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Distribution and Enrichments of Abundant and Trace Elements in Al-Khassa Sub Basin Soil, Kirkuk, Northeastern of Iraq

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Abstract

This study focused on the soil of the Al-Khassa Sub Basin, thirty-four soil samples were collected from different areas of land use and differences in human activity.

Physicochemical properties of the soil were examined Hydrogen Potential (pH), Organic Matter (O.M), Loss Of Ignition (L.O.I), Total Organic Carbon (TOC), Cation Exchange Capacity (CEC) and Total Hydrocarbon (THC).

Hydrogen Potential (pH) showed that the soil is alkaline above seven with a mean 7.98.

Organic Matter (O.M) of the study area with a mean 1.28 % and high value found in Agricultural areas.Cation Exchange Capacity (CEC) with a mean 42.64 (cmol/kg) that is proportional to the granular size of the soil that silty clay. Both Total Organic Carbon (TOC) and Total Hydrocarbon (THC) acceptable concentration values compared to the soils of the arid region.

In the present study abundant elements (Calcium (Ca), Silicon (Si), Aluminum (Al), Magnesium (Mg), Sulfur (S), Potassium (K), Chloride (Cl), Titanium (Ti) and Phosphorous (P)) and Trace element(Chromium (Cr), Manganese (Mn), Nickel (Ni), Zinc (Zn), Vanadium(V), Copper(Cu), Lead(Pb), Arsenic (As), Cobalt (Co), Mercury (Hg) and Molybdenum (Mo)) that have been analyzed in this study and compared with the limits to elements distribution in world soil and local study of Lesser Zab.

Elements that are higher than standard Ca, Cl, Cu, As,Hg, Mo, Zn because of excessive use of fertilizers and pesticides and poor irrigation practice and other anthropogenic sources. High concentration elements (Ni, Ca, Co) as a result of the weathering of the parent rocks, it occurs naturally in soils. Other elements that were partially higher than the standard is (K, Cr, P, S, Mg) only in dense agricultural areas.

Elements that were lower than Standard (Ti, Al, Si, Mn, V, Pb) represent the unpolluted elements at some locations the sub-basin because they are elements that increase in urban and industrial areas that are not available in the Al-Khassa Sub Basin, main activity and land use of sub basin were rural area and cultivated land.

The results of the enrichment factor (EF) and the contamination factor (CF) are calculated for contamination assessment. The Enrichment factor (EF) of the sub-basin is EF 2 depletion to minimal enrichment, indicating no or minimal pollution, but there is a real beginning of contamination of the magnesium element EF 2-5 moderate enrichment, indicating a real beginning of contamination of the magnesium element. indicating of moderate pollution due to the presence of farms that were use of magnesium sulfate fertilizers by villagers at sedan.

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The results of the Contamination Factor (CF) showed that the region is low to moderate contamination
Except for the contamination factor of magnesium in Mam Rash (S22), Belgrad (S10) was very high degree of contamination of Cf > 6, and in Sedan (S25), Gurgay Shammar (S11), and Obarick (S32) was considerable degree of contamination of magnesium 3 < Cf < 6 because of the three villages was agricultural area that use of magnesium fertilizer.
Phosphor (P) contamination factor is moderate in Heon (S7), Ali Makaeel (S20) because they are villages that use phosphate fertilizers beside occurrence of poultry farms.

Keywords: Contamination factor (Cf) ,Enrichment factor (Ef), Soil Contamination, Local Geochemical Factor .

توزيع وإغناء العناصر الوفيره و النزرة في تربة حوض الخاصه الثانوي، كركوك، شمال شرق العراق

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الخلاصه

ركزت هذة الدراسة على حوض الخاصة الثانوي, حيث تم جمع 34 عينة تربة في مناطق مختلفة الاستخدام الارضي والنشاط البشري .

تم فحص الخواص الفيزيائية والكيمائية للتربة تتمثل بالرقم الهيدروجيني والماده العضوية ومفقودات الاشتعال واجمالي الكربون العضوي وسعة التبادل الكاتيون واجمالي الهيدروكاربون .

حيث اظهرت النتائج من الرقم الهيدروجيني ان التربة قلوية فوق السبعه بمتوسط 7.98. والمادة العضوية لمنطقة الدراسة بمتوسط 1.28% حيث ان قيمتها عالية في المناطق الزراعية وان السعة تبادل الكاتيون بمعدل 42.64 مول /كغم يتناسب مع الحجم الحبيبي للتربة المتراوحة مابين الرمل الناعم والغرين والطين. وان قيم الكاربون العضوي الكلي واجمالي الهيدروكاربون هي مقبولة بالنسبة لترب المناطق الجافة وشبة الجافة.

في هذة الدراسة العناصر الوفيرة المقاسة هي الكاليسيوم والسيليكون والالمنيوم والمغنيسيوم و والكبريت والبوتاسيوم والكلوريد والتيتانيوم والفسفور , والعناصر النزرة متمثلة بالكروم , المنغنيز ,النيكل,الزنك, الفناديوم, النحاس , الرصاص , الزرنيخ , الرصاص , الزرنيخ, الكوبلت , الزئبق , المولبيوديوم ثم تمت مقارنتها مع التواجد الطبيعي للعناصر في ترب العالم والدراسة المحلية للزاب الصغير.

تراكيز العناصر التي كانت اعلى من المعدلات الطبيعية كانت الكاليسيوم , الكلوريد , النحاس , الزئبق , المولبيديوم , الزنك بسبب الاستخدام المفرط للاسمدة والمبيدات الحشرية وسوء ممارسات الري وغيرها من المصادر البشرية .

