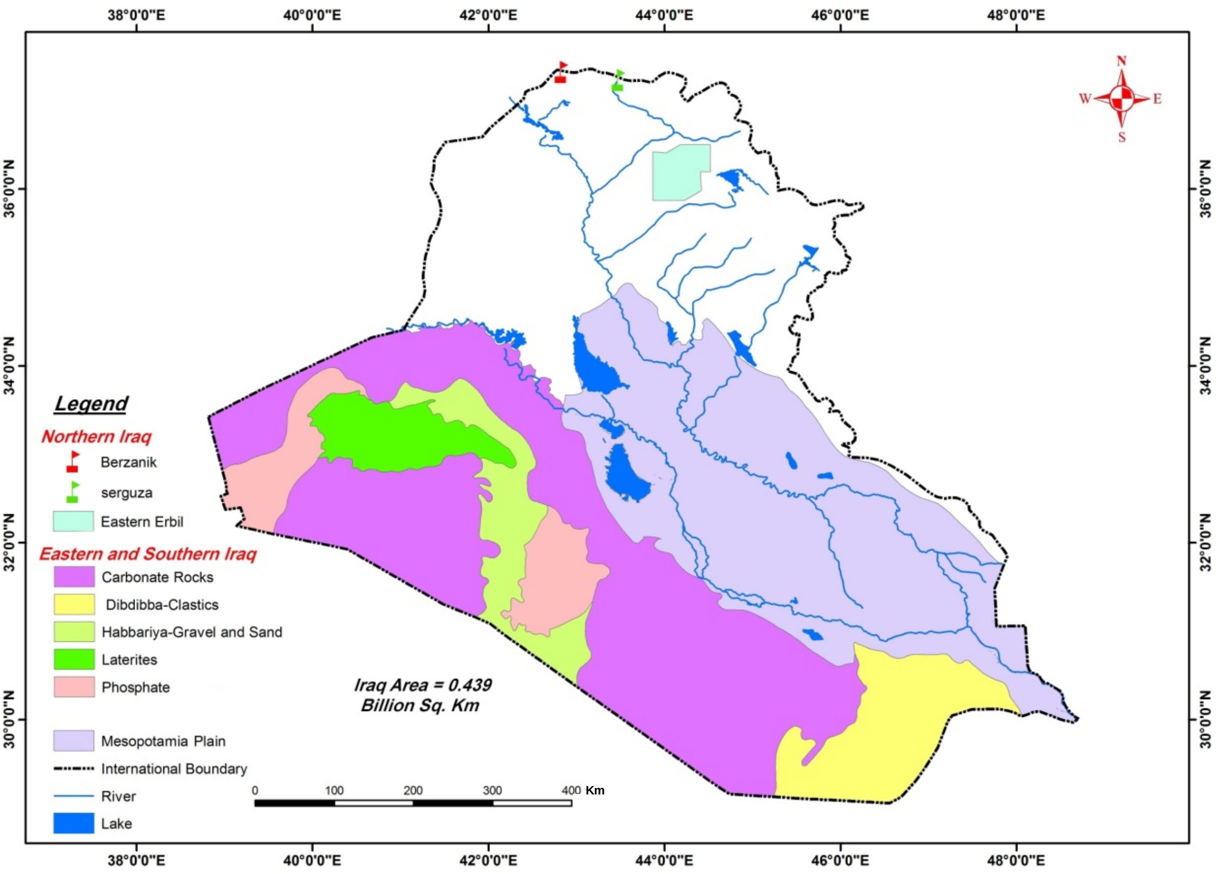


Fig.1: Location map of the surveyed areas

QUATERNARY GEOLOGY AND CLIMATIC CONDITIONS

The Quaternary sediments of Iraq are generally classified according to genesis (Yacoub and Barwary, 2002) as:

- Areas of accumulation; which include the Mesopotamia basin, depressions in the Western and Southern deserts and synclinal areas in the folded zones.
- Areas of denudation; which include high lands and plateaus in the desert, hills and mountains in the fold and thrust belt.
- Areas of authigenic sedimentation; which include low lands of shallow groundwater and high evaporation rate (gypcrete and/ or calcrete terrains).

▪ The Desert Terrain

It is characterized by relatively flat rocky terrain with structural ridges and isolated hills. The elevation ranges from 6 m (a.s.l) in the SE to 987 m (a.s.l) in the NW. It is includes sedimentary rocks of various types and origins (Permian – Quaternary), gently dipping and occasionally karstified. It is mostly made up of carbonate rocks, with subordinate exposure of phosphorite, shale, laterites, quartz sand, sand (Dibdibba Formation) and gravel – sand (Horan – Hab'bariyah). Major valleys cross the desert terrain, flowing mostly towards the Euphrates River basin (Hamza, 2007 and Ma'ala, 2009).

In heavy pluvial episodes of the Pliocene and Pleistocene huge amounts of siliciclasts were transported via major valleys from Arabia to the depocenter of the Mesopotamia (Dibdibba Formation and Wadi Al-Batin Fan) (Ma'ala, 2009 and Yacoub, 2011).

Most of the desert terrain is covered by thin veneer of immature residual soil (0.3 – 0.5) m thick. Moderate erosion and slight accumulation of transported sediments occur in main depressions and valley courses.

The Quaternary sediments of the desert were categorized by Yacoub and Barwary (2002) as:

- Residual soil.
- Slope sediments.
- Depression and valley fill deposits.
- Terraces.
- Horan – Hab'bariyah gravel – sand deposits.
- Gypcrete.
- Calcrete.
- Aeolian sediments.

▪ **The Mesopotamia**

It has been a flood plain subsiding basin since the Pliocene. More than (180) m thick fluvial sediments have accumulated during the Quaternary period, brought by the rivers Tigris, Euphrates and tributaries from the mountainous areas of Turkey, Syria (the Euphrates), Iran and N and NE Iraq (the Tigris) (Aqrawi *et al.*, 2006 and Yacoub, 2011). These giant rivers and their tributaries cross various types of igneous, metamorphic and sedimentary rocks before they reach the Mesopotamia basin. The Mesopotamia basin is generally a flat terrain, gently elevated from about 1 m (a.s.l) in the south to about 140 m (a.s.l) in the north, near the Himreen Range (Fig.2).

Over the years of no flooding and poor drainage, salination of the upper parts occurred and gypsiferous soil dominates large parts of this province. Marsh and lacustrine deposits are common in the southern parts. In the central parts aeolian deposits are common.

The main Quaternary units recognized in the Mesopotamia sediments were listed by Yacoub and Barwary (2002) as:

- Floodplain deposits.
- Crevasse splay deposits.
- Depression fill deposits.
- Marsh deposits.
- Sabkhas.
- Tidal flat deposits.
- Aeolian deposits.
- Sheet run – off deposits.
- Alluvial fan deposits.

▪ **The Folded Terrain (East Erbil Region)**

It is generally (1000 – 1500) m (a.s.l) in elevation, dominated by carbonate and clastic rocks of Cretaceous and Tertiary age, forming ridges of anticlinal structures with relatively thick Quaternary synclinal fill deposits (Yacoub and Barwary, 2002).

In these areas the products of denudation are mainly transported and deposited in the piedmont plains along the foothills of the mountain ranges. They grade from gravelly alluvial fans at the outlets of the foothills streams to sheet run-off down slope, then to slope sediments, and developing to wide valleys along which, river terraces are developed (Yacoub and Barwary, 2002).

- **The Imbricate Terrains (Serguza and Berzanik Localities)**

These two localities are situated in the extreme north of Iraq in the high mountain region, with elevations generally more than (1500) m (a.s.l) (Fig.2). Various types of Quaternary sediments are formed there; overlying carbonate rocks sequences of Mesozoic and Tertiary age. The Quaternary sediments are influenced by source rocks, stream or river order and morphologic position. The main Quaternary sediments recognized in these terrains are intermountain plains, synclinal depressions and valley fill deposits (Yacoub and Barwary, 2002). Both localities (Serguza and Berzanik) are known for their Zn – Pb – pyrite mineralization, hosted by carbonate rocks of Triassic and Jurassic age. Their oxidation products form yellowish brown gossans along mineralized fault plains and areas surrounding mineralization outcrops (Al-Bassam, 1980). No mining works ever existed in the past in these localities, and the contamination of local soil is a natural process. The soils at both localities are mostly residual, being the product of weathering and alteration of neighboring country rocks.

GRAIN SIZE, MINERALOGY AND SOIL pH

Previous studies on grain size distribution show that the soil in the Desert terrain is dominated by sand and silt fractions with minor clay and very minor gravel (rock fragments),whereas the Mesopotamia sediments are dominated by clay fraction, followed by silt and minor sand fractions. The following results were reported (Al-Nuaimi *et al*., 2010):

– **Desert soil:** clay fraction: (15 – 23) %, silt fraction: (13 – 50) %, sand fraction: (30 – 65) % gravel (rock fragments): (3 – 9) %.

– **Mesopotamia sediments:** clay fraction: (41 – 57) %, silt fraction: (37 – 53) %, sand fraction: (1 – 13) %, gravel: non.

The mineral constituents (XRD results) are clay minerals, carbonates, quartz and feldspar. In the desert soil the clay mineralogy consists mainly of: smectite and palygorskite with subordinate amounts of kaolinite and illite. In the Mesopotamia sediments the clay mineralogy is dominated by smectite, chlorite and illite mainly with subordinate amounts of palygorskite and kaolinite. Up to 50% carbonate minerals were recorded in the soil and sediments of both terrains (Al-Bassam *et al*., 2004).

The soil is alkaline in both terrains (generally the pH is 8 – 9) (Al-Rawi *et al*., 1976, Ali *et al*., 2013). Moreover, the Mesopotamia surface sediments and the eastern parts of the Desert (bordering the Euphrates River) are saline to extremely saline, with numerous salt-water springs flowing along the Euphrates – Hit – Abu Jir Fault Zone (Shehata and Mahmoud, 1982).

CLIMATIC CONDITIONS

Most of Iraq can be described as a desert as far as rainfall and evaporation rates are concerned according to Iraqi Meteorological Organization (2000). The territory west of the Euphrates River recives less than (100) mm annual rainfall and in most of Mesopotamia it is between (100) and (150) mm/year. In the folded terrains, it is (400 – 500) mm/year and more than (500) mm/year in the imbricate terrain (Fig.2). In contrast, the evaporation rate is more than (3000) mm/year in the desert and Mesopotamia, decreasing to about (2000) mm/year in the folded terrain and to less than (2000) mm/year in the imbricate high mountainous terrain (Fig.2). According to the updated world map of the "Koppen – Geigre Climate classification" (Kottek *et al*., 2006) the majority of the surveyed areas lie within the region of main arid climate, with steppe precipitation and hot temperature conditions. In the northern parts of Iraq (imbricate terrain and some of the folded terrain) the climate may be classified as semiarid according to Kottek *et al*. (2006), considering annual rain fall, evaporation, temperature and humidity rates.

The generally dry and warm to hot climate dominating most of Iraq has had its influence on the type of Quaternary sediments and soil developed, being generally immature, without profile zonation, generally with minor mineralogical and chemical alterations compared to source rocks (Buday and Hak, 1980 and Shehata *et al*., 1987). The main changes have been size degradation of these rocks to gravel, sand, silt and mud by erosional factors and mechanical transportation, rather than by chemical weathering processes. The latter may be felt more in the higher altitudes of the folded and imbricate terrains, where climatic conditions are relatively more favorable.

It must be stressed that the climatic conditions were different in Iraq in the Pleistocene, where more pluvial periods and temperate climate existed (Aqrawi *et al*., 2006). The present day climate is an extension of the Mid Holocene climatic conditions, which have dominated the region for almost the past 6000 years B.P. (Al-Jubouri and Al-Amiri, 2000).

Source of geochemical data employed in this study:

– Al-A'asam and Sulaiman, 1979.
– Al-Bassam, 1977.
– Al-Bassam, 1980.
– Buday and Hak, 1980.
– Al-Bassam and Shehata, 1982.
– Shehata and Mahmoud, 1982.
– Hana and Al-Hillali, 1986.
– Shehata *et al*., 1987.

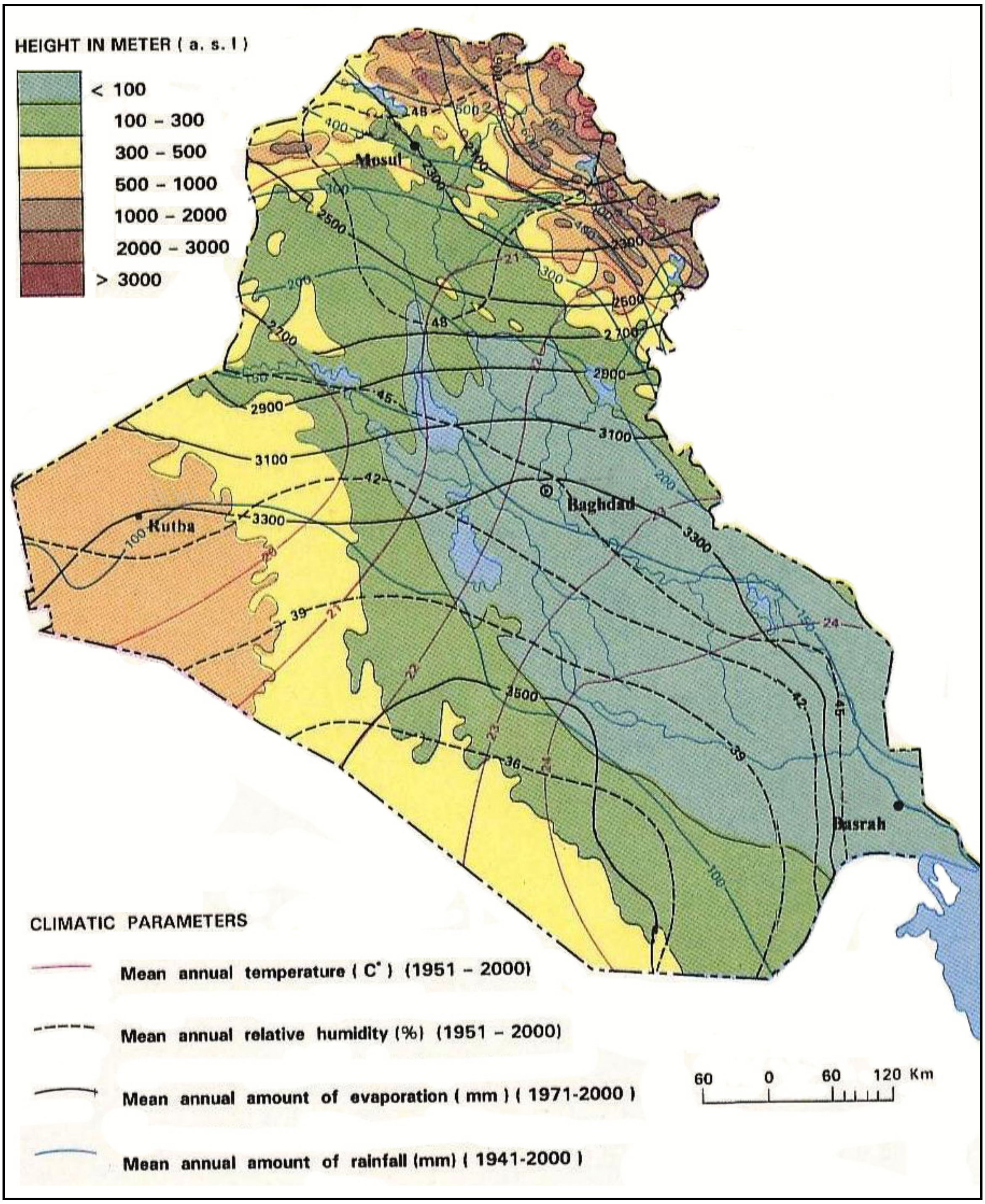


Fig.2: Climatic map of Iraq. (Iraqi Meteorological Organization, 2000)

PROCEDURES

▪ Sampling Procedures

Soil and Recent sediments samples were collected from the upper 25 cm section by digging a shallow pit using soil auger. All samples were sieved using a nylon cloth and the (– 80) mesh fraction was collected, air dried and kept in polyethylene bags for analysis. The average sampling density was as follow: Desert terrain: about one sample per 11 Km^2, Mesopotamia: about one sample per 53 Km^2, E. Erbil: about one sample per 7 Km^2, Serguza and Berzanik about one sample per 0.005 Km^2 and 0.007 Km^2 respectively (Table 1).

Table 1: Areas covered by soil surveys

Location	Area (km^2)	No. of samples	Sampling density Km^2/sample
Regional surveys			
1. Desert	197100	17653	11.2
1.1. Carbonate	118600	10742	11.0
1.2. Phosphate	20400	2238	9.1
1.3. Laterites	13300	1399	9.5
1.4. Dibdibba	20500	1541	17.2
1.5. Hab'bariyah	18300	1733	10.6
2. Mesopotamia	113000	2131	53.0
3. Folded terrain – East Erbil	2711.5	384	7.1
Detailed surveys			
4. Imbricate terrain			
4.1. Serguza	1.693	324	0.005
4.2. Berzanik	3.492	508	0.007
Total	**312816.7**	**21000**	

Note: The total area of Iraq is 439000 Km^2
Area covered by this study is 71% of total area of Iraq.

▪ Analytical Procedures

All analyses were carried out at Iraq Geological Survey, following GEOSURV Work Procedures, documented later in Al-Janabi *et al*. (1992).

P_2O_5: colorimetry by Autoanalyser following $HClO_4$ digestion.
SO_3: colorimetry by Autoanalyser following dilute HCl digestion.
Al_2O_3 and TiO_2 colorimetry by Autoanalyser following conc. HCl and HNO_3 digestion.
Pb, Zn, Cu, Cr, Ni and V: Atomic absorption spectrophotometry, following conc. HCl and HNO_3 digestion.

The Mesopotamia sediments were analysed for trace elements by spectrographic analysis (Jarrel Ash) using the method described in Spackova *et al*. (1982) and adapted by Iraq Geological Survey work procedures.

U: Fluorometry, after conc. HNO_3 digestion and fusion with sodium fluoride.
Fe total (as Fe_2O_3): Titration with $K_2Cr_2O_7$.
K: Atomic absorption spectrophotometry after conc. HNO_3, $HClO_4$ and HF digestion.
Detection limits for trace elements:
Pb 1.0 ppm, Zn 0.1 ppm, Cu 0.1 ppm, Cr 0.8 ppm, Ni 1.0 ppm, V 0.5 ppm, U 0.01 ppm. International and local standards were used for calibration.

▪ **Spatial Analysis Computer Programs**

1. The applied GIS methodology for the spatial analysis of the geochemical elements involved the following steps:

─ **Exploratory Spatial Data Analysis (ESDA):** Using ArcGIS 9.3 software for the geochemical elements to study the following:
- Data distribution
- Global and local outliers
- Trend analysis

─ **Geostatistical Analyst:** extension for advanced surface modeling using deterministic and geostatistical methods in ArcGIS 9.3 software and calculates summary statistics (Mean, Median, Std. Dev. and Threshold).

─ **Spatial Interpolation for Geochemical Elements Data**: Using ArcGIS 9.3 software, while ordinary kriging is applied by involving the following procedures:
- Semivariogram and covariance modelling
- Model validation using cross validation
- Surfaces generation of the geochemical elements

2. Statistical Basic: Includes the following:
- Compute a wide selection of descriptive statistics for selected elements
- Produce a Histogram for selected elements and fit to it the normal distribution
- Computation of correlation coefficient and Factor analysis

RESULTS

The results are presented as tables showing main statistical parameters (no. of sample, minimum, maximum, mean, median and standard deviation) for the sample populations covering all areas included in this study, in addition to subareas classified according to underlying, lithology in the Desert terrain (Table 2). Furthermore, statistically calculated threshold values for all elements analysed in the samples of the Desert and Mesopotamia are presented and the same parameters were recalculated after subtracting values above threshold to present background range values (Table 3). Correlation coefficients and factor analyses for the Desert and Mesopotamia data are presented in Table (4). Frequency distribution histograms are presented in Fig.3 (a to m) for Desert terrain and in Fig.4 (a to m) for the Mesopotamia. Spatial distribution maps of elements in the Desert terrain are presented in Fig.5 (a to m) and for the Mesopotamia terrain in Fig.6 (a to m). World soil range of trace elements is presented in Table (5). Median values of the trace elements in the surveyed areas are presented in Table (6) and recommended background values are presented in Table (7).