تراكيز العناصر التي كانت اعلى بشكل جزئي محصورة فقط على المناطق الزراعية الكثيفة لعناصر الفسفور , الكروم, البوتاسيوم, المغنيسيوم, الكبريت,

انا الاعناصر التي تتواجد بتراكيز اقل من المعايير العالمية والمحلية للتربه هي الرصاص , الفيناديوم , المنغنيز, السليكون, المنيوم, تيتانيوم لان النشاط الغالب في الحوض هي المناطق الريفية

لتقييم التلوث تم حساب معامل الاغناء ومعامل التلوث, حيث وجد بان عامل الاغناء هو اقل من 2 يشير الى ان عدم وجود تلوث عدا بداية حقيقية لتلوث المغيسيوم عامل الاغناء تراوحت مابين 2 الى 8 يشير الى اغناء متوسط بسبب استخدام سماد كبريتات المغنيوسوم .

اما معامل التلوث اظهر ان تلوث المغنيسيوم كان في مام راش وبلغراد حيث كانت القيم اقل من 6 وفي كوركي شمار وسيدات واوباريك بدرجه تلوث اقل من 3 بسبب ان القرى تستخدم سماد المغنسيوم .

معامل التلوث للفسفور عالي في هيون وعلي ميكائيل لانها قرى تستخدم الاسمدة الفوسفاتية وحاوية على حقول دواجن .

1.Introduction:

Soil is an important compartment receiving a significant amount of pollutants from different sources every year. Generally, soil not only serves as sink for the chemical pollutants but also acts as a natural buffer by controlling the transport of chemical elements and substances to the environment [1]. Abundance and trace elements are found ubiquitously in both polluted and unpolluted soil layers of many ecological systems. These toxic elements cannot be degraded or destroyed but only are accumulated in soil, water, and sediments. Heavy metals in soils may either be found naturally or generated from anthropogenic activities. However, anthropogenically origin sources related to the metal-enriched sewage sludge in agriculture, fertilizer, livestock manures, application of metal-based pesticides, municipal wastes, and agricultural activities [2].

The contamination of agricultural soil by toxic elements such as heavy metals attracts the interest of people not only because metals can build up in the soil but also because metals can be accumulated in crops, where they cause a significant potential risk to human health[3].Soils contaminated by toxic elements from agricultural activities have raised serious concern in recent decades regarding potential risk to human health through the direct intake, bio accumulation through food chain, and their impacts on ecological system [4].

So far, there is no environmental study that tracks and indicates the pollution that occurs to the soil of the Al-Khassa Sub Basin . after constructing of Al-Khassa dam in 2010, that lead ti increase the villigesm residents with agricultural activity throughout the basin.

Agriculture is the dominant land-use and large amounts of agrochemical have been applied to the farming areas of this region. Metals and pesticides in soils can reach the aquatic ecosystems by leaching, soil erosion, and surface runoff. Protection of the soil quality of Al-Khassa Sub Basin is of great importance for conserving the Soil and water quality in Sub-Basin.

Al-Khassa Sub Basin is a part of the Al-Adhaim River Basin (Al-Khassa stream is one of the three main tributaries of Al-Adhaim River), that's suffering from many environmental pollution problems due to anthropological activity impact on soil quality.

Agriculture is the most common land use, and the farming regions of the study site have been heavily sprayed with agrochemicals. Leaching, soil erosion, and surface runoff can transport metals and pesticides from soils to aquatic habitats. The Al-Khassa Sub Basin soil quality must be protected in order to preserve the soil and water quality.The main objectives of the study were to observe any possible contamination by toxic elements in soils in Al-Khassa Sub Basin and then to identify their natural and anthropogenic sources by using contamination assessment factor which may be used as a diagnostic tool for determining the degree of pollution in the soil assessment, beside, using the geochemical index.

2.Study site :

Al-Khassa Sub-Basin is located in the northeastern part of Kirkuk Province/ Iraq, about 21 km from the Centre of Kirkuk City. The area is located between longitudes (44° 28' 00" E - 44° 49' 00"E), and the latitudes (35° 30' 00" N - 35° 43' 00" N). It covers a total area of 468 km2. that includes about (32) villages (Figure 1). Al-Khassa Sub-Basin is characterized by a series of long, sinuous fold mountains trending northeast separated by valleys in the middle and eastern parts, whereas it is undulating in the west, near the site of the dam and the surrounding areas of the reservoir (the area is hilly terrain and sloping toward southwest). The study area is bounded by North Chamchmal Anticline in the northeastern, Shwan Sub-Basin in northwestern and Qara Hanger Sub- Basin in the south of the study area. Generally, the elevations of ground surface are ranged from 440 a.s.l in the west near the Al-Khassa reservoir, to 910 m a.s.l. towards northeast near Chamchamal Anticline.Three Formations were exposed in the area from the oldest (Injana, Mukdadiya, Bai-Hassan Formations and Quaternary deposits).

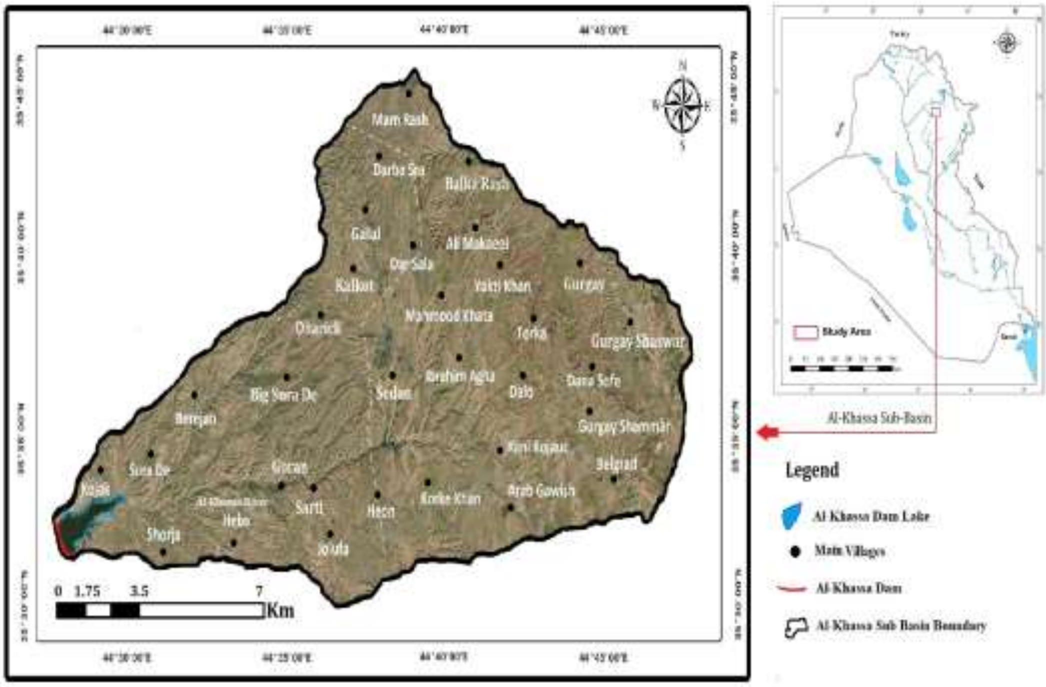

Figure 1: Location Map Al-Khassa Sub Basin.

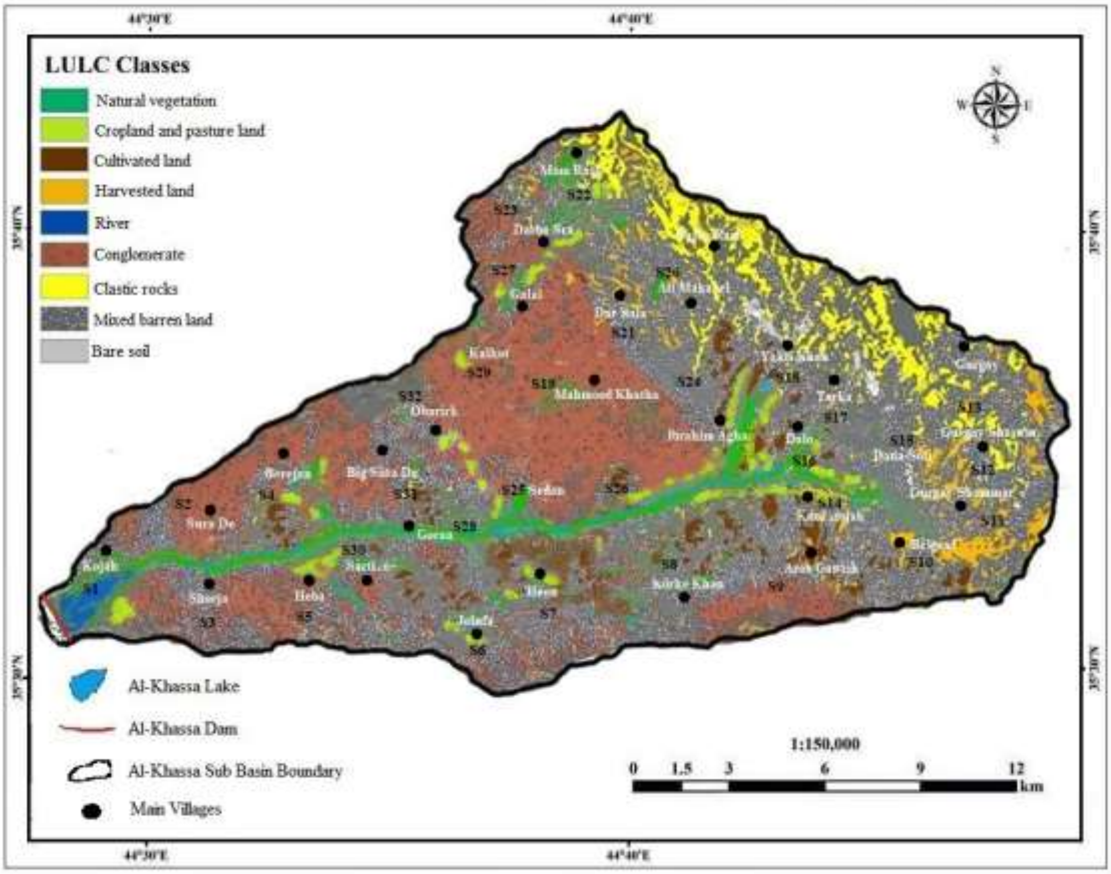

Figure 2: Soil Sample of Al-Khassa Sub Basin.

3.Material and method :

Soil samples were taken systematically with a density of one sample per 4 square kilometers to get a uniform coverage of the study area[5]. The samples were adopted depending on the change and impact of land use, most of which were inhabited villages, agricultural areas and animal pastures.

The location of sampling sites was geo-referenced by using a Geographical Positioning System (GPS) instrument (GPS etrex vista). Soil samples were collected during the field work Approximately 2-3 kg of sampling material for each sampling site was collected in polyethylene bags and labeled, soil sample was taken from 35-45 cm depth. In addition to field description and photo documentation of sampling sites. All samples were air-dried and sieved to collect sample fractions of less than 2 mm for chemical analysis [6].

Chemical and physical properties were performed in ALS Environmental Lab.Mississauga,Canada, and soil samples were analyzed for major oxides and heavy metals contents by digested solutions are determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), in accordance with the procedures approved by the analytical laboratory of ALS Environmental Lab in January 2021.