Table 2: Statistical parameters of the surveyed areas

2a: Region: Desert terrain: Underlying lithology: carbonates, phosphorite, shale, silica-sand, laterites (2D area: 0.1971 million Km^2)

Ser. No.	Element	Unit	No. of Samples	Range		Mean	Median	Std. Dev.
				Min.	Max.			
1	P_2O_5	%	17612	0.01	14	0.24	0.2	0.25
2	K_2O		17652	0.005	14	1.36	1.4	0.51
3	Al_2O_3		17653	0.11	16.4	6.89	7	2.01
4	Fe_2O_3		17653	0.07	9.85	3.57	3.62	1.12
5	TiO_2		17614	0.01	5.6	0.59	0.58	0.19
6	SO_3		3115	0.02	44.3	5.68	0.9	8.7
7	Cu	ppm	17613	1	200	25	25	10
8	Pb		5325	1	60	8.5	8	5.6
9	Zn		16854	2	253	67	66	22
10	Cr		17614	0.6	900	112	106	46
11	Ni		17614	1	360	73	70	27
12	V		6967	3	420	94	90	41
13	U		17614	0.01	19	0.3	0.1	0.5

2b: Region: Mesopotamia terrain: Underlying lithology:
Flood plain deposits; sand; silt and mud (2D area: 0. 113 million Km^2)

Ser. No.	Element	Unit	No. of Samples	Range		Mean	Median	Std. Dev.
				Min	Max			
1	P_2O_5	%	2129	0.02	1.16	0.17	0.16	0.08
2	K_2O		2130	0.04	2.87	1.01	0.99	0.51
3	Al_2O_3		2131	0.12	19.37	6.03	6.1	2.41
4	Fe_2O_3		2131	0.04	10.8	3.14	3.02	1.29
5	TiO_2		2131	0.01	1.98	0.46	0.46	0.2
6	SO_3		939	0.01	45.67	10.13	4.8	11.41
7	Cu	ppm	2059	1	85	18	16	11
8	Pb		1976	1	46	6.8	5	5.2
9	Zn		244	20	117	56	56	16
10	Cr		2131	4	2000	282	190	268
11	Ni		2131	1	870	99	85	65
12	V		1968	4	380	76	70	45
13	U		2044	0.1	11	0.3	0.1	0.5

2c: Region: Folded terrain/ East Erbil (2D area: 2711.5 Km^2)
Underlying lithology: Limestone, dolostone, gravel – sand and gypsum

Ser. No.	Element	Unit	No. of Samples	Range		Mean	Median	Std. Dev.
				Min	Max			
1	Fe_2O_3	%	381	0.5	6.4	3.3	3.2	0.8
2	Cu	ppm	380	4	100	31	28	14
3	Pb		379	2	210	20	16	20
4	Zn		369	3	131	62	60	18
5	Cr		380	17	1750	435	319	320
6	Ni		384	10	1200	178	100	188
7	V		380	15	1525	133	105	107

2d: Region: Imbricate terrain/ Serguza (2D area: 1.693 Km^2)
Underlying lithology: Limestone, dolostone and gossan of Pb – Zn – pyrite mineralization

Ser. No.	Element	Unit	No. of Samples	Range		Mean	Median	Std. Dev.
				Min	Max			
1	Fe_2O_3	%	324	0.35	45.75	6.18	5.93	4.05
2	Cu	ppm	324	3	300	49	46	28
3	Pb		324	2	1600	90	38	175
4	Zn		324	29	9125	308	131	648
5	Cr		324	8	7250	395	280	680
6	Ni		324	17	1200	266	240	184
7	V		323	10	1000	220	190	149

2e: Region: Imbricate terrain/ Berzanik (2D area: 3.492 Km^2)
Underlying lithology: limestone, shale and gossan of Zn – Pb – pyrite mineralization

Ser. No.	Element	Unit	No. of Samples	Range		Mean	Median	Std. Dev.
				Min	Max			
1	Fe_2O_3	%	491	0.24	9.48	4.24	4.4	1.99
2	Cu	ppm	491	4	154	31	32	13
3	Pb		491	10	190	79	87	34
4	Zn		491	16	950	129	111	103
5	Cr		491	22	238	119	119	50
6	Ni		491	10	893	100	89	69
7	V		491	3	520	87	83	61

2f: Region: Desert terrain/ carbonate domain (2D area: 0.1186 Km^2)

Ser. No.	Element	Unit	No. of Samples	Range		Mean	Median	Std. Dev.
				Min	Max			
1	P_2O_5	%	10701	0.01	14	0.21	0.2	0.18
2	K_2O		10741	0.005	5.7	1.42	1.48	0.52
3	Al_2O_3		10742	0.11	16.4	6.74	6.9	1.92
4	Fe_2O_3		10742	0.07	9.85	3.58	3.61	1.05
5	TiO_2		10703	0.01	2.02	0.58	0.59	0.17
6	SO_3		1489	0.02	44.3	7.4	1.66	9.72
7	Cu	ppm	10702	1	200	26	25	9.4
8	Pb		3173	1	60	8.5	8	5.7
9	Zn		9943	7	210	67	66	19
10	Cr		10703	1	900	112	106	46
11	Ni		10703	1	360	76	72	29
12	V		3837	3	380	89	90	40
13	U		10703	0.01	15	0.3	0.1	0.5

2g: Region: Desert terrain/ laterites domain (2D area: 0.0133 million Km^2)

Ser. No.	Element	Unit	No. of Samples	Range		Mean	Median	Std. Dev.
				Min	Max			
1	P_2O_5	%	1399	0.03	2.57	0.25	0.2	0.22
2	K_2O		1399	0.1	14	1.25	1.22	0.48
3	Al_2O_3		1399	0.9	14.9	8.02	8	1.65
4	Fe_2O_3		1399	0.56	7.23	3.99	4.02	0.74
5	TiO_2		1399	0.1	1.56	0.58	0.56	0.14
6	SO_3		72	0.1	11.21	0.95	0.62	1.79
7	Cu	ppm	1399	4	58	26	25	6.4
8	Pb		933	1	33	9	8	5.5
9	Zn		1399	18	193	74	70	21
10	Cr		1399	16	226	107	102	26
11	Ni		1399	8	180	72	70	21
12	V		1030	15	250	90	90	20
13	U		1399	0.07	9	0.6	0.7	0.4

2h: Region: Desert terrain/ phosphorite domain (2D area: 0.0204 million Km^2)
Underlying lithology: phosphorite, shale and carbonates

Ser. No.	Element	Unit	No. of Samples	Range		Mean	Median	Std. Dev.
				Min	Max			
1	P_2O_5	%	2238	0.01	9.1	0.4	0.28	0.51
2	K_2O		2238	0.02	6	1.23	1.21	0.48
3	Al_2O_3		2238	0.5	14.2	7.45	6.3	2.0
4	Fe_2O_3		2238	0.07	7.29	4.02	4.04	1.13
5	TiO_2		2238	0.03	1.21	0.58	0.58	0.16
6	SO_3		227	0.03	27.1	1.1	0.51	2.51
7	Cu	ppm	2238	3	92	26	25	11
8	Pb		1196	1	45	8.33	8	5.52
9	Zn		2238	2	204	73	73	19
10	Cr		2238	0.7	332	106	105	30
11	Ni		2238	3	180	66	66	20
12	V		1356	4	340	104	95	39
13	U		2238	0.1	8	0.6	0.4	0.7

2i: Region: Desert terrain/ Dibdibba domain (2D area 0.0265 million Km^2)
Underlying lithology: Sand and gravel

Ser. No.	Element	Unit	No. of Samples	Range		Mean	Median	Std. Dev.
				Min	Max			
1	P_2O_5	%	1541	0.01	0.65	0.1	0.09	0.06
2	K_2O		1541	0.08	10.3	1.09	1.11	0.41
3	Al_2O_3		1541	0.18	14.5	5.63	5.7	1.81
4	Fe_2O_3		1541	0.13	7.8	2.46	2.55	1.08
5	TiO_2		1541	0.01	2	0.54	0.54	0.26
6	SO_3		634	0.07	38	7.55	1.03	9.39
7	Cu	ppm	1541	2	75	21	20	8.3
8	Zn		1541	5	132	38	39	14
9	Cr		1541	3	700	124	108	75
10	Ni		1541	5	320	68	66	30
11	U		1541	0.01	14	0.5	0.3	0.8

2j: Region: Desert terrain/ Hab'bariyah domain (2D area 0.0183 million Km^2)
Underlying lithology: Gravel, sand and clay sediments

Ser. No.	Element	Unit	No. of Samples	Range		Mean	Median	Std. Dev.
				Min	Max			
1	P_2O_5	%	1733	0.02	1.16	0.27	0.22	0.14
2	K_2O		1733	0.1	2.8	1.45	1.5	0.45
3	Al_2O_3		1733	0.2	15	7.25	7.4	2.25
4	Fe_2O_3		1733	0.2	9.77	3.52	3.57	1.12
5	TiO_2		1733	0.04	1.8	0.65	0.64	0.19
6	SO_3		693	0.03	29.3	2.27	0.66	4.89
7	Cu	ppm	1733	5	127	27	27	10
8	Pb		23	2	13	7.2	7	2.7
9	Zn		1733	10	253	81	79	28
10	Cr		1733	7	224	113	112	31
11	Ni		1733	12	204	73	72	23
12	V		744	5	420	103	100	59
13	U		1733	0.04	19	0.2	0.1	0.7

Table 3: Statistical parameters after removing anomalous values
3a: Desert terrain

Ser. No.	Element	Unit	No. of Samples	Range		Mean	Median	Std. Dev.	Primary Threshold
				Min	Max				
1	P_2O_5	%	17282	0.01	0.74	0.21	0.2	0.11	0.74
2	K_2O		17204	0.005	2.38	1.32	1.38	0.46	2.38
3	Al_2O_3		17364	0.11	10.90	6.8	7	1.92	10.91
4	Fe_2O_3		17391	0.07	5.81	3.53	3.6	1.07	5.81
5	TiO_2		17609	0.01	1.80	0.58	0.58	0.18	1.81
6	SO_3		2905	0.02	23.02	3.99	0.77	6.09	23.08
7	Cu	ppm	17092	1	45	24	24	7.8	45
8	Pb		5084	1	19	7.7	7	4.4	19.7
9	Zn		16317	2	111	65	66	19	111
10	Cr		17022	0.6	204	106	105	31	204
11	Ni		17518	1	117	69	69	21	117
12	V		6673	3	175	88	90	31	176
13	U		17225	0.01	1.3	0.24	0.1	0.23	1.3

3b: Mesopotamia terrain

Ser. No.	Element	Unit	No. of Samples	Range		Mean	Median	Std. Dev.	Primary Threshold
				Min	Max				
1	P_2O_5	%	2061	0.02	0.33	0.16	0.16	0.06	0.33
2	K_2O		2072	0.04	2	0.98	0.96	0.46	2.03
3	Al_2O_3		2105	0.12	10.8	5.94	6	2.29	10.85
4	Fe_2O_3		2092	0.04	5.72	3.08	2.99	1.20	5.72
5	TiO_2		2059	0.01	0.86	0.44	0.46	0.16	0.86
6	SO_3		891	0.01	32.63	8.68	4.01	9.76	32.95
7	Cu	ppm	1981	1	40	16	15	7.9	40
8	Pb		1895	1	17	6.02	5	3.5	17.2
9	Zn		237	20	87	54	55	14	88
10	Cr		2026	4	810	238	180	176	818
11	Ni		2045	1	229	91	83	49	229
12	V		1898	4	164	71	66	38	166
13	U		1992	0.1	1.24	0.2	0.1	0.21	1.3

Table 4: R – mode correlation coefficients and factor analysis

4a: Desert terrain

	P_2O_5	K_2O	Al_2O_3	Fe_2O_3	TiO_2	Cu	Pb	Zn	Cr	Ni	V
K_2O	-0.22										
Al_2O_3	-0.21	0.35									
Fe_2O_3	-0.26	0.42	0.80								
TiO_2	-0.03	0.04	0.04	0.05							
Cu	-0.07	0.17	0.54	0.52	0.01						
Pb	0.15	-0.04	-0.04	-0.07	0.03	-0.04					
Zn	0.27	0.12	0.44	0.40	0.02	0.34	0.13				
Cr	0.07	0.22	0.37	0.40	0.04	0.22	0.20	0.45			
Ni	0.05	-0.06	0.39	0.31	0.02	0.36	0.26	0.43	0.54		
V	-0.05	-0.02	0.34	0.36	0.01	0.49	0.04	0.18	0.23	0.40	
U	0.59	-0.11	-0.23	-0.24	-0.02	-0.08	0.06	0.10	-0.02	-0.08	-0.06

Factor Score Coefficients
Extraction: Principal components

Variables	Factor 1	Factor 2	Factor 3	Factor 4
P_2O_5	0.02	0.50	0.00	0.00
K_2O	-0.36	0.01	0.48	-0.07
Al_2O_3	0.10	-0.02	0.26	-0.05
Fe_2O_3	0.06	-0.04	0.30	-0.07
TiO_2	-0.22	-0.08	0.10	0.20
Cu	0.37	0.06	0.06	-0.17
Pb	-0.16	-0.10	-0.13	0.58
Zn	0.00	0.26	0.21	0.12
Cr	-0.10	0.03	0.15	0.36
Ni	0.22	-0.06	-0.12	0.36
V	0.50	-0.05	-0.18	-0.05
U	-0.01	0.52	0.07	-0.14

Eigenvalues
Extraction: Principal components

Value	Eigenval	% total Variance	Cumul. Eigenval	Cumul. %
1	3.62	30.17	3.62	30.17
2	1.98	16.50	5.60	46.67
3	1.18	9.87	6.78	56.54
4	1.12	9.36	7.91	65.89

4b: Mesopotamia terrain

	P_2O_5	K_2O	Al_2O_3	Fe_2O_3	TiO_2	Cu	Pb	Zn	Cr	Ni	V
K_2O	0.13										
Al_2O_3	0.05	-0.06									
Fe_2O_3	0.40	0.11	0.67								
TiO_2	0.22	0.26	0.25	0.50							
Cu	-0.21	0.08	-0.41	-0.51	-0.19						
Pb	0.13	-0.30	0.50	0.52	0.32	-0.40					
Zn	0.32	0.11	0.14	0.37	0.11	-0.23	0.10				
Cr	0.17	0.40	-0.05	0.27	0.01	-0.13	0.03	0.05			
Ni	0.01	-0.01	0.04	0.06	0.23	-0.30	0.16	0.14	0.00		
V	0.10	0.05	0.50	0.62	0.33	-0.44	0.55	0.31	0.28	0.26	
U	0.31	0.27	0.29	0.48	0.43	-0.34	0.36	0.44	0.10	0.28	0.63

Factor Score Coefficients
Extraction: Principal components

Variables	Factor 1	Factor 2	Factor 3	Factor 4
P_2O_5	-0.07	-0.04	-0.12	0.57
K_2O	-0.13	0.53	0.09	-0.01
Al_2O_3	0.34	-0.04	-0.19	-0.11
Fe_2O_3	0.26	0.10	-0.20	0.11
TiO_2	0.06	0.15	0.23	-0.15
Cu	-0.16	0.09	-0.09	-0.03
Pb	0.30	-0.13	-0.03	-0.12
Zn	-0.12	-0.16	0.07	0.56
Cr	0.07	0.53	-0.13	-0.15
Ni	-0.12	-0.10	0.71	-0.11
V	0.21	0.11	0.13	-0.11
U	0.00	0.06	0.27	0.19

Eigenvalues
Extraction: Principal components

Value	Eigenval	% total Variance	Cumul. Eigenval	Cumul. %
1	4.09	34.12	4.09	34.12
2	1.70	14.18	5.80	48.30
3	1.15	9.58	6.94	57.87
4	1.07	8.95	8.02	66.82

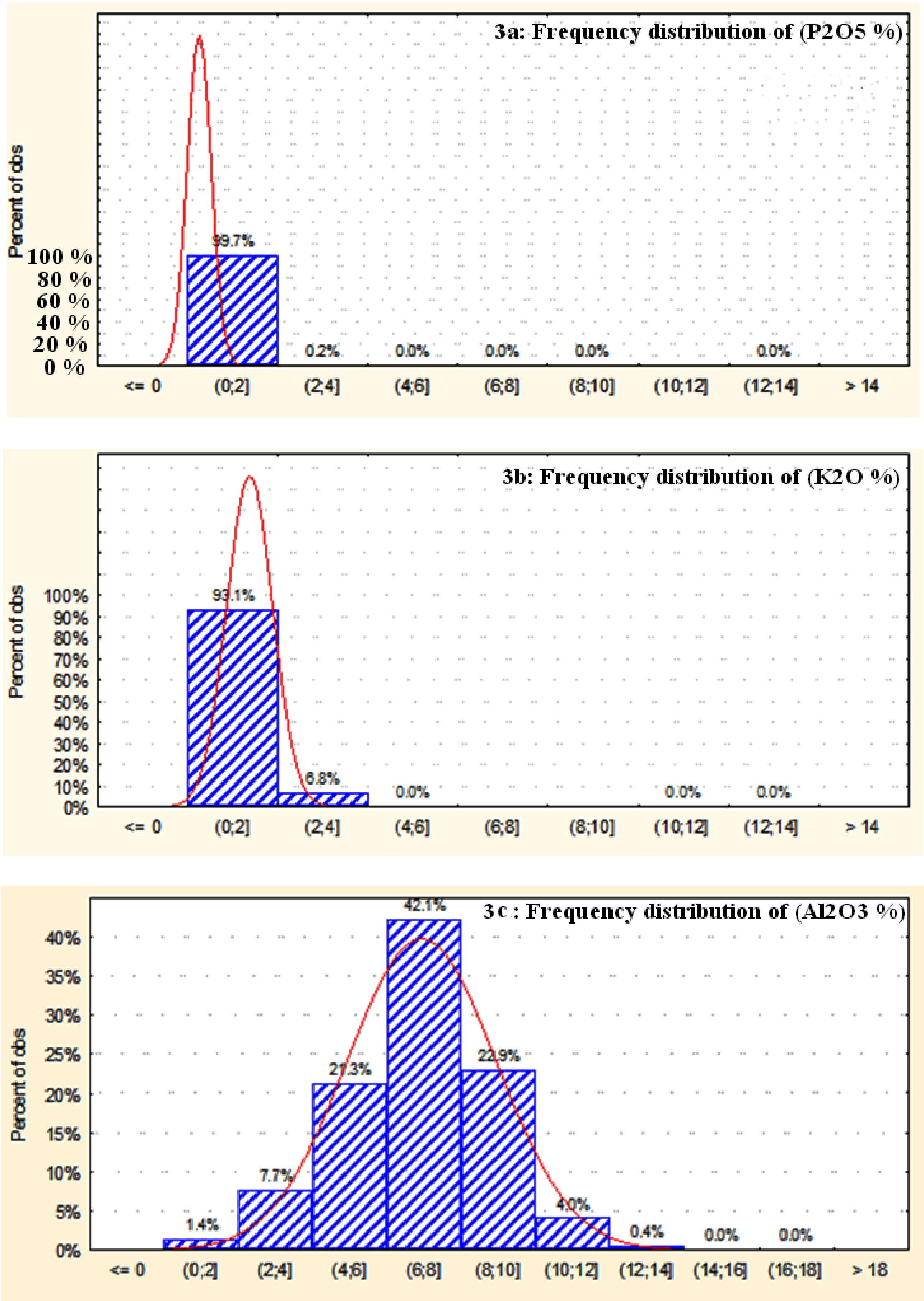
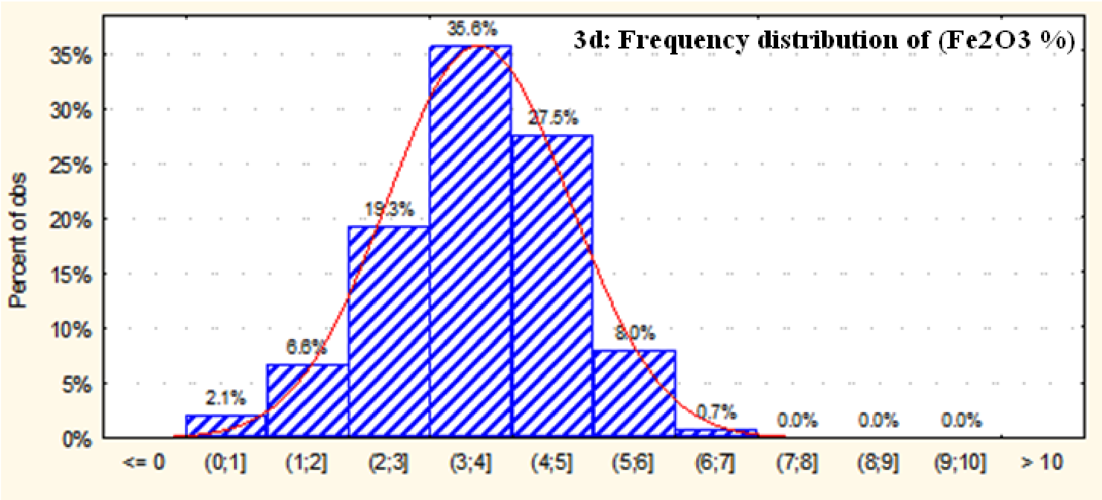
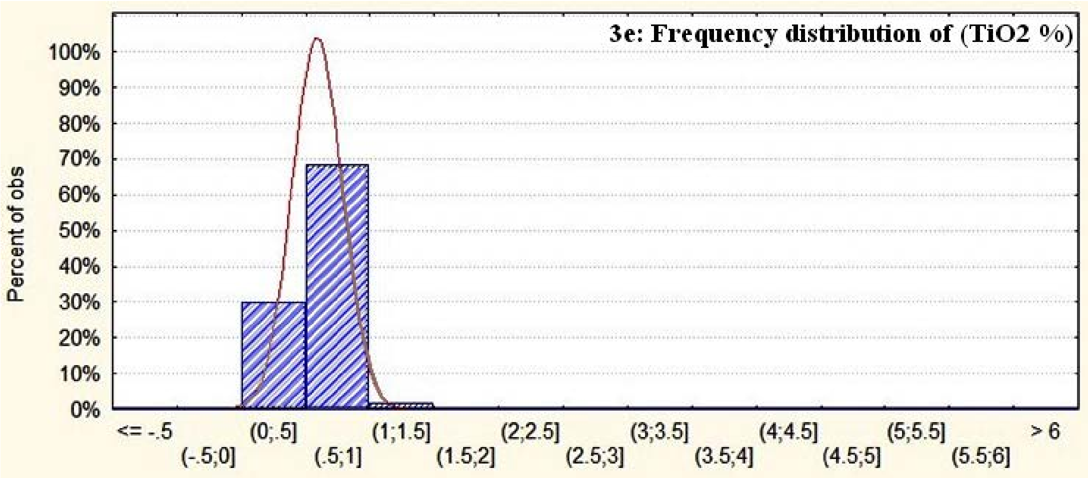
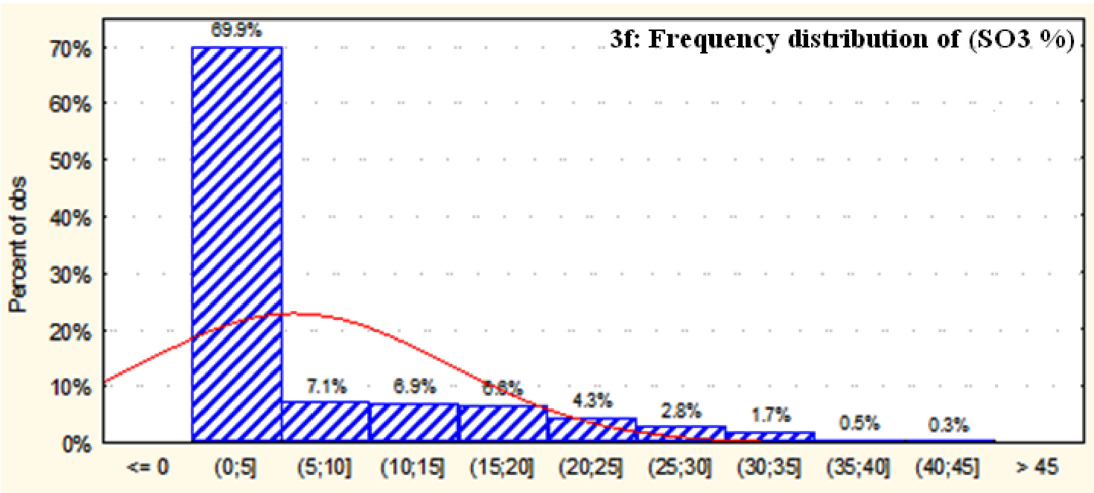