4.Physico-chemical parameters of soil :

Both chemical and physical properties were performed in ALS Environmental lab .Mississauga, Canada .Each soil sample is analyzed for (pH), Organic Mater (O.M), Loss of Ignation(L.O.I), Total Organic Carbon (TOC), Cation Exchange Capacity (CEC) and Total Hydrocarbon (THC) in accordance with the procedures approved by the analytical laboratory of ALS Environmental Lab .

Table 1: Shows the measured chemical parameters of the soil samples

Chemical Parameter	Minimum	Maximum	Mean	Standard
pH	7.1	9.9	7.98	More than 7 [6]
O.M%	0.55	2.1	1.28	1-2 in arid to semi arid [8]
L.O.I %	8.6	30	19.10	-------
TOC%	0.9	4.1	2.65	more than five [8]
CEC(cmol/kg)	31	65	42.64	-------
THC(mg/kg)	16	76	40.29	less than 100 [13]

Hydrogen potential (pH) of soil ranges from 7 to 9.9 with a mean of 7.98 (Table 1), all soil samples which considered as slightly alkaline except (S2, S7, S8, S9, S12, S21) considered moderately alkaline and (S25, S22) were strongly alkaline with value more than 9 [7].

Solid-phase carbonate is found in alkaline soils (pH > 7) and bicarbonate was the major anion in the solution. Calcium and magnesium carbonates create a pH range of 7 to 8.5, depending on CO2 and Ca^{+2} or Mg^{+2} ion concentrations.[7].

The organic matter content of the soil sample ranges from 0.55% to 2.1% with a mean of 1.28% (Table 1). The maximum value was measured in sample S23 from the agriculture area of Darba Sra in the north part of the Al-Khassa Sub Basin, while the minimum value in virgin land sample S34 from the west part of Al-Khassa Sub Basin. All soil samples are accepted according to global standard of organic matter[8] of agricultural area soil (1-2)% in arid to semi-arid regions.

Cation Exchange Capacity (CEC) values in soil samples range from 31 to 65 cmol/kg with a mean value of 42.64 cmol/kg (Table 1).CEC increases when grain sizes decrease, so CEC is considered high in all soil samples. This is due to the influence of soil grain sizes (silt and clay are dominant size).

Loss of Ignition (L. O. I.) gives a reasonable approximation of the soil's organic composition; the percentage of dry weight lost during ignition may subsequently be determined. In the current study's ignition range (8.6 - 30) % with a mean 19.10 %, the residual ash sample can be utilized for carbonate analysis[7].

Total Organic Carbon (TOC) in soils is widely distributed over the earth's surface occurring in almost all terrestrial and aquatic environments [9].In the current study TOC range from 0.9% to 4.1%with a mean value of 2.65% (Table 1). TOC results in the current study are considered acceptable for the arid region [10].

Total Hydrocarbon (THC) there are a variety of interactions that may occur between inorganic and organic soil components, as well as organic contaminants, soil organic matter, and clays, all of which can have a substantial influence on solid-liquid extraction. Furthermore, the moisture content of the soil influences the solvent extraction of chemicals from soil or sludge samples[11]. Thermal measurements of the extracted solvent have several inherent issues; not all petroleum hydrocarbons respond uniformly to infrared measurement, and comparing the unknown to a reference combination can result in substantial systematic errors[12, 13]. The following guiding values for total oil hydrocarbons content in soil are provided by the regulation on the assessment of environmental pollution:

Normal soil: Less than 100 (mg/kg)

Alert values for sensitive soils: 200 mg/kg;

Alert values for less sensitive soils: 1000 (mg/kg)

For current study the value of THC were ranged (16mg/kg-76mg/kg) with the mean 40.29mg/kg which considered a normal soil.

5Abundant and Trace element of soil:

Soil sample were analyzed for abundant and trace element contents by digested solutions were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) performed in ALS Environmental Lab. Mississauga, Canada.

The element concentrations were determined using 5.0 g of each sample, which was sieved in a 2 mm sieve and powdered to 0.063m. Heavy metals are abundant in soil, and their impact on the ecosystem is well documented [8]. As a result, the soil may be a source of heavy metals that are discharged into the overlying water through natural and human processes [9]. In the present study abundant elements (Calcium (Ca), Silicon (Si), Aluminum (Al), Magnesium (Mg), Sulfur (S), Potassium (K), Chloride (Cl), Titanium (Ti), Phosphorous (P)) and Trace element (Chromium (Cr), Manganese (Mn),Nickel (Ni), Zinc (Zn), Vanadium (V), Copper(Cu), Lead(Pb), Arsenic (As), Cobalt (Co), Mercury (Hg) , and Molybdenum (Mo)) that have been analyzed, the a mean concentration values of elements in the soil of Al-Khassa Sub Basin have been compared with natural occurrences of trace elements in soil across the world [14] and local study of Lesser Zab[15].