Fig.3: Frequency distribution histograms of the elements in the Desert terrain







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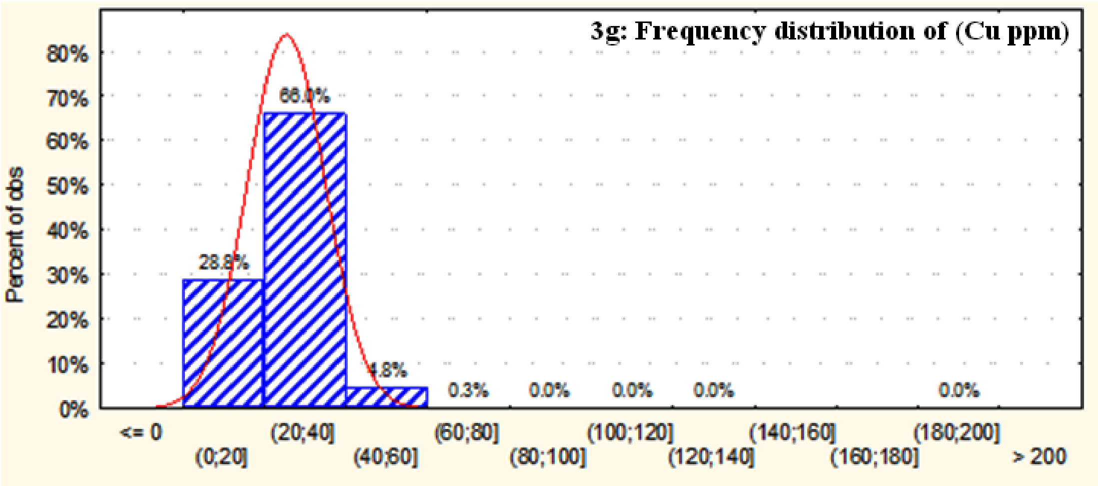

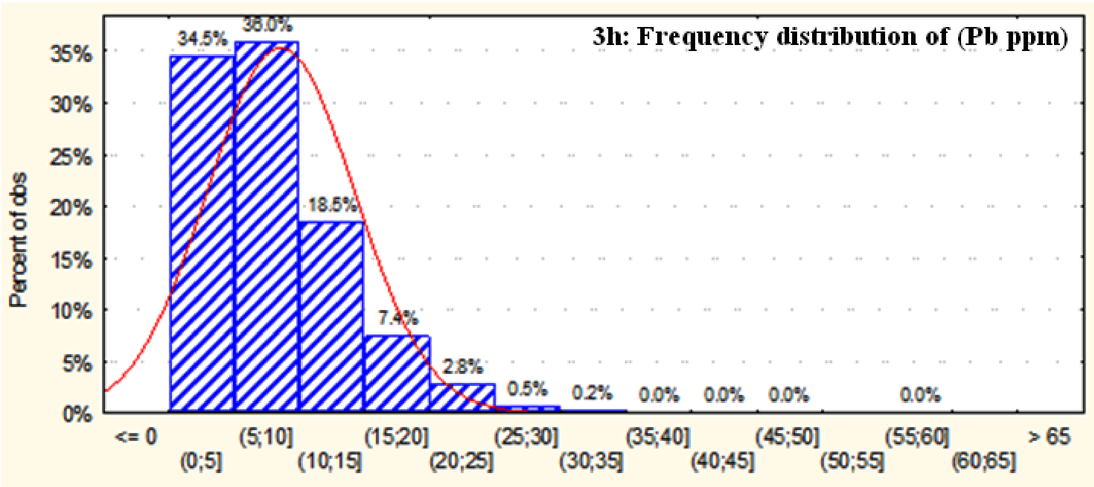

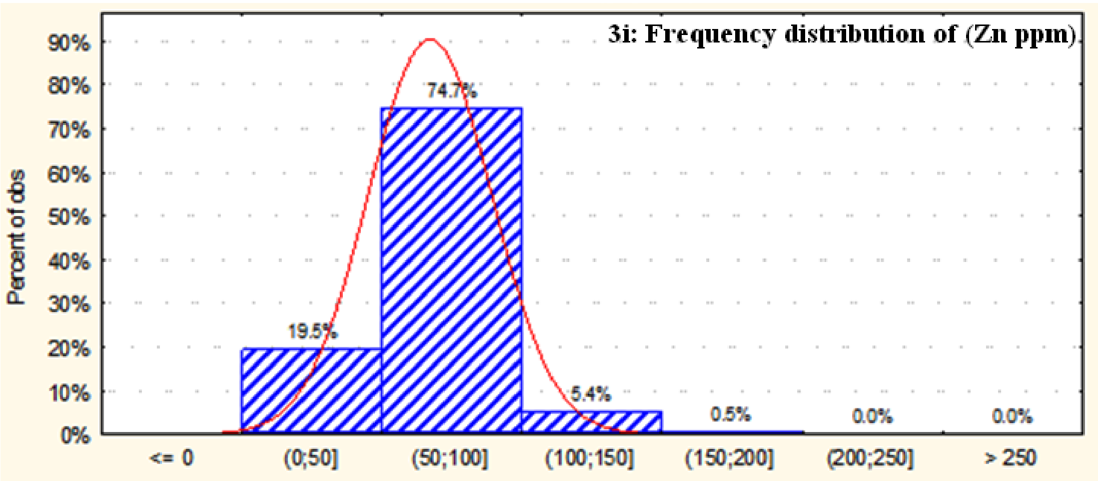

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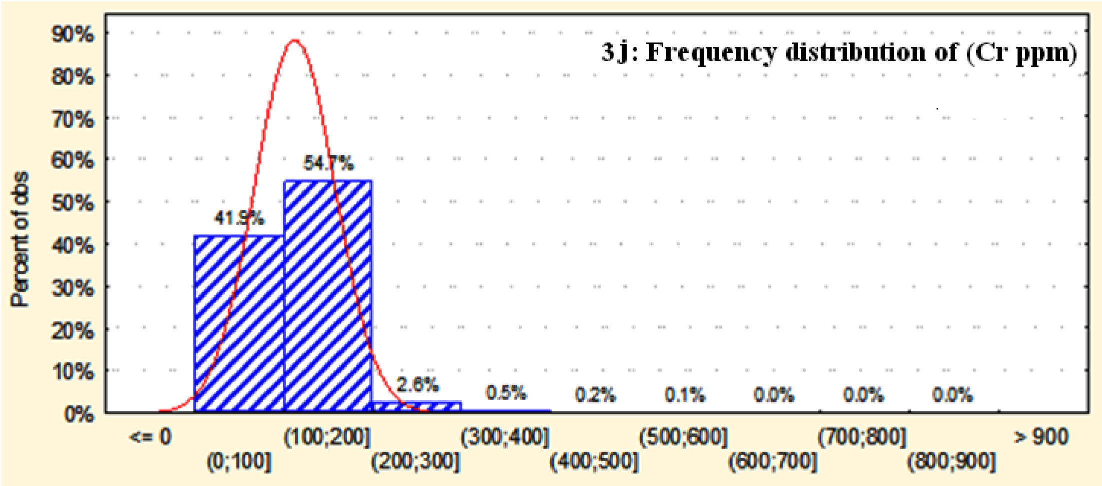

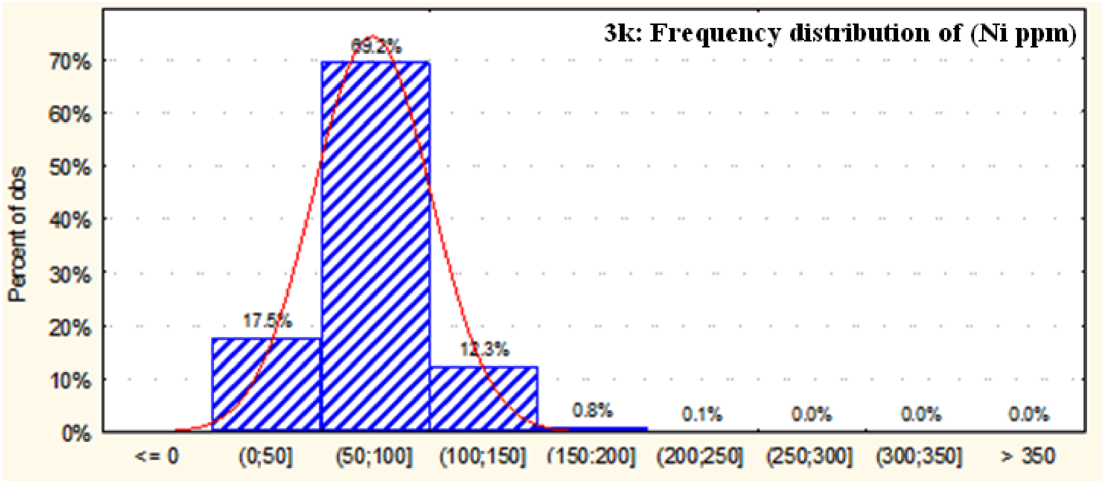

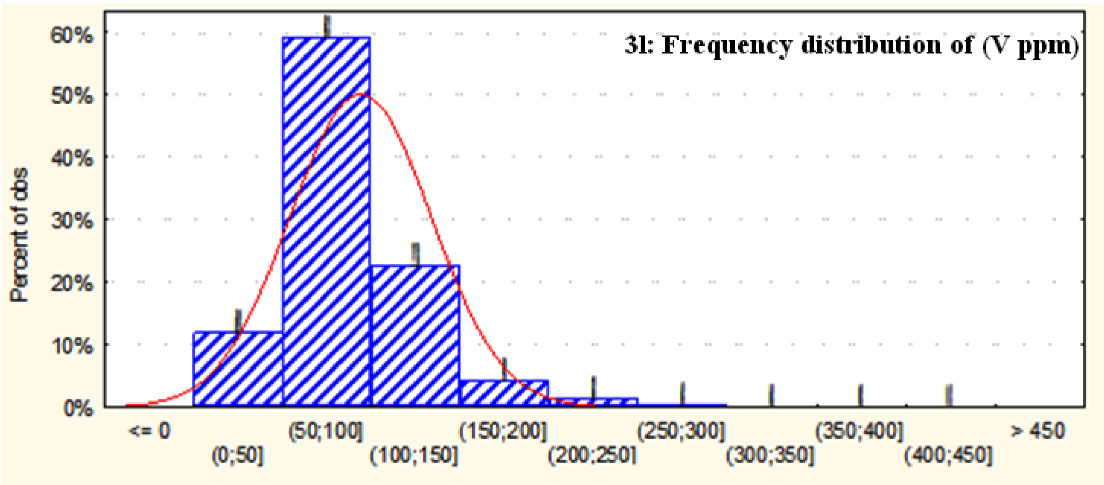

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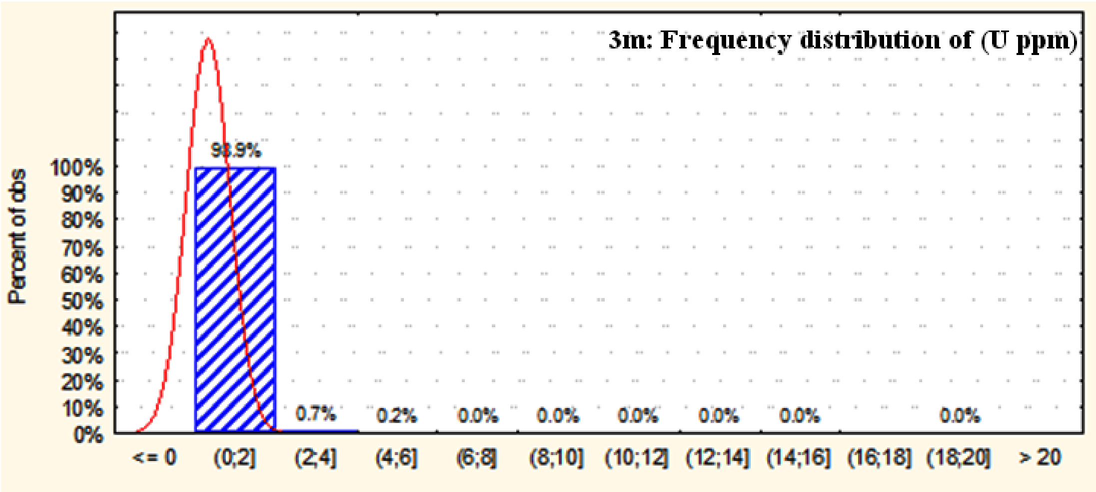

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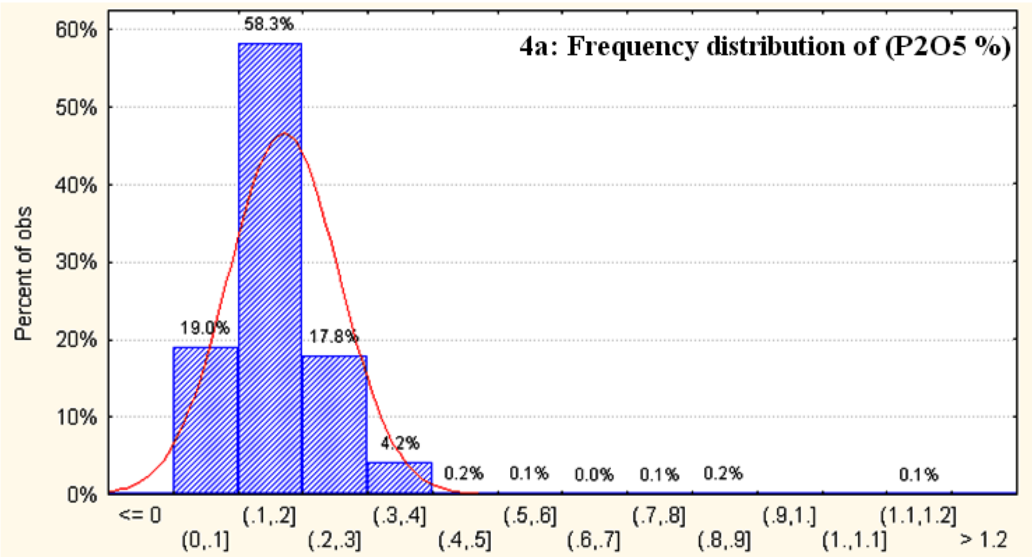


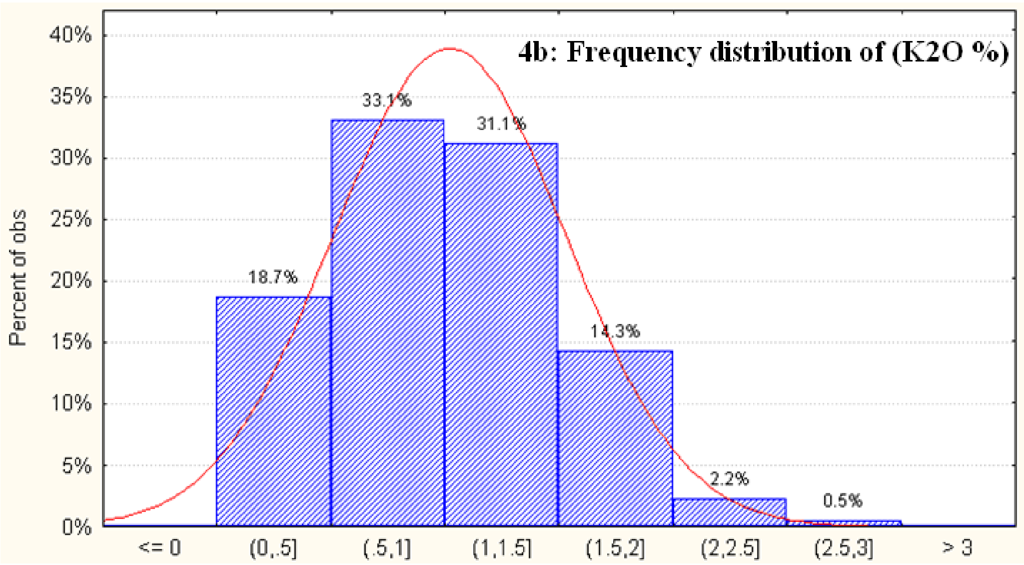
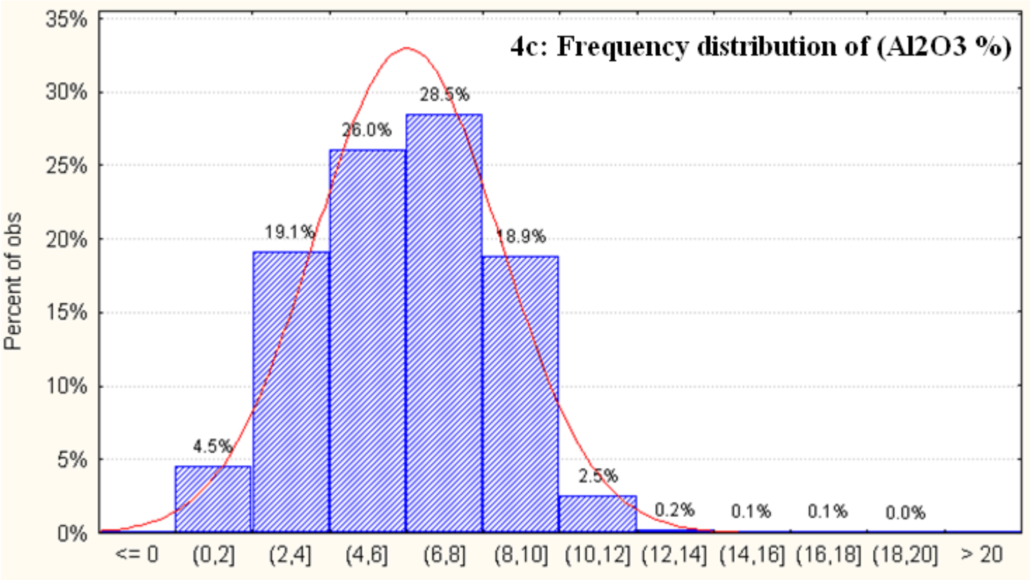
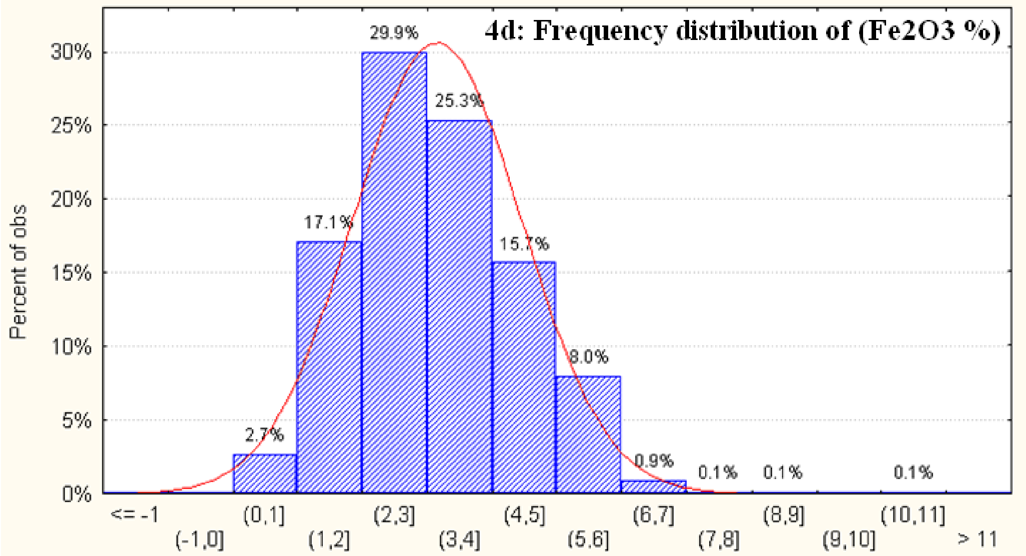
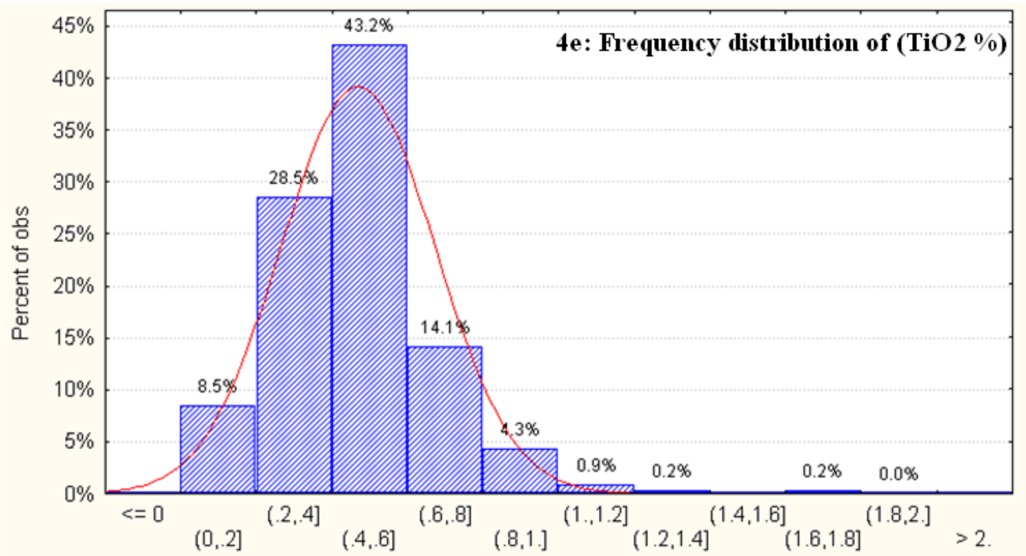


Fig.4: Frequency distribution histograms of the elements in the Mesopotamia terrain







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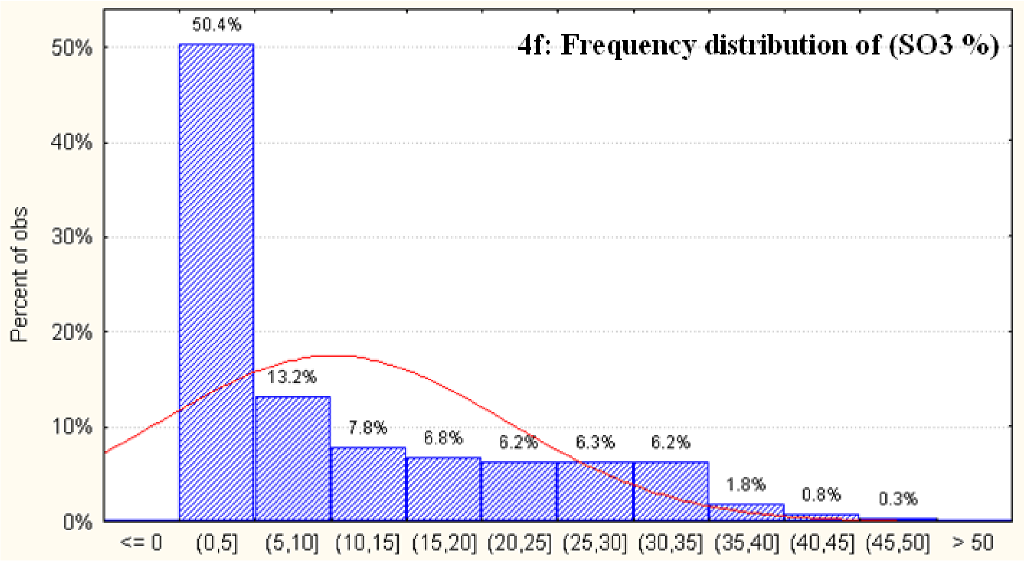

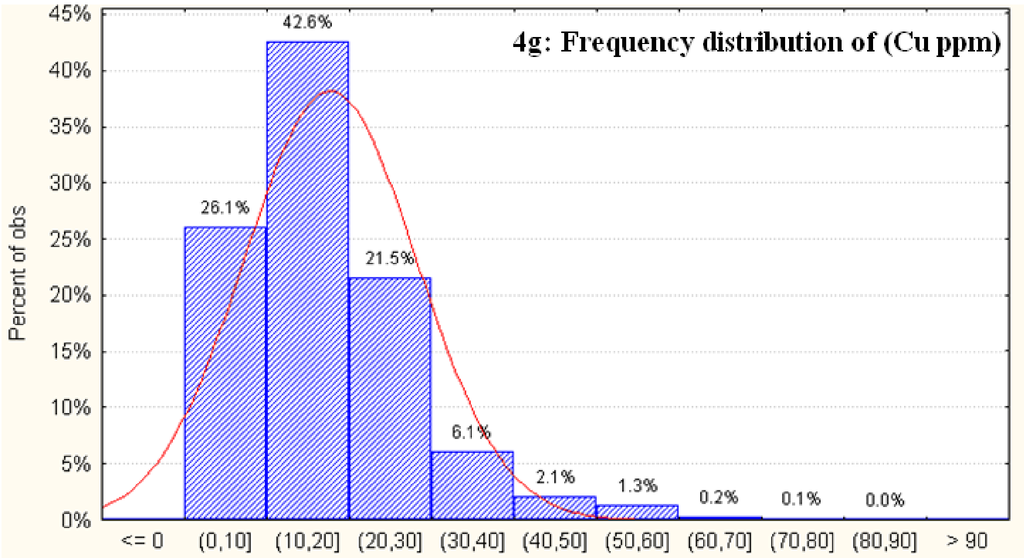

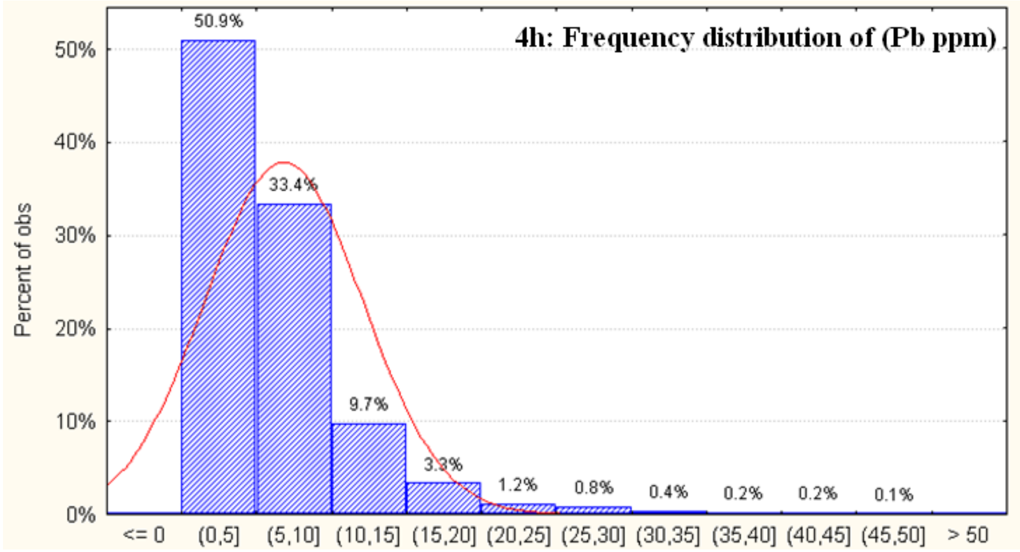

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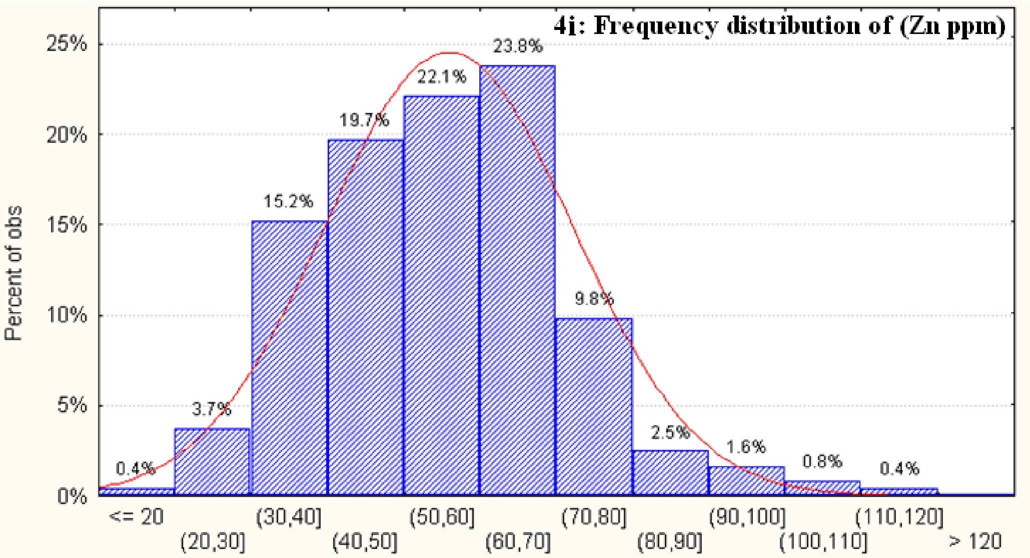

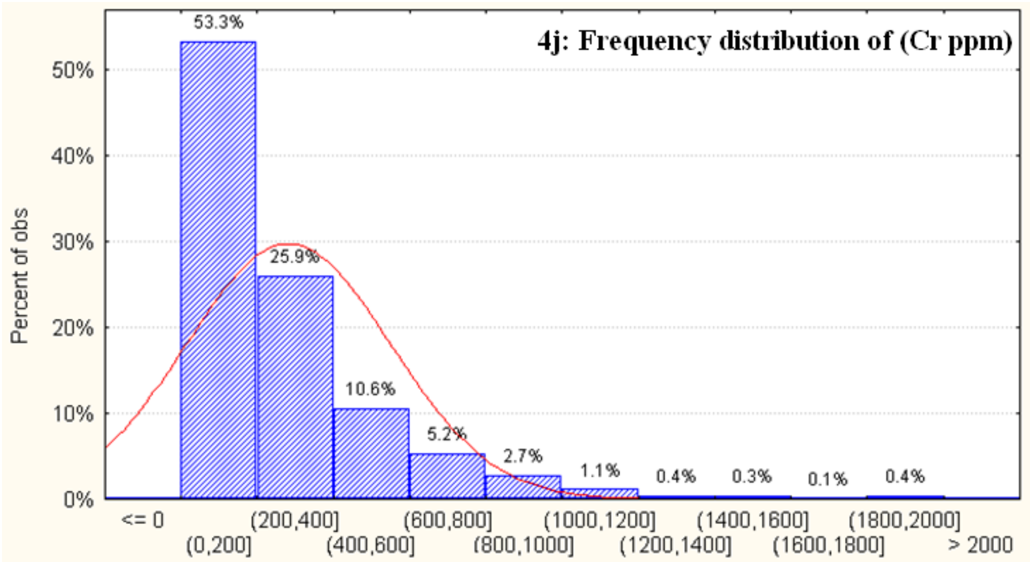

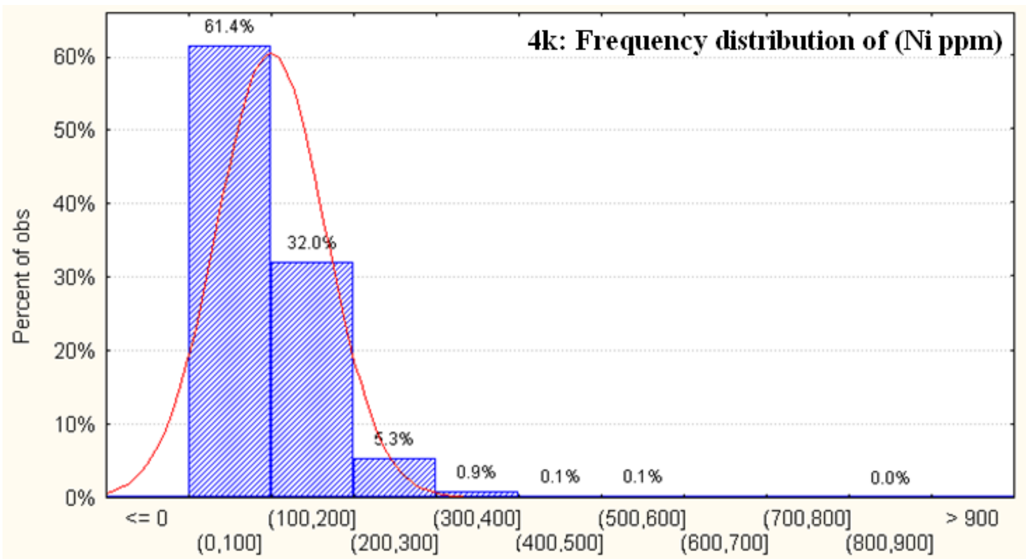

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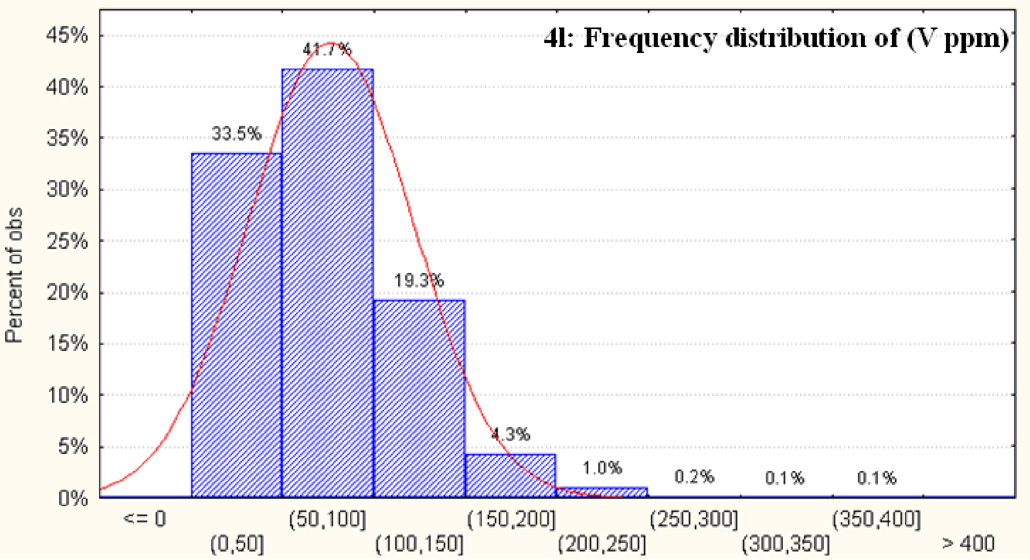