Table 2: Abundant and trace elements analysis results of soil samples

Soil sample no.	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V
S1	6487	44453	24395	305	812	604	6724	230000	1676	23
S2	31970	54263	21000	397	878	653	9301	221557	15845	60
S3	3485	46986	22000	396	832	784	8320	160008	6481	55
S4	5784	48792	99250	425	742	602	10020	183471	7999	30
S5	6485	35895	39274	436	810	521	9340	179385	5686	40
S6	6278	42351	75000	401	720	514	7401	163282	8102	26
S7	7054	44215	28522	1831	735	706	21050	150087	2532	34
S8	8396	42563	20100	468	765	689	12042	190004	9685	33
S9	3458	64856	42000	325	986	756	8320	201452	10141	28
S10	32989	49858	99250	471	986	656	16205	234524	2885	29
S11	39868	56986	80001	468	989	901	15251	223965	12151	30
S12	9652	43975	80200	986	911	889	12085	152486	10258	45
S13	8548	63541	35122	1211	898	989	9638	162585	13135	33
S14	5489	35995	28634	852	850	524	7350	163210	4865	36
S15	6832	43281	21002	932	980	898	13025	150024	8487	30
S16	31970	77739	33565	1047	1100	968	13055	197230	6785	44
S17	14896	52879	34020	1986	1875	875	8323	153000	3658	29
S18	17982	56432	24775	1652	1365	852	12000	184232	13355	28
S19	11970	68548	32525	969	1785	874	9986	157985	14575	40
S20	24876	58952	45287	1898	1100	921	3020	154124	8584	40
S21	23656	64325	34250	1364	1128	745	15222	150085	8745	39
S22	34878	55852	25685	1245	1201	647	22414	221511	5785	66
S23	14529	65696	42055	896	1758	988	9762	182457	11020	45
S24	8346	76542	40585	986	989	986	9632	150048	6358	38
S25	86281	54289	42010	1586	1454	884	14050	175896	3568	30
S26	9838	35686	53820	1421	1245	906	8352	173859	8745	38
S27	9454	46895	35021	1356	1253	802	8635	162589	9680	27
S28	23794	43585	24783	973	1010	576	7210	19325	6487	44

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S29	23569	79898	23222	865	1012	501	10505	163588	14141	35
S30	8865	53315	54100	1447	1328	555	11025	180041	4878	32
S31	7397	47865	20525	974	989	625	8320	193858	10100	41
S32	25879	34852	32505	958	898	666	13025	214888	9858	29
S33	2285	37845	21000	454	776	850	7200	152222	1111	20
S34	2879	35985	23025	354	789	452	6210	144455	1251	19

Soil sample no.	**Cr**	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Hg**	**Mo**	**Pb**
S1	33	101	22	178	175	120	68	2.3	465	2.4
S2	44	174	33	256	180	157	89	4.3	741	5.5
S3	39	120	29	235	171	158	64	2.8	520	2.6
S4	58	177	36	275	171.2	133	70	4.7	470	3.9
S5	32	140	37	180	173	300	82	4.4	612	3.4
S6	50	178	40	244	168	200	66	2.6	533	4.1
S7	66	136	23	173	166	300	76	2.4	700	4.8
S8	55	120	34	184	171	345	63	3.4	480	5
S9	40	145	28	164	166	239	81	2.4	725	2.6
S10	69	122	47	191	172	136	78	3.6	796	4.9
S11	77	160	43	197	170	216	76	3.1	637	3.1
S12	78	155	42	182	172.2	125	66	2.1	721	5.1
S13	84	138	47	190	166	210	79	4.6	499	2.5
S14	65	145	46	172	169	170	75	3.1	530	3.4
S15	59	135	23	210	177	301	79	3.2	732	4.2
S16	101	179	31	256	170	357	89	3.7	741	5.5
S17	110	152	24	170	172.1	235	82	4.1	425	5.6
S18	140	172	44	256	172	357	67	3.4	460	5
S19	133	174	38	183	177	352	73	4.1	741	4
S20	124	144	34	256	174	357	81	4.6	741	3.5
S21	53	173	46	260	188	370	89	5	430	5.5
S22	133	150	37	256	170	357	90	5	741	4
S23	96	135	43	190	154.2	287	83	4.2	611	3.7
S24	88	166	26	176	179	234	63	4.8	420	2.4
S25	63	152	36	182	175.5	178	78	2.4	712	3.3
S26	66	175	31	200	163	137	75	2.6	601	2.3
S27	56	132	46	176	155	305	83	2.9	511	4.9
S28	94	125	34	181	173	212	77	4.1	560	4.1
S29	81	115	48	278	172	225	67	2.8	721	3.6
S30	90	151	37	185	174	320	81	2.5	501	4.8
S31	74	132	41	210	172	244	76	2.1	514	2.9
S32	90	122	36	183	155	198	87	2.7	711	4.4
S33	33	101	23	162	168	120	68	2.3	465	2.4
S34	38	118	21	177	144	132	63	1.9	421	2.3

Table 3: Maximum, Minimum, And a mean of Element Concentrations in Soil Sample and Limits to Elements Distribution in World Soil [14], [15]

Soil Sample No.	Min	Max	Mean	Vinogradov, 1959	Al-Saadi, 2016
Mg (ppm)	2285	86281	16650.5	6300	
Al (ppm)	34852	79898	51917.3	71300	48908
Si (ppm)	20100	99250	39956.1	330000	212108
P (ppm)	305	1986	951.0	800	392
S (ppm)	720	1875	1057.3	850	90879
Cl (ppm)	452	989	745.8	450	
K (ppm)	3020	22414	10706.4	13600	7669
Ca (ppm)	144455	234524	178569.5	13700	1084
Ti (ppm)	1111	15845	7900.3	4600	90879
V (ppm)	19	66	35.7	100	
Cr (ppm)	32	140	73.8	200	72
Mn (ppm)	101	179	144.5	850	512
Co (ppm)	21	48	35.4	8	10.7
Ni (ppm)	162	278	204.9	40	78
Cu (ppm)	144	188	169.8	20	15
Zn (ppm)	120	370	237.8	50	37
As (ppm)	63	90	76	5	
Hg (ppm)	1.9	5	3.3	0.1	
Mo (ppm)	420	796	593.7	2	
Pb (ppm)	2.3	5.6	3.8	17	5.14

Calcium (Ca) ranging (144455 - 234524) ppm with a mean value of 178569.5 ppm all stations have exceeded the limit of its natural abundance in world soil [14]. Comparing the a mean of the current study with local studies was higher than that of the study [15] of soil in Lesser Zab basin, Calcium exceeded the limit of limits to elements distribution in world soil [14].