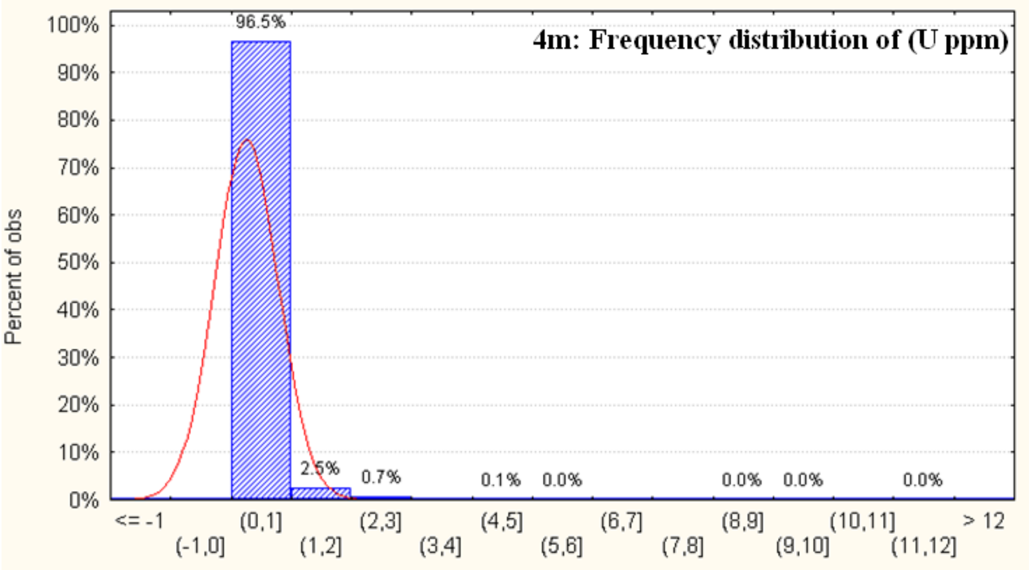

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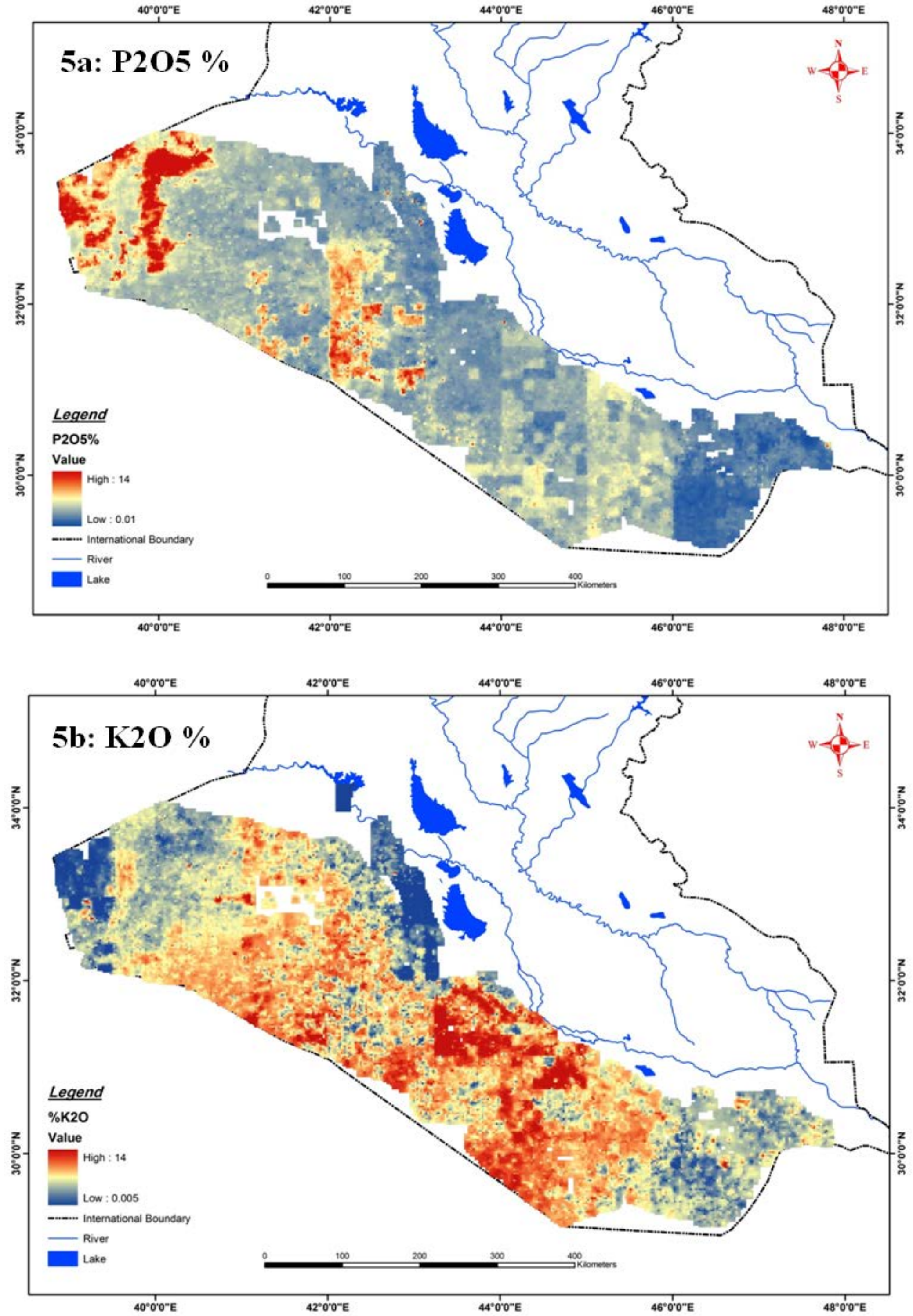
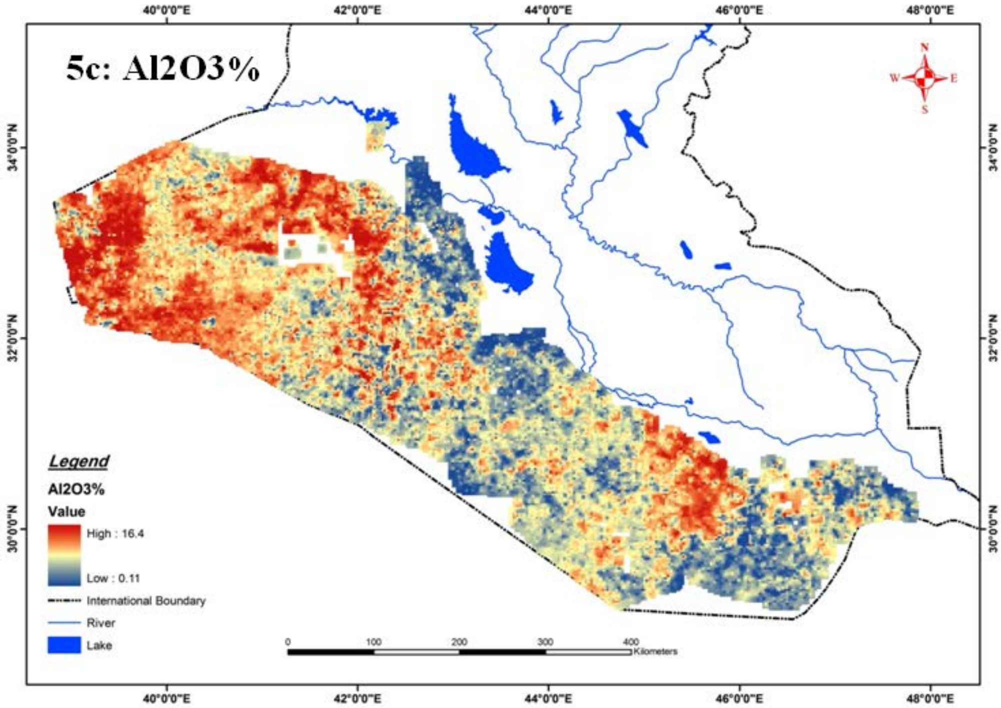
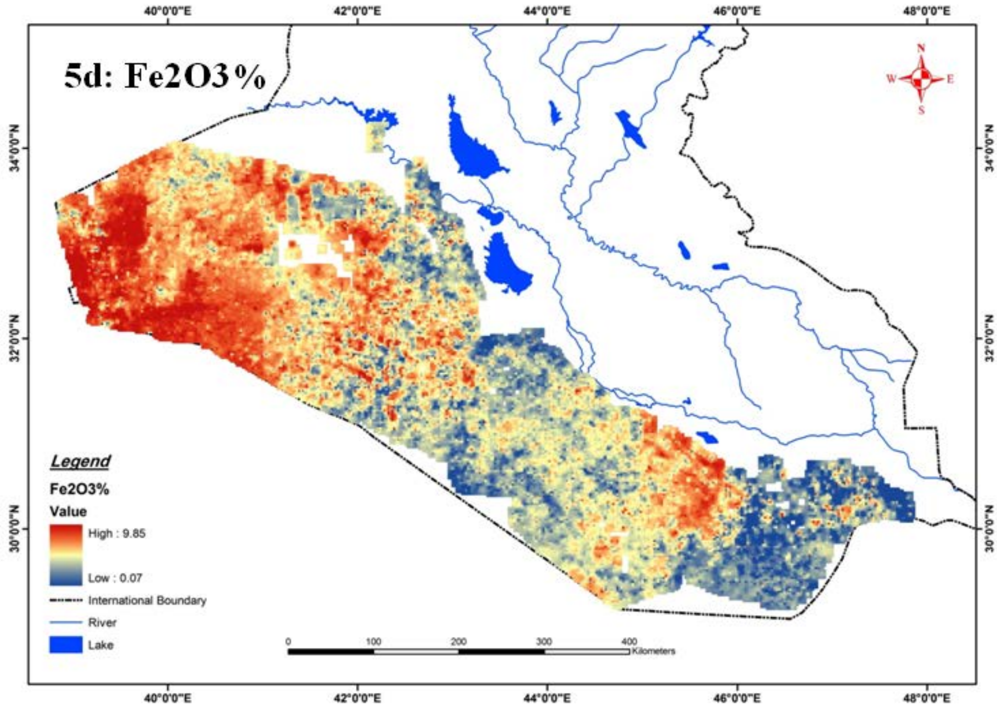


Fig.5: Spatial distribution maps/ Desert terrain





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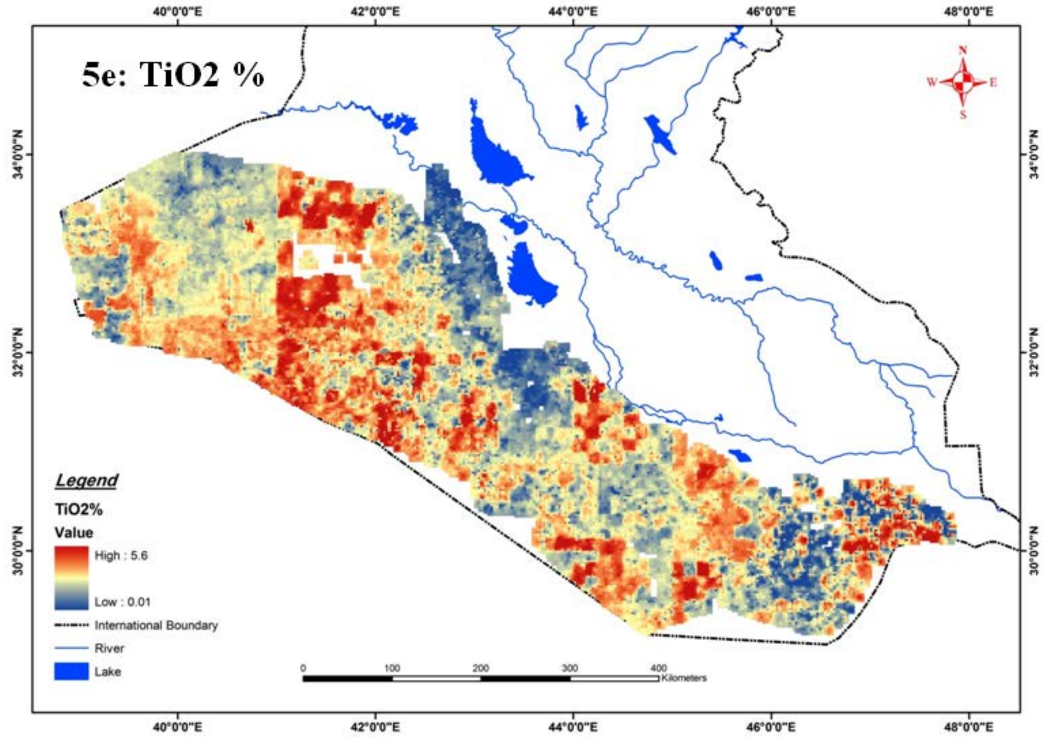

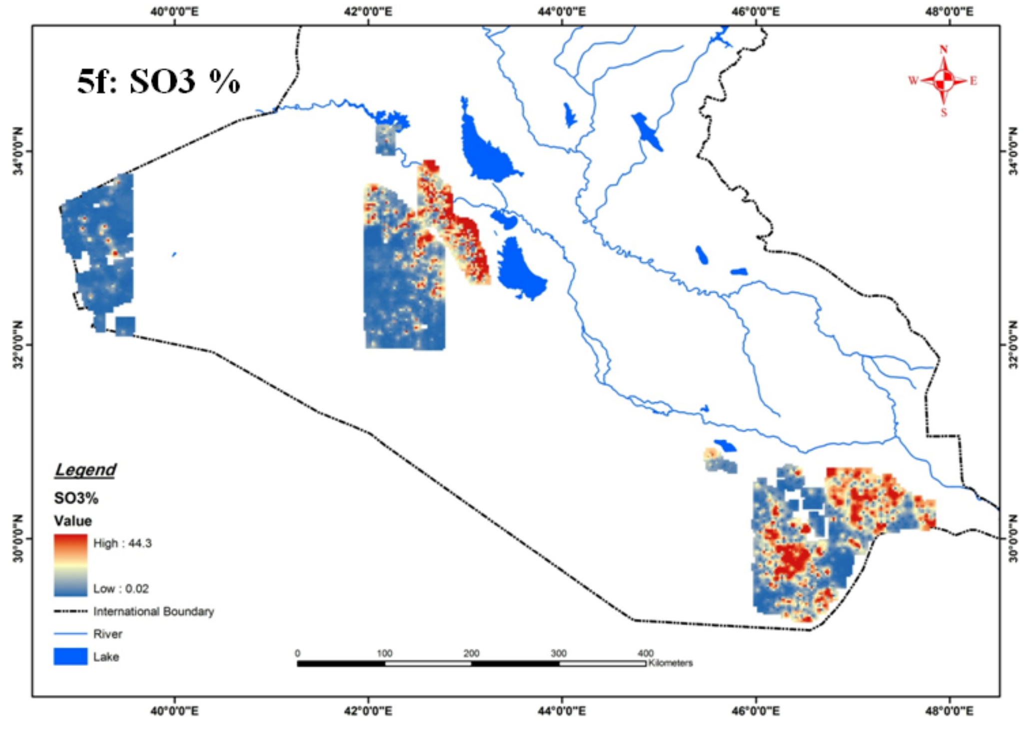

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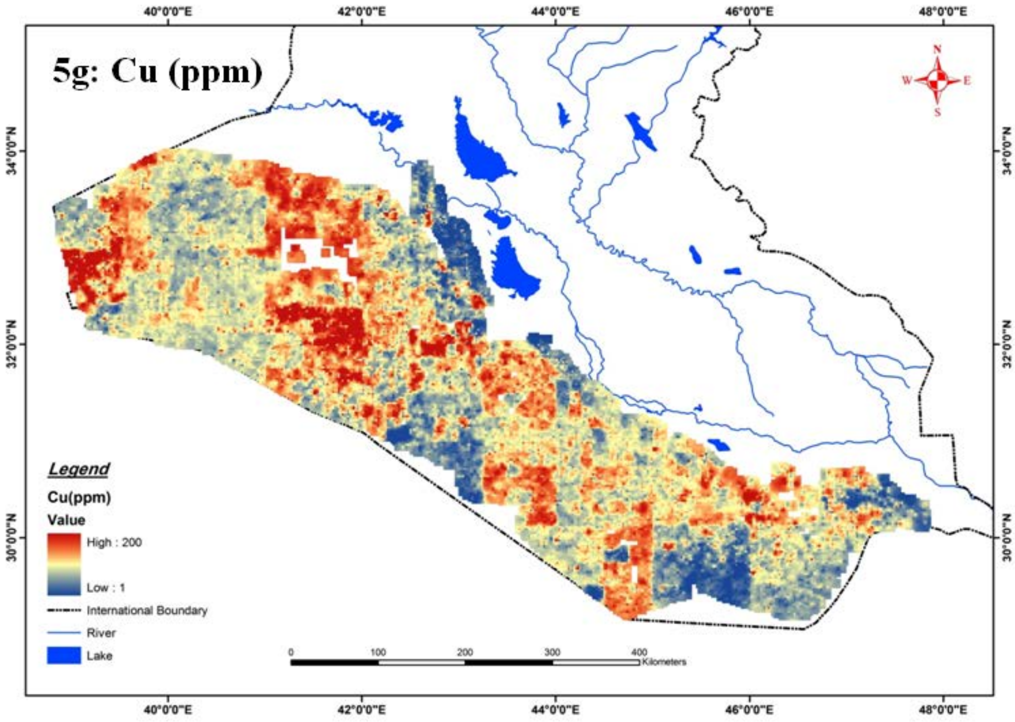

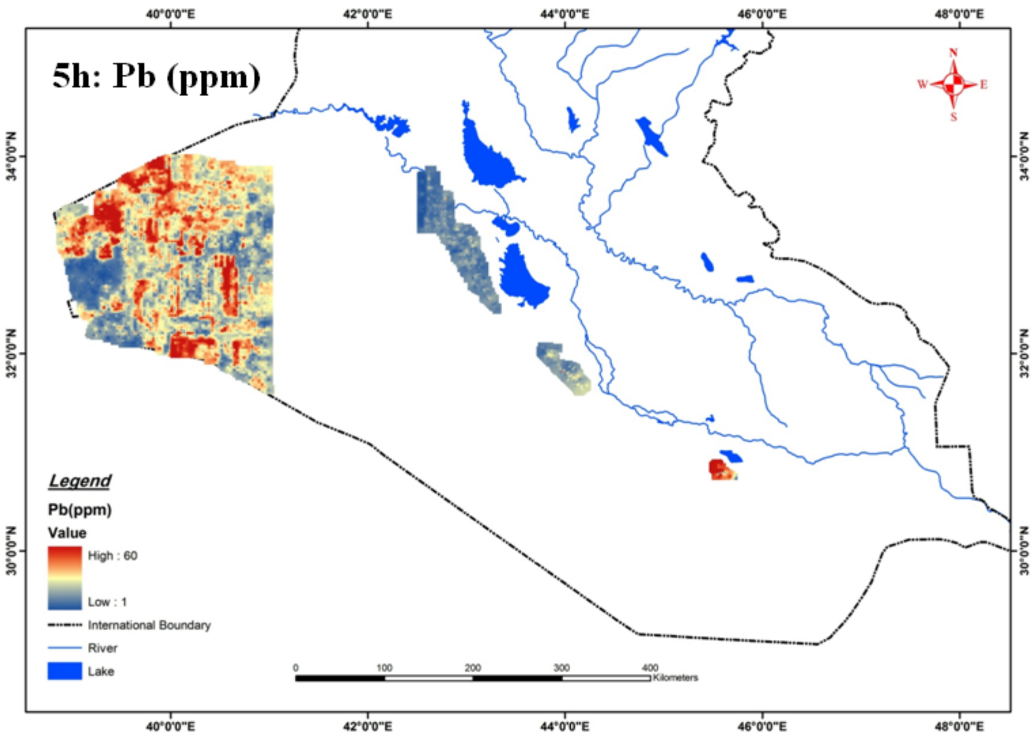

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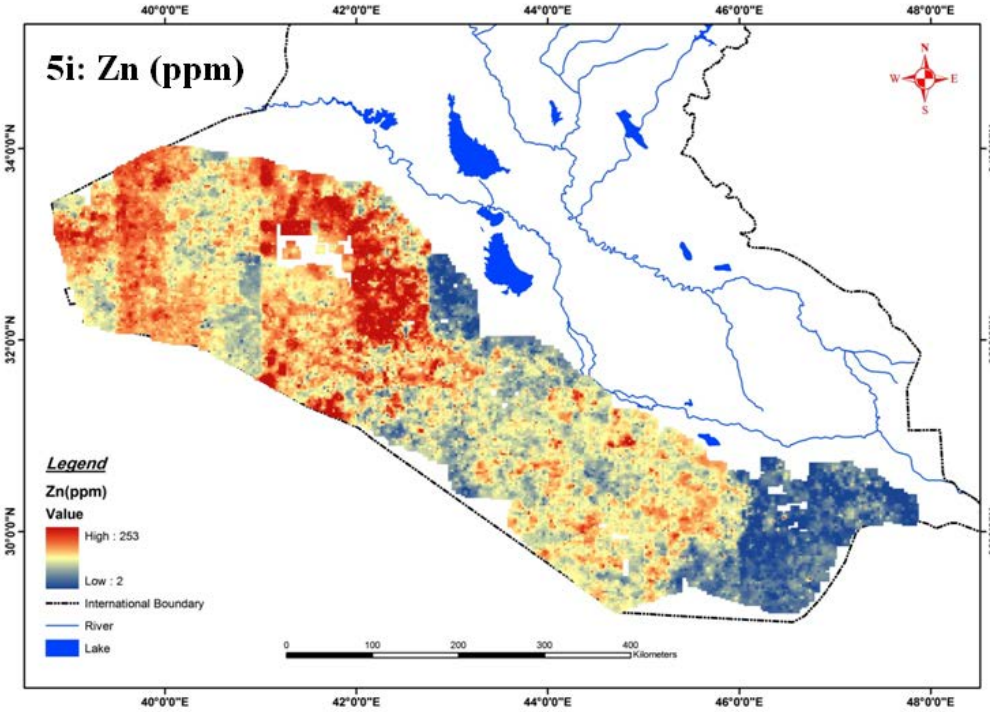

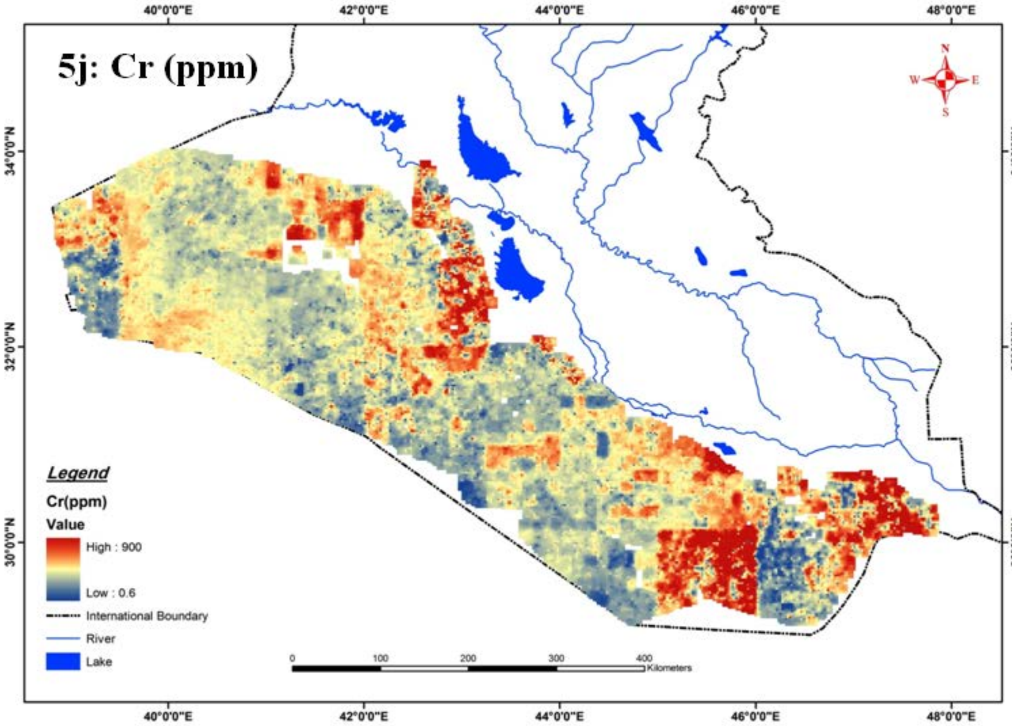

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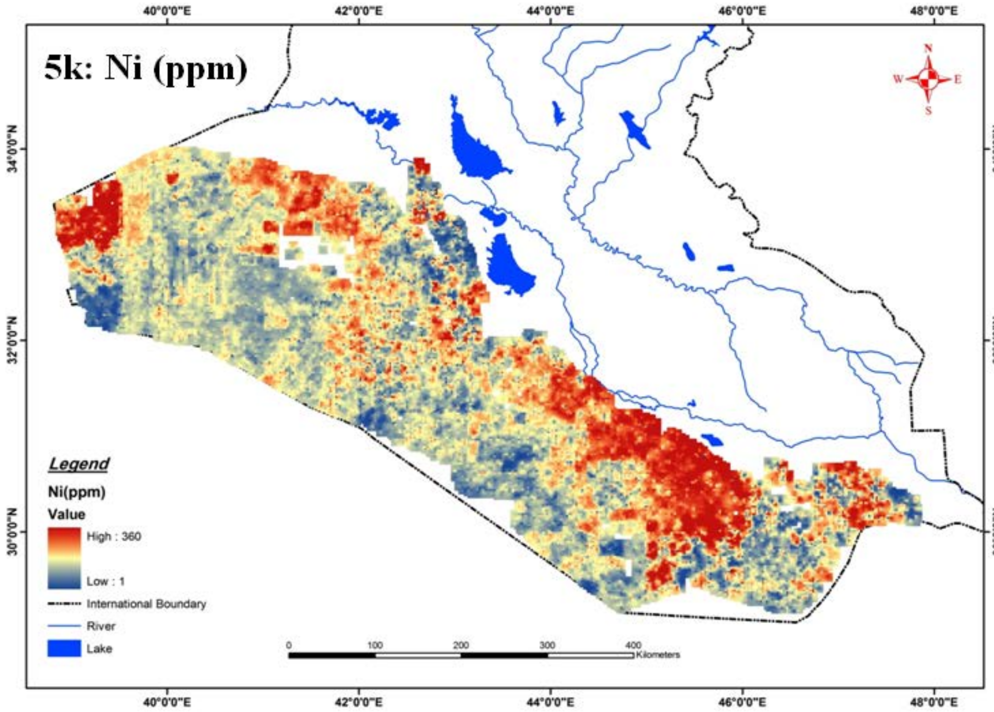