Silicon (Si) in soil ranges from 20100 to 99250 ppm with a mean value was 39956.1 ppm, and to compare with the other studies has shown that Si mean concentration value was lower than that of Lesser Zab [15], and has accepted the limits to elements distribution in world soil[14].

Aluminum (Al) in soil ranged from 34852 to 79898 with a mean value of 51917.3 ppm and this value within the limits of its world natural abundance [14] except of S29 which is higher, and was close with a mean concentration value of Lesser Zab [15] of soil except of (S2, S4, S9, S10, S11, S13, S16, S17, S18, S19, S20, S21, S22, S23, S24, S25, S26, S29, S30).

Magnesium (Mg) in soil ranged from 2285 to 86281 with a mean value of 16650.5 ppm and most detected values of Mg were out of abundant limits in world soils except (S1, S3, S4, S9, S14, S33, S34)[14]. Magnesium has increased due to the heavy use of magnesium sulfate fertilizers in the study area the increase value of magnesium might be due to agricultural activity.

Sulfur (S) in soil ranged from 720 ppm to 1875 ppm with a mean 1057.3 ppm and all detected values of S were out of abundant limits in world soils except (S1, S3, S4, S5, S6, S7, S8, S33, S34) Sulfur was much less than [15]. Sulfur is high because of the presence of sulfate mineral as gypsum and use of Fungicide on plants corps in agricultural area .
Potassium (K) in soil ranges from 3020 to 22414 a mean value was10706.4 ppm which was considered within naturally existent limits in world Soil [14] except (S7, S10, S11, S21, S22, S25) (Table 3).

But higher than Lesser Zab except (S1, S6, S14, S20, S28, S33, S34) [15], the presence of potassium may be due to the use of Iraqi fertilizer (NPK) and Muriate of Potash Mop.

Chloride (Cl) in soil ranges from 452ppm to 989ppm has a mean value of 745.8 ppm and was exceeded its natural abundance the world soil limit [14].The increase in chloride might be interpreted due to agriculture activity with applying of Muriate of Potash MOP which is potassium and chloride fertilizer world wide .

Titanium (Ti) is metallic element and is present at an estimated average concentration in the upper continental crust between 0.3 and 0.31% by weight[16]. Ti has been detected in soil samples of Al-Khassa Sub Basin in soil ranged from 1111 to 15845 with a mean value of 7900.3 ppm. Ti mean value was greater than [14],except for (S10, S11) but was lower the [15].

Phosphorous (P) ranged from 305 to 1986 have a mean value of 951.0 ppm, soil samples lower than natural abundance soil [14] 800ppm and greater than [15] (Table 3
).The main source of P in the soil of the Al-Khassa Sub-Basin could be from phosphate fertilizer.

Chromium (Cr) ranged from 32 ppm to 140 ppm with the mean concentration of 73.8 ppm. This mean value less than the natural occurrence limits in world soil [14] and a little higher than the local study at Lesser Zab soil[15]except (S11, S12, S13, S16. S17, S18, S19, S22, S23, S24, S28, S29, S30, S31, S32) the maximum Cr concentration value 140 ppm was detected at S18. From the spatial distribution of Cr concentration in soil samples, it is clear that the high concentration is distributed mainly in the northern and northeastern parts of the main basin, and that might be connected to the parent rocks beside anthropologic activity at the basin.

Manganese (Mn) range (101-179) ppm. which the mean value of 144.5 ppm which was less than its natural abundance in world soil limits[14] and less than that of local soil sample [15].

Nickel (Ni) occurs naturally in soils as a result of the weathering of the parent rocks , the underlying geology, and soil-forming processes strongly influence the amount of Ni in soils [17]. Nickel (Ni) ranged 162 ppm to 278 ppm with a mean concentration value of 204.9 ppm. It considered greater than abundant limits in soil[14] and [15], The surface soil of the Al-Khassa Sub-Basin is characterized by a relatively high level of Ni. The high content of Ni is probably due to the parent rocks in the northeastern part of the main basin.

The samples of the upper and middle parts of the main basin are richer in Ni than the lower part indicating that lithogenic origin was the main source of Ni even though the anthropogenic sources cannot be ignored especially of agricultural land.

Zinc (Zn) range (120- 370) ppm with a mean concentration value 237.8 ppm, and higher than world soil [14] and [15] a mean value and all detected values are exceeded Zn natural abundant in world soil (Table.2) Regarding LULC map, the highest value of Zn content measured in agriculture land class. Distribution of high Zn content suggests that the geogenic origin is the dominant source of Zn nonetheless the agriculture activities (fertilizer) is also an important source.

Vanadium(V)was existing in soil ranging from 19 ppm to 66 ppm with a mean concentration value of 35.7 ppm which was less than the natural occurrences of trace elements in world soil[14].

Copper(Cu)concentration value range 144 ppm to 188 ppm and with a mean concentration value of 169.8 ppm. Cu was out of its natural abundance in world soil [14], and higher than the study of [15] soil in Lesser Zab. According to the LULC map, the agriculture land class has the highest concentration of Cu (Table 3).

Lead (Pb) has a mean concentration of 3.8ppm which was lower the world soil (17ppm)[14] and lower than [15] except (S2, S16, S17).

Arsenic (As) range from 63 ppm to 90 ppm with a mean concentration value of 76 ppm which was more than its natural abundance in world soil [14]. The presence of Arsenic was due to fertilizer and pesticide [16].

Cobalt (Co) ranging from 21 ppm to 48 ppm a mean concentration value was 35.4 ppm higher to the natural abundance in world soil[14] and the local study at Lesser Zab soil[15]. The main concentration in the agricultural land was the highest. The spatial distribution also displayed that the highest concentration of Co was mainly distributed in the upper and middle part of the sub-basin.

Mercury (Hg) range from 1.9 ppm to 5.0 ppm with a mean value 3.3 ppm higher than natural abundance in world soil [14], Mercury was found in high concentration in agricultural area in Al-Khassa Sub Basin was due use of Agricultural Chemical as fungicide, mildwicide or pesticide [17, 18]. Molybdenum (Mo) range from 420 ppm to 796 ppm had a mean concentration 593.7 ppm. This mean value more than its natural occurrence limits in world soil [14]. There are also many fertilizer formulations with molybdenum added, which will work well to increase the availability of the element in most plants.

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5 **Assessment of soil contamination**

5.1 Local geochemical backround calculation:

The method that has been used in this study depended on standards deviation (SD) method, the iterative 2SD technique (average +2SD) is mainly used to define background value because it approximates the original data set to normal distribution this technique detailed by[19-21] is based on the assumption that data set beyond the average +2SD are alliteratively omitted until all value lie within the range (normal distribution) the local geological background shown in (Table 3). In order to evaluate if the chemical element concentration in the soil from natural or anthropogenic sources, enrichment factor is calculated for all studied soil samples using zirconium (Al) as a reference element. Indirect geochemical background obtained from the computation of statistical background methods are used as reference background. In the current study, Al is used as a reference element for geochemical normalization because of the following reasons: (1) Al is associated with fine solid surfaces sediments; (2) its geochemistry is similar to that of many heavy metals and (3) its natural concentration tends to be uniform[22].

5.2 Enrichment factor (EF)

Pollution indices such as Enrichment Factor (EF) are powerful tools for processing, analyzing, and conveying raw environmental information.

$EF= (C_x /C_y)_S/(C_x /C_y)_{RS}$ ………{ equation .1}

Where C is the measured concentration of the examined metal in the soil sample (mg/kg), Cy is the concentration of the immobile element in the sample (Al), and (Cx /Cy) is the concentration of element X to the immobile element ratio in the selected reference

sample[19]. Aluminium that have been chosen as immobile element in this study.
Increasing in EF value indicate increasing metals supply from anthropogenic activity. There are five contamination categories are recognized on the basis of the enrichment factor values based on the enrichment ratio methodology [23]: (1) EF<2 depletion to minimal enrichment indicating of no or minimal pollution (2) EF 2-5 moderate enrichment, indicating of moderate pollution (3) EF 5-20 significant enrichment, indicating of a significant pollution (4) EF 20-40 very highly enriched, indicating a very strong pollution (5) EF>40 extremely enriched, indicating an extreme pollution.

Enrichment factor results can be summarized that most of soil sample with EF<2 and the rest soil samples with EF 2-5, indicating that most of soil of the Sub- Basin had depletion to minimal pollution . Wheres, and some soil sample had a moderate pollution. The only exception among the soil sample was S25 with EF 5-20 indicating a significant pollution by magnesium Mg due to the heavy use of magnesium fertilizer at Sedan site (S25).

Table 4: Show the enrichment factor (EF) result and local geochemical background.

Element	EF<2	EF 2-5	EF 5-20	Local geochemical background (ppm)
Mg	Most of Sample	S2, S10, S11, S16, S18, S20, S21, S22, S28, S29, S32	S25	8000
Al	All sample	------	------	41212
Si	Most of Sample	S4, S10, S11, S12	------	31000
P	Most of Sample	S7, S13, S16, S17,S18, S20 ,S21	------	600
S	Most of Sample	S17, S19, S23	------	814
Cl	All sample	------	------	666
K	Most of Sample	S7, S10, S22	------	8045
Ca	Most of Sample	S1, S10	------	112515
Ti	Most of Sample	S2	------	7895
V	Most of Sample	S1, S2, S22	------	25
Cr	Most of Sample	S18	------	67.5
Mn	All sample	------	------	100
Co	All sample	------	------	25
Ni	Most of Sample	S2, S3, S4, S6 S16, S19, S21, S22, S23 , S29	------	110
Cu	All sample	------	------	155
Zn	Most of Sample	S5, S7, S8, S15, S16 ,S17, S18, S19, S20, S21, S22, S27, S30	------	145
As	Most of Sample	S2 , S5, S9, S16, S17, S20, S21, S22, S23 ,S27, S30	------	40
Hg	Most of Sample	S2, S3, S4, S8, S10 , S11, S13, S14, S15, S16, S17, S18, S19 ,S20 , S21 ,S22, S24, S28	------	1.5
Mo	Most of Sample	S1, S3, S4, S6, S8, S13, S14, S17, S18, S21, S23, S24 ,S27, S28, S30, S31, S33	------	300
Pb	S1, S3, S9, S11, S12, S26, S31, S33, S34,	Most of Sample	------	1.5

5.3 Contamination factor (Cf)

The contamination factor is used to determine the contamination status of the Al-Khassa Sub Basin soil. The Cf is the ratio obtained by dividing the concentration of each metal in the soil (C_M) by the background (C_B) value (Varol 2011)[24]. Hence, Cf values can evaluate the enrichment of one given metal in the sediments over a period of time:

$$CF = \frac{C_{metal}}{C_{background}}$$

………{ equation .2}

Where, C_M is a concentration of an individual metal in sediments and C_B is the background concentration of the individual metal.