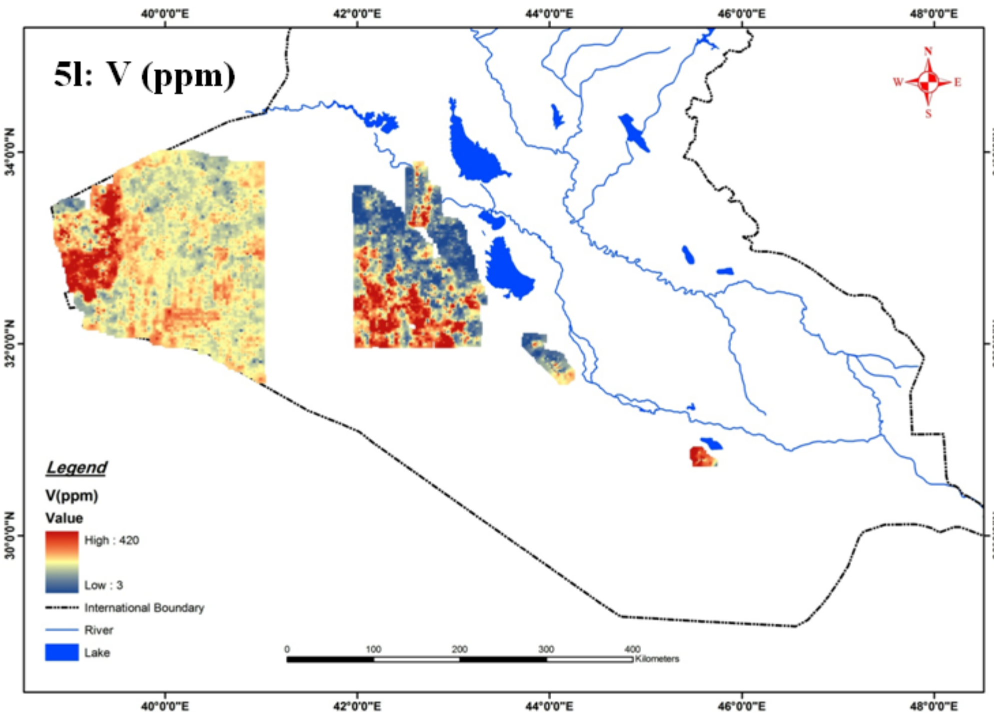

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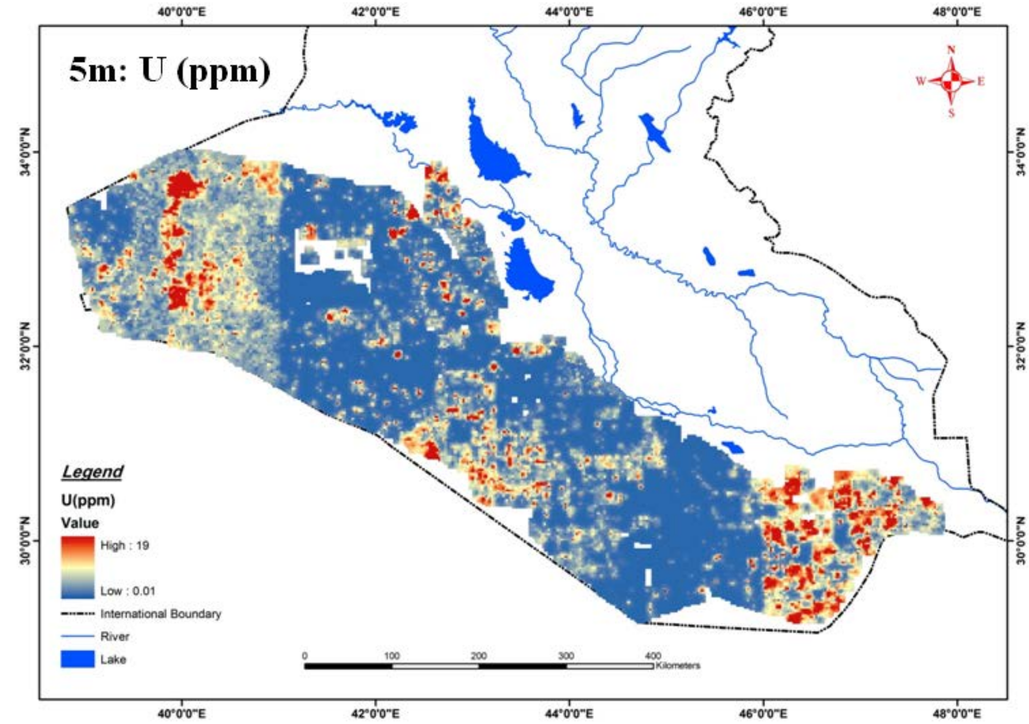

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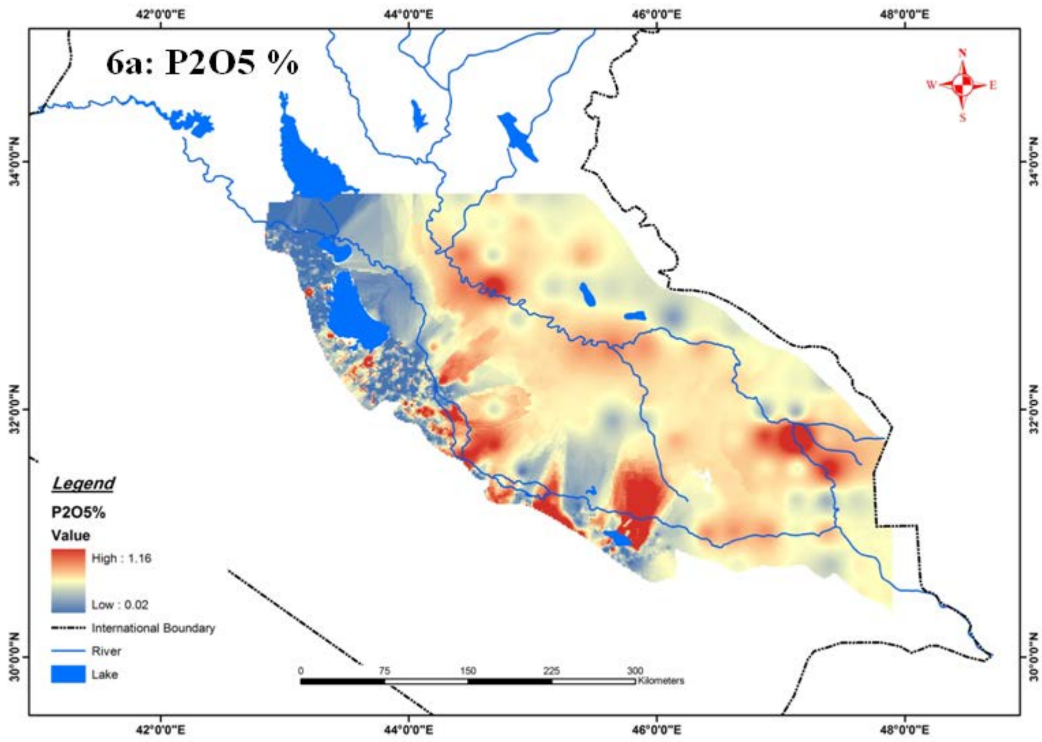
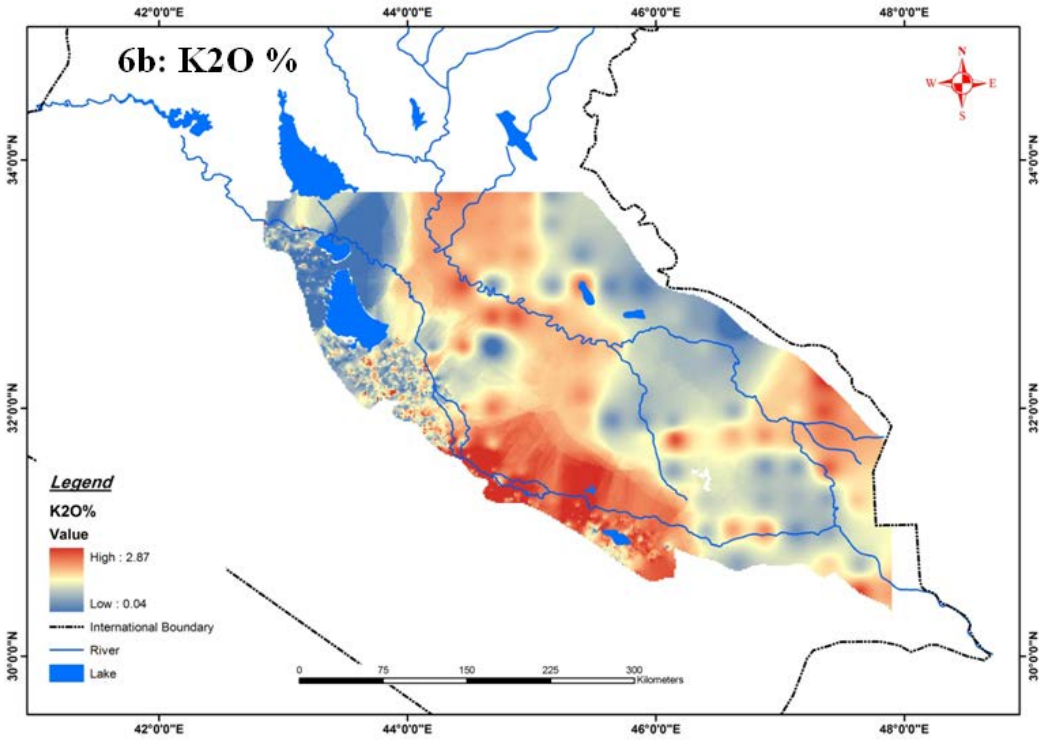
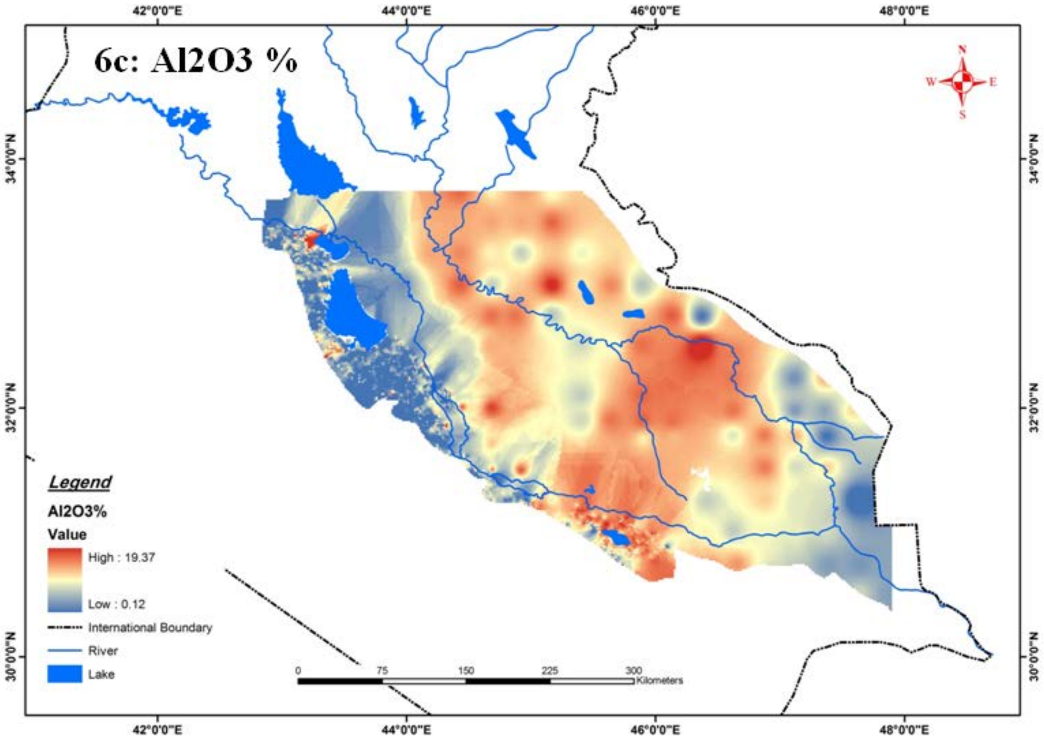


Fig.6: Spatial distribution maps/ Mesopotamia terrain





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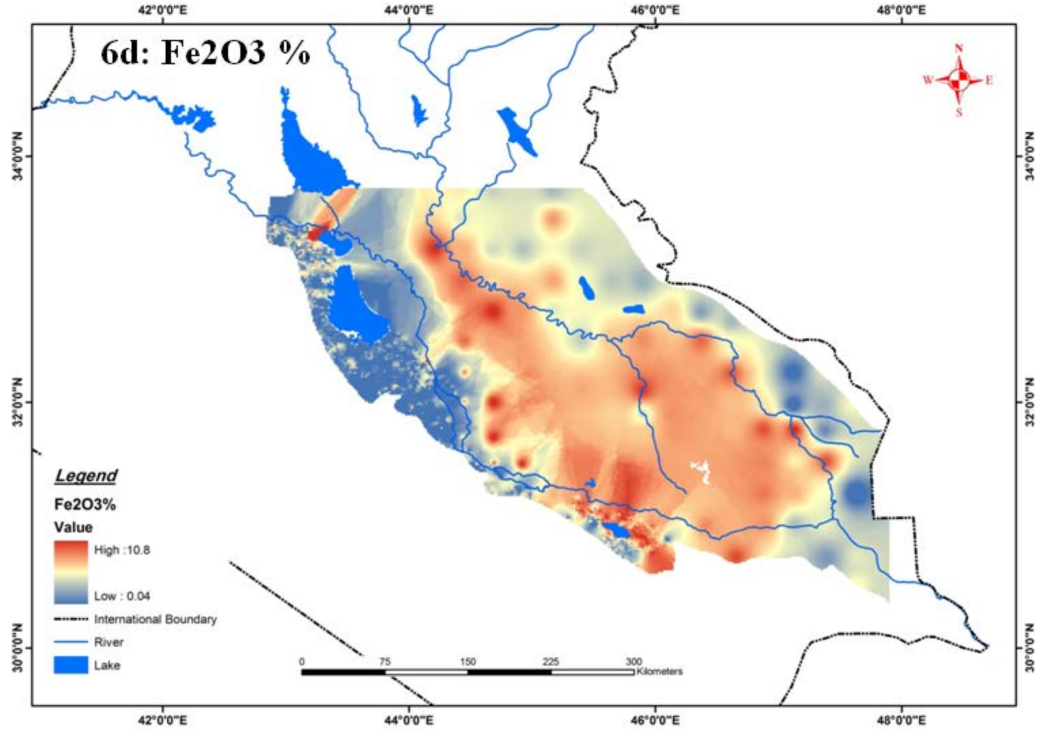

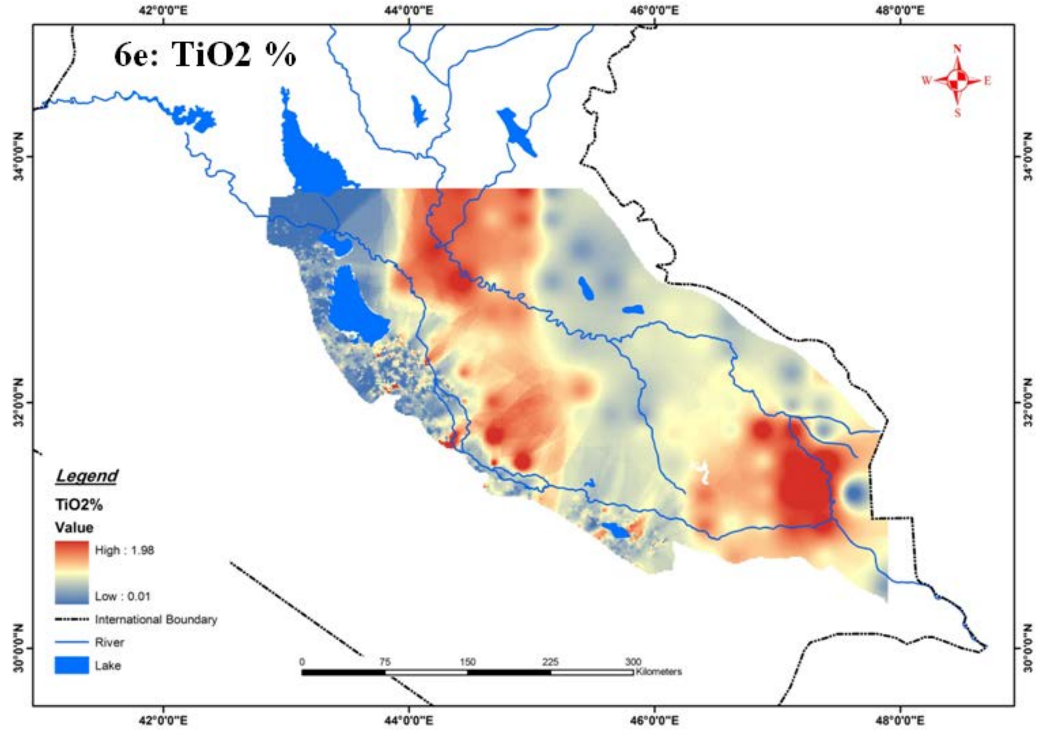

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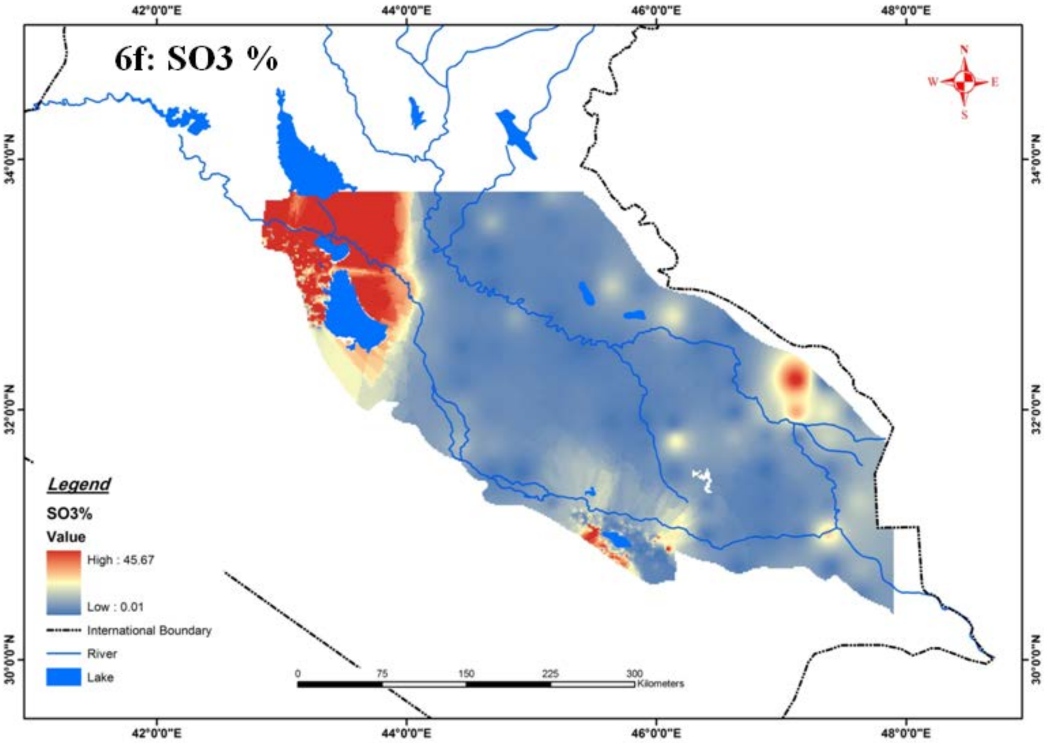

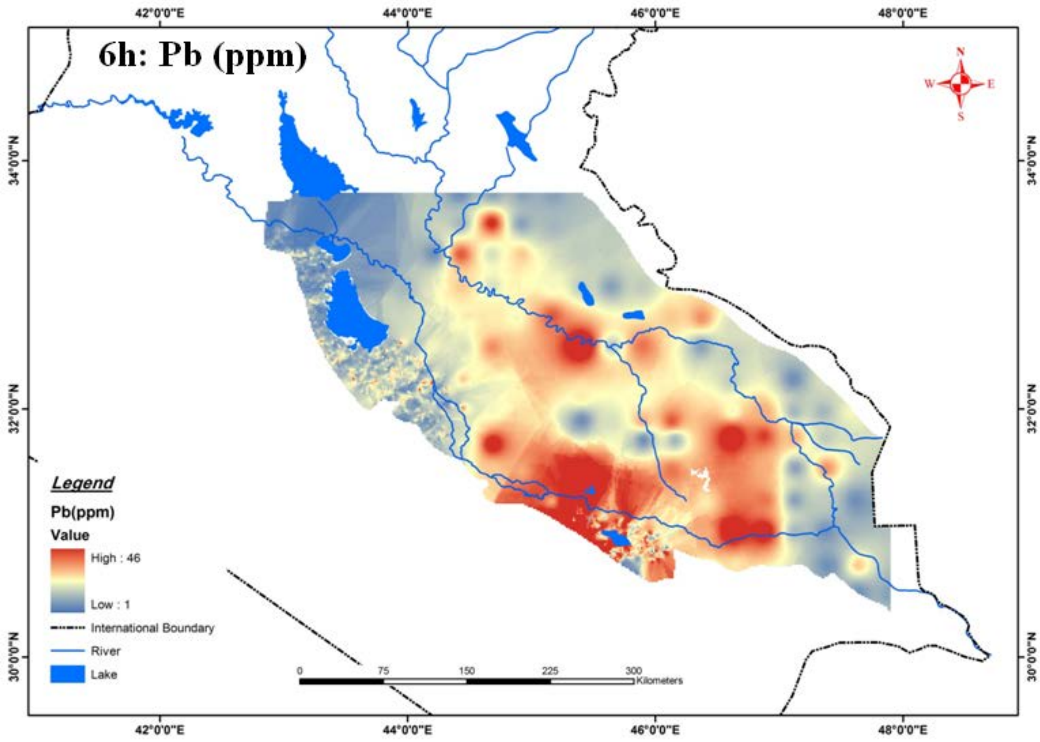

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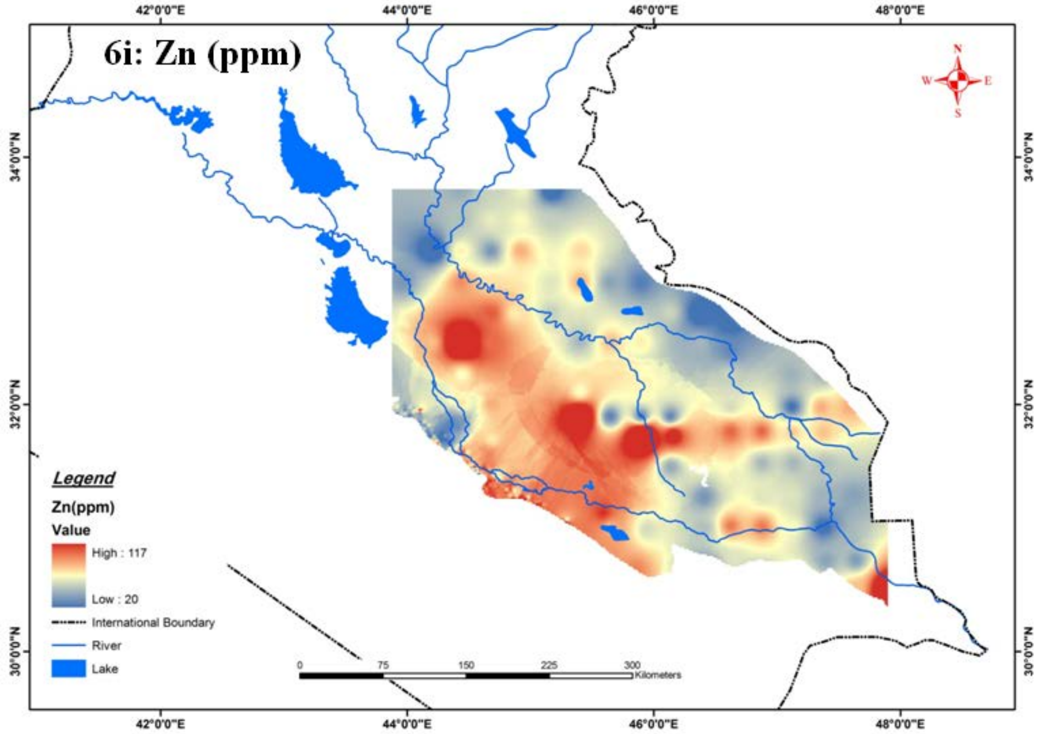

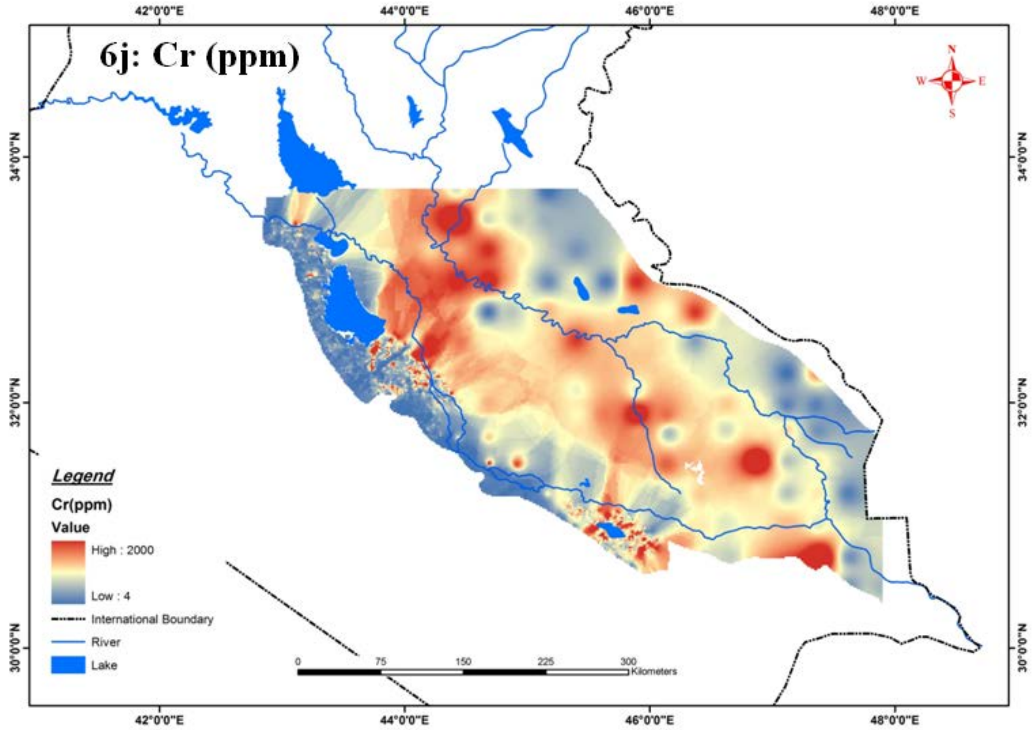

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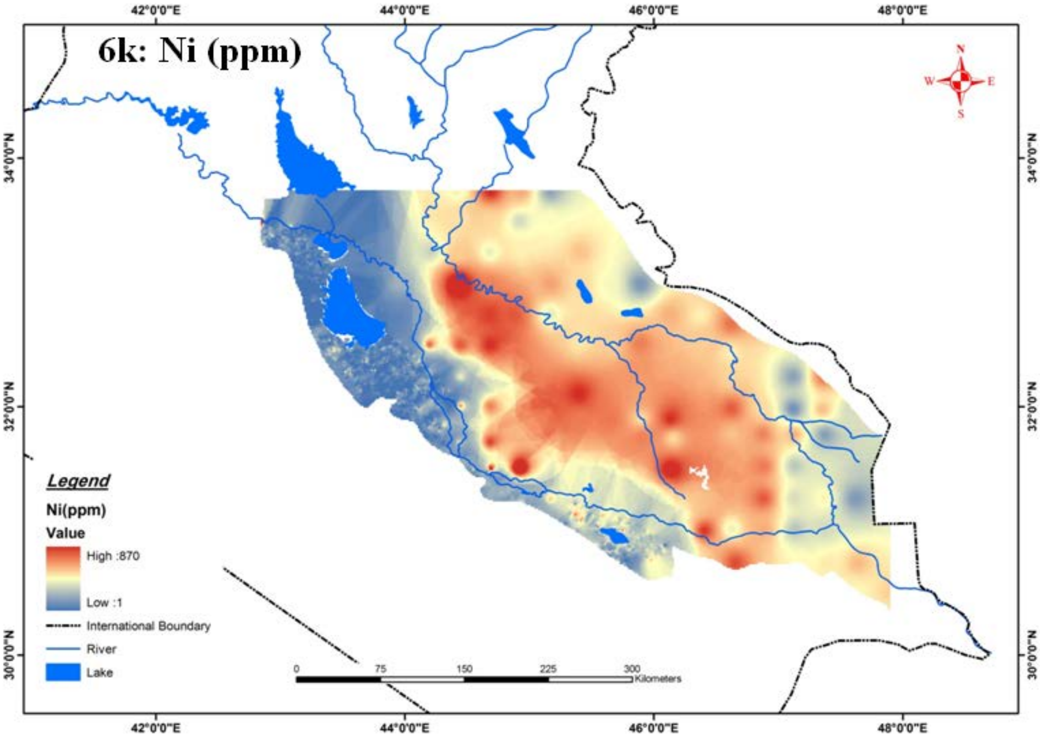

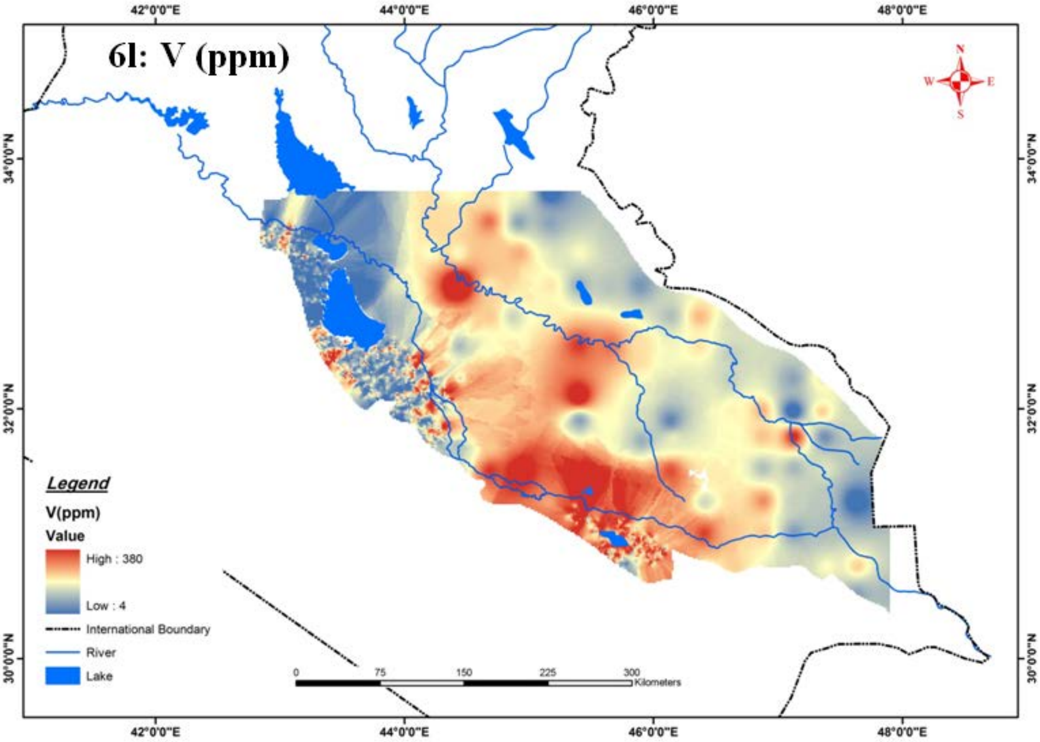

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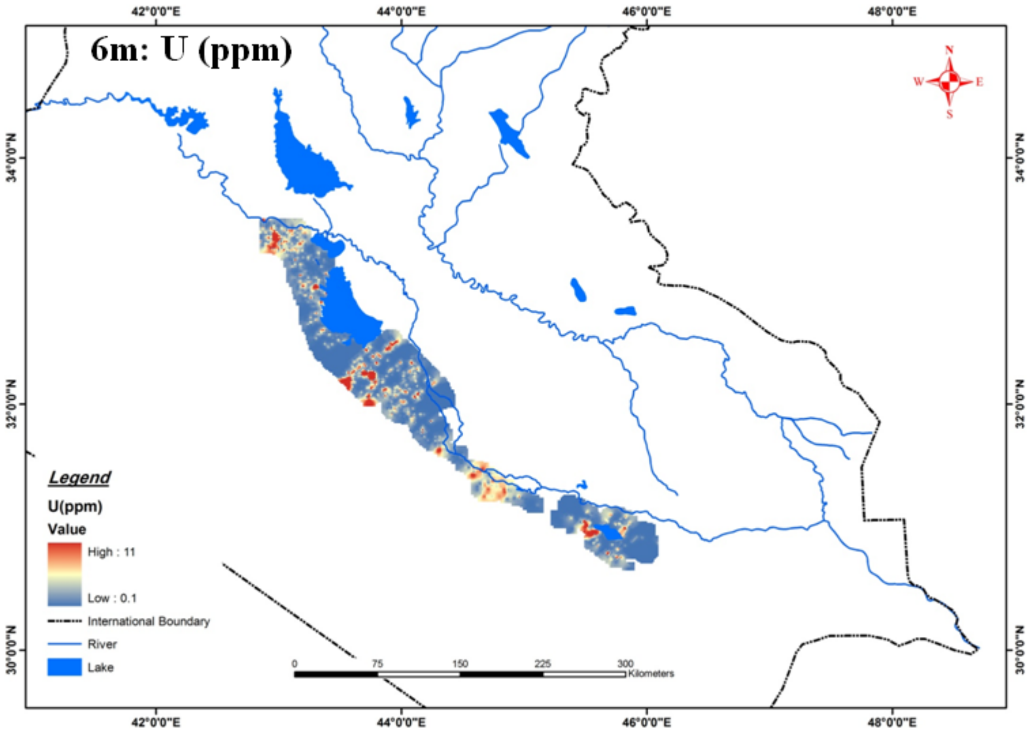

Continue Fig.6:

Table 5: World soil range and average concentrations of the analysed trace elements (ppm)

	(1)	(2)	(3)	(4)
Cu	20	13 – 24	15 – 40	
Pb	10	3 – 189	15 – 25	
Zn	50	17 – 125	tr. – 900	
Cr	200	7 – 221	200 – 540	
Ni	40	0.2 – 450	50 – 500	
V	100	18 – 115	tr. – 300	
U	1.0	–	–	0.79 – 11

(1) Hawkes and Webb (1962).
(2) Kapata – Pendias and Pendias (2001).
(3) Aubert and Pinta (1977).
(4) UNSCEAR (1993).

Table 6: Actual median values of the surveyed areas (ppm)

Element	Desert	Mesopotamia	E. Erbil	Serguza	Berzanik
Cu	25	16	28	46	32
Pb	8	5	16	38	87
Zn	66	56	60	131	111
Cr	106	190	319	280	119
Ni	70	85	100	240	89
V	90	70	105	190	83
U	0.1	0.1	n.a.	n.a.	n.a.

n.a.: not analysed

Table 7: Range and median values of the trace elements geochemical data of the Desert and Mesopotamia samples (ppm)

	Actual data		**Recommended background**	
	Range	**Median**	**Range**	**Median**
Desert				
Cu	1 –200	25	1 – 45	24
Pb	1 – 60	8	1 – 19	7
Zn	2 – 253	66	2 – 111	66
Cr	0.6 – 900	106	0.6 – 204	105
Ni	1 – 360	70	1 – 117	69
V	3 – 420	90	3 – 175	90
U	0.01 – 19	0.1	0.01 – 1.3	0.1
Mesopotamia				
Cu	1 – 85	16	1 – 40	15
Pb	1 – 46	5	1 – 17	5
Zn	20 – 117	56	20 – 87	55
Cr	4 – 2000	190	4 – 810	180
Ni	1 – 870	85	1 – 229	83
V	4 – 380	70	4 – 164	66
U	0.1 – 11	0.1	0.1 – 1.2	0.1

DISCUSSION

It has been a common practice among environmental geochemists in Iraq and other countries to compare with "Average Shale" content of trace elements (Turekian and Wedepohle, 1961) or Average Earth Crust concentrations to define enrichment or depletion of these elements caused by anthropogenic processes (Kassir *et al*., 2011; Akoto *et al*., 2008; Al-Haidarey *et al*., 2010; Guimaraes *et al*., 2011; Loska *et al*., 2003; Rabee *et al*., 2011; Yisa, *et al*., 2012; Nomaan *et al*., 2012, among others). They went further by using these reference element concentrations in calculating factors and indecies such as "geoaccumulation index" (I geo) of Muller (1969) or "Enrichment factor" (EF) of Buat – Menards (1979) or Pollution Load Index (PLI) of Tomlinson *et al*. (1980) to measure quantitatively metals contamination or pollution in soils and recent sediments.

The controversy in these practices is that neither "Average Shale" of Turekian and Wedepohl (1961) nor Earth Crust abundance of trace elements resemble soil in any respect. Even World averages of trace elements in soil, suggested by many pioneer authors such as (Hawkes and Webb, 1962, Aubert and Pinta, 1979, among others), should be strictly considered for comparison only and not to drive conclusions based on such comparison regarding anthropogenic contamination or pollution. Using any of these reference averages in formulas as the "natural" or "normal" background concentration of an element is completely misleading and may result in bias conclusions. The significantly wide range of mean elements concentration of soil in various countries of the world reported in Kapata – Pendias and Pendias (2001) argues for the weak and unjustifiable marking of a grand world mean or average of trace elements concentration in soil. Nevertheless, using such grand mean values in determining environmental pollution, qualitatively or quantitatively lacks sound scientific base.

Trace metals concentrations in sediments should be compared with those in sediments of the same source rocks and depositional environment and soils should be compared with those that have developed in similar climate and have underwent similar pedogenic processes. Moreover, the total content of trace metals in soil samples (obtained by total digestion of samples) should be considered cautiously since the greater part of the concentration is not necessarily available to plants or can be mobilized to ground – or surface water, which are the main elements of the environment. Only that part of the metal that is weakly bonded to soil components and may be available for mobilization, in ionic form, under specific natural pH and Eh soil conditions, is to be considered as environmental hazard. The radioactive elements and their daughter products are obviously an exception to this statement.

In this work, minor element (oxides), directly related to parent rocks and their concentration in soil is geogenic, were also analysed and their spatial distribution in the Desert and Mesopotamia terrains was demonstrated together with statistical treatment of the analytical data. These are P_2O_5, K_2O, Al_2O_3, Fe_2O_3 and TiO_2. The affinity of the analysed trace elements to these minor geogenic elements was also studied to illustrate the role of parent rocks on trace elements concentration and distribution in the studied terrains. Sulfate (SO_3) was analysed in the Mesopotamia samples to show the influence of soil salinization on the concentration and background values of the trace elements analysed. It was also analysed in selected parts of the Desert terrain for comparison.

Moreover, natural geochemical background range and mean values for the trace elements: Cu, Pb, Zn, Cr, Ni, V and U are presented for two major provinces in Iraq with negligible anthropogenic activity. The results are compared to soil analysis in other localities in Iraq. Significant differences occurred, which emphasize the role of source rocks, climatic conditions and soil – forming processes on the natural geogenic concentration of these elements and their spatial distribution.

▪ **Minor Components (P_2O_5, K_2O, Al_2O_3, Fe_2O_3, TiO_2, SO_3)**

─ **P_2O_5:** Exhibits a narrow range where more than 99% of the samples in the Desert contain less than 2% P_2O_5 with negligible outliers approaching 14% P_2O_5. Mean and median values are close enough to consider normal distribution. The Mesopotamia samples show clear normal distribution and lower background values than the desert reflecting parent rock influence. Removing anomalous concentration yielded background range of (0.01 – 0.74) % P_2O_5 (median 0.2 %) for the Desert samples and (0.02 – 0.33) % P_2O_5 (median 0.16%) for the Mesopotamia samples.