Cf has been used to classify contamination levels into four categories[25, 26], with Cf 1 indicating low contamination, 1 Cf 3 indicating moderate contamination, 3 Cf 6 indicating significant contamination, and Cf > 6 indicating extremely high contamination.

Based on Cf values showed that the region was low to moderate contamination except for the contamination factor of magnesium in Mam Rash (S22), Belgrad (S10) was very high degree of contamination of Cf > 6, Gurgay Shammar (S11), and Obarick (S32) was considerable degree of contamination of magnesium 3 < Cf < 6 because most of these sites are villages with farmlands using magnesium fertilizers. Phosphor (P) contamination factor is considerable degree of contamination in Heon (S7), Ali Makaeel (S20) because of use phosphate fertilizers and contain many poultry farms at these sites.

Table 5: Show Contamination Factor (Cf) of Soil Sample.

Cf< 1		1 < Cf < 3	3 < Cf < 6	Cf > 6
Low degree of contamination		Moderate degree of contamination,	Considerable degree of contamination	Very high degree of contamination
Si	S1, S2, S3, S7, S8, S14, S15, S18, S22, S28, S29, S31	Most of the stations	NO	No
P	S1, S2, S3, S4, S5, S6, S8, S9, S10, S11, S12, S33, S32, S33,	Most of the stations	S7,S20	No
S	S1,S4,S5,S6,S7,S8, S33, S34,	Most of the stations	No	No
Cl	S1,S2,S4,S5,S6,S27,S28,S29,S30,S34	Most of the stations	No	No
K	S1,S7,S14,S20,S28,S33,S34	Most of the stations	No	No
Ca	No	All the stations	No	No
Ti	S1, S3, S5, S7, S10, S14, S16, S17, S22, S24, S25, S28, S30, S30, S33, S34	Most of the stations	No	No
V	S1, S32	Most of the stations	No	No
Cr	S1,S2,S3,S4,S5,S6,S8,S9,S14, S15,S21,S25, S26,S27,S33,S34	Most of the stations	No	No
Mn	No	All the stations	No	No
Co	S1, S7, S15, S17, S34	Most of the stations	No	No
Ni	No	All the stations	No	No
Cu	S23, S34	Most of the stations	No	No
Zn	S1, S4, S10, S12, S26, S33, S34	Most of the stations	No	No
As	No	All the stations	No	No
Mg	S1, S2, S3, S4, S5, S6, S7, S9, S14, S15, S31, S33, S34	Most of the stations	S10, S11, S32	S22,S25
Al	S5, S14, S26, S32, S33, S34	Most of the stations	No	No
Hg	No	All the stations	No	No
Mo	No	All the stations	No	No
Pb	No	All the stations	No	No

6.Conclusions and discussion

1- Physicochemical Properties of the soil were examined Hydrogen Potential (pH), Organic Matter (O.M), Loss Of Ignition (L.O.I), Total Organic Carbon (TOC), Cation Exchange Capacity (CEC) and Total Hydrocarbon (THC).

Hydrogen potential (pH) showed that the soil was alkaline above seven with a mean 7.98.

Organic Matter (O.M) of the study area with a mean 1.28 % and high value found in agricultural areas.Cation Exchange Capacity (CEC) with a mean 42.64 (cmol/kg) that is

proportional to the granular size of the soil that silty clay. Both Total Organic Carbon (TOC) and Total Hydrocarbon (THC) acceptable concentration values compared to the soils of the arid region.
2- Abundant Elements (Calcium (Ca), Silicon (Si), Aluminum (Al), Magnesium (Mg), Sulfur (S), Potassium (K), Chloride (Cl), Titanium (Ti) and Phosphorous (P)) and Trace element (Chromium (Cr), Manganese (Mn), Nickel (Ni), Zinc (Zn), Vanadium(V), Copper(Cu), Lead(Pb), Arsenic (As), Cobalt (Co), Mercury (Hg) and Molybdenum (Mo)) that had been analyzed in this study and compared with the natural occurrences of trace elements in world soil [14] and local study of Lesser Zab [15].
3-Elements that were higher than standard Ca,Cl,Cu, As, Hg, Mo, Zn because of excessive use of fertilizers and pesticides and poor irrigation practices and other anthropogenic sources .
4-High concentration elements (Ni, Ca, Co) occurs naturally in soils as a result of the weathering of the parent rocks.
5- Elements that are partially higher than the standard is (K, Cr, P , S, Mg) only in dense agricultural areas.
Elements that were lower than standard (Ti, Al, Si, Mn, V, Pb) given the idea that was not polluted with such elements, that usually increased in the industrial regions that is not the case of Al-Khassa Sub-Basin.
6-For contamination assessment the results of the enrichment factor (EF)and the Contamination factor(CF) are calculated, Enrichment Factor (EF) of sub-basin is EF<2 depletion to minimal enrichment indicating of no or minimal pollution, but some sites showed moderate enrichment EF (EF 2-5) indicating of moderate pollution, the only expectation was site S25 had EF (5- 20) indicating a significant pollution by magnesium (Mg), due to heavy use of magnesium fertilizer at Sedan site (S25).
7-The results of the Contamination Factor (CF) showed that the region was low to moderate contamination

except for the contamination factor of magnesium in Mam Rash (S22), Belgrad (S10) is very high degree of contamination of Cf > 6, Gurgay Shammar (S11), and Obarick (S32) was considerable degree of contamination of magnesium 3 < Cf < 6 because of the two villages are agriculture area that use of magnesium fertilizer. Phosphor (P) contamination factor is moderate in Heon (S7), Ali Makaeel (S20) because of domination of agricultural activity. Phosphor (P) contamination factor was moderate in Heon (S7) and Ali Makeael (S20) because of phosphate fertilizer besides spreading poultry farm at these two sites.

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