Spatial distribution of P_2O_5 in the Desert terrain clearly demonstrates its geogenic relation to parent rocks where higher values coincide with phosphorite-shale domains (Akashat and Nukhaib). Strong positive correlation with uranium exists, which demonstrates the radioactivity of the marine phosphorites, and the geochemical affinity of U towards phosphate minerals. This is also demonstrated in the factor analysis (Factor 2, Desert samples). In the Mesopotamia, the spatial distribution of P_2O_5 shows higher values associated with the Tigris and Euphrates river basins which might indicate anthropogenic influence of using phosphate fertilizers in agriculture.

─ **K_2O:** Exhibits a narrow range in the Desert samples where more than 97.5% of samples contain less than 2.4% K_2O with a few anomalous samples approaching 14% K_2O. Mean and median values are close enough to consider normal distribution. Removing anomalous values, the range is (0.005 – 2.38) % K_2O (median 1.4%). Normal distribution is also shown in the Mesopotamia samples with insignificant outliers above 2% K_2O. Range (0.04 – 2.87) % K_2O (median 0.99% K_2O). Removing anomalous values resulted in insignificant change of these parameters.

Spatial distribution of potassium show elevated values in the middle part of the Desert; higher values were encountered in soil overlying carbonates and also in soils from the Habbariya sediments. On the otherhand, higher values of potassium were found along the gypsum – halite continental salt deposits associated with Hit – Abu Jir Fault System, where potassium salts may be expected in these deposits in minor concentrations.

– **Al_2O_3:** Alumina is usually a residual component in soil and closely connected with parent rocks composition. It shows normal distribution in the Desert and Mesopotamia samples, where median values are 7% Al_2O_5 (range 0.11 – 10.9%) and 6.0% (range 0.12 – 10.8%) respectively. Higher median values are noticed in soils overlying laterites domain (median 8.0% Al_2O_3) and phosphate – shale domain (median 7.45% Al_2O_3), which demonstrates the geogenic influence on Al content in the soil samples. Alumina is positively correlated, in the desert samples, with Fe and K indicating their common presence in the alumino – silicates (clay minerals) components of soil. In the Mesopotamia samples, alumina is positively correlated with Fe and Ti. The clay mineralogy is somewhat different in the two terrains; smectite and palygorskite are dominant in the Desert, whereas chlorite and illite are dominant in the Mesopotamia which may explain such variation. Factor no. 3 controls the distribution of Al, K and Fe in the desert samples and Factor no. 1 in the Mesopotamia controlling Al and Fe, which may be related to the abundance of the fine (clay) fraction in the samples.

– **TiO_2:** Titanium minerals are of the most resistant during weathering and Ti is the least mobile element. Hence it is a typical geogenic component in soil. It exhibits a normal distribution in both terrains with a median value of 0.58% TiO_2, (range 0.01 – 5.6% TiO_2) in the Desert samples and 0.46% TiO_2 (range 0.01 – 1.98 TiO_2) in the Mesopotamia samples. Median values were the same after removing anomalous values, and are within world average range for soil (Aubert and Pinta, 1977).

Spatial distribution of TiO_2 in the Desert terrain shows high values in the laterrite – dominated region, emphasizing the residual nature of the element. However, the higher values in the north and south of Mesopotamia may be related to the abundance of the clay – rich fine fraction in sediments especially in the south. Titanium shows normal distribution patterns in the Desert and Mesopotamia samples. It is controlled by Factor no. 4, together with Pb, Cr and Ni which may indicate heavy minerals fraction of the soil. In the Mesopotamia it is controlled by Factor no. 3 together with Cr and V and by Factor no. 2 with potassium suggesting more than one host for Ti. Titanium has no significant correlation with any of the analysed elements in the Desert samples, whereas, in the Mesopotamia samples, it is positively correlated with a number of elements including Al, Fe and K which may suggest common presence in clay minerals.

– **SO_3:** The sulfate in the studied soil is not related to parent rocks; it is enriched in the soil due to authigenic salinization by poor drainage, hot and arid climate, where evaporation rate is 200 – 300 times the rainfall rate in these terrains. It shows a log – normal distribution in both terrains. In the desert areas covered by sampling, the upper range value approaches typical gypsum composition, and is associated with saline soils west of Tharthar and Razzazah lakes, as well as with the soil overlying the Dibdibba terrain in the south, where inland sabkhas are common. The same pattern of distribution may be noticed in the Mesopotamia, where sabkhas of the Razzazah lake show the highest values. Removing anomalous values gave a range of (0.02 – 23) % SO_3 (median 0.77% SO_3) for the Desert (partly covered terrain) and (0.01 – 32.6) % SO_3 (median 4.0% SO_3) for the Mesopotamia samples. It is negatively correlated with all elements demonstrating its authigenic replacement of the original soil components.

▪ **Trace Elements (Cu, Pb, Zn, Cr, Ni, V and U)**

Soils are considered as sinks for trace elements; therefore, they play an important role in the environmental cycling of these elements (Kapata – Pendias and Pendias, 2001). The factors controlling trace elements concentration in soil are mainly influenced by: parent rocks, pH – Eh, drainage, climate, time, clay fraction content and organic matter content, among other factors. Hence, soil mineralogy and chemistry are dynamic and evolving with time.

― **Cu:** General world soil content of Cu ranges from traces to 250 ppm with an average range of (15 – 40) ppm (Aubert and Pinta, 1977) and 13 – 24 ppm (Kapata – Pendias and Pendias, 2001). It is highly depended on parent rocks and generally high in soils of arid regions.

Copper shows generally a log – normal distribution in the soils of both terrains. Higher upper range and median values were encountered in the Desert samples compared with these from Mesopotamia. Copper in the former ranges (1 – 200) ppm (median 25) ppm and in the latter the Cu range is (1 – 85) ppm (median 16 ppm). Removing anomalous concentrations (above the threshold) brought the background range to (1 – 45) ppm (median 24 ppm) in the Desert samples and (1 – 40) ppm (median 15 ppm) in the Mesopotamia samples. Spatial distribution shows relatively higher values of Cu in soils overlying phosphate – shale, Habbariya and laterites domains in the Desert terrain, but no definite trend was noticed in the Mesopotamia samples.

The role of parent rocks, vegetation and climate, are demonstrated when these values are compared with soil of the folded and mineralized soils of the imbricate terrains (East Erbil, Serguza and Berzanik). In East Erbil, Cu ranges from (4 – 100) ppm (median 31 ppm), in Serquza the range is (3 – 300) ppm (median 49 ppm) and in Berzanik the range is (4 – 154) ppm (median 31 ppm). In the Desert samples and Mesopotamia samples, copper is positively correlated with Al and Fe suggesting clay minerals as host. It is controlled by Factor no. 1 in both populations, together with Ni and V in the Desert samples and with Fe, Al and Ni in the Mesopotamia samples. The variation in the type of clay minerals in the soil of these two terrains may be the cause or such variation.

― **Pb:** Lead concentration in soil of the world is highly variable. In subdesert and saline soil a background range was reported as (20 – 45) ppm (Aubert and Pinta, 1977). A grand average value for world soil was reported as (10) ppm (Hawkes and Webb, 1962).

During weathering, lead (as Pb^{2+}) forms carbonates, incorporated in clay minerals, in Fe – Mn oxides and in organic matter. Its concentration in soil is highly dependent on parent rocks (Kapata – Pendias and Pendias, 2001).

Lead in the Desert and Mesopotamia samples show a log – normal distribution. The range is (1 – 60) ppm (median 8 ppm) in the former and (1 – 46) ppm (median 5 ppm) in the latter. Removing anomalous concentrations (higher than threshold value) brought the background range to (1 – 19) ppm (median 7 ppm) in the Desert samples and (1 – 17) ppm (median 5 ppm) in the Mesopotamia samples. Spatial coverage in the Desert terrain, however, is limited to the western part. In the Mesopotamia higher values of Pb are noticed in the saline soils of mid Euphrates basin (Najaf – Nasiriyah) and further south in the marshland.

Lead is positively correlated with P, Cr, Zn and Ni in the Desert, probably suggesting some association with the phosphorites, but the limited spatial coverage of Pb in this terrain make such suggestion only a speculation. In Factor analysis of the Desert data, it is grouped together with Cr, Ni and Ti under Factor no. 4, which might suggest heavy minerals multiple hosts for lead.

In the Mesopotamia samples, Pb is positively correlated with Fe, P, Ni, Al, Cr, V and K suggesting multiple hosts; among which are clay and heavy minerals. In the factor analysis of the Mesopotamia data, Pb is grouped under Factor no. 4 together with P and V which might add organic matter as another possible host of Pb in this terrain.

The role of climate, soil development, vegetation and parent rocks is demonstrated when the background of Pb in the Desert and Mesopotamia soils is compared with those of East Erbil area (range 2 – 210 ppm and median 16 ppm). The influence of parent rocks is well shown in the Pb concentration of the soils of Serguza and Berzanik, where the weathering of Pb – Zn – pyrite mineral showings in both areas have contributed to the soils geogenic enrichment by Pb and other base metals. The background of Pb in Serguza soil is (2 – 210) ppm (median 38 ppm) and in Berzanik soil is (2 – 1600) ppm (median 87 ppm).

─ **Zn:** The grand range of Zn in world soil is reported as (trace – 900 ppm) and is believed to be dependent on parent rocks more than pedogenic processes (Aubert and Pinta, 1977). It is high in the soils of arid regions and saline alkaline soils. An average value of Zn in world soil was reported as 50 ppm (Hawkes and Webb, 1962). Zinc substitutes for Mg^{2+} in silicate minerals and is mobile in acid oxidizing environment. Kapata – Pendias and Pendias (2001) reported world soil background range of (17 – 125) ppm.

In the Desert soil, Zn concentration range is (2 – 253) ppm (median 67 ppm), and in the Mesopotamia soil, the range is (20 – 117) ppm (median 56 ppm). The distribution is log – normal in both terrains. Removing anomalous concentrations (higher than threshold) yielded a background range (2 – 111) ppm (median 66 ppm) in the Desert soils and (20 – 87) ppm (median 55 ppm) for the Mesopotamia soils, which are both, within world range for Zn in soil.

Spatial distribution of Zn show lower concentrations (median 39 ppm) in soils overlying fluvial sandstones (Dibdibba Formation) and higher values in soils overlying phosphorite – shale and Hab'bariyah Gravel – Sand domains (median values 73 ppm and 81 ppm Zn, respectively).

Zinc is positively correlated with Al, Fe and P in Desert samples demonstrating its association with clay minerals as one host and with phosphate minerals (substituting for Ca^{2+} in francolite) as another host. It is controlled by two factors (2 and 3), both are parent rocks factors; Factor no. 2 is related to phosphorite and Factor no. 3 is related to clay minerals. In the Mesopotamia samples, Zn main correlation is with potassium, which is also demonstrated in the factor analysis (Factor no. 2), suggesting mica and illite as the main host of Zn in these sediments.

─ **Cr:** Chromium was reported to be rich and very rich in the soils of arid and semi arid regions; up to 2400 ppm Cr was reported in soils of such regions (Aubert and Pinta, 1977). A grand average for world soil was reported as 200 ppm (Hawkes and Webb, 1962) and a world background range was reported as (7 – 221) ppm by Kapata – Pendias and Pendias (2001).

Chromium is present as Cr^{3+} in most soils, usually hosted within mineral structures or with Fe^{3+} oxyhydroxides. It is slightly mobile (only in very acid media), and usually its compounds are very stable in soil. Parent rocks are the main factor controlling its concentration in soil and sediments.

Chromium distribution in the studied soil samples is log – normal; well – emphasized in the Mesopotamia sediments. The concentration range in the Desert samples is (0.6 – 900) ppm (median 105 ppm) and in the Mesopotamia samples the range is (4 – 2000) ppm (median 190 ppm). Removing anomalous concentrations, the background range is (0.6 – 204) ppm (median 105 ppm) for the former and (4 – 810) ppm (median 180 ppm) for the latter. The Desert soil background is within world range values, but the Mesopotamia samples exhibit a higher upper background range.

The higher background range in the Mesopotamia sediments is mainly due to source rocks composition in the NE of Iraq, where basic and ultrabasic, chromite bearing igneous complexes are common. Chromite was identified in the Mesopotamia sediments within the heavy minerals fraction (identified by X – ray diffraction) (Hana and Al-Hilali, 1986). Based on a reconnaissance survey, Zainal (1978) found elevated Cr and Ni concentrations in the sediments of North and NE parts of the Mesopotamia and attributed this to the sediments transported from the Zagros igneous complexes by tributaries of the Tigris River (especially the Adhaim River).

Within the Desert terrain, relatively higher concentrations were noticed in soils overlying fluvial sand deposits (Dibdibba Formation) and also in the Habbariya Sand – Gravel domain. In the Mesopotamia terrain, Cr spatial distribution show higher values in the northern parts which may demonstrate the proximity to the source area in the Zagros Mountains.

Chromium main correlation is with Fe, Ni and Al in the Desert samples and with Ti and Ni in the Mesopotamia samples. In factor analysis, it is grouped under Factor no. 4 in the Desert sample, together with Pb, Ni and Ti, whereas in the Mesopotamia samples, it is grouped under Factor no. 3, as the major variable, together with Ti and V.

─ Ni: Nickel is easily mobilized during weathering and co-precipitated with Fe – Mn oxides or organically bound in soil (Kapata – Pendias and Pendias, 2001).

Nickel content in soil is highly dependent on climate and parent rock composition. It is higher in soil of arid regions than temperate and boreal regions. World range for soil is (tr. – 5000) ppm, reported range for Ni in soil of arid regions is (50 – 300) ppm and in saline alkaline soils (40 – 100) ppm (Aubert and Pinta, 1977). In recent literature, Kapata – Pendias and Pendias (2001), reported world range for Ni in soil as (0.2 – 450) ppm.

Nickel in the soil samples of the Desert terrain show a weak trend of log – normal distribution with a range of (1 – 360) ppm (median 70 ppm). In the Mesopotamia, it is clearly of log – normal distribution, with a range (1 – 870) ppm (median 85 ppm). Removing values above threshold resulted in a background range of (1 – 117) ppm (median 69 ppm) for the Desert samples and (1 – 229) ppm (median 83 ppm) for the Mesopotamia samples.

Spatial distribution of Ni show elevated values in the southern part of the Desert terrain as well as the extreme western part of the Desert. The former may be linked to the Euphrates – Hit – Abu Jir Fault System and associated salinas. The range of Ni in the Desert soils is generally within world range whereas the range in the Mesopotamia sediments is higher. The significant elevated background values in the Mesopotamia samples demonstrate the influence of source rocks composition of the Zagros igneous complexes as a major factor.

In East Erbil soil samples, Ni content is higher. The range is (10 – 1200) ppm (median 100 ppm). In Serguza and Berzanik soils, Ni range is (17 – 1200) ppm (median 240 ppm) and (10 – 893) ppm (median 89 ppm) respectively. Type and origin of soil in East Erbil, together with the proximately of weathered mineralization in Serguza and Berzanik areas are controlling factors of such Ni enrichment in these areas relative to the Desert and Mesopotamia samples.

Nickel correlates positively with Al and Fe in the Desert and Mesopotamia samples, suggesting its presence in clay minerals as well as with Fe – oxides which demonstrates Ni typical geochemical affinity. However, in factor analysis, Ni is grouped together with Ti and Pb under Factor no. 4, and with Cu and V under Factor no. 1, together with Al, Fe and Cu, and to a lesser extent under Factor no. 3 with Cr, Ti and V.

— V: Vanadium content in soil is believed to be close to parent rocks. A grand world range was reported as (tr. – 400) ppm. In arid regions the range is (tr. – 300) ppm in alkaline saline soil it is (55 – 130) ppm and the Mediterranean soils it is (70 – 180) ppm (Aubert and Pinta, 1977). In recent literature, the range was quoted as (18 – 115) ppm (Kabata – Pendias and pendias, 2001).

During weathering, the mobility of V is dependent on the host minerals, but finally it remains in oxides. Variation of V content in soil is believed to be inherited from parent rocks (Kabata - Pendias and pendias, 2001).

Vanadium shows log – normal distribution in the Desert and Mesopotamia samples. The range of V in the soil samples of the Desert terrain is (3 – 420) ppm (median 90 ppm) and in the Mesopotamia samples it is (4 – 380) ppm (median 70 ppm). Removing anomalous values the background range is (3 – 175) ppm (median 90 ppm) in the Desert and (4 – 164) ppm (median 66 ppm). These values are comparable to world range values.

In East Erbil the upper range for V is higher (15 – 1525) ppm (median 105), in Serguza it is (10 – 1000) ppm (median 190 ppm) and in Berzanik it is (3 – 520) ppm (median 83 ppm). The high upper range values in these areas may be related to mineralized soil samples in Serguza and Berzanik and may be attributed to the organic – rich soil of East Erbil.

Vanadium is positively correlated with Al, Fe, Cu, Ni, Cr and Zn in the Desert samples suggesting strong association with clay minerals. In factor analysis, it is grouped under Factor no. 1, together with Cu, Ni and some extent Al, which emphasizes the same association. In the Mesopotamia samples, V is positively correlated with Fe, Ni, Pb, Ti, Cu, Al and Cr suggesting association with Fe – oxides and heavy minerals. In factor analysis, vanadium is controlled by Factor no. 3 with Cr and by Factor no. 4 with P and Pb. The former may suggest presence in the heavy mineral fraction and the latter suggest a possible relation to organic matter.

Vanadium is analysed in selected areas of the desert terrain, which show higher values in the western part in association with the phosphorite – shale rock assemblages as well as some high values in Habbariya gravel – sand domain. The spatial distribution of V in the Mesopotamia sediments show higher values in mid-Euphrates region in association with saline sediments within the domain of the Euphrates – Hit – Abu Jir Fault system and salt water springs.

─ **U:** Uranium, if not introduced to the soil environment by anthropogenic activities, is strongly related to parent rocks, and its concentration in soil shows a wide range. A world average of U in soil was reported as (1) ppm (Hawkes and Webb, 1962). In more recent literature a background range was reported as (0.3 – 11.7) ppm (UNSCEAR, 1993). Uranium is found in various concentrations in all rock types; among which are marine phosphorites, sandstones and black shale. Uranium may be introduced geogenically to soil by the weathering of and mobilization from uraniferrous parent rocks or by uranium – bearing groundwater. Uranium is present in two valencies, U^{4+}, which is less mobile, and U^{6+} which is very mobile in the secondary environment, and may be found in secondary uranium minerals in soil or in association with Fe – Mn oxides, or with organic matter.

The Desert samples show U range of (0.01 – 19) ppm (median 0.1 ppm) and the limited number of samples in the Mesopotamia show a range of (0.1 – 11) ppm (median 0.1 ppm) both are within world average values, but the Desert samples exhibit a higher upper range.

Removing anomalous values (above threshold) a background range of (0.01 – 1.3) ppm (median 0.1 ppm) was obtained for the Desert soil and (0.1 – 1.2) ppm (median 0.1 ppm) was obtained for the Mesopotamia sediments. These background ranges are well within world range values.

Uranium shows a poorly expressed log – normal distribution in the Desert samples; about 99% of the values are less than 2 ppm, and only 1% of the population exhibit higher values. In the Mesopotamia samples U shows a log – normal distribution where more than 97% of the population contains less than 1 ppm U.

Significant variation of U range and median values exists in soil overlying different lithologies in the Desert terrain demonstrating parent rock influence. Soils overlying laterites, phosphorites and sandstones (Dibdibba Formation) exhibit higher median values than those overlying carbonates and Habbariya gravel – sand deposits. This is shown in the spatial distribution map of uranium in the desert terrain. Uranium only positive correlation is with P_2O_5 in the Desert samples, which is well demonstrated in Factor no. 2.

CONCLUSIONS

- The trace elements analysed in the soils of Iraq show significant variations in their background range and median values controlled by parent or source rocks, climatic conditions pedogenic processes and drainage.
- The soils and surface sediments of the Desert and Mesopotamia terrains are immature with little modifications or alterations by pedogenesis and have undergone size degradation and sorting by fluvial processes. Salinization of the upper part of the Mesopotamia sediments is induced by poor drainage, little rainfall and very high evaporation rates.
- The achieved background and median values of the elements analysed in the soil and sediments of the Desert and Mesopotamia terrains fall within the values reported for uncontaminated soil of the world.
- The distribution and concentration of minor elements (Ti, Al, Fe, K and P) in the samples analysed from the Desert are largely controlled by the underlying lithology, whereas in the Mesopotamia samples, their concentration in the sediments appears to have been mainly influenced by the type of source rocks of the rivers Euphrates, Tigris and tributaries. The Zagros suture rock complexes have had the major role.
- The background range values obtained in this study provide useful, important and reliable reference information for environmental and geochemical exploration surveys.

- There are no unified background norms that can represent all Iraqi soils due to the significant geogenic variations shown in this work and the wide background range values. Each area should be taken on its own merits.
- The results of this work show that there are no scientific justification to use single figure average or mean values for the background and using values such as "world average soil" or "average shale" or "Earth crust" in calculating environmental parameters and estimating pollution degree, may result in serious misleading conclusions.

